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**PLASMA-ENABLED DESIGN OF HYBRID CARBON
NANOSTRUCTURES FOR ENERGY STORAGE
APPLICATIONS**

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PLASMA-ENABLED DESIGN OF HYBRID CARBON NANOSTRUCTURES FOR ENERGY STORAGE APPLICATIONS

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Doctoral Dissertation
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PLAZEMSKO OMOGOČENO OBLIKOVANJE
HIBRIDNIH OGLJIKOVIH NANOSTRUKTUR ZA
SHRANJEVANJE ENERGIJE

Doktorska disertacija

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To my father, mother, brother, all family members and friends.

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Abstract

Carbon, one of the most abundant materials in the earth crust, has gained research attention owing to its high structural stability, electrical conductivity, optical and thermal properties. Additionally, the possibility of tailoring carbon materials at nanoscales makes them promising materials for many applications, including energy storage, sensors, bio-medical and electronics. One of the highest potential applications of carbon-based nanomaterials are energy storage devices to store energy considering the increasing demand for alternative energy resources for fulfilling consumer needs. Therefore, enormous efforts were already employed to design advanced carbon materials for energy storage by nanostructure design, surface engineering and nanocomposite formation. However, most commonly used synthesis and processing techniques are limited due to the high energy and high-temperature requirements for the fabrication, large time consumption, and uncontrollability of the nanoengineering. Thus, developing a new technique for the controllable nanoengineering of advanced carbon materials at a large scale that is more efficient is necessary for application-oriented purposes.

In this PhD dissertation, plasma-enabled techniques are used for developing advanced carbon-based electrodes for energy applications. In order to attain the research objectives, the PhD research has been designed into three stages: (i) developing plasma techniques for fabricating carbon nanostructures, (ii) designing hybrid carbon-based electrodes, and (iii) exploring energy storage performances of the designed electrodes. A cold low-pressure plasma is explored in the first stage as a promising approach for designing advanced carbon materials at the nanoscale. We tested different plasma systems for the synthesis of carbon nanostructures. In all cases, a radio-frequency power generator was used for plasma discharge. The first approach was the deposition of carbon nanostructures from vapour phase to the solid phase using carbon-containing gases in plasma as the precursors. In the second approach, we have established an alternative technique by growing carbon nanostructures by the surface reformation of a solid precursor using an argon/ hydrogen gas mixture. In both cases, we investigated the influence of plasma discharge parameters on the nanostructures growth mechanisms.

In the second stage of this PhD research, we demonstrated the ability of plasma for surface engineering and heteroatom doping in both low-pressure and atmospheric conditions. In the former, carbon nanostructures were exposed to nitrogen-containing low-pressure plasmas for fabricating the nitrogen-doped carbon nanowalls. Furthermore, in the latter, at atmospheric conditions, entangled carbon nanotubes were treated with a plasma jet of inert gas. We revealed the surface engineering mechanisms in both cases and determined the changes in the surface properties.

In the final stage, we designed hybrid carbon-based nanostructures for energy storage applications. We have chosen the plasma-enabled techniques that were used in the first and second stages of our investigation for designing carbon nanostructure platforms and, in addition, a thermal annealing technique for designing carbon/metal sulphide hybrid composite. Afterwards, we have studied the electrochemical properties of the fabricated electrodes for batteries and supercapacitors and demonstrated that the fabricated electrodes were delivering one of the best performances among similar carbon-based materials.

The presented PhD dissertation offers insight into the superiority of plasma-enabled techniques for designing hybrid carbon-based electrodes. In addition, the method offers a 2-in-1 package, as one can also tailor the properties of the synthesised electrodes either during the synthesis process or afterwards. Examples of using such plasma techniques have been demonstrated in the thesis for the preparation of electrodes that have superior properties when used as electrodes for lithium-ion batteries or supercapacitors.

Povzetek

Ogljik, eden izmed najbolj zastopanih materialov v zemeljski skorji, je pritegnil pozornost raziskovalcev zaradi visoke strukturne stabilnosti, električne prevodnosti, optičnih in termalnih lastnosti. Poleg tega so ogljikovi materiali obetavni za številne aplikacije, vključno s skladiščenjem energije, senzorji, biomedicino in elektroniko zaradi možnosti prilagajanja teh materialov na nanoskali. Ena izmed najobetavnejših aplikacij ogljikovih nanomaterialov so naprave za shranjevanje energije, saj se potrebe potrošnikov po alternativnih energetskih virih povečujejo. Zato je že bilo veliko truda vloženega v oblikovanje naprednih ogljikovih materialov za skladiščenje energije z oblikovanjem nanostrukture, površinskim inženirstvom in tvorbo nanokompozitov. Vendar pa so najpogostejše uporabljene sintezne in obdelovalne tehnike omejene zaradi visokih energetskih in visokotemperaturnih zahtev izdelave, slabe kontrole nanoinženiringa in počasnega procesa rasti. Zato je za industrijske namene potreben razvoj nove bolj učinkovite tehnike za nadzorovano nanoinženirstvo naprednih ogljikovih materialov v velikem obsegu.

V tej doktorski disertaciji se plazemske tehnike uporabijo za razvoj naprednih elektrod za energetske aplikacije, ki temeljijo na ogljiku. Da bi dosegli raziskovalne cilje, je doktorska raziskava oblikovana v tri faze: (i) razvoj plazemskih tehnik za izdelavo ogljikovih nanostruktur, (ii) zasnova hibridnih elektrod na ogljikovi osnovi in (iii) raziskovanje zmogljivosti shranjevanja energije zasnovanih elektrod. V prvi fazi se raziskuje hladno nizkotlačno plazmo kot perspektivni pristop za snovanje naprednih ogljikovih materialov na nanoskali. Testirali smo različne plazemske sisteme za sintezo ogljikovih nanostruktur. V vseh primerih je bil uporabljen radiofrekvenčni generator za napajanje plazemske razelektritve. Prvi pristop je bil plazemsko nalaganje ogljikovih nanostruktur iz parne v trdno fazo, kjer se je uporabilo pline, ki vsebujejo ogljik, kot prekursorje za sintezo. V drugem pristopu smo vzpostavili alternativno tehniko z rastočimi nanostrukturami ogljika s površinsko reformacijo trdnega vzorca s pomočjo plazme iz mešanice plinov argon/vodik. V obeh primerih smo raziskali vpliv parametrov plazemske razelektritve na mehanizme rasti nanostruktur.

V drugi fazi tega doktorskega raziskovanja smo dokazali zmožnost plazme za površinsko inženirstvo in heteroatomsko dopiranje tako pri nizkem tlaku kot pri atmosferskih pogojih. Tako so bile ogljikove nanostrukture izpostavljene nizkotlačnim plazmam, ki vsebujejo dušik, za sintezo z dušikom obogatenih ogljikovih nanozidov. Z atmosfersko plazmo iz inertnega plina pa se je obdelalo vzorce prepletenih ogljikovih nanocevk. Razkrili smo mehanizme površinskega inženiringa v obeh primerih in določili spremembe v površinskih lastnostih. V zadnji fazi smo oblikovali hibridne nanostrukture na osnovi ogljika za namene shranjevanja energije. Za pripravo ogljikovih nanostrukturnih platform smo izbrali plazemske tehnike, ki so bile uporabljene v prvih dveh fazah naše raziskave. Poleg teh smo se poslužili še tehnike žarjenja, s katero smo oblikovali hibridni kompozit ogljik/kovinski-sulfid. Nazadnje smo premerili elektrokemijske lastnosti izdelanih elektrod za baterije in superkondenzatorje. Meritve so pokazale, da so naše elektrode med podobnimi materiali na osnovi ogljika ene najboljših. Predstavljena doktorska disertacija ponuja vpogled v superiornost plazemskih tehnik za oblikovanje hibridnih elektrod, ki temeljijo na ogljiku. Poleg tega te metode ponujajo „paket 2-v-1“, saj lahko prilagajajo lastnosti sintetiziranih elektrod bodisi med postopkom sinteze bodisi pozneje. Primeri uporabe plazemske tehnike so bili v doktorski nalogi prikazani za pripravo elektrod z vrhunskimi lastnostmi za uporabo kot elektrode za litij-ionske baterije ali superkondenzatorje.

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Abbreviations

1D	...	One Dimension
2D	...	Two Dimension
3D	...	Three Dimension
AC	...	Alternating Current
NH ₃	...	Ammonia
a-C	...	Amorphous Carbon
Ar	...	Argon
APPJ	...	Atmospheric Pressure Plasma Jet
BP	...	Bucky Paper
CCP	...	Capacitively Coupled Plasma
C ₂	...	Carbon Dimer
CNF	...	Carbon Nanofiber
CN	...	Carbon Nanostructure
CNT	...	Carbon Nanotube
CNW	...	Carbon Nanowall
CF ₄	...	Carbon Tetra Fluoride
CVD	...	Chemical Vapour Deposition
CV	...	Cyclic Voltammetry
DC	...	Direct Current
DV	...	Divacancy
EIS	...	Electrochemical Impedance Spectroscopy
EBEP	...	Electron Beam Excited Plasma
ECR	...	Electron Cyclotron Resonance
eV	...	Electron Volt
FLG	...	Few Layer Graphene
FC	...	Fluorocarbon
FIB	...	Focused Ion Beam
FTIR	...	Fourier Transform Infrared Spectroscopy
GCD	...	Galvanostatic Charge-Discharge
GO	...	Graphene Oxide
He	...	Helium
HAADF-STEM	...	High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy
HC	...	Hydrocarbon
H ₂	...	Hydrogen
H ₂ S	...	Hydrogen Sulphide
ICP	...	Inductively Coupled Plasma
LIB	...	Lithium-Ion Batteries
CH ₄	...	Methane

MW	...	Microwave
MWCNT	...	Multi-Walled Carbon Nanotube
NP	...	Nanoparticle
NEXAFS	...	Near Edge X-Ray Absorption Fine Structure
Ni	...	Nickel
Ni foil	...	Nickel Foil
Ni ₃ N	...	Nickel Nitride
N ₂	...	Nitrogen
NVCN	...	Nitrogen Doped Vertical Carbon Nanotube
NCNW	...	Nitrogen-Doped Carbon Nanowall
NVGN	...	Nitrogen-Doped Vertical Graphene Nanosheet
OCN	...	Oriented Carbon Nanostructures
O ₂	...	Oxygen
PECVD	...	Plasma Enhanced Chemical Vapour Deposition
PUR	...	Polyurethane
RF	...	Radio Frequency
RF gel	...	Resorcinol Formaldehyde Gel
SEM	...	Scanning Electron Microscope
SAED	...	Selected Area Diffraction Pattern
SiO ₂	...	Silicon Oxide
SV	...	Single Vacancy
SWCNT	...	Single-Walled Carbon Nanotube
SERS	...	Surface Enhanced Raman Spectroscopy
TEM	...	Transmission Electron Microscope
Ni ₃ S ₂	...	Trinickel Disulphide
UV-VIS	...	Ultraviolet-Visible Spectroscopy
VCN	...	Vertical Carbon Nanotube
VGN	...	Vertical Graphene Nanosheet
VHF	...	Very High Frequency
XRD	...	X-Ray Diffraction
XPS	...	X-Ray Photoelectron Spectroscopy

Chapter 1

Introduction

1.1 Importance of Nanoengineered Advanced Carbon Materials

Carbon-based materials are well-known for multi-purpose applications, including electrodes for energy storage, gas sensors, catalysis, field emission techniques and electronic devices [1]–[7]. From structural and morphological to electrical features, their unique characteristics have made them a promising material for future applications. Nanoengineering strategies of carbon materials, including nanostructure design, optimisation of hybrid composites, surface functionalisation and heteroatom doping, improve the properties of the carbon materials. Due to the advanced applications, nanostructure design and surface modifications of carbon at the nanoscale have attracted research attention since the early 1990s. As a result, several nano-sized carbon materials have already been reported depending on their size, dimension, crystal structure, morphology, and orientation [8]–[11]. Commonly used forms of carbon nanostructures are graphene, a crystalline form of the fullerene family, an allotrope of carbon consisting of a single layer of carbon atoms arranged in a 2D honeycomb lattice, which is one of the main constituents in other forms of carbon nanostructures. Another form of carbon allotropes is graphite, which consists of multiple layers of graphene sheets with an interlayer distance of ~ 0.34 nm. Rolled forms of graphene are known as carbon nanotubes. Depends on the number of graphene layers, nanotubes are distinguished into single-walled carbon nanotubes and multi-walled carbon nanotubes. The arrangement of graphene sheets in conical shape results in the formation of carbon nanofibers. Compared to the horizontal graphene, stacking of graphene sheets perpendicular to a substrate surface forming carbon nanowalls, each nanowall consists of multiple graphene and has a thickness of several tens of nanometers. Nanostructured carbon materials have dimensions in the range of several nanometres to few microns, depends on their morphology and orientation. Modifications of carbon to different allotropes with the nanometer scale are highly influenced by their synthesis method. Thus, numerous approaches have been emerged for the nanostructured modification and process of carbon materials. This chapter provides an insight into synthesis, processing and applications of carbon nanostructures, starting with the identification of the conventional synthesis techniques and processing of nanostructured carbon materials (Section 1.2), a brief introduction to the plasma-enabled techniques and their advantages for the nanostructuring of carbon materials (Section 1.3) and a potential of carbon nanostructures for energy storage applications (Section 1.4). Following these, the motivation of this dissertation and the major objectives of the dissertation are outlined in Section 1.5.

1.2 Conventional Techniques for the Synthesis and Processing of Carbon Nanostructures and Challenges

As carbon nanostructures are industrially very important, it does not surprise us that several chemical and physical approaches have already been developed to synthesise and process nanoscale carbon materials, especially to design graphene, carbon nanotubes, and graphitic carbon forms. One set of such physical methods is exfoliation and cleavage techniques, which are considered one of the easiest techniques to produce 2D carbon nanostructures. Exfoliation is, in principle, a repeated peeling process of bulk carbon material to produce nanoscale carbon by breaking the bonding between carbon layers using mechanical or chemical energy [12]–[14]. E.g. high-quality graphene layers can be produced from the highly oriented pyrolytic graphite (HOPG) sheet by the continuous peel-off process. Another promising approach to designing different carbon nanostructures are chemical vapour deposition (CVD) techniques [15]. In CVD techniques, carbon nanostructures are produced from the gaseous phase to the solid phase at higher temperatures ($\sim$ above 900 °C) [16]. Carbon-containing gases are used as precursors, and the carbon nanostructures are usually deposited onto a solid substrate. CVD processes have already been reported for producing graphene, carbon nanotubes, carbon nanofibers and other nanocarbons [17]–[19]. In another approach, carbon nanostructures have been synthesised using laser ablation techniques. In laser ablation, the synthesis system consists of a furnace chamber and a laser source [20], [21]. The laser system is focused on a carbon-containing target to ablate the carbon in the form of a nanomaterial. The structural quality and morphology of the carbon nanostructures are determined by the furnace temperature used in the experimental setup. Usually, high-quality carbon nanostructures are produced at elevated temperatures by using ablation methods. Nevertheless, another technique in line with physical nanostructure synthesis is epitaxial growth of carbon nanostructures by the controlled layer-by-layer stacking [22]–[24]. These techniques yield high-quality carbon nanostructures. Other chemical techniques have been demonstrated for the production of carbon nanostructures; Chemical reduction of graphite oxide, pyrolysis of carbon-rich polymers [18], [25], hydrothermal carbonisation of carbon-containing precursors, sol-gel methods [26], [27], thermal reduction of organic compounds, and electrodeposition are various alternative techniques that form carbon nanostructures, including graphene, graphite, carbon nanotube, carbon nanowall and carbon nanofibers. However, all the above-mentioned techniques have limitations for the large-scale production of carbon-based nanostructures for practical applications. Among all these techniques, CVD is commonly used to produce carbon nanostructures because of its ability for mass production. However, the requirement of high temperature during the CVD growth process is a bottleneck that needs to be resolved for large-scale applications [13], [16], [28].

The features of carbon nanostructures towards easy surface processing are one of the best qualities for advanced applications. Surface processing or surface engineering of carbon nanostructures is the manipulation of carbon surfaces by introducing defects, heteroatoms, and functional groups [29]–[32]. Heteroatom doping or functional groups can improve the electrical, optical and electronic properties of the carbon nanostructures. Surface-engineered carbon nanostructures can be produced in two methods: one method is processing of nanostructures during their growth [33], [34], and the other is processing of prepared nanostructures by post-treatment [28], [35]–[40]. Post-treatment of carbon nanostructures has been gaining research attention due to its capability of controlling the functional entities on the nanostructure during

the processing time compared to the processing during the growth. Surface processing and heteroatom doping in the carbon lattice are highly influenced by the structural defects formed on the nanostructure during the growth or processing time. Moreover, CVD techniques, thermal treatment, segregation growth, solvo-thermal process, and arc discharge processing are the widely used approaches for the surface engineering of carbon nanostructures [31], [32]. Nevertheless, all these techniques are limited for producing carbon nanostructures with a high concentration of doped atom/functional groups due to their limits on creating surface defects. Therefore, an alternative technique to synthesise high-quality carbon nanostructures and process carbon nanostructures to attain a high concentration of surface functionalities in controlled manner is required for the large-scale production of advanced carbon nanostructures.

1.3 Advantages of Plasma-Enabled Synthesis and Processing of Carbon Nanostructures

Compared to the conventional techniques, plasma-enabled techniques can produce high-quality carbon nanostructures with a high controllability over the structure and morphology. Plasma is commonly known as the “fourth state of matter”, composed of fully or partially ionised gas, i.e. ions, electrons and neutral species. A plasma-enabled approach working at low-temperatures is an alternative solution for producing carbon nanostructures at favourable industrial conditions [41]. Plasma-enhanced chemical vapour deposition (PECVD) is one kind of technique to produce high-quality carbon nanostructures [10], [42]–[47]. In this process, the carbon nanostructure growth occurs from the gas phase to the solid phase. In the general principle of PECVD, a carbon source gas introduces into a reactive chamber, generates the plasma by an electromagnetic field, and allows the source gas to get chemically active by the partial ionisation, dissociation and electron excitation. These species are then transported to the substrate material and initiate the growth of nanostructure. During this time, the substrate is heated either by the plasma-heating effects (due to the ion bombardment and exothermal chemical reactions on the surface, e.g.: recombination) or by using an external heating system [48], [49]. The substrate temperature is one of the determining factors for the structure, quality and morphology of the final carbon nanostructure. During nanostructure growth, some specific conditions have to be fulfilled, such as a sufficient amount of high energy particles at the growth zone and a balanced flux of carbon atoms to the growing nanostructures. In a plasma-enabled approach, these conditions can be easily achievable by selecting optimum plasma discharge parameters such as plasma power, electron temperature, and surface potential.

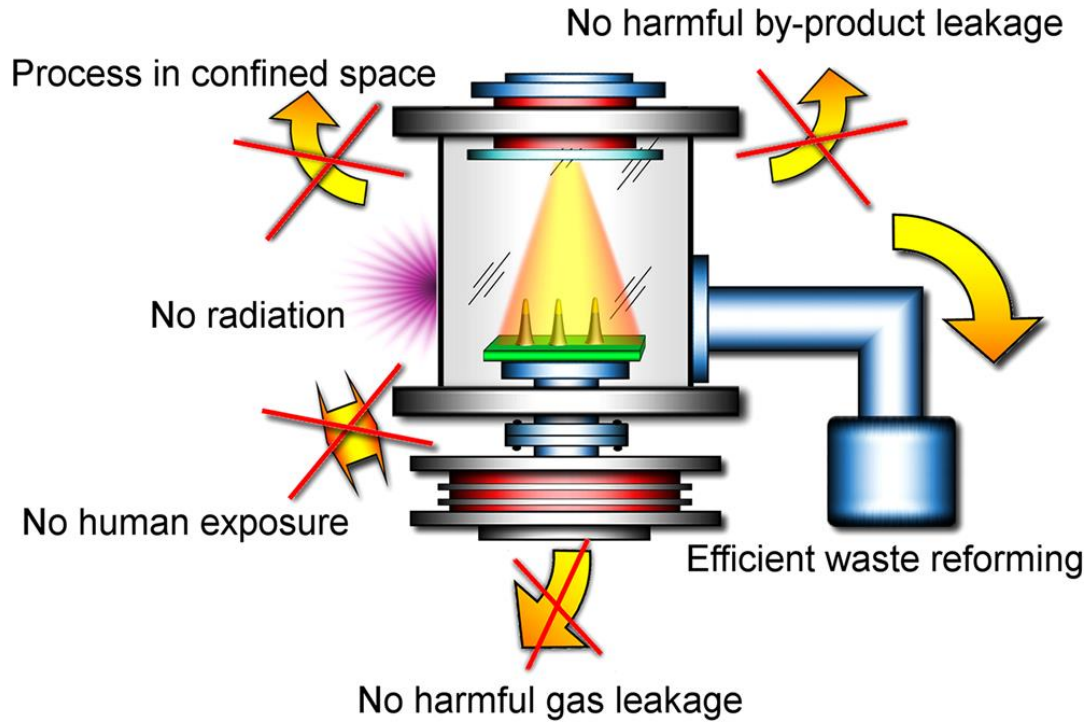


Figure 1: Safety of plasma nanofabrication approaches confined space for conducting the process, no severe radiation outside the reactor, no leakage of harmful by-products or gases, no significant human exposure [50].

To achieve these specific conditions, a typical PECVD system is built with three major parts: plasma generator with connected antennas, plasma chamber and precursor gas [28], [48]. Varying the generator or plasma power, changing the geometry of antennas or plasma chamber, and changing the composition ratio of gases could lead to the formation of different nanostructures. Depending on the used plasma generators, the plasma system can be divided into different categories: microwave, radiofrequency, direct current, and their combinations. In all cases, the plasma generator is coupled with the plasma chamber using different antennas such as inductive coils, parallel plate electrodes or pin to plate electrodes. Depending upon the pressure, plasmas can be low-pressure ($1\text{--}10^4$ Pa) or atmospheric pressure. In a PECVD process, ions can elevate the substrate temperature and surface diffusion after the ionisation, and electrons can participate in the chemical reactions. Highly reactive radicals will be deposited onto the substrate. By adjusting the plasma power, gas flow rate, pressure inside the plasma system and the potential of the substrate surface, it is possible to control the quality, structure, morphology, orientation and growth rate of deposited carbon nanostructures. With PECVD, carbon nanostructures, including graphene, diamonds, carbon nanotubes, carbon nanofibers, and carbon nanowalls, have already been prepared [10], [42], [43], [51]–[56]. Apart from the PECVD techniques, plasma-enabled surface reformation of solid/liquid precursors has also been explored to produce carbon nanostructures [57]–[59]. Several studies revealed that high-quality carbon nanostructures with ordered structure and morphology could be easily fabricated from honey, coconut oil, and honeycomb using plasma-enabled techniques. In addition, all these studies demonstrate the efficiency of plasma-enabled approaches to produce the final carbon nanostructures much faster than the other conventional technique with superior growth rate and controllability. The plasma process is conducted in a closed reactor, where a controlled atmosphere is used, and human respiratory tracts remain isolated from the harmful volatile compounds. In addition, carbon

nanostructures are usually produced by the decomposition of methane, and acetylene-like gases, which are not harmful to the environment. Therefore, the environmental benign nature of plasma-enabled techniques is highly appreciated in the industrial sectors. A schematic of a closed PECVD system and its environmental benign features is presented in Figure 1.

Besides the benefits of plasma for carbon nanostructure synthesis, the ability of plasma to engineer and functionalise the surface controllably is also important for industrial adaptation of the carbon nanostructures [60]–[63]. The plasma-enabled surface treatment process to incorporate heteroatoms in the carbon atoms during the growth and after the growth is an interesting strategy to tune the electrical properties of carbon. Nitrogen, boron and oxygen are commonly used as the heteroatoms to tune the properties of carbon nanostructures to desired features, including electrical, electrochemical and catalytic properties. It is well-known that plasma can achieve a higher concentration of heteroatoms in bulk than other conventional techniques due to its ability to create surface defects and incorporate heteroatom simultaneously [64]. Besides, the ability of plasma surface treatment using suitable reactive gases is proven for changing the surface wettability of carbon materials from hydrophilic to hydrophobic and vice-versa. Therefore, enhancing the controllability of the existing plasma systems or designing new plasma systems to ensure much higher controllability could be a potential technique to produce high-quality carbon nanostructures on a large scale. High electrical conductivity, layered structures, easy functionalisation features, and the possibility to tailor the electrical and electrochemical properties of carbon nanostructures are well suitable for the next generation applications, including batteries, supercapacitors, gas sensors, solar cells and others.

1.4 Potential of Hybrid Carbon Nanostructures for Energy Storage Applications

The rising concerns on the worldwide energy demands and global warming push forward the development of clean and renewable energy storage devices [65]–[67]. Currently, lithium-based batteries and their graphite electrodes dominate the commercial markets. However, the spread of renewable energy storage devices demands suitable high performing electrode materials to deliver high energy storage performances [68]. Energy storage is a potential application of the carbon-based nanomaterials due to their impressive structural integrity and stability upon cycling for long-term use compared to other electrode materials [69], [70]. However, carbon nanostructure electrode often shows moderate discharge capacity and unsatisfactory rate capability [71], [72]. Therefore, it is critical to improve the electrochemical performances by tailoring the surface by a heteroatom, functional groups and a combination with high capacity material, e.g., transition metal sulphides [30], [39], [73], [74]. Surface-engineered carbon nanomaterials can possess advantages such as active sites for pseudocapacitance, shortened diffusion pathways, excellent ionic and thermal conductivity and enhanced electrochemical performance [75]. As a result of surface engineering (e.g., nitrogen-doped carbon), carbon electrodes can deliver higher performance. For further improvement of the electrode, one can consider other high capacity materials to combine with carbon. Transition metal sulphides are well-known to deliver high capacity during electrochemical reactions. However, their poor electrical conductivity and structural degradation are bottlenecks used as advanced electrodes for energy storage materials [76]–[78]. However, designing hybrid carbon-based nanostructures with transition metal sulphides would bring forth the best properties from each material to ensure electrical conductivity, high capacity and structural stability. Several studies exposed the potential of these kinds of

carbon/metal sulphide hybrids as an excellent electrode material for supercapacitors, lithium-ion batteries and sodium-ion batteries. Characteristic features of carbon nanostructures make them one of the best platforms for composite preparation due to their structural stability, affinity towards easy functionalisation and surface engineering. Carbon nanostructures fabricated directly on the substrate with metal nanoparticles in the backbone could be an easy solution for designing hybrid carbon/metal sulphide-based advanced electrodes. Most of the currently available techniques for designing carbon-based electrodes are high-temperature annealing, chemical reduction, and CVD process, which are time-consuming and energy-consuming. In addition, most of these electrode fabrication techniques involve polymeric binders to cast the active material on the current collector, which can cause side effects in the electrochemical reactions. Consequently, a fast and facile approach that enables the synthesis and processing of carbon nanostructures directly on the substrates at low-temperature conditions could lead to a paradigm shift in the field of advanced electrodes for energy storage applications and could address the major problems concerning the energy demands. Moreover, we have identified that developing a plasma-enabled technique could address this problem and contribute to the needs of industrial demands.

1.5 Motivation and Thesis Objectives

The increasing demand for power backup solutions and renewable energy resources for fulfilling consumer requirements has prompted the development of advanced electrochemical energy storage devices such as batteries and supercapacitors [79]–[81]. Supercapacitors have many practical applications and have attracted research attention due to their high power density, long cycle life, and fast charge-discharge rate properties [82]–[84]. Amid available battery technologies, lithium-ion batteries (LIBs) have high specific energy and power density, long cycle life, no memory effect, and high load capabilities [85]–[87]. However, the features of these devices have to be further modified for advanced applications [88], [89]. Since the electrochemical performance of a device of choice is mainly influenced by the employed electrode material, novel electrode materials are essential to address the challenges related to high energy/power density, safety, higher performance, and long lifespan. Ideal characteristics of such electrodes include high electrical conductivity, chemical inertness, mechanical resistance, large electrochemically active area, large surface area, and low cost. Therefore, a far greater understanding of designing advanced electrodes is essential for the sustainable development in energy storage. Electrodes for electrochemical energy storage are expected to meet three criteria; A high electrical conductivity for charge carrier transport between the electrode and electrolyte interfaces. Second, a high surface area, since capacity scales with the interfacial area. Third, an excellent electrode electrochemical stability avoids unwanted reactions with the electrolyte and the decreased stability in long-term cycling [90], [91]. Endeavours to find alternative anode materials have resulted in several potential candidates with excellent electrochemical properties, i.e. carbon, transition metal oxides, and metal sulphides [76], [92]–[97].

Among the widely researched materials, carbon-based electrode shows superior stability, high electrical conductivity and structural integrity for long-term applications compared to other varieties. However, their low-discharge capacity and poor rate capabilities have to be resolved for practical applications. One of the efficient strategies to overcome these problems is nanoengineering of carbon nanostructures with heteroatom doping or combining them with high capacity materials. Recently much attention is dedicated to the transition metal sulphides due

to their higher discharge capacity, high redox activity, easy preparation, and low cost. Despite the named advantages, metal sulphide-based electrode materials for energy storage applications are still limited due to poor electrical conductivity and material fragmentation during electrochemical reactions, which decrease stability performance. An effective strategy that emerged to tackle these issues is compositing the metal sulphide-based materials into a highly conductive and stable carbon matrix (e.g. graphene, carbon nanotubes, carbon nanofiber, carbon nanowall) [98], [99]. Furthermore, the direct growth/deposition of electrode materials on the current collector is considered as an alternative strategy to provide free-standing hierarchical nanostructure-based electrodes to eliminate resistivity-related issues due to the use of binders during electrochemical testing [100], [101]. Most of the currently available electrode designing techniques are wet-processes that require complicated chemical methods and high-temperature assistance. Therefore, developing an alternative fast and feasible electrode-designing technique could provide a paradigm shift in future studies in energy storage and conversion devices.

In this dissertation work, a systematic study of the current state of the art is performed to identify the missing links in the use of carbon-based electrodes for energy storage devices to overcome the above-mentioned barriers. These gaps are mainly associated with the synthesis and processing of carbon nanostructures. Therefore, the ultimate goal of the dissertation is to develop a feasible technique to design novel hybrid carbon-based electrode materials. For this reason, a low-pressure radio-frequency plasma system is used in this work for the synthesis and processing of carbon nanostructures. A detailed investigation is carried out on the influence of plasma-discharge parameters on the growth mechanism of carbon nanostructures. The effect of plasma-enabled surface treatments on carbon nanostructures is studied using different gases (nitrogen, ammonia, helium, and argon) and different plasma conditions (low-pressure and atmospheric pressure). These synthesised/processed carbon nanostructures are combined with transition metal sulphides for designing binder-free electrodes for energy storage devices (Li-ion batteries and supercapacitors), and the electrochemical performance is tested. Based on the identified possibilities for tackling the challenges, the main objectives of the dissertation work are as follows:

Objective 1: Exploration of low-pressure plasma-enabled green approaches for the direct growth of carbon nanostructures on solid substrates and optimisation of the growth conditions.

Plasma-enabled direct growth of carbon nanostructures on solid substrates is highly influenced by the plasma discharge parameters and type of the plasma system. Therefore, the first objective is to design three different types of plasma systems and use different plasma conditions to check the feasibility of carbon nanostructure synthesis with different morphology and dimensions, and optimise the growth conditions. Two systems should deposit carbon nanostructures from the vapour phase, while the last one should use a solid precursor, e.g. polymer, to synthesise carbon nanostructures. Reformation of polymer gels to the carbon nanostructure should be achievable using hydrogen-containing plasma based on the background literature. As an example, a mixture of argon and hydrogen low-pressure RF ICP plasma should be used in the surface reformation of resorcinol-formaldehyde-based polymer gels. As a part of Objective 1, plasma discharge conditions such as plasma power, plasma treatment time and gas mixture ratios are to be varied during the surface reformation process to identify their influence on the formation of carbon nanostructures (Chapter 3.1). A low-pressure radio-frequency inductively coupled plasma should

be designed in order to identify the growth mechanism of the carbon structures and to optimise the growth conditions. This objective is covered in Chapter 3.2. Furthermore, the nucleation and the initial growth structure and structural transformation processes on a suitable substrate should be systematically investigated. Among other parameters that influence the growth, Objective 1 looks at substrate temperature and the presence of catalytic material in detail. The chapter that covers this part of Objective 1 is Chapter 3.3. The findings of this objective are expected to identify the best plasma-based alternative approach for designing advanced carbon nanostructures directly on solid substrates.

Objective 2: Designing surface-engineered carbon nanostructures using plasma-enabled heteroatom doping and plasma surface functionalisation.

Surface engineering of carbon nanostructures is critical for potential applications. Conventional chemical and physical surface engineering is challenging due to uncontrollability of precise surface modification. Therefore, applying a reliable plasma-enabled approach is a key for designing surface-engineered carbon nanostructures with desired functionalities. Additionally, surface engineering after the growth of carbon nanostructures could enable better control over the modification. Surface engineering of carbon nanostructures should be achievable by heteroatom doping, atomic etching and surface functionalisation. Thus, the carbon nanostructures should be subjected to surface modification after the growth process. The heteroatom doping and functionalisation should be fulfilled by exposing carbon nanostructures to nitrogen-containing plasma, e.g. low-pressure nitrogen or ammonia RF plasma could have the desired effects. Nitrogen plasma treatment should result in the formation of nitrogen-incorporated carbon nanowall, while ammonia plasma treatment results in the formation of amino-functionalised carbon nanowall along with incorporated nitrogen. Different plasma post-treatment conditions should be investigated to control the concentration and configuration of nitrogen groups and identify the role of structural defects for the successful nitrogen incorporation mechanism. Together with the outcomes, the most probable nitrogen incorporation mechanism in graphene lattice should be illustrated. The objective is covered in Chapter 4.1. In a second case, entangled carbon nanotubes deposited on polyurethane membrane should be treated with inert plasma using an atmospheric pressure plasma jet system for surface modification. The part of Objective 2 covers the effect of mild plasmas at atmospheric conditions on the surface of carbon nanostructures. Therefore, mild plasmas, like argon and helium, should be tested and comprehensive analysis of the effects done. Findings of this part of objective are explained in Chapter 4.2. The effect of plasma treatment on the surface of carbon and plasma-induced changes in electrical properties should be revealed in Objective 2. These findings are expected to identify the ability of plasma for the controlled surface engineering of carbon nanostructures.

Objective 3: Design hybrid electrodes by tailoring-plasma designed carbon nanostructures with pseudocapacitive materials.

Surface-engineered carbon nanostructures are promising platforms for designing advanced functional materials by combining them with pseudocapacitive materials. These functional materials can be used as suitable electrode materials for different energy storage applications. Therefore, suitable pseudocapacitive materials must be identified for combining with plasma-

designed carbon nanostructures. The plasma-deposited carbon nanostructures should be considered for designing hybrid electrodes. A low-temperature thermal annealing technique should also be considered along with the plasma techniques to design the hybrid electrode. Different types of electrode fabrication techniques should be used. In the first approach, carbon nanostructures should be deposited on a catalytic conductive substrate using plasma techniques explained in Objective 1. Then these plasma-designed carbon nanostructures should be directly exposed to sulphur-containing gas for a low-temperature treatment. In the second approach, the plasma-designed carbon nanostructures should be treated with nitrogen plasma and then exposed to sulphur treatment. In both cases, sulphur-treated plasma deposited and plasma surface-engineered carbon nanostructures should be analysed with standard characterisation techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Raman spectroscopy for understanding the chemical and physical characteristics. Together with the thermal annealing technique, different plasma-enabled approaches explained in Chapter 3 and Chapter 4 are expected to design advanced hybrid electrodes in Chapter 5.

Objective 4: Exploring the energy storage performances of the designed carbon nanostructure-based hybrid electrodes.

The electrochemical energy storage performance of designed electrodes is a critical factor in exploiting the tested plasma-enabled approach for further applications. The information about the specific capacity and cyclic stability of the designed materials are key factors for accepting the material in energy storage-related industries. Therefore, we have planned to investigate the energy storage performance of the prepared electrodes as an active material for lithium-ion batteries and supercapacitors as Objective 4. The energy storage performance of the electrodes should be evaluated by obtaining specific capacity, rate capability and cyclic stability during the electrochemical reaction using galvanostatic charge/discharge curves, cyclic voltammetry, and electrochemical impedance spectra analyses. Further electrochemical kinetic studies should be conducted to understand the electrochemical charge storage mechanism of the electrode materials. The part of Objective 4 to understand the electrochemical features of the prepared carbon-sulphide hybrid electrode for supercapacitors based on the electrochemical performances is presented in Chapter 5.1. At the same time, the charge-storage properties of the electrodes for lithium-ion batteries are shown in Chapter 5.2. Both research studies are anticipated to reveal the potential of plasma-designed carbon nanostructures-based hybrid electrodes for delivering high electrochemical performances, as aimed in Objective 4.

Considering the advantages, motivation and objectives of the experimental research work, this dissertation exposes the capability of different cold low-pressure plasma for the precise structure-controlled synthesis and doping of different 1D, 2D or 3D carbon nanostructures, resulting in carbon hybrid nanostructures. Also, exploring the possibilities of using these hybrid structures as advanced electrodes for energy storage such as supercapacitors and batteries.

Chapter 2

Oriented Carbon Nanostructures by Plasma Processing: Recent Advances and Future Challenges

This chapter critically reviews plasma-enabled synthesis and processing techniques for designing hybrid carbon nanostructures. Despite being already used for the synthesis of carbon nanostructures; plasma techniques are not yet regarded as “conventional techniques”. Conventional chemical and physical techniques, including chemical vapour deposition, exfoliation, and hydrothermal processes, are widely used to synthesise and process carbon nanostructures. However, the large scale application of these techniques is limited due to their requirement of high-temperature, low control over the structural quality nanostructure, and high time consumption. On the contrary, plasma-enabled techniques are presented as a promising fast, and facile environmentally friendly approach for the synthesis and designing of carbon nanostructures, which overcome the majority of drawbacks of the conventional techniques. Besides, plasma-enabled techniques, especially at low-pressure, allow the designing of high-quality carbon nanostructures. These techniques also offer the post-processing of the synthesised structures, including incorporation, doping and functionalisation of carbon materials with heterogeneous atoms or functional groups. Furthermore, this chapter provides an overview of the currently available plasma techniques for designing hybrid carbon nanostructures and highlight the basic principles and state-of-the-art low-pressure plasma techniques for synthesising and processing carbon nanostructures with a focus on two-dimensional carbon nanostructures.

This chapter addresses thesis Objective 1.

Regarding my contribution: I made the extensive literature review and wrote the complete initial version of the paper by comparing the current trends in plasma-enabled techniques for designing hybrid carbon nanostructures.



Review

Oriented Carbon Nanostructures by Plasma Processing: Recent Advances and Future Challenges

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Abstract: Carbon, one of the most abundant materials, is very attractive for many applications because it exists in a variety of forms based on dimensions, such as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D). Carbon nanowall (CNW) is a vertically-oriented 2D form of a graphene-like structure with open boundaries, sharp edges, nonstacking morphology, large interlayer spacing, and a huge surface area. Plasma-enhanced chemical vapor deposition (PECVD) is widely used for the large-scale synthesis and functionalization of carbon nanowalls (CNWs) with different types of plasma activation. Plasma-enhanced techniques open up possibilities to improve the structure and morphology of CNWs by controlling the plasma discharge parameters. Plasma-assisted surface treatment on CNWs improves their stability against structural degradation and surface chemistry with enhanced electrical and chemical properties. These advantages broaden the applications of CNWs in electrochemical energy storage devices, catalysis, and electronic devices and sensing devices to extremely thin black body coatings. However, the controlled growth of CNWs for specific applications remains a challenge. In these aspects, this review discusses the growth of CNWs using different plasma activation, the influence of various plasma-discharge parameters, and plasma-assisted surface treatment techniques for tailoring the properties of CNWs. The challenges and possibilities of CNW-related research are also discussed.

Keywords: carbon nanostructures; carbon nanowall; graphene nanowall; plasma-enhanced chemical vapor deposition

1. Introduction

The unusual characteristic properties, from structural and morphological to electrical, of two-dimensional (2D) carbon nanostructures have made them an attractive material for a wide range of applications. Their investigation was started in the early 1980s after various carbon nanostructures

were distinguished based on their dimension. Fullerene, which belongs to a zero-dimensional (0D) carbon nanostructure, was reported first [1], followed by one-dimensional (1D) carbon nanotubes (CNTs). Carbon roses were the first reported 2D carbon nanostructures [2]. Then, the first vertical sheet-like structures, that is, carbon nanowalls (CNWs)/graphene nanowalls (GNWs), were reported in 2002 [3]. However, the actual development of 2D material research started to bloom with the isolation of graphene in 2004 [4] and the later realization that 2D carbon nanomaterials are composed of graphene sheets in various compositions. The milestones in carbon nanostructure research are shown in Figure 1. The importance of graphene is that it is the building block of many carbon nanomaterials: Fullerene (0D) is graphene wrapped in a sphere, CNTs (1D) are graphene rolled into tubes, and CNWs are graphene sheets with open boundary and sharp edges normal to the substrate surface. All these structures can be single-layered or multilayered graphene sheets with different interlayer spacing. CNWs are self-assembled, vertically-oriented arrays of open boundary structured few graphene sheets, which are separated with an interlayer spacing of several nanometers and with a large surface area. Their height is in the range of 1–2 μm , with a thickness in the order of several nanometers. Good thermal and electrical characteristics with a high mechanical stability of CNWs make them an attractive material for a wide range of applications, such as catalyst supporters for fuel cells [5,6], catalytic activity towards oxygen reduction reaction [7], battery electrode materials [8–10], templates for fabrication of nanostructures [11–13], gas sensor materials [14], resistive switching memory devices [15], field emission devices [16–18], and superhydrophobic surfaces [19].

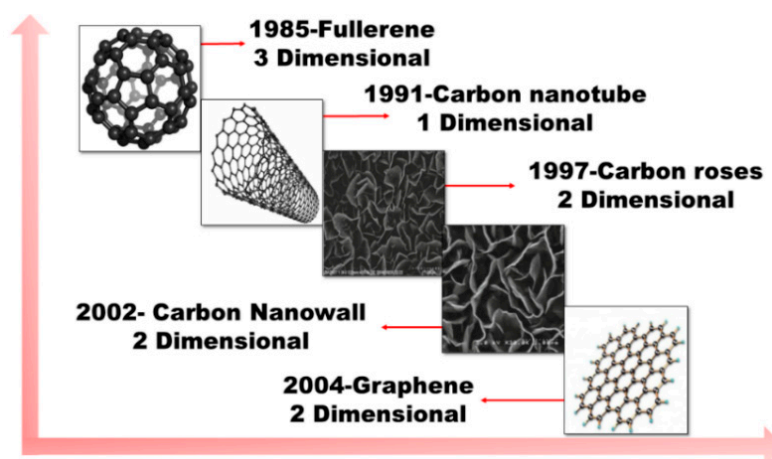


Figure 1. Milestones in carbon nanostructure research.

The conventional micromechanical exfoliation, chemical vapor deposition (CVD), and epitaxial growth techniques have been used for the synthesis of single- or multilayered graphene and other 2D graphene forms [20]. However, none of these techniques are assured regarding the structure quality, size control, and rate of growth; exfoliation techniques suffer from structure defects, the shape, and uncontrollability of size. Thermal CVD techniques enable the growth of high-quality 2D carbon nanostructures, but the synthesis is limited due to the need for very high temperatures in the range of 1000–1700 $^{\circ}\text{C}$ [21–23]. Epitaxial growth also requires a high temperature (1500 $^{\circ}\text{C}$) for the growth process to attain the high-quality 2D carbon nanostructures [23]. This indicates that all these techniques are not able to supply a large-scale synthesis and processing of 2D carbon nanostructures which would be needed for industrial applications. Thus, improved techniques are needed. One of them could be a group of synthesis methods connected with reactive gaseous plasma. There are already many reports on plasma or plasma-assisted synthesis of 2D carbon nanostructures, including CNWs, few-layer graphene sheet (FLG), graphene, etc. [3,24–28]. As different applications demand specific material properties, the way in which CNWs are synthesized matters greatly. Plasma-enhanced chemical vapor deposition (PECVD) has already been shown to deposit high-quality CNWs [29,30]. During PECVD, one can control the growth rate of CNWs by controlling the discharge parameters of plasma

(gas selection, power density, substrate material and temperature selection, etc.) [31]. The ability to alter the physical and chemical properties of material simultaneously during deposition is one of the main advantages of plasma techniques. The properties can be modified by surface functionalization, exchange of atoms in the crystal structure (e.g., material doping), and defect density control. Compared to conventional chemical synthesis routes, plasma-based techniques also offer the large-scale synthesis of 2D carbon nanostructures [32].

Compared to other established synthesis techniques, plasma offers control over the growth of CNWs, with enhanced physical and chemical properties at large-scale. As such, this paper will try to describe the general principles of plasma-enhanced synthesis of oriented 2D carbon nanostructures and finding the influence of different discharge parameters on nanostructure growth. Furthermore, it will deal with plasma parameters and particles and present how this knowledge can be useful in plasma chemistry for the functionalization of CNWs, which can be done after synthesis or even during growth itself. In addition to functionalization, the study will also immerse into finding the advantage of plasma techniques for doping the CNWs. The review will conclude with identifications of challenges and possibilities of plasma-assisted CNW synthesis and their future applications.

2. Plasma: Potential Approach for Carbon Nanowall (CNW) Synthesis

Plasma synthesis of CNW can follow two paths: Either deposition of carbon species and followed growth of CNW or restructuring of carbon material and growth of CNW on top of it. The first one is plasma vapor deposition, and it is the most common; thus, the majority of this chapter will be about that. The general principle of PECVD techniques for CNW growth is the gas phase deposition process, where the carbon source gas is introduced into the plasma, where it gets chemically activated through partial ionization, dissociation, and even electron excitation. These radicals are then transported to the substrate at optimal condition, namely optimal substrate temperature, and the synthesis of nanostructured CNWs occurs.

Plasma is generated by the application of a strong electromagnetic field, which accelerates electrons to collide with the neutral gas. This leads to the dissociation, ionization, and excitation, which form numerous species—more electrons, ions, photons, and radicals, as well as excited background gas. Based on the electron temperature, plasma can be distinguished as high-temperature plasmas (above 10 eV) and low-temperature plasmas (<1 eV). Another criterion is based on the temperature which separates into equilibrium and nonequilibrium plasmas, where the temperature of ions is equal to the electron temperature in the former, and nonequal in the latter case. Plasmas can also be atmospheric or low-pressure (10^2 – 10^4 Pa). When plasma is used for material synthesis or processing, each of its particles play a significant role: (1) Energetic ions cause sputtering of material, elevate the substrate temperature, and increase surface diffusion; (2) electrons are involved in the chemical reactions by supplying activation energy; (3) photons which are generated during the de-excitation of the plasma molecules, atoms, and ions heat the substrate and take place in the photochemical reactions; (4) highly reactive radicals are deposited and react with the substrate or chemically etch the sample; (5) a fraction of the undissociated source gas is also involved in chemical reactions on the substrate [33]. Additionally, one can further influence ion and electron energy by biasing the sample and chemical reactions on the surface through external heating of the sample. These various factors make plasma a versatile tool for chemical synthesis, deposition, and surface treatment. The combination of plasma species–substrate interactions also enables a wide selection of substrates, since many chemical reactions and deposition processes can occur at much lower temperatures compared to, for example, thermal CVD, which occurs at a temperature above 1000 °C [34]. In this aspect, low-temperature and low-pressure PECVD techniques have emerged as an important method for the large-scale synthesis of CNWs.

A PECVD method is a system with typically low pressure to control the purity of the deposition. However, there can be different plasma sources, power supplies, and antenna combinations, which have different characteristic properties, and consequently, CNW depositions have different features. A PECVD system mainly consists of three major parts; they are (i) plasma generator (plasma source and antennas); (ii) gas (precursor and etchants); (iii) vacuum heating chamber, usually a quartz tube (substrate placed, and plasma interactions occur for the deposition). Based on the plasma generators, plasma sources, such as a microwave (MW), radio frequency (RF), direct current (DC), and their combinations, are widely used for CNW synthesis. Figure 2 shows the different plasma systems for the growth of CNWs based on the plasma sources. Microwave plasma-enhanced chemical vapor deposition (MWPECVD) is a high-frequency plasma system with a MW generator that has a frequency of approximately 2.45 GHz. The MW is generated from the MW source and coupled to the vacuum heating chamber either via a traverse rectangular cavity guide or using an external antenna, which produces a higher electric field effect inside the chamber. The wave propagation mode in the traverse rectangular cavity guide coupled MW system is transverse electric mode (TE). The electromagnetic waves in the waveguide interact with the plasma discharge to form a standing wave. An external tuner is used for controlling the waveguide length to attain the maximum electric field in the growth region. In TE mode, the electrons do not experience any change in the electric field and gain energy through the collision between background gases. The low dimension (wavelength) of the collimated MW drives the TE mode to attain the maximum electric field, which increases the electron-neutral collision and produces radicals for the deposition process. The TE–MWPECVD system is typically operated under 100–600 W. The high power may damage the quartz tube and vacuum system. The quasi-optical nature of MW made them difficult to confine and leads to diffraction in the tube, which results in the lower growth rate and non-uniformity in the morphology of CNWs. An external antenna is placed to the vacuum chamber used to couple the dominant cylindrical waveguide to the system through transverse magnetic (TM) mode wave propagation. This external antenna can increase the intensity of the electric field at the substrate surface placed inside the chamber in the form of a plasma ball. This plasma ball covers the substrate entirely and helps to control the substrate temperature and promotes the uniform growth of CNWs [29,35].

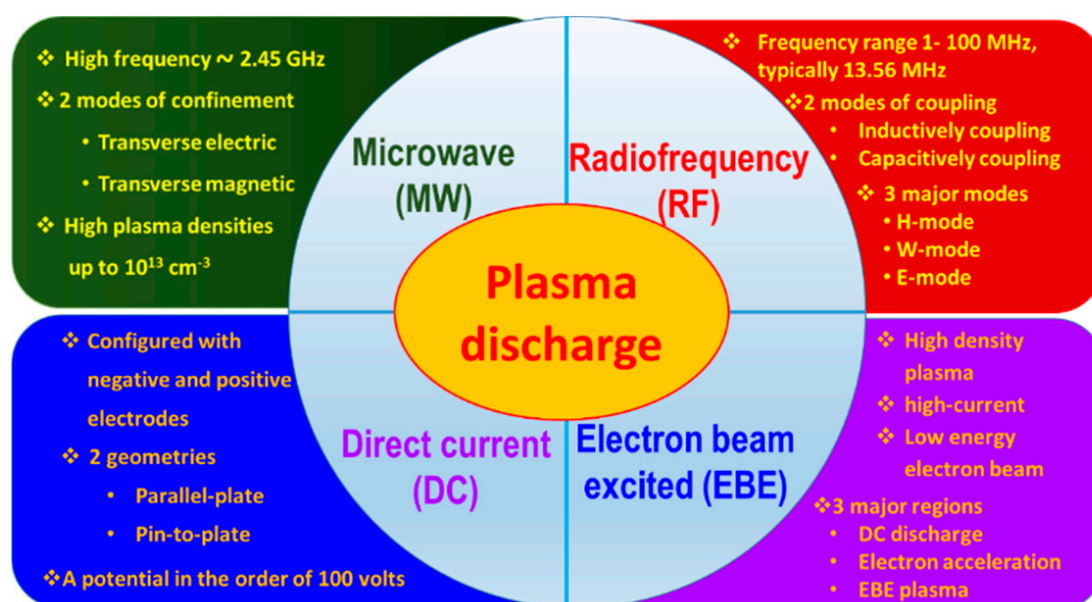


Figure 2. Different plasma systems for the carbon nanowall (CNW) growth.

RF plasma systems are another type of AC plasma system, where RF waves with a frequency in the range of MHz (typically 13.56 MHz) are coupled to the plasma sources by two different antennae; they are inductively coupled plasma (ICP) and capacitively coupled plasma (CCP). The energy from the RF generator to the plasma system is coupled through these couplings in three modes, that is, evanescent electromagnetic mode (H), propagating wave mode (W), and electrostatic mode (E) [35]. In ICP systems, the energy from the RF generator is coupled through the inductive coils, which stimulates the magnetic field in the ICP discharges. Azarenkov et al. proposed that the discharge length and plasma densities in an RF system can be varied by changing the external magnetic field and keeping other plasma parameters fixed [36]. This magnetic field induces a low amount of high-frequency electric field for the ionization, which is suitable for operating under low pressure. Based on the geometry, different antennas used in an ICP system for the plasma discharge are distinguished into two types: Planar geometry and cylindrical geometry. In a planar geometry, a coil antenna of flat metal is used as the electrode. In cylindrical geometry, an inductive coil is surrounded on the quartz tube. Here, the inductive coil can produce partially longitudinal transverse electromagnetic waves by changing the magnetic field, which is coupled with evanescent electromagnetic waves (H-mode) to plasma. In helicon plasma systems, the coil is coupled to the RF generator through the helical spring-like structure, and a propagating wave (W-mode) helicon plasma is obtained by the effect of the magnetic field (100–300 G) [35]. A theoretical study to optimize the various antennas as a potential plasma source to produce IC plasma by Gogolides et al. stated that, the electric field was scale with the number of loops of the coil for a constant current [37]. Compared to the ICP systems, a CCP system consists of two parallel plate electrodes, where the electrostatic waves (E-mode) are produced in between these two parallel plate electrodes, which are capacitively coupled to the RF source for the plasma discharge. ICP plasmas have more advantages compared to the plasma produced by CCP mode, that is, they are capable of producing very high electron density and reactive species (up to approximately two orders of magnitude higher than the standard CCP plasmas under a similar plasma condition), self-regulating control of the ion energies due to the collision, low electron temperature, and plasma sheath potential, with uniform plasma discharge parameters along the radial and axial directions [38]. Due to the lower electron density and electron energy in CCP mode, successful growth of CNWs became hard using a capacitively coupled plasma-enhanced chemical vapor deposition (CCPECVD) system as an independent source [39,40]. Therefore, CCP mode is usually combined with other high-density plasmas for attaining a higher growth rate of CNWs. The combinations of different modes with CCP widely used for enhancing the CNW growth are: CCP+ICP, CCP+MW, and CCP+IC H₂ [41,42]. In all these combinations, the carbon-containing gases are dissociated to form radicals by the electric field produced between parallel plate electrodes [42].

Compared to the two abovementioned plasma systems, plasma in a direct current (DC) system is produced by the glow discharge between two electrodes (cathode and anode) when DC passes through the gas in between the electrode. The DC glow discharge can be produced between the electrodes in two modes: (i) Parallel-plate and (ii) pin-to-plate. In a parallel plate DC discharge, a sufficient potential is applied between two parallel plate electrodes to break down the gas composition. The ionization of gas molecules increases by increasing the electric field between the electrodes, and the glow discharge is produced. A strong electric field and an ion flux between the electrodes enhance the growth rate and orientation of the CNWs. In an asymmetrical pin-to-plate electrode system, a sharp pin (typically tungsten) is attached to a planar electrode, and the high-intensity electric field is produced near the tip. This high electric field enhances the ionization rate of gas molecules and helps with the massive production of CNWs [14,43]. DC power sources are also used for the plasma discharge in electron beam excited plasma (EBEP) to achieve high-density plasma, where the plasma is produced by a high-current and low-energy electron beam. The electron current is controlled by the discharge current and electron beam energy is controlled by accelerating voltage. An electron beam excited plasma-enhanced chemical vapor deposition (EBEPECVD) system mainly consists of a DC plasma discharge region, electron acceleration region, and EBEP region. A cathode (usually

LaB₆) produces electrons and sustains the DC plasma to extract an electron beam. The electron beam causes the dissociation of gas molecules by providing sufficient energy. EBEP enables the production of highly ionized plasma at low pressures by adjusting electron beam energy close to the maximum electron impact ionization energy of the source gas. The higher density of source gas inside the EBEP system increases the pressure inside the chamber, which assists in controlling the morphology of CNWs [44,45]. In addition to these plasma-enhanced deposition techniques, several reports on the growth of carbon nanostructures and graphene flakes have been successfully demonstrated by arc discharge plasma [46,47]. The first reported petal-like 2D carbon nanostructures were also synthesized by arc discharge. However, the lack of available literature on the vertical growth of CNWs through arc discharge plasma shows that the focus on CNW growth through arc discharge plasma is not exploited well. All these plasma systems mentioned above imply that the large-scale production of CNWs is highly influenced by the density of plasma activated species. The effect of plasma-activated species on the growth of CNWs will be discussed in the forthcoming sections of this review.

A summary of the CNW depositions with different plasma sources and discharge parameters that were reported is in Table 1. The extensive studies on the growth of CNWs using different plasma sources reveal that the structure and morphology of CNWs can be altered by varying the gas proportion and gas flow rate. A higher flow of gas mixtures gives a higher growth rate of CNWs and higher rate of etching effect. However, a higher concentration of gases inside plasma systems increases the pressure inside the plasma system, which degrades the stability of plasma discharge and retards growth. Plasma surface interactions can heat the substrate surface to a certain extent, which also influences the morphology and structure of CNWs. However, the presence of energetic electrons and other active species in plasma keep the heat effects lower compared to thermal CVD. CNWs with a similar morphology can be synthesized by varying discharge parameters and plasma sources. On the other hand, similar plasma sources with different discharge conditions provide the opportunity to synthesize CNWs with a different morphology, interlayer spacing, height-uniformity, and thickness. For example, considering the works reported on MWPECVD-synthesized CNWs, the features of CNWs were changed by varying the flow rate, growth time, and temperature [3,25,26,48]. Alternatively, vertically-oriented CNWs with similar features were reported using two entirely different plasma systems; radio-frequency capacitively coupled plasma-enhanced chemical vapor deposition (RFCCPECVD) and direct current plasma-enhanced chemical vapor deposition (DCPECVD) and at different growth time [41,45,49]. CNWs with similar structural properties were reported using the same plasma source, the source gas, and plasma power but varying growth time and flow rate of gas [3,25]. On the other hand, CNWs with different morphologies were synthesized using different source gases and growth temperature [31,50]. In general, it was found that the morphology of CNWs was greatly influenced by the high density of carbon atoms, temperature, and pressure inside the plasma system. In all these cases, high-density MW, radio-frequency inductively coupled plasmas (RFICP), and DC plasmas are mainly used for the production of a large number of carbon dimers (C₂ radicals) and hydrogen radicals for the deposition process. All the RFCCP systems are combined with either a high-density ICP system or external radical injections to achieve a large number of H radicals to remove the amorphous carbon (a-C) phase. Furthermore, in all cases, the substrate temperature is kept below 400–850 °C for the vertical growth of CNWs, which is much lower than the average temperature of the thermal CVD process (operational temperature 1200 °C).

Table 1. Overview of plasma-enhanced syntheses for different two-dimensional (2D) carbon nanostructures *.

Plasma Source	Source Gas	Parameters					Nanostructure and Characteristics	Ref.
		Temperature (°C)	Pressure (Torr)	Flow Rate (sccm)	Growth Time (min)	Power (W)		
MW	CH ₄ :H ₂	650–700	1	40:10	8–10	500	CNW, Uniformly oriented carbon sheets	[3]
	acetylene, ammonia	High	10	Flow ratio <1	10	500	CNW, Grape like and aggregate structure	[24]
	H ₂ , CH ₄	-	1.7	80:20 and 80:5	0.17–15	500	CNWs with a higher growth rate	[25]
	CH ₄ /H ₂	700	40	200 sccm Ratio: 1:8	1–50	2000	FLG, vertically-aligned sheets with thickness 4–6 atomic layers	[26]
	CH ₄ /H ₂	350	2.2 × 10 ^{−3}	-	10	1300	CNWs with 660 nm height	[51]
	CH ₄ , H ₂ , Ar	100–400	<1 Torr	30, 50, 20	1–2	16,000	Graphene sheets, A continuous graphene film with 294 mm width	[27]
	C ₂ H ₂ :Ar	240	<1 Torr	10, 200	2–4	1200	Few layer graphene sheets with spacing 0.345 nm	[28]
	CH ₄ /H ₂	450–700	20	80:1	1	1400	High-quality centimeter scale graphene sheet	[48]
	He, H ₂ , CH ₄	680	atm	1, 25, 25	30	350	Vertically grown carbon nanowall	[31]
RFICP	CH ₄ , H ₂ /Ar	Low	1	1100	0–60	600	High-quality graphene layers with significant growth kinetics	[52]
	CH ₄ /H ₂	680	90 mTorr	0:100–95:5	-	900	Free-standing sub-nanometer graphite sheets	[53]
	CH ₄ , Ar	700–850	10–60 mTorr	7, 1.4	30–60	500	The growth of carbon nanowalls	[45]
	Al(acac) ₃ , Ar	350, 425, 500	8 Pa	1.66, 40	50	500	CNWs with different structures	[50]
RFCCP	C ₂ F ₆ , CH ₄ , CHF ₃ , C ₄ F ₆ , and H ₂	500	100 mTorr	Carbon precursor: 15, and 30	3–8 h	400	Vertical growth of carbon nanowalls	[41]
	C ₂ F ₆ , H ₂ (Radical injection)	600	0.1–1.2	50, 100	30 Min–10 h	MW/VHF 250/300	The highly reliable growth of carbon nanowall	[42]
	C ₂ F ₆ , H ₂	580	1.2	50, 100	30 s to 60 min	MW/VHF 250/270	Vertically standing CNWs with a uniform height	[49]
RF plasma beam	C ₂ H ₂ , H ₂ , Ar	700	0.0075–2.25	1–20, 1–20, 100–1000	60	50–500	CNWs with large surface area and sharp edges	[54]
	Ar, H ₂ , C ₂ H ₂	200–700	1	1050, 25, 1	60	300	Various nanostructures including CNWs	[55]
EBEP	CH ₄ /H ₂	570	10–30 mTorr	-	10–90	Electron-voltage ~60–100 V	Vertically aligned well definite CNW	[45]
DC	Ar:H ₂ , CH ₄ , Ar	700	atm	1000, 0.15, 1.35	30 s–10	0–10 kV	CNWs	[56]

* Al(acac)₃: Aluminium acetylacetonate, MW: Microwave, FLG: Few-layer graphene sheet, RFICP: Radio-frequency inductively coupled plasma, RFCCP: Radio-frequency capacitively coupled plasma, RF: Radio frequency, EBEP: Electron beam excited plasma, DC: Direct current, VHF: Very high frequency.

Carbon-containing aromatic compounds were also successfully employed for the large-scale growth of CNWs. Lehmann et al. described the growth of CNWs using paraxylene as the precursor in an RF-ICP system [57]. The morphology of carbon nanostructure changes from nanofibers, nanowalls to interconnected nanowalls concerning the flow rate decreases from 5 mL/h to 0.5 mL/h. It was observed that the number of defects in the carbon nanostructures increased with the decrease in the flow rate. The interconnected CNWs contain atomic defects, mainly due to the twisting and bending of nanowalls in different directions, were formed at a low flow rate. Giese et al. reported the growth of CNWs from a single source metal organic precursor $\text{Al}(\text{acac})_3$ using an RFICP system [50]. The powdered form of the precursor was transported into the chamber using an evaporator bed with the assistance of Ar gas. The growth of CNWs was explained by the function of substrate bias and substrate temperature. The curled thin CNWs with the large surface area, higher wall height, and higher surface densities were deposited at the highest value of temperature and bias. The solid aromatic precursor provides an advantage to dop metallic nanoparticles in the CNW lattices with a uniform distribution. Bundaleska et al. reported the advantage of the aromatic precursor, containing functional groups to achieve CNW growth with a higher number of defects [58]. The mixture of ethanol and ammonia was used in an MW atmospheric condition for the growth and nitrogen doped CNWs were deposited on the substrate. Therefore, the growth of CNWs from aromatic precursors containing different functional groups would be a potential method to control the growth in the desired manner; with functional entities, uniform height distribution, etc.

An alternative plasma synthesis to PECVD is the direct surface growth of CNWs from a bulk carbon precursor using plasma-assisted carbonization. Ostrikov et al. reported a method for the growth of vertical graphene sheets (VGS) from natural honey [59]. A Si substrate was coated with liquefied honey and loaded in an RFICP system. An $\text{Ar}:\text{H}_2$ gas mixture with a flow rate of 10:7 sccm was used for surface treatment on honey. After 10 min of carbonization, VGS grew with an average sheet length of 200–300 nm and graphitic edges composed of 5–6 graphene layers. In a similar process, Ostrikov et al. reported the vertical growth of graphene sheets using melted honeycomb as the precursor [60]. The growth of vertical graphene was carried out in the same conditions as above and showed an average length of 200 nm and a thickness of 2 μm for nanowall. Similar to the PECVD mechanism, these reports also state that the substrate temperature of the growth process is very low (400–450 $^\circ\text{C}$) compared to thermal CVD.

From all the results mentioned above, CNWs possess a common morphology, even when synthesizing with different plasma techniques and at extremely different growth conditions. Thus, it is very important to understand the general growth mechanism of CNWs. In this review, an attempt is made to explain the general mechanism of CNW growth and the influence of different factors on growth and morphology. The upcoming sections are discussing the impact of various discharge parameters (gas species, plasma power, electric field, and substrate temperature) on the growth mechanism of CNWs.

3. Growth Mechanism of Vertically-Oriented Carbon Nanostructures in Plasma-Enhanced Chemical Vapor Deposition (PECVD)

The common morphology of CNWs arises due to the common mechanism for the growth of CNWs, which can proceed through the production of radicals in plasma, plasma–surface interaction, nucleation, and coalescence of carbon radicals and area selective growth to the vertical orientation. A schematic diagram of the CNW growth mechanism is shown in Figure 3.

The ignition of plasma inside the chamber affects the initiation of CNW growth through the ion-stimulated plasma–substrate surface interaction and production of specific radicals for the growth through the dissociation of gas molecules. The substrate used for the deposition is in direct contact with the plasma and, thus, the ion stimulated plasma–surface interaction creates defects on the substrate surface, which acts as an immobilized free radical capable of forming dangling bonds with the radicals produced from the plasma. On the boundary between plasma and surface, a self-organized plasma

sheath is formed, which modifies the energy and flux of the radicals to move towards the substrate to initiate the deposition. Formation of the nucleation site for vertical growth is the first step. The radicals dissociated from the gas source are absorbed or migrate to the surface and are attached to the defects via the dangling bonds. Absorption of this radical species in the early stage of growth forms a thin layer of carbon film with a thickness 20 nm parallel on the substrate called a buffer layer [61,62] (some authors report it as the carbidization layer [26] or graphitic layer [63]) composed of both graphitic and amorphous carbon. Along with the growth time, more carbon radicals get dissociated and attach to this layer in the form of carbon nanoislands, where nucleation initiates. These nanoislands or vertical graphene nuclei (VG nuclei) also have a dangling bond to attach more carbon atoms to it and act as the nucleation center for the growth of nanosheets. When a sufficient level of force is acquired at the grain boundaries of the sheets, it leads to curling the edges of top layer sheets vertically along with the direction of the electric field. The curling of the nanosheets to the vertical form is highly influenced by the plasma sheath, since the sheath contains a large number of incoming carbon species with high surface mobility and induces an electrical field perpendicular to the substrate. These vertically-oriented sheets grow faster compared to the parallel sheet, since the reactive carbon species are attached to the vertical graphene sheets more easily, and coalescence occurs. Thus, the parallel graphene sheets are shadowed by this faster vertical growth [64]. Eventually, the height of the graphene sheets increases with the growth rate rather than the thickness, resulting in the formation of nanowall. The growth of nanowalls increases with the growth time and they are grown throughout the substrate to form an interconnected structure with finite interlayer spacing [63]. The significant species responsible for the initiation, coalescence, and orientation has not yet been revealed well. However, radicals with high surface diffusion, such as carbon and small hydrocarbon/fluorocarbon (HC/FC) molecules, can provide edge growth of the CNWs.

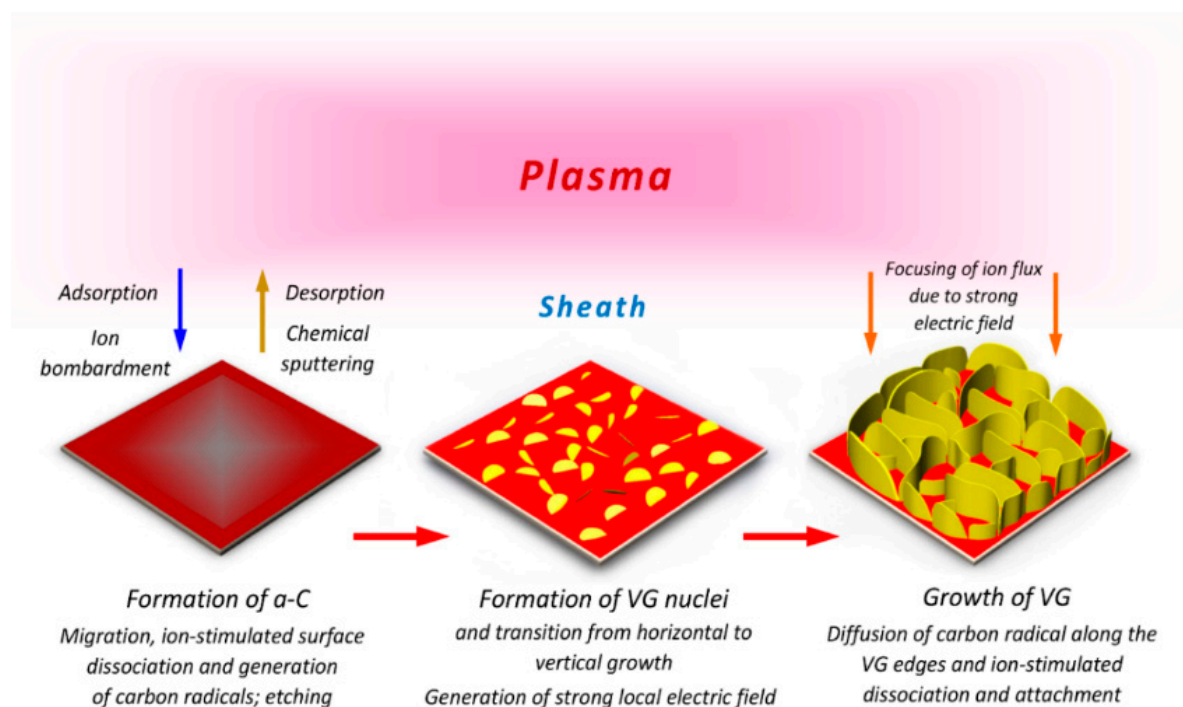


Figure 3. Schematic diagram of a plasma-enhanced deposition.

Baranov et al. developed a theoretical model to investigate the key factors for the growth of vertically-oriented CNWs [65]. The model gives an insight into the processes taking place in the nucleation and orientation of CNWs in plasma systems. These calculations are fitted to a larger number of experimental data from various authors to match the macroscopic parameters to the

microscopic growth process. This study proposes that ion bombardment and ion flux highly influence the growth of CNWs. Furthermore, the model agrees with the influence of surface activation via defect formation for the nucleation. The influence of the electric field on the vertical growth also confirms this and proposed that focusing ion current to the edges enhances the edge growth. This model also suggests that the sophisticated control over all these parameters will allow the formation of larger and denser arrays of CNWs. However, plasma surface interaction and surface activated defects can influence the growth mechanism up to the formation of the buffer layer [66]. Therefore, it is very important to understand the effect of various plasma-discharge parameters on the initial and vertical growth of CNWs after buffer layer formation. Apart from the plasma–surface interactions, the composition of plasma gases also determines the quality of prepared CNWs. In addition, there are other important parameters with which one can influence the CNWs' growth and quality: Electric field determines the vertical orientation; growth time regulates the height of CNWs; temperature of substrate and gas pressure influence the morphology and growth rate; concentration of carbon radicals determines the rate of the deposition and morphology, etc. All the flexibility of plasma deposition offers a variety of CNWs with different properties. However, it can be a challenge to find optimum parameters for the optimal growth of CNWs for specific needs.

4. Influence of Gas Sources and Gas Proportion

Considering the fact that CNWs are grown with a similar structure and morphology under various discharge conditions, reactive gas species play a key role in the growth of high-quality CNWs. The gaseous species for CNW growth can be classified as (i) carbon-containing precursor gases (HC or FC), which produce carbon radicals for the CNW growth via plasma-enhanced deposition; (ii) etchant gases for the removal of a-C (H_2 , O_2), to assist with the growth of high-crystalline CNWs; and (iii) dopant gases (N_2 , NH_3) when doping of CNWs is required. There is a variety of gas mixtures reported for the growth of CNWs, such as CH_4/H_2 [3,25], $Ar/CH_4/H_2$ [67], $Ar/C_2H_2/H_2$ [68], $Ar/C_2H_2/NH_3$ [69], CH_4/NH_3 [70], and C_2H_2/NH_3 [71]. Many more are listed in Table 2, together with the significant effect of radical species on the CNW morphology.

Table 2. Overview of different gases and plasma sources used for the synthesis of 2D carbon nanostructures and main influence of radical species *.

Precursor	Flow Rate (sccm)	Plasma Source	Structure and Properties	Effect of Radical Species
$CH_4:H_2$	20:80 & 5:80	MWPECVD	CNWs with higher growth rate with thickness 20 nm	Hydrogen radicals help the plasma ignition and enhance the growth rate by higher carbon dimer density [25]
	200 sccm Ratio: 1:8	MWPECVD	FLG, vertically aligned sheets with thickness 4–6 atomic layers	The average dimensions of the flakes reduce with increase in hydrogen flow compared to CH_4 flow rate [26]
	1:80, 1:40, 1:10	MWPECVD	High-quality centimeter scale graphene sheet	The flow of more CH_4 in a ratio of 80:1 leads to the production of high-quality graphene monolayer without defects [48]
	0:100–95:5	ICPECVD	Free-standing sub-nanometer graphite sheets	H radicals help with producing carbon nanosheets with thickness 1 nm with an average height of 250 nm [53]
	-	EBEPECVD	Vertically aligned well definite CNW	The height of the CNW increased by 3 times and spacing between individual layers increased by 5–10 times [45]
CH_4 , H_2 , Ar	3–7.5, 12.4, 10–50	ICPECVD	Ordered carbon nanostructures	The electron density growth influenced by the rise of argon density [72]
CH_4 & $Ar:H_2$	1 & 100 (90:10)	ICPECVD	High-quality graphene layers with significant growth kinetics	A single layer of graphene sheets formed due to the high H radical density with help to etch C atoms [52]

Table 2. Cont.

Precursor	Flow Rate (sccm)	Plasma Source	Structure and Properties	Effect of Radical Species
Ar:H ₂ , CH ₄ : Ar, OH radicals	1000, 0.15:1.35	DC-atm	CNWs	OH radicals effectively remove a-C, increases CNW crystallinity and enhance the initial nucleation process [56]
CH ₄ , Ar	7, 1.4	ICPECVD	The growth of carbon nanowalls	H and Ar radical helps to remove the amorphous carbon and CNW with a smooth surface, saturated morphology and thickness grown [31]
C ₂ F ₆ , CH ₄ , CHF ₃ , C ₄ F ₆ , and H ₂	15, and 30	CCPECVD	Vertical growth of carbon nanowalls	Injection of H radicals to the fluorocarbon radicals produce <i>sp</i> ² bonds on the surface and form a continuous network to form CNW [41]
C ₂ F ₆ , H ₂ , O ₂	50, 100, 256	CCPECVD	The highly reliable growth of carbon nanowall	O ₂ plasma chamber cleaning increases the growth of CNWs with good reproducibility [42]
C ₂ F ₆ , H ₂ , O ₂	50, 100, 5	CCPECVD (Radical injection)	Vertically standing CNWs with a uniform height	O ₂ influence the effective removal of amorphous carbon from the CNW surface and controlling the nucleation [49]
H ₂ , C ₂ H ₂ :NH ₃	100, Ratio < 1	DCPECVD	Vertically aligned carbon nanostructures	The high amount of NH ₃ in the system increases the etching rate by producing large H radicals and remove amorphous carbon between the structures [73]

* MWPECVD: Microwave plasma-enhanced chemical vapor deposition, ICPECVD: Inductively coupled plasma-enhanced chemical vapor deposition, EBEPECVD: Electron beam excited plasma-enhanced chemical vapor deposition, CCPECVD: Capacitively coupled plasma-enhanced chemical vapor deposition, DCPECVD: Direct current plasma-enhanced chemical vapor deposition.

The HC/FC gases and their mixtures with other gases (H₂, O₂, Ar, etc.) are the widely used carbon-containing gas sources for CNW growth, which dissociated in the plasma system to form various radicals, such as carbon dimers, small HC/FC radicals, and F/C radicals. Consider the HC precursor, which can effectively produce different hydrocarbon radicals as the provider of carbon dimer, by the plasma discharge. In the case of HC gases, for example, CH₄ containing gas can easily produce CH_x radicals as the C₂ provider for the CNW nucleation through the radical recombination and dissociation [74]. However, in C₂H₂ gas, carbon dimers were produced from the direct dissociation of HC≡CH with a strong C≡C bond [75]. The density of different radicals produced by different plasma sources may vary with the growth conditions, which further varies the morphological features of CNWs. In an RF plasma, a higher density of CH_x (x = 1, 2, 3) radicals mainly contributes to the production of carbon dimers. On the other hand, in an MW plasma, HC gas species are directly dissociated into CH_x and C₂ radicals with approximately equal densities. Most of all, the experimental investigations confirm the importance of C₂ radicals for the nucleation and coalescence of carbon nanosheets [75–77]. Investigations on the radical density of C₂ radicals in MW and RFICP systems shows that the radical density of C₂ ranging from 10¹¹–10¹³ cm^{−1} is favorable for the initial growth of carbon nanostructures [78,79]. The growth of CNWs in an RFICP system by supplying CH₄/H₂ and C₂H₂/H₂ gas mixtures was compared by Zhu et al. [53,77–79]. The thickness of the CNW synthesized using C₂H₂/H₂, and CH₄/H₂ gas species was about 1–2 nm and less than 1 nm, respectively. The higher thickness in the first case is mainly due to the higher density of C₂ radicals produced by the direct dissociation C₂H₂ gas. Teii et al. described an MW system that contains a large number of C₂ radicals for synthesizing CNWs even in the hydrogen-poor condition by employing C₂H₂/Ar/N₂ gas [75]. Similar to HC systems, FC gas mixtures are dissociating into a large number of CF₃ radicals, which are providing the carbon dimers for the CNW growth. However, the absence of H atoms in the system slows down the growth initiation due to the inefficient abstraction of fluorine from CF_x radicals to produce C₂ radicals. Therefore, an additional H source is coupled to the FC systems to achieve sufficient H radicals for the high-quality growth of CNWs. The mechanism of growth in the FC systems can briefly be described as: Production carbon atoms from fluorocarbon radicals, removal of F-atoms from carbon atoms by reacting with H radicals, migration or adsorption of C-atoms on the

substrate surface, and formation of nanoislands on the surface through dangling bonds. Finally, the nanostructure is continuously grown on the surface [49].

Following the precursor gases, etchant gases are mainly supplied to the system for the effective removal of the amorphous interface phase and to enhance the growth. As mentioned in the above section, the assistance of H for the abstraction of bonding atoms from the radicals on the surface is explained in various reports, mostly in the FC gas plasma [41,49,80,81]. The presence of H atoms in the plasma system assists in the nucleation of the carbon radical and simultaneously acts as the etchant gas for a-C [3,53,82]. Furthermore, H atoms are more reactive with a-C atoms than the sp^2 and sp^3 hybridized carbon atoms, which helps with the removal of the a-C phase and results in the formation of highly crystalline CNWs with sharp edges. Similarly, some reports show that oxygen and nitrogen also assist in the effective removal of a-C from the surface. Kondo et al. explained the effect of O_2 radicals on the successful growth and removal of a-C on the substrate [49]. The study investigated the nucleation and growth of CNWs using FC gases with and without the presence of oxygen. The presence of O radicals is capable of reducing the defects and suppressing the carbon nucleation and retarding the formation of the interface layer, which leads to the formation of carbon nanostructures without any interface layers. Additionally, O_2 promotes the vertical growth of CNWs from the nuclei by removing this horizontal interface nucleus. Hydrogen–oxygen combined OH radicals are also capable of removing the a-C carbon. The reports by Bo et al. [56] and Chateai et al. [83] indicate that OH radicals have much more capability than H atoms for the effective removal of a-C. The advantage of nitrogen as an etching agent was described by Chuang et al. by supplying C_2H_2/NH_3 as the gas source. Here, the NH_3 molecules dissociate into different radicals and provide sufficient H atoms for the efficient removal of a-C [73]. Neutral gases, like argon, are also supplied to the plasma system for enhanced CNW growth. Most of the MW-based growth by HC gases is assisted by the argon, since Ar has a higher excitation and ionization potential compared to hydrogen. Thus, the interaction between the plasma activated species and Ar is dominated by the elastic collisions and the energy loss through the inelastic collisions reduced. In this way, the addition of argon increases the electron temperature and enhances the plasma stability. Moreover, the addition of argon into the plasma system promotes the production of C_2 through the direct dissociation of gas sources. There are several reports observing that higher Ar concentration in the plasma enhances the carbon dimer concentration, which is a benefit in the high degree of graphitization [75]. The presence of Ar enables to provide the high-quality growth of CNWs by increasing plasma stability and moderating the growth rate. The main features of the influence of different gaseous species on the growth of CNWs are shown in Figure 4. Along with the source and etchant gases, some dopant gases are also used when CNWs requires doping. Doping of CNWs and surface functionalization of CNWs by various gases for tailoring the properties are discussed in detail in this review later. In addition to the mixture of source gases, the concentration of the gas species, the flow rate of gases, and the proportion of the gas, mixtures also significantly affect the nucleation and coalescence of CNWs.

The proportion and flow rate of gas into the plasma system also has a significant role in the growth of CNWs. The requirement of optimum concentration of carbon and the etchant gases for the growth mechanism was already discussed in the above section, which highly determines the structure, morphology, and properties of the CNWs deposited on the substrate. The experimental study on the influence of the concentration of carbon gases on the growth of CNWs was carried out by Wang et al. [84]. The concentration of precursor CH_4/H_2 gas was controlled by various flow rates (0–100%). The study reveals that the density of GNW sheets was highly influenced by the CH_4 concentration, which is responsible for the nucleation of carbon radical and initial growth. A higher nucleation rate with small lateral size was observed at a higher concentration of precursor gas (40–100%). The various structures of CNWs formed at the different CH_4 concentration are shown in Figure 5a–c. Wu et al. gave a good description of the effect of flow rate of the gaseous mixture on the growth mechanism [85]. Figure 5d–i shows the SEM images of different CNW morphologies according to different flow rates in his experiment. The CNWs were grown on Au (cc. 20 nm) coated

Si substrates using CH_4/H_2 as a precursor gas in an MWPECVD system at growth temperature of 650–700 °C. The impact of flow rate on the structure and morphology of CNW growth is observed by the varying flow rate of the CH_4/H_2 mixture from 30, 10, 6, 4, to 1 sccm. At 30 sccm, a-C with column structures was observed. A further decrease in the flow rate led to the evolution of tube-like carbon structures. Finally, the high-quality CNWs were formed at a flow rate between 4–8 sccm. Moreover, the further decrease in the flow rate led to the formation of a-C on the substrate. This indicates that the morphology of the final product, even in the same system with the same discharge conditions, was highly affected by the flow rate of gas into the system.

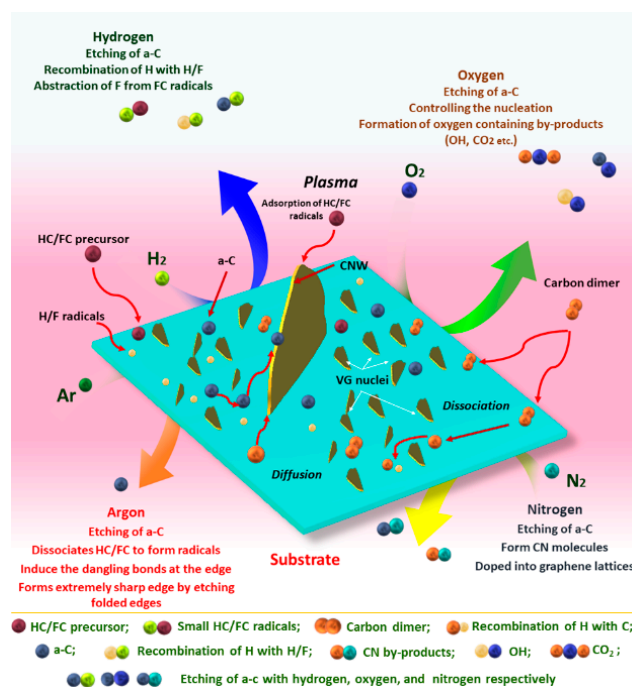


Figure 4. Effect of different radical species on the growth of carbon nanowalls.

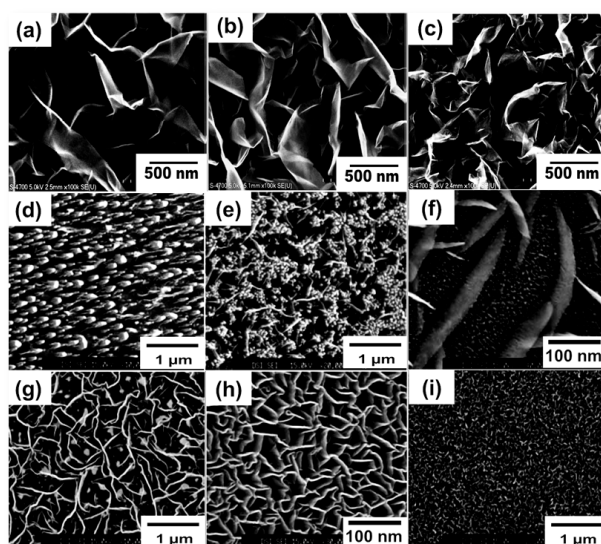


Figure 5. SEM images of graphene nanowalls (GNWs) with different CH_4 concentration (a) 10%, (b) 40%, (c) 100%. Reprinted with permission from the authors of [84]. Copyright Elsevier 2004. SEM images of carbon grown at different H_2/CH_4 flow rate ratios: (d) 30, (e) 15, (f) 10, (g) 6, (h) 4, (i) 1 sccm. Reproduced with permission from [85]. Copyright Royal Society of Chemistry 2004.

Lehmann et al. described the effect of the flow rate of the aromatic precursor on the growth of CNWs [57]. Aromatic paraxylene (P-xylene) was inserted to an RFICP system as the precursor. Plasma power of 150 W, a substrate temperature of 450 °C and pressure between 4.6–7.5 Pa for 20 min were the observed optimum conditions for the CNW growth. The flow rate of the liquid precursor to the system varied from 0.5–5 mL/h (0.01–0.08 sccm) to obtain different morphologies. SEM analysis on the deposited material is shown in Figure 6a–c, which displays the growth of carbon nanofibers (CNF) with a height of 2.2–6 µm, which were produced by a flow rate between 3–5 mL/h. Free-standing CNWs with a height of 1.4–2.2 µm grew at a flow rate of 1–2 mL/h. Interconnected CNWs with a height of 1.1–1.6 µm were deposited at a flow rate of less than 1 mL/h. The investigation stated that the decrease in flow rate increases the interconnection between the nanostructures to form interconnected CNWs from CNF and the height decreases in the order of 33%.

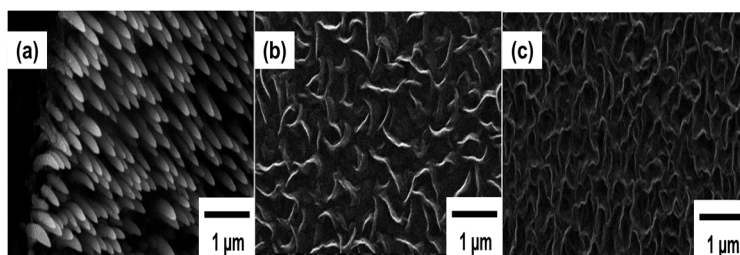


Figure 6. SEM images of (a) a tilted view of carbon nanofibers (CNF) and a top view of (b) freestanding CNW and (c) interconnected CNW. Reproduced with permission from [57]. Copyright Royal Society of Chemistry 2016.

Similar to these carbon-containing gases, the flow rate of etchant gases also influences the growth mechanism. Kondo et al. investigated the effect of the flow rate of H₂ gas on the nucleation and growth of CNWs [86]. A multibeam RFICP system was used for the investigation by supplying an FC precursor source and H₂ as the etchant gas. The H₂ gas was inserted into the system by the direct radical injection mechanism and by an radical ICP system. The morphological changes of the CNWs by the influence of H radicals were studied by the synthesis of CNWs for 35 min at various flow rates of 0, 3, 5, 7, and 10 sccm. A thin layer of carbon was formed on the substrate without an H radical. An increasing H radical flow rate up to 3 sccm initiated the carbon nanoparticle deposition. A further increase to 5 and 7 sccm produced CNWs with an interlayer spacing of 10–20 nm and sheet thickness of less than 5 nm. The height of CNWs was also influenced by the H radical flow. The maximum height for CNWs was observed at a flow rate of 5 sccm. In all other cases, the height decreased with increasing the flow rate, that is, the optimum density of the H radical inside the system highly influenced the vertical growth of CNWs. Suzuki et al. have also investigated the effect of hydrogen on CNW growth by the MW system [87]. Compared to the previous case, Suzuki et al. investigated the variation in the morphology by changing the H₂/CH₄ ratio in between 0–4. The morphology of CNWs varied from a wavy and densely distributed to a linear and sparsely distributed manner on the substrate with increasing the flow rate ratio. Moreover, the wall height increased with increasing the H₂/CH₄ flow ratio. At lower flow rate ratios, the hydrogen did not actively participate in the graphitisation due to the poor H radical condition, while at a higher flow rate ratio, hydrogen participated in the effective removal of a-C from the substrate to form high-quality CNWs. The enhancement of the morphology and crystallinity of CNWs by the addition of O₂ was described by Takeuchi et al. [88]. CNWs were synthesized by RFICP with a radical injection system by employing a C₂F₆/H₂ mixture. The addition of N₂ and O₂ to a system slightly changed the morphology and properties of the CNWs. N-doped CNWs were formed by the insertion of N₂ with higher crystallinity and density. Thus the proportion and optimum flow of various gas species into the system influence the overall growth mechanism of CNWs, which in turn altered the pressure inside the plasma system.

The growth rate of CNWs varies with varying flow rates, which also changes the pressure inside the system, a logical consequence. Thus, the growth of CNWs can also be influenced by the operating pressure. In low-pressure RFICP systems, the total pressure inside the chamber is controlled by regulating the flow rate of gases inserted. The inductive coil stimulates the magnetic field and sustains a breakdown voltage for the dissociation. Therefore, the influence of pressure on the growth can be explained as similar to the effect of the flow rate of gases. On the other hand, in RFCCP, DC, and MW coupled with electrode based plasma systems, dissociation of gaseous species takes place under a certain breakdown voltage, which is described as the function of pressure (p) and the distance between the electrodes (d). This influence of breakdown voltage on gas dissociation is described by Paschen's law [89]. A Paschen's curve indicates that the breakdown voltage decreases with decreasing p and d . Most of the PECVD synthesis is carried out at low pressure. Thus, the p - d values should always be less than its critical values. In most of all the PECVD systems, the distance between the electrode is usually fixed as a constant. Therefore, the breakdown voltage and growth can be influenced by varying the pressure, which means the value of p has to be lower than its critical value. The change in pressure also determines the mean free path of electrons, since the electron mean free path is inversely proportional to the pressure. The low pressure inside the system can increase the mean free path of electrons, which increases the (i) electron temperature via two successive collisions and (ii) stability of plasma. Following this, the plasma becomes capable of providing a sufficient amount of electrons with a higher energy and enhances the ionization rate, which results in the optimal growth rate of CNWs. Low pressure means low flow of gas species through the system and lower growth rate. However, the quality of CNWs at low pressure could be higher than the high-pressure plasma, since the lower growth rate effectively removes the a-C from the surfaces. Hiramatsu et al. reported the influence of pressure for the synthesis of vertical nanographene networks to determine the balance between the gas composition [90]. A mixture of CH_4/Ar inside an RFICP was used for the growth of CNWs at total pressure ranges from 15 to 20 mTorr. This low-pressure operation in an ICP system was capable of enhancing the effective ion bombardment with the surface for the successful nucleation of CNWs. However, the wall density decreased and interlayer spacing increased with the slight increase of total pressure. The investigation by Takeuchi et al. showed that the pressure inside the system influences the growth rate and the radical density, as well [91]. A very high frequency (VHF) CCP+MW PECVD system employed with a $\text{C}_2\text{F}_6/\text{H}_2$ gas mixture was used to study the effect of pressure on the radical density. The increase in pressure from 13.3 to 80 Pa kept the C atom density constant, while the H atom density increased. The important finding in this study was that the ratio between H/CF_x in an FC system is important for the formation of CNWs. The height of the deposited CNWs decreased, and interlayer spacing increased with the increase in pressure. The graphitization of well-oriented CNWs increased with changing pressure to the maximum as well. Similar to the low-pressure PECVD systems, the growth of CNWs at atmospheric pressure (atm) also illustrated the effect of pressure on growth. Bo et al. reported the high growth rate of CNWs using atmospheric normal pin-to-plate DC glow discharge plasma [56]. The strong electrical field produced near the tip enhanced the initiation and growth of CNWs. The gas flow rate was elevated to reach high pressure, which further improved the growth rate. Yu et al. also reported the advantage of pin-to-plate DC plasma to produce high electric field near the tip with atmosphere conditions for the enhanced growth [14]. These all studies confirm that the mixture of gas species, the proportion of gas mixtures, and flow rate of gases play a significant role in the growth mechanism. Ostrikov et al. explained that the formation of nanostructures on the substrate in a PECVD process was mainly influenced by the insertion and consumption of gas species, where the consumption of gas species was regulated by the substrate temperature, which in turn was affected by plasma power [92]. In this aspect, it is very important to find the influence of plasma power, electric field, and substrate temperature on the synthesis of CNWs.

5. Electric Fields and Plasma Power

Nanowall growth is initiated by the nucleation and coalescence of carbon radicals to form graphene sheets on the substrate. Thus, the curling of these sheets to vertical orientation is the following step. As described in the chapter about the growth mechanism, the curling of nanosheets into a vertical orientation is highly influenced by the electric field. Yang et al. explained that the variation in the microstructure during CNW deposition was mainly due to the high electrical field perpendicularly aligned to the substrate, which is provided by plasma [93]. This electrical field promotes the generation of sp^3 -hybridized C atoms as the nucleation center for vertical growth. Wu et al. explained the effect of the strong lateral electrical field on the CNW growth in an MW system [85]. The study revealed the influence of the electric field with surface plasmons induced by gold particles to alter the growth of nanowalls in very localized areas. A growth model by Zhu et al. proposed that the electric field in a plasma system enhances the growth through edges and induces the orientation perpendicular to the substrate [63]. A schematic of the growth model using CH_4/H_2 gas species for the growth of CNWs is presented in Figure 7. The curling of nucleated graphene sheets was initiated when the sp^2 bonded network in the graphene sheets overcame the activation energy barrier for the distortion. A strong electric field perpendicular to the substrate helps to overcome the activation barrier on the edges and sheets bend into the direction of the electric field. The elimination of dangling bonds at the edges by the etchant gases reduced the total energy, which further reduced the probability of edges to bond with each other. A theoretical model on the key factor for the growth of CNWs by Baranov et al. explained that an increased electric field helps to focus ion current to the sharp nanoflake edges on enhancing the height of nanowall [65].

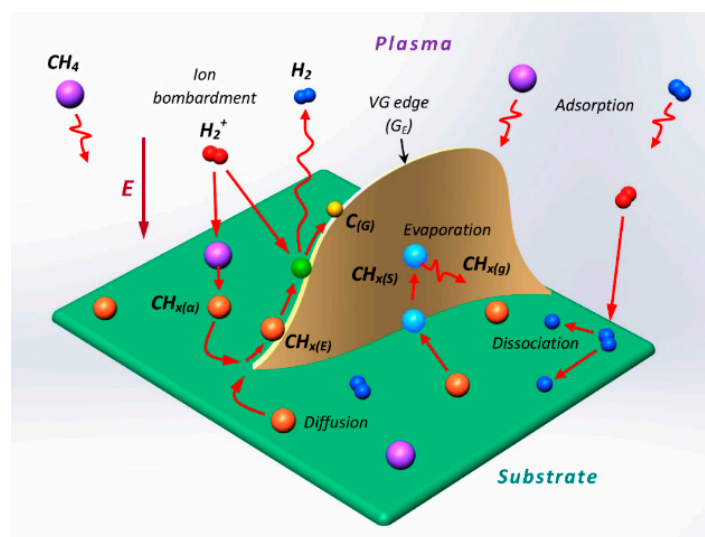


Figure 7. A schematic explanation of the CNW growth model. E: The direction of an electric field; $CH_{x(g)}$: HC growth species; $C_{(G)}$: Graphene sheets; H: Atomic hydrogen used as an etchant. $CH_{x(\alpha)}$: a-C etched along with H atoms in the form of hydrocarbon (HC); VG edge: Edges of vertically-oriented CNWs. Reproduced with permission from [63]. Copyright Elsevier 2007.

Similar to the radical species, neutral gas species also play an important role in the growth mechanism. The collision of neutral atoms and ions, which accelerate through the plasma sheath, enhances the growth rate and creates more defects on the nanowalls [63]. The intensity of the electric field can be externally controlled by varying the plasma power. Zhu et al. described that the growth rate and morphology of CNWs were increased with increasing the power from 500 to 1200 W [63]. High plasma power induces a high electric field on the plasma sheath above the substrate, causing elevation of the substrate temperature and forcing the nanosheets to curl up to a vertical form with a higher growth rate. Yang et al. also explained the better growth of CNWs at a higher power by

regulating RF plasma power from 50 to 200 W [93]. The SEM images of CNWs deposited by different plasma power are shown in Figure 8, where enhanced growth is observed at 200 W. Therefore, the formation of the carbon nanostructure using a high plasma power shows a strong correlation with the electric field effect to form a vertical structure.

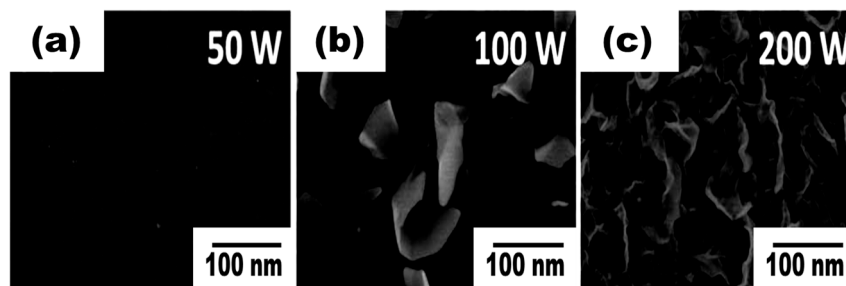


Figure 8. SEM images of GNWs under different plasma power, (a) 50 W, (b) 100 W, (c) 200 W. Reproduced with permission from [93]. Copyright Royal Society of Chemistry 2013.

6. Substrate Temperature

The energy transfer into a PECVD system is carried out mainly by the transfer of electrical energy via plasma, and thermal energy via heating effects. Compared to the thermal CVD systems, growth in PECVD occurs at a relatively lower temperature due to the effects of plasma activated species. In low-pressure PECVD systems, the electrons gain more energy than the ions in plasma through the external electric field. The elastic collisions of electrons can transfer the kinetic energy in relatively smaller amounts than the ions. The electron temperature is much higher than the temperature of ions, but the transfer of energy to other plasma components from electrons is lower because of the extremely low mass of electrons [94]. Thus, the heat transfer inside the plasma becomes low (<1 eV). However, the higher temperature generated by the strong electric field with high-intensity plasma can offer the possibility to transfer the heat to the substrate more effectively by reactive species and ion-based reactions on the surface [95,96]. In addition to this, the neutral gas temperature in high-density plasmas is typically raised, too. This helps the active species to enhance the nucleation and coalescence to form CNWs by forming dangling bonds to the surface defects. The studies on the synthesis of carbon nanostructures show that if the temperature is not fixed exactly, the plasma heating effects promote the substrate temperature and growth. Therefore, the approximate growth–temperature regimes for various carbon nanostructures can be expected as: Graphene growth 400–700 °C [97], initial growth of CNWs 400–600 °C [64,98] and vertical growth of CNW/GNW 500–850 °C [41,98]. Figure 9 shows the growth regimes to initiate the growth to form different carbon nanostructures.

Kim et al. studied the effect of substrate temperature on CNW growth using the CH_4/H_2 gas mixture in an MW system [98]. The CH_4/H_2 gas mixture was introduced into the chamber at a flow rate of 30/15 sccm and the pressure inside the chamber was maintained at 10^{-2} Torr. The CNWs were synthesized on the *p*-type Si substrate at a plasma power of 1000 W. The surface images of CNWs at different substrate temperatures are presented in Figure 10a–f. The deposition of carbon is observed from the temperature of 750 °C. Elevation of temperature to 800 °C destroyed the nucleated structure of carbon atoms and flattened on the substrate. On further increase to 850 °C, 900 °C, and 950 °C, the vertical growth of highly interconnected CNWs was observed with the reduced surface area. The elevation of the temperature also resulted in changes in the surface properties. The contact angle of the CNWs increased linearly until 850 °C and then decreased, where the highly interconnected CNWs with the low surface area was formed. Thus, the elevation of temperature can enhance the growth rate of CNWs and modify the morphology, and further increase leads to the modification of the surface properties.

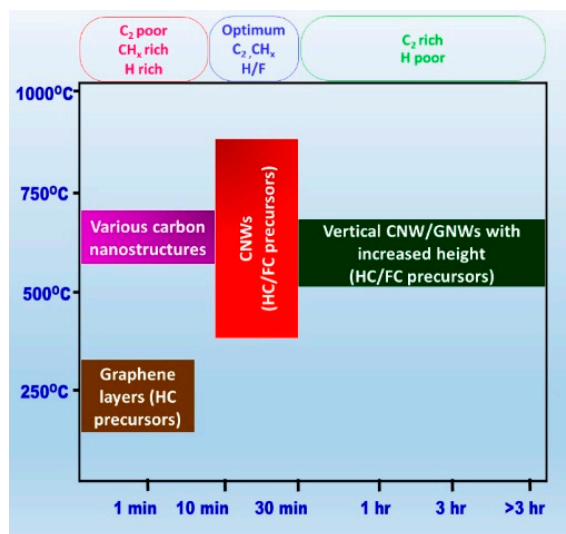


Figure 9. Summary of time–temperature growth regimes for the initial growth of different carbon nanostructures.

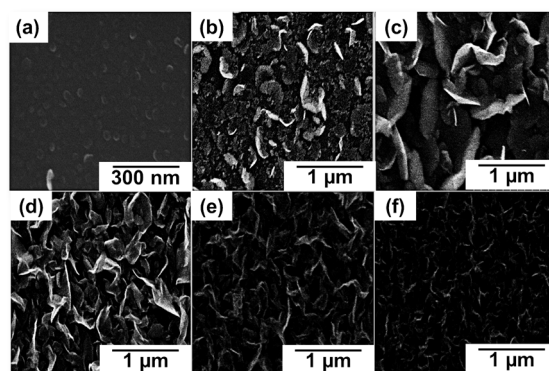


Figure 10. SEM images of the CNWs according to the following growth temperatures: (a) 700 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C, (e) 900 °C, and (f) 950 °C. Reproduced with permission from [98]. Copyright Elsevier 2014.

Once all the discharge parameters are set for the growth of CNWs and plasma generation, the growth of CNWs is initiated by the substrate surface activation, which promotes the selective area growth of CNWs. The growth mechanism and properties of CNWs can be influenced by the plasma parameters. On the other hand, the properties of CNWs can be modified by different plasma treatments after the growth, which is one of the main advantages of plasma-assisted techniques. The following part of the review will mainly focus on the surface treatment of CNWs with plasma generated by different gases.

7. Plasma Assisted Surface Modification and Doping

Enhancing the properties of CNWs specifically through surface treatment or surface functionalization is the main advantage of plasma techniques. Functionalization of the surface is a simple tool for incorporating different functional entities, such as reactive radicals, metallic nanoparticles, and pendant molecules, into the graphene lattice and modifying their properties for various applications. Plasma functionalization can be performed in two ways: (i) In-situ treatment, modification, and functionalization of CNWs during growth, when dopant gas is added into the carbon precursor mixture; or (ii) through post processing treatment. Effects of the in-situ treatment with different gases during growth were already discussed in the *Influence of Gas Sources and Gas Proportion* section of this article. Thus, this section is mainly focused on the plasma post processing

on CNWs by using different plasma gas compositions. Usually, a hydrogen plasma treatment helps to produce high-quality carbon nanostructures by removing the HC groups and contaminants and is also observed through changed wettability of the surface [19,99–101]. Adding oxygen to plasma synthesis of CNWs results in the etching of a-C and the formation of oxide groups and carbonyl groups [19,49]. However, high energy plasma with a high density of oxygen ions can destroy the crystallinity of carbon nanostructures through continuous etching [102]. Oxygen plasma treatment is also an effective tool for tuning the band gap of graphene sheets, since it disrupts the atomic ordering in the graphene layer and forms an oxygen-containing functional groups [103]. The use of nitrogen plasma post-treatment enhances the doping and grafting of the amino functional groups into the CNW structure, which modifies the electrical, electronic, and field emission properties, which can be beneficial also for improving the sensing capability of the material [75,104,105]. Similarly, argon plasma post-treatment influences both electronic and surface properties of carbon nanostructures [17,106]. Argon plasma treatment is generally used to enhance the removal of a-C, mostly through kinetic interactions, and by the prolonged Ar treatment on the edges of nanowalls results in the thinning of the wall and enhances the electronic properties and field emission characteristics [17]. Use of fluorinated gases in post-treatment can lead to controlling the surface wettability properties of CNWs [107]. Such effects are also seen when adding fluoro-based gases into in-situ synthesis systems. Adding boron to plasma gas mixtures during synthesis leads to the formation of B-doped CNWs, which enhances the field emission properties and also participates in the bandgap tuning [108,109]. Additionally, the electrochemical properties of CNWs were enhanced by boron doping [110]. The optical and electronic properties of carbon nanostructures can be tuned by using chlorine-containing plasma, too [111]. To summarize, the use of plasma treatment can lead to either the formation of functional groups (e.g., carbonyl, hydroxyl, carboxyl), an increase in the number of defects due to the removal C atoms from the lattice (e.g., by Ar treatment), or doping of impurities into the graphene lattice (e.g., N and B-doping). Various plasma-assisted surface treatment/doping techniques using different gases reported so far are summarized in Table 3.

Table 3. Different plasma treatments on 2D carbon nanostructures and observed modifications.

Plasma Treatment	Morphology	Changes in the Structure/Property	Ref.
Hydrogen	FLGs	Few layers of highly crystalline graphene sheets with few defects	[26]
	Petal-like nanosheets	Carbon nanosheets from CNTs with a thickness 300 to 500 nm	[99]
	CNWs	Large area free standing CNWs in a well-isolated manner	[112]
		Thin CNW films with ultra-low total reflectance (0.13%) for black body coating	[113]
		Controllable high-quality growth with good electric performance	[114]
	Few-layer graphene	Semiconducting sheets with one magnitude less carrier mobility and two order increase in sheet resistance	[115]
	Thin layer graphene sheets	Defects due to hydrogen plasma make fluctuations in optical properties	[116]
Oxygen	CNWs	A surface roughened layer formed with a higher surface area	[101]
	Thin carbon films	Re-structured carbon coatings with higher scratch resistance	[117]
	CNWs	Alters the adhesive macrophage properties	[118]
	CNWs	Increasing the surface activity of CNWs to act as a template for fabricating nanostructured materials	[119]
	CNWs	O ₂ plasma addition effectively increases the graphitization of carbon nanowalls and controlling the nucleation of CNW growth	[49]
	Few graphene sheets	Enhancing the <i>p</i> -type semiconducting behaviors of graphene nanosheets with strong photoluminescence effect	[120]
	Multilayer graphene sheets	The exponential decrease of conductance and transconductance	[121]
	Graphene sheets	Transformation of semi-metallic nature of graphene sheets into semiconducting via the opening of a band gap	[103]

Table 3. Cont.

Plasma Treatment	Morphology	Changes in the Structure/Property	Ref.
Argon	Single layer graphene	Increases the photoresponse by Ar plasma-induced defects	[122]
	Graphene paper	Reduced the aggregation and forms surface protrusions and improves field emission properties	[123]
	CNW	Induce dangling bonds on the surface and resulting in the formation of nucleation sites	[124]
	GNWs	Field emission properties of GNWs increases by improving graphitic order and removing impurities	[17]
	CNWs	Continuous change in the morphology from 1D to 2D with an increase in Ar flow	[54]
	FLGs	Field emission properties enhanced by forming sharp edges and defects	[125]
Nitrogen	CNWs	Electrical conductance of N-doped CNWs increases compared to undoped CNWs, N-doped CNWs exhibits <i>n</i> -type conduction, N act as donor	[126]
	Graphene sheets	Varying <i>p</i> -type conducting behavior to <i>n</i> -type with increasing N-concentration and possess spin-polarized band structure	[127]
	CNWs	<i>n</i> -type conductivity ranging from 1.9 to 330 $\Omega^{-1} \text{ cm}^{-1}$ due to nitrogen incorporated defects in the amorphous carbon	[75]
	CNWs	The drastic increase in the electron emission current from the CNW edges treatment from 1 to 100 μA	[128]
	CNWs	Higher electrochemical reactivity for the N-doped CNWs	[129]
	CNWs	Maintain <i>p</i> -type conducting behavior and increases the carrier mobility	[130]
Other plasmas	Fluorination in the a-C	Hydrophobicity of a-C films enhanced by fluorinated plasma treatments	[131]
	Boron-doped graphene	The bandgap of the B-doped graphene widened to 0.54 eV from 0 eV	[109]
	Chlorinated graphene sheets	The large surface area with uniform morphology and possess a <i>p</i> -type semiconducting behavior	[132]
	Chlorinated graphene sheets	Reduces the sheet resistance and enhance optical transparency via C-Cl bonds	[111]

Vizireanu et al. investigated the effect of post surface plasma treatment of CNWs using H_2 , O_2 , N_2 , tetrafluoroethane ($\text{C}_2\text{H}_2\text{F}_4$), and sulphur hexafluoride (SF_6) plasmas [19]. Randomly distributed CNWs with an average height of 1.5 μm , a length of 0.8 μm , and a thickness of 10–20 nm were used in the experiment. Morphological investigation unveiled that the post-treatment using H_2 , O_2 , and N_2 caused thinning of the walls and branching towards each other. $\text{C}_2\text{H}_2\text{F}_4$ plasma treatment caused the formation of a fluorine thin film on the CNW surface, while SF_6 plasma treatment led to the rounding of edges by smoothening the sharp edges of CNWs. The formation of carbonyl, aldehyde, epoxy, peroxide, and aromatic quinoides during plasma post-treatment by all the gas mixtures was observed through vibrational spectroscopic analysis, and the formation of additional FC groups in the $\text{C}_2\text{H}_2\text{F}_4$ and SF_6 plasma conditions was also described. The wettability studies on the materials described the increased hydrophilicity of the CNWs after H_2 , O_2 , and N_2 plasma treatments, while the formation of fluorocarbon groups on the structure by $\text{C}_2\text{H}_2\text{F}_4$ and SF_6 plasma treatment resulted in the superhydrophobicity of CNWs. In most hydrogen-containing plasma treatments, hydrogen is used as the in-situ agent to control growth and purity, due to the critical role of hydrogen for growth discussed earlier. However, hydrogen plasma post-treatment is mainly used for controlling the surface wettability by forming H-bonds on the edges and leads to the formation of superhydrophilic surfaces, which are widely used for sensing applications. Jiang et al. found that the hydrogen-plasma post-treatment can remove the oxygen atoms absorbed in the nanowall surface, which enhances CNWs adsorption capabilities [101]. Hydrogen plasma post-treatment is capable of modifying the surface through strong etching and forms a roughened layer on the nanowall surface with a large number of graphite bumps. Elias et al. showed that hydrogenation in graphene lattices could change the hybridization of sp^2 bonded carbon atoms to sp^3 bonds, which further results in the transformation of band structure from semimetal to insulators [133]. The term for this process is bandgap opening, which is an important aspect for electronic device applications.

In contrast to hydrogen plasma treatment, fluorine-containing plasma post-treatment resulted in the hydrophobic nature of the surface (superhydrophobic in some cases) by forming F-terminated bonds on CNWs. This was also demonstrated in the study by Vizireanu et al. mentioned above. Furthermore, Watanabe et al. also came to the same conclusion that H-terminated or O-terminated CNWs have a hydrophilic nature, whereas F-terminated CNWs have a hydrophobic nature. The as-synthesized CNWs were treated with Ar plasma at atmospheric conditions, which leads to the formation of H/O-terminated CNWs by the incorporation of oxygen into the lattice through the dissociation of oxygen molecules in the air, while CF_4 plasma led to the formation of F-terminated CNWs [106,134]. Figure 11a shows the water contact angle (WCA) of CNWs as a function of plasma post-treatment time. It is observed that Ar plasma treatment makes the surface more superhydrophilic through surface oxidation during the treatment. On the other hand, treatment with CF_4 plasma makes the surface more superhydrophobic. Deposition of a fluorinated polymer layer by the CF_4 radicals causes a superhydrophobic effect on CNWs. Thus, the formation of O-terminated CNWs leads to hydrophilic surfaces, whereas that of F-terminated CNWs by FC plasma leads to hydrophobic CNW surfaces. The effect of Ar post-treatment on the enhancement of field emission properties of CNWs was explained by Qi et al. [125] and Cui et al. [135]. The Ar post-treatment was efficiently removing the a-Cs, sharpening the edges, and removing the folded edges. The atomically thin edges of CNWs acquired by the optimum Ar plasma post-treatment show the maximum field emission properties. Ar ion bombardment on to the CNW edges causes the thinning of edges and created several defects on the edges, and these defects act as the additional emission sites, resulting in the enhanced field emission.

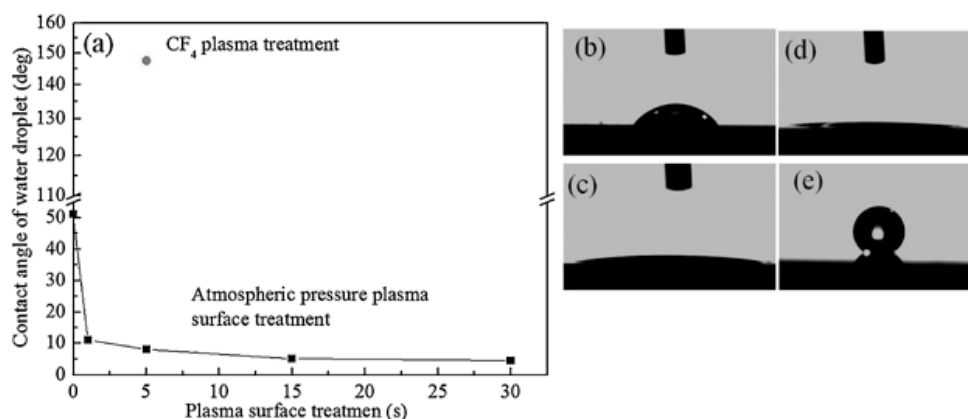


Figure 11. (a) Contact angles of water droplets on CNWs as a function of the plasma treatment time, (b) as-grown CNWs, (c) CNWs after Ar atmospheric pressure plasma treatment for 5 s, (d) CNWs after Ar atmospheric pressure of plasma treatment for 30 s, and (e) CNWs after CF_4 plasma treatment for 5 s. Reproduced with permission from [106]. Copyright John Wiley and Sons 2013.

An oxygen plasma post-treatment influences both the edges and the interstitial sites of the CNWs to form different functional groups. The presence of the O-terminated carbon structure improves the surface wettability properties, which also increases the reaction with electrolytes in energy storage devices. Sahoo et al. reported the effect of oxygen plasma treatment to enhance the electrochemical performance of CNWs [136,137]. Formation of different oxygen-containing functional groups after oxygen plasma post-treatment enhances the capability of CNWs to interact with electrolyte rapidly, which further increases the specific capacitance of the material. Chen et al. also reported the effect of oxygen plasma post-treatment in enhancing the reaction of CNWs with enzymes for electrochemical sensors to detect lactate enzyme [138]. Gokus et al. and Wang et al. explained the effect of oxygen plasma treatment on graphene to modify the photoluminescent (PL) properties [120,139]. The significant amount of oxygen in the graphene lattice enhances the PL properties of CNWs by the transition of energy from π band to the defect energy band related to oxygen atoms.

Nitrogen plasma post-treatment is widely used for incorporating nitrogen to the graphene lattice to produce N-doped CNWs. The nitrogen plasma post-treatment can significantly enhance the electrical and electronic properties of the CNWs. Cho et al. modified the conductivity and carrier mobility of CNWs by nitrogen doping while keeping the morphology and edges of CNWs intact [130]. Compared to in-situ N_2 plasma during the growth of CNWs, N_2 post-treatment on CNWs shows an improved carrier concentration and carrier mobility. The former leads to bulk nitrogen doping and consequential formation of higher topological defect densities and a decrease in the conductivity; the latter largely influences only the edges of CNWs, where the N atom is attached to the graphene edges and results in the higher charge carrier mobility and, thus, conductivity. Figure 12 shows the improved electrical properties of CNWs after nitrogen plasma post-treatment.

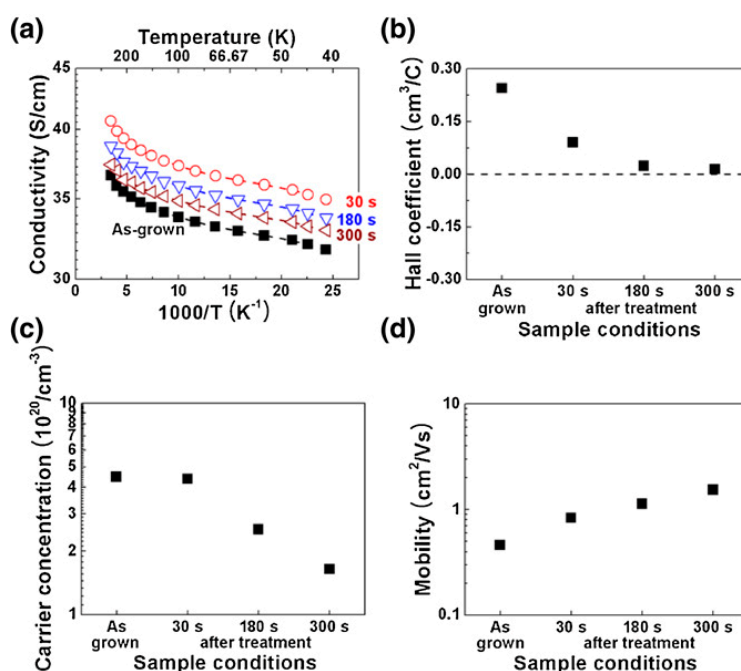


Figure 12. Temperature dependences of (a) electrical conductivities, (b) Hall coefficients, (c) carrier densities, and (d) carrier mobilities of the CNWs before and after post-growth N_2 gas plasma treatments. Reproduced with permission from [130]. Copyright The Japan Society of Applied Physics 2014.

The concentration of bulk N-doping during growth can be controlled by the flow rate of nitrogen to the system, which was shown by Takeuchi et al. in the FC/ H_2 plasma synthesis [126]. The inclusion of N in the lattice changes the conduction type of CNWs to n -type from p -type. Uniform distribution of N-doping was controlled by the flow rate of N_2 gas, where N-concentration increased with the increase in N_2 flow. Dias et al. investigated the amount of nitrogen doped into CNW lattice by nitrogen plasma post-treatment and reported a high doping level of 5.6% [104]. The Ar- N_2 plasma post-treatment was used for nitrogen doping on the self-standing graphene sheets. The evolution of the concentration of nitrogen on the graphene lattice with respect to plasma treatment time is displayed in Figure 13. The nitrogen plasma treatment leads to the formation of different N-graphene by forming pyrrolic-N, pyridinic-N, and quaternary nitrogen. Recently, Bundaleska et al. reported the large-scale synthesis of 0.4% N-doped free-standing graphene sheets via a highly cost-efficient microwave plasma system [58]. The in-situ N-doping was carried out using ethanol and ammonia as the precursors, with IR and UV irradiation post-treatment. The irradiation causes heating, which activates the defects through subsequent bond recombination and enhances the capability of N-doping. Tatarova et al. explained the synthesis of free-standing N-doped graphene via MW plasma system and reported 0.2% of N-doping [140]. The electrochemical properties of N-doped graphene showed a good electrochemical response, with negligible interfacial resistance. Chi et al. reported the higher

concentration of N-doping on CNWs at 7.6%, which is suitable for use as an electrode for electric double layer super capacitors [141]. Yen et al. showed that the in-situ doping of N in CNWs exhibits maximum specific capacitance in aqueous electrolyte [142]. Wang et al. reported the photoluminescence effect from the N-doped carbon tips [143]. Bundaleska et al. reported the highest level of N-doping up to 25% on graphene sheets through Ar–N₂ post-treatment in an MW plasma [144]. The highest level of N-doping into graphene lattice can be suitable for various applications. All the investigations on N-doped CNWs confirmed the enhanced electrical properties of CNWs through nitrogen doping.

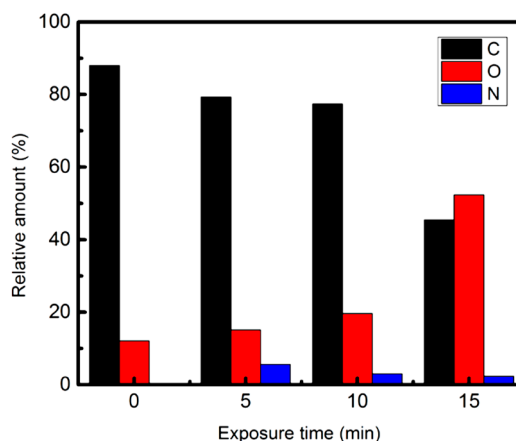


Figure 13. Evolution of the elemental composition of N-graphene with plasma treatment time ($P = 600$ W, N₂–Ar (10–90%), $p = 1$ mbar). Reproduced with permission from [104]. Copyright IOP publishers 2016.

The complex behavior of plasma surface chemistry on the growth and modification of CNWs is not fully understood. However, functionalization is mainly occurring at the edges, which helps to control the surface chemistry of CNWs. Attaining substantial edge growth rather than the production of a large number of nucleation centres is one of the main future goals through different plasma treatments. Most recently reported CNWs contain an amorphous structure in their morphology, which can be reduced by in-situ treatment with the optimum concentration of etchant gases to achieve high crystalline CNWs with high quality. Plasma surface treatment always opens the chances for surface functionalization and doping on the CNW structures. The functionalization on the graphitic edges of CNWs through plasma post-treatment using different gases may result in the development of a new electronics era based on edge electronics. Tuning electrical, optical, morphological, and chemical properties of CNWs using plasma surface treatment can be applied in the fields of electronics, optics, energy, and so on, which are yet to be explored in depth.

8. Challenges and opportunities

The synthesis of open boundary structured CNWs has been widely investigated. The main challenges of CNW synthesis are structure controlled growth, large-scale production, high growth rate, and low-temperature growth. The vertically-oriented structure and morphology with thin edges of CNWs strongly enhance their surface and electrical properties, which are widely applicable to potential applications. Therefore, a better understanding of the optimum conditions for the structure controlled growth is one of the main challenges to be resolved, which can be explained by studying the influence of discharge parameters on the growth of CNWs. The challenges arise due to different growth parameters such as: Low-pressure plasma results in a low growth rate, high temperature, and high power plasma-treatment, sometimes destroying the structure of CNWs and the presence of dominant amorphous nature in hydrogen-poor conditions. Thus, it is critical to choose the suitable gas source with an optimum flow rate and proportion to maintain the optimum pressure inside the system for the enhanced growth. Additionally, the selection of a-C etchant source gases is critical to increasing

the crystallinity of CNW. The growth rate under different plasma conditions reported until now is not sufficient for industrial-scale production. Until now, the mostly reported plasma-enhanced growth of CNWs was carried out via the gas phase deposition of carbon radicals onto the substrate. There are very few works available on the growth of CNWs or vertical carbon nanostructures via a surface growth mechanism or using aromatic precursors. The surface growth of vertically-oriented structures may give more control over the thickness and size of the nanostructures. Furthermore, it is critical to fabricating isolated free-standing CNWs, which can be useful for a variety of applications.

Opportunities of CNWs are the possibilities of applications. The major applications of CNWs in different fields are displayed in Figure 14. Considering the structure and morphology of CNWs, the large surface area of CNWs is one of the main advantages, which can be widely used for energy device applications and gas storage devices. The vertically-oriented structure with interlayer spacings can be a suitable material for the catalyst supporter in the fuel cells. Highly branched CNWs with a large surface to volume ratio is a potential material for gas sensing applications. Exfoliation of CNWs from the substrate can open up possibilities for using them as membrane filters. Plasma-surface treatment with different gases is useful for modifying the properties of CNWs for specific applications. Sharp edges with the high crystalline nature of CNWs are suitable for field emission applications. F-terminated CNWs with higher stability against degradation are suitable for hydrophobic coatings, which can be achieved through either fluorine-containing plasma treatment or growth from FC precursors. Nitrogen plasma-treatment can produce N-doped CNWs with improved electrical properties and capacitance. The maximum percentage of N-doping in CNWs so far reported is approximately 25%, which can be useful for various electrical and electrochemical applications. Production of CNWs from the nitrogen-containing precursor (e.g., aromatic precursor contains amino groups) can be an alternative method to enhance the concentration of nitrogen both in interstitial and edges of CNWs. Oxygenated CNWs can become able to produce a PL effect, applicable for designing optoelectronic devices. Hydrogenation or surface functionalization with hydrogen plasma enhances the hydrophilic properties of CNWs, which enhances the reaction towards electrolytes in electrochemical energy storage devices to provide better results. Moreover, this hydrophilic nature promotes their applications in biosensing, energy storage devices, and catalytic reactions. The intrinsic electrical property (without any functional groups/dopants) of CNWs is not yet revealed; investigating the intrinsic behavior of CNWs will be a great step for the next generation of electronic devices.

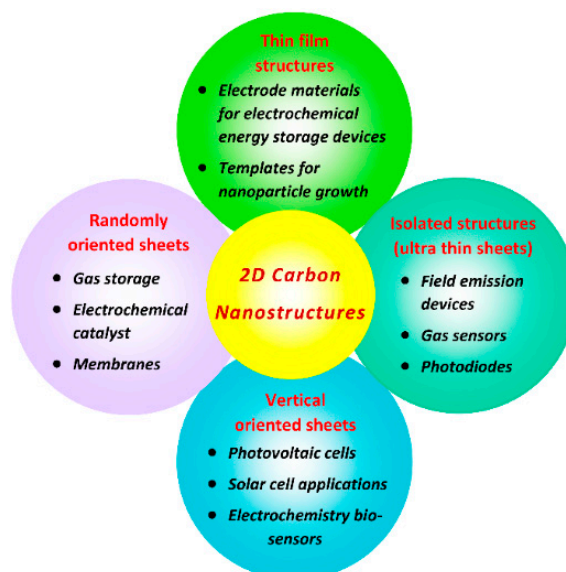


Figure 14. Schematic representations of possible applications of CNWs/other 2D carbon materials.

9. Conclusions

The open boundary structure, vertical alignment with interlayer spacing, and high crystallinity of 2D CNWs has extended carbon-related research into various areas. Employing different gaseous and aromatic precursors to a PECVD system, which are activated by different plasma sources, has successfully demonstrated the synthesis of vertically-oriented CNWs. There have been many studies to identify the parameters responsible for the growth; starting from the precursor gas, the mode of plasma coupling, plasma power source, the pressure inside the system, duration of growth, and electric field to substrate temperature. All these were systematically presented in this paper. In addition to this, the major advantage of plasma synthesis is the production of highly pure 2D carbon materials in a rather controllable manner. However, the responsible plasma species and growth mechanisms still have gaps to be deeply explored. Moreover, the future challenges in CNW research are also connected with: The control of the height uniformity with large interlayer spacing and higher crystallinity; bridging the low growth rates for upscaling; precise isolation of single nanowalls; and uniform doping of nitrogen on CNW lattices with higher concentration.

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Chapter 3

Plasma-Enabled Approaches for Designing Carbon Nanostructures

Chapter 3 deals with the different plasma-enabled approaches for designing oriented carbon nanostructures. The considered carbon nanostructures are nanotubes, nanowalls and nanoforests, which are commonly investigated in application-oriented research. As the applications mainly rely on the ability to engineer the carbon structures at the nanoscale, a fast and facile reproducible method for the large-scale production of carbon nanostructures is required.

Plasma-enabled techniques are capable of designing carbon structures at the nanoscale with high controllability and structural quality. Plasma can achieve the growth of nanostructures at a fast growth rate without additional heating at low energy consumption. Additionally, it can produce carbon nanostructures at a large scale without producing any hazardous by-products. Therefore, we have investigated the use of cold low-pressure plasma to synthesise high-quality carbon nanostructures with different morphologies and dimensions.

This chapter describes our efforts to develop the best plasma technique for the fast synthesis of carbon nanostructures. Thus, we have formulated different plasma-enabled approaches for the synthesis. In the first approach, we have experimented with a simple plasma reformation technique for the surface reformation of polymer gels to carbon nanostructures. We used a low-pressure inductively coupled radio-frequency plasma with a mixture of argon and hydrogen gases. The idea was that the argon/hydrogen plasma would reform the polymer surface, and carbon would form nanostructures. In the second approach, we applied a cold plasma-enhanced chemical vapour deposition (PECVD) system to fabricate carbon nanostructures. A radio-frequency plasma generator inductively coupled to the plasma chamber with a carbon source gas flow was used for the synthesis. The motivation for using inductively coupled plasma was the rapid production of carbon nanostructures at ambient conditions. In the last approach, we explored the ability of a low-pressure radio-frequency plasma, which was capacitively coupled with the plasma chamber for the synthesis process. The idea behind using capacitively coupled plasma was to produce carbon nanostructures at low temperature and low plasma power. We successfully realised all approaches, and synthesised the high-quality carbon nanostructures. The detailed description and results are described in the following subchapters:

- 3.1. Oriented Carbon Nanostructures from Plasma Reformed Resorcinol-Formaldehyde Polymer Gels
- 3.2. Low-Pressure Plasma-Enabled Synthesis of Vertical Carbon Nanostructures
- 3.3. Low-temperature low-power PECVD synthesis of vertically aligned graphene

This chapter addresses thesis Objectives 1 and 2.

Chapter 3.1

Oriented Carbon Nanostructures from Plasma Reformed Resorcinol-Formaldehyde Polymer Gels

Chapter 3.1 demonstrates an alternative plasma-enabled technique for designing carbon nanostructures from the solid precursor. Resorcinol-formaldehyde-based polymer gels were used as the solid precursor in this study. The radio-frequency inductively coupled plasma was used to reform the surface of polymer gel into carbon nanostructures. Here, we researched the influence of plasma discharge conditions (gas flow rate, plasma power, and treatment time) on the structural reformation of polymer gels and demonstrated the possibility of growing oriented carbon nanostructures. We established that, at lower plasma power ($<200\text{W}$), it is hard to reform the polymer surface to carbon nanostructures. Also, a short plasma-treatment time ($<5\text{ min}$) was insufficient for the successful reformation. We optimized that plasma surface treatment for 8 min at a power of 250 W is sufficient for the surface reformation for polymer gels to carbon nanostructures. Then the prepared carbon nanostructures were tested for the gas sensing properties towards ethanol detection at atmospheric conditions. The developed novel technique presented in this study could be used as an alternative environmentally friendly processing technique for designing high-quality carbon nanostructures from solid precursors, including oils, polymer gels, and other bio-wastes. Therefore, this process would result in beneficial reformation/degradation of organic materials and produce a valued carbon material.

Regarding my contribution: I conducted all the experiments, contributed to the surface analysis and chemical composition analysis of carbon nanostructures, tested sensors for ethanol vapours response and jointly wrote the paper with all the other co-authors.



Article

Oriented Carbon Nanostructures from Plasma Reformed Resorcinol-Formaldehyde Polymer Gels for Gas Sensor Applications

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Abstract: Oriented carbon nanostructures (OCNs) with dominant graphitic characteristics have attracted research interest for various applications due to the excellent electrical and optical properties owing to their vertical orientation, interconnected structures, electronic properties, and large surface area. Plasma enhanced chemical vapor deposition (PECVD) is considered as a promising method for the large-scale synthesis of OCNs. Alternatively, structural reformation of natural carbon precursor or phenol-based polymers using plasma-assisted surface treatment is also considered for the fabrication of OCNs. In this work, we have demonstrated a fast technique for the synthesis of OCNs by plasma-assisted structure reformation of resorcinol-formaldehyde (RF) polymer gels using radio-frequency inductively coupled plasma (rf-ICP). A thin layer of RF polymer gel cast on a glass substrate was used as the carbon source and treated with rf plasma under different plasma discharge conditions. Argon and hydrogen gases were used in surface treatment, and the growth of carbon nanostructures at different discharge parameters was systematically examined. This study explored the influence of the gas flow rate, the plasma power, and the treatment time on the structural reformation of polymer gel to produce OCNs. Moreover, the gas-sensing properties of as-prepared OCNs towards ethanol at atmospheric conditions were also investigated.

Keywords: inductively coupled plasma; oriented carbon nanostructures; plasma surface treatment; polymer gel; Raman spectroscopy

1. Introduction

Carbon nanostructures (CNs) have several unique structural, morphological, and electrical properties [1]. Owing to their structure, morphology, and preferential orientation, CNs have gained research attention in different fields of electronic, gas sensing, and energy storage applications. The structure, morphology, and orientation of CNs can be tuned by the parameters of the growth process. The orientation of surface-bound CNs can be arbitrary, horizontal, or vertical to the substrate. Among them, vertical OCNs are considered to be a promising material for the industrial and practical applications due to their high-aspect-ratio, large specific area, and good electrical properties that can improve the material performance. Commonly investigated forms of such CNs are vertical carbon nanotubes [2,3], vertical graphene sheets [4–10], and carbon nanofibers [3,11,12], which are already exploited for various applications such as electronic devices [13,14], sensors [15], renewable energy storage devices [16–18], catalyst supporters [19,20], etc. As the applications mainly rely on the

capability of successful nano-tailoring of the number of atomic layers deposited in a specific orientation, a reproducible method for the large-scale synthesis is one of the major obstacles for the mass production of OCNs. Conventional micromechanical exfoliation, epitaxial synthesis, and growth methods can produce thin-layered nanostructures, but cannot be implemented for large-scale production [21]. To overcome this issue, plasma-assisted techniques are considered as a promising technique for the large-scale synthesis of CNs, which allows control over their structure and morphology [22,23]. During a plasma-deposition process, precursor gas molecules are dissociated in the plasma and deposited onto the substrate in solid-state. Thus far, various CNs have been synthesized by different PECVD techniques using microwave plasma [6,24], radio frequency inductively coupled plasma (rf-ICP) [25,26], and rf-capacitively coupled plasma (rf-CCP) assisted by H radical injection [27–29]. However, the use of flammable gases, such as methane, and the need for external substrate heating during the plasma deposition are the main challenges during the plasma-enabled synthesis for obtaining reproducible results.

Inspired by the recent studies on thermal annealing of natural precursors to obtain CNs, several investigations are reported on the alternative plasma-assisted single-step synthesis of OCNs from environmentally-friendly precursors, such as coconut oil [30], honey [31], butter [32], honeycomb [33], etc. Apart from these precursors, phenol derived xerogels and aerogels are also considered as the precursor sources for the preparation of porous carbon nanoparticles and nanostructures with large surface area [34,35]. Among all varieties of phenol-based polymer gels, resorcinol-formaldehyde (RF) gel is considered as a favorable precursor for the synthesis of open-cell foam-like structured CNs [36] due to their cross-linked polymer network and thermosetting properties [37]. Additionally, it has been reported that RF gel-based structures can be graphitized by catalytic activity upon thermal annealing [38–41]. However, thermal annealing of phenol-derived gels for the synthesis of CNs is limited due to the requirement of high temperature (900–1800 °C) and lower controllability on the final structure. As plasma surface-treatment has already been used for the orientation-controlled synthesis of the CNs (horizontal to vertical) compared to the thermal annealing methods [32,33], we have explored the possibilities of plasma-assisted techniques for the surface modification of RF xerogels to synthesize OCNs. Modification of the amorphous RF gel to crystalline OCNs (so-called graphitization) by the plasma treatment can alter the morphology, exposed surface area, and functionality, as well as the electrical conductivity of the material. Moreover, the optimized vertical alignment of such CNs contributes to the relatively larger exposure of the active surface compared to the initial arbitrary orientation. Plasma-assisted modification of the carbon species or plasma-deposited CNs are usually formed with a large number of reactive surface sites generated either by the reactive surface carbon atoms or by the surface defects, which can be useful for various applications. Additionally, exploiting the applications of these structures for the detection of commonly used gases can be a new approach for the material-efficient fabrication of OCN based gas-sensors [42].

We demonstrated an environmentally-friendly fast and facile synthesis of OCNs by the plasma-assisted structural reformation of RF xerogel cast on a glass substrate. An rf-ICP ignited by a mixture of Ar and H₂ gases was used for the surface treatment. Additionally, the proposed synthesis method did not require external substrate heating to produce OCNs. The systematic investigation on the influence of plasma discharge parameters and treatment time on the structural reformation of CNs enabled us to find the optimum conditions for synthesizing OCNs. Structural graphitization, defect generation, and improvement in the orientation of OCNs by plasma surface treatment were confirmed by various surface analytical techniques. The obtained results are used to explain a possible mechanism of the structural reformation of RF gel to graphitized OCNs using an energy-efficient plasma surface treatment technique. The defect-rich properties of CNs reveal the functionality for gas sensing applications potentially at low-temperatures (20–80 °C).

2. Materials and Methods

2.1. Synthesis of RF Xerogel

All chemicals used in the present study were obtained from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany). RF aqua gel was prepared by dissolving resorcinol (99% purity), formaldehyde (37.6%; methanol stabilized), and sodium bicarbonate (Na_2CO_3) in distilled water. A typical gel formulation contained 0.29 M resorcinol, 0.57 M formaldehyde, and 4.0 mM sodium carbonate as the catalyst. The RF mixture was transferred into a 20 mL glass vials and sealed. The glass vials were then kept in the oven at 85 ± 3 °C for 24–36 h. The gelation could occur in approximately 30 h. The solution progressively changed color from clear to yellow, then to orange, and deep red as a function of the reaction time during the gelation process (Figure S1). Prepared RF gels were cast on a borosilicate glass substrate using a doctor blade with a thickness of approximately 100 μm and dried at room temperature to form RF xerogel.

2.2. Plasma-Assisted Synthesis of OCNs

Plasma surface treatment on the RF gel was conducted in an rf (13.56 MHz) inductively coupled plasma system that consists of an 80 cm long glass tube with a diameter of 4 cm and a wall thickness of 3 mm. The rf generator was inductively coupled to the system by using a nine-turn water-cooled copper coil. The RF gel was cast on a glass substrate and placed in the glass tube in the center of the coil. Argon and hydrogen gases were used for the discharge. The chamber was pumped down to 3 Pa using a rotary pump before the experiments, and the pressure was increased up to 55 Pa during the experiments. Based on our preliminary experiments, the influence of plasma parameters on the surface deformation was investigated in detail by varying one plasma parameter while keeping other parameters constant. In this study, we investigated the influence of plasma power, gas flow rate, and treatment time; the experimental conditions used in the experiment are listed in Table 1. There was no external heating source used during the plasma treatment, and the substrate temperature was below 300 °C. The schematic diagram of the experimental setup for the plasma-assisted synthesis of the CNs is presented in Figure S2.

Table 1. Experimental conditions for plasma-assisted structure reformation of RF gel to CNs.

Sample	Plasma Power (W)	Flow Rate Ar:H ₂ (sccm)	Growth Time (min)
1	200	100:50	8
2	250	100:50	8
3	300	100:50	8
4	250	50:50	8
5	250	50:100	8
6	250	100:100	8
7	250	100:50	1
8	250	100:50	3
9	250	100:50	5

2.3. Gas Sensing Measurement

Prepared OCNs were peeled off from the glass substrate and placed on a wet polyurethane membrane (GSM 3 g/m², Pardam Nanotechnology, Roudnice nad Labem, Czech Republic) and vacuum filtered to make good adhesion between the membrane and CNs. The sensing property of the OCNs was investigated by measuring the change in sensor resistance using a home-built sensing device, as reported earlier [43]. For preparing the sensor, the OCNs filtered on PU membrane was cut into a

dimension of 1.5 cm × 1.5 cm placed on a sensing chip with conductive contacts and connected to the source meter. The resistance was measured by using a Keithley 2460 (Tektronix Inc., Beaverton, OR, USA) high current source-meter at a constant input current of 10 mA, and the data were evaluated with the help of a computer. Two identical 250 mL conical flasks were used as the sensing chamber during the experiment, and ethanol was used as the sensing gas. Ethanol was transferred to one flask, and the other flask was filled with the ambient air. During the sensing measurement, the sensor was manually moved from the “empty” flask to the flask with ethanol (gas on phase), and the sensor was put in the saturated vapor above the ethanol surface. Later, the sensor was put back in the empty flask (gas off phase). The schematic of the experimental setup for the sensor measurements is presented in Figure S3. The time for sensing and recovery process during the gas on and gas off phase was assigned as 180 s. The flasks were heated simultaneously to different temperatures (20, 40, 60, and 80 °C) using an electric hotplate stirrer and measured the sensing capability towards different ethanol concentrations. The response of the sensor was calculated from:

$$\text{Sensor response} = \frac{R_g - R_a}{R_a} \quad (1)$$

where R_g is the resistance of a sensor after inserting ethanol, and R_a is the resistance of the sensor in air. The concentration of ethanol vapors at each temperature was calculated using Dalton’s law of partial pressure, and the vapor pressure at different temperatures is given in Supplementary information file, Table S1.

3. Characterization Techniques

The surface morphology of the plasma reformed OCNs was analyzed by scanning electron microscope (SEM, JSM 7600F, JEOL Ltd., Tokyo, Japan). The phase composition and the crystal structure of the samples were investigated by the transmission electron microscope, operating at 200 kV (TEM, JEM-2100, Jeol Ltd., Tokyo, Japan). Raman spectra were recorded at various points of the samples to study the structural changes of the nanostructures after plasma treatment using NTEGRA confocal Raman spectrometer (NT-MDT SI, Moscow, Russia) at an excitation wavelength of 633 nm with an incident power ~3 mW at a spot size of 50 μm. The alteration of the crystallinity of the products was assessed by X-ray powder diffractometer (XRD, Philips Analytical PW 3050/60 X’Pert PRO, PANalytical, Almelo, The Netherlands) employing $K\alpha$ irradiation and operating at 45 kV and 40 mA, using incident beam monochromator, while spectra were recorded with a step size of 0.001° in characteristic range of 10–30°. The X-ray photoelectron spectroscopy (XPS PHI-TFA XPS spectrometer, Physical Electronics Inc., Chanhassen, MN, USA) analysis was employed to evaluate the surface composition and chemical bonding of the nanostructures using an Al-monochromatic X-ray source at the energy of 1486.6 eV. The changes in the functional entities of the RF xerogel after the plasma surface treatment were analyzed by Fourier transform infrared spectroscopy (FTIR). FTIR spectrum was recorded by GX FTIR spectrometer (Perkin Elmer Inc., Waltham, MA, USA) equipped with a photoacoustic detector. The spectra were obtained over wavelengths between 4000 and 500 cm^{−1} (mid-infrared region) with 8 cm^{−1} resolution by averaging 64 scans.

4. Results and Discussions

To understand the effect of plasma treatment on the RF gel morphology, a series of CNs were synthesized at different plasma conditions. The first parameter varied during the experiment was plasma power (200–300 W), while keeping flow rate (100:50 sccm) and growth time (8 min) constant. During the plasma surface treatment of RF gel cast on a glass substrate, the first observation is a noticeable change of color from deep red to black, which can be due to the changes in structure and morphology of precursor. Thus, the change in surface morphology of the RF gel after each plasma treatment was analyzed by SEM, and the effect of plasma power on the surface morphology of CNs is presented in Figure 1a–c. The morphological characteristics of CNs with respect to each plasma

power suggests that the structure is changing with the increase in power. At a power of 200 W, a microscale flat film with randomly distributed fibrils is formed on the substrate (Figure 1a). At a power of 250 W, densely-packed vertically oriented thick flakes, with a thickness of ~80–100 nm, are observed (Figure 1b). At a further increase of power to 300 W, a free-standing individual flake-like structure is observed (Figure 1c). The CNs are damaged when using the power of 300 W, and while comparing CN growth at powers of 150 and 250 W, it is observed that the growth is more significant in the latter. Consequently, the power of 250 W was taken as an optimum plasma power for investigation of the influence of gas flow rate and treatment time on CN growth. The flow rate of the gas mixture is also considered as a key factor on the surface reformation. Thus, the plasma treatment was conducted at different flow rates (pressure) of Ar: H₂ as 50:50 sccm (31 Pa), 50:100 sccm (41 Pa), and 100:100 sccm (53 Pa) at a constant plasma power (250 W) and treatment time of 8 min. A microporous structure is observed at a gas mixture ratio of 50:50 sccm (Figure 1d). When the flow ratio is 50:100 sccm, randomly distributed thick fiber-like structures are formed on the substrate (Figure 1e). A further change in the flow ratio to 100:100 sccm leads to the formation of dense CNs with randomly distributed nanofibers (Figure 1f). Evaluation of the influence of flowrate also confirms that densely packed OCNs are growing from RF gel after 8 min of surface plasma treatment at a plasma power 250 W and gas flow ratio 100:50 sccm.

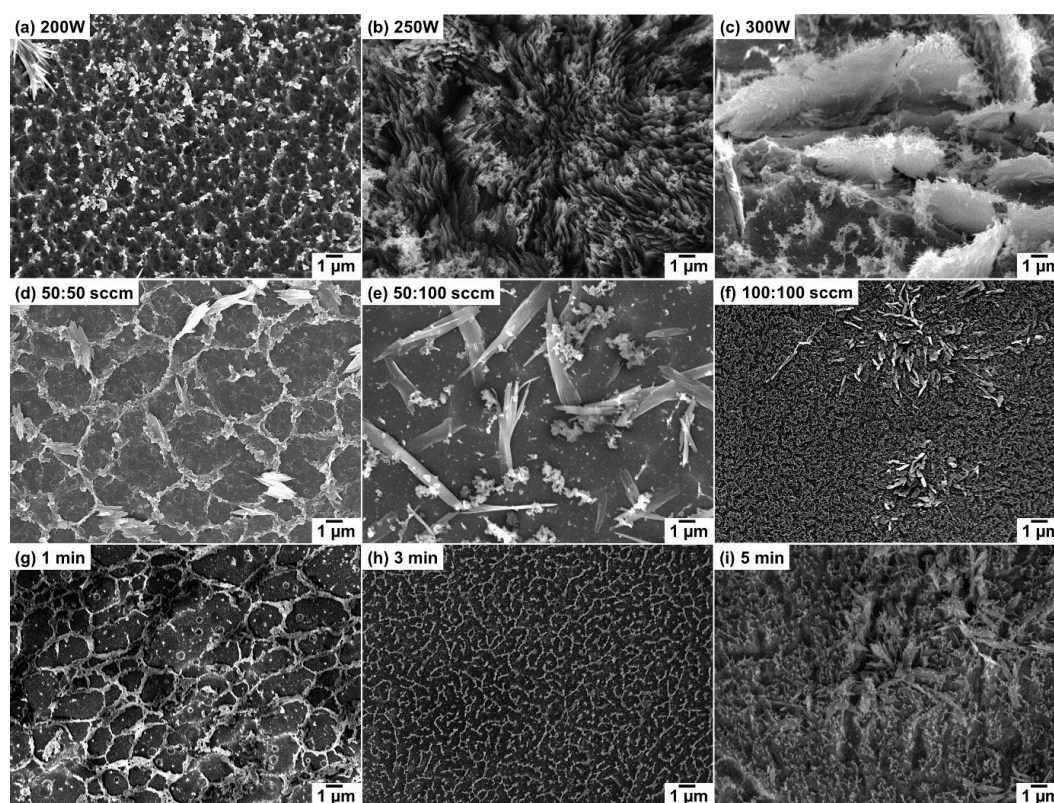


Figure 1. Secondary electrons (SE) SEM micrographs of carbon structures after plasma surface treatment on RF gel at different treatment conditions: (a–c) different power at 100:50 sccm and 8 min; (d–f) different flowrates at 250 W and 8 min and (g–i) different time at 250 W and 100:50 sccm.

Thus, to investigate the formation of OCNs by plasma processing, time-dependent plasma treatment was performed. The progress of morphology was investigated at different treatment times, 1, 3, 5, and 8 min, as presented in Figure 1b, g, h, i, respectively. The morphology of RF gel treated for 1 min resembles an interconnected ring-like structure with large interspacing. After 3 min of plasma treatment, the surface is filled with a broken ring-like structure (Figure 1h). Further increase of treatment time to 5 min leads to the formation of the combined ring and fiber-like structures on the

substrate, where the fiber-like structures seeded on the surface are also seen after 3 min treatment. The longest plasma treatment of 8 min resulted in the removal of ring-like structures and the formation of densely packed OCNs (Figure 1b). Additionally, further plasma treatment longer than 8 min has resulted in the erosion of all of the precursors from the substrate. High-resolution micrographs of the time-dependent growth of CN structures during the plasma treatment process are presented in Figure 2a–d. The nucleation of the CN structures started after 3 min treatment, and the growth is facilitated with time. The CN structures after 8 min treatment are in the form of vertically orientated flake-like structures (Figure 2c, d).

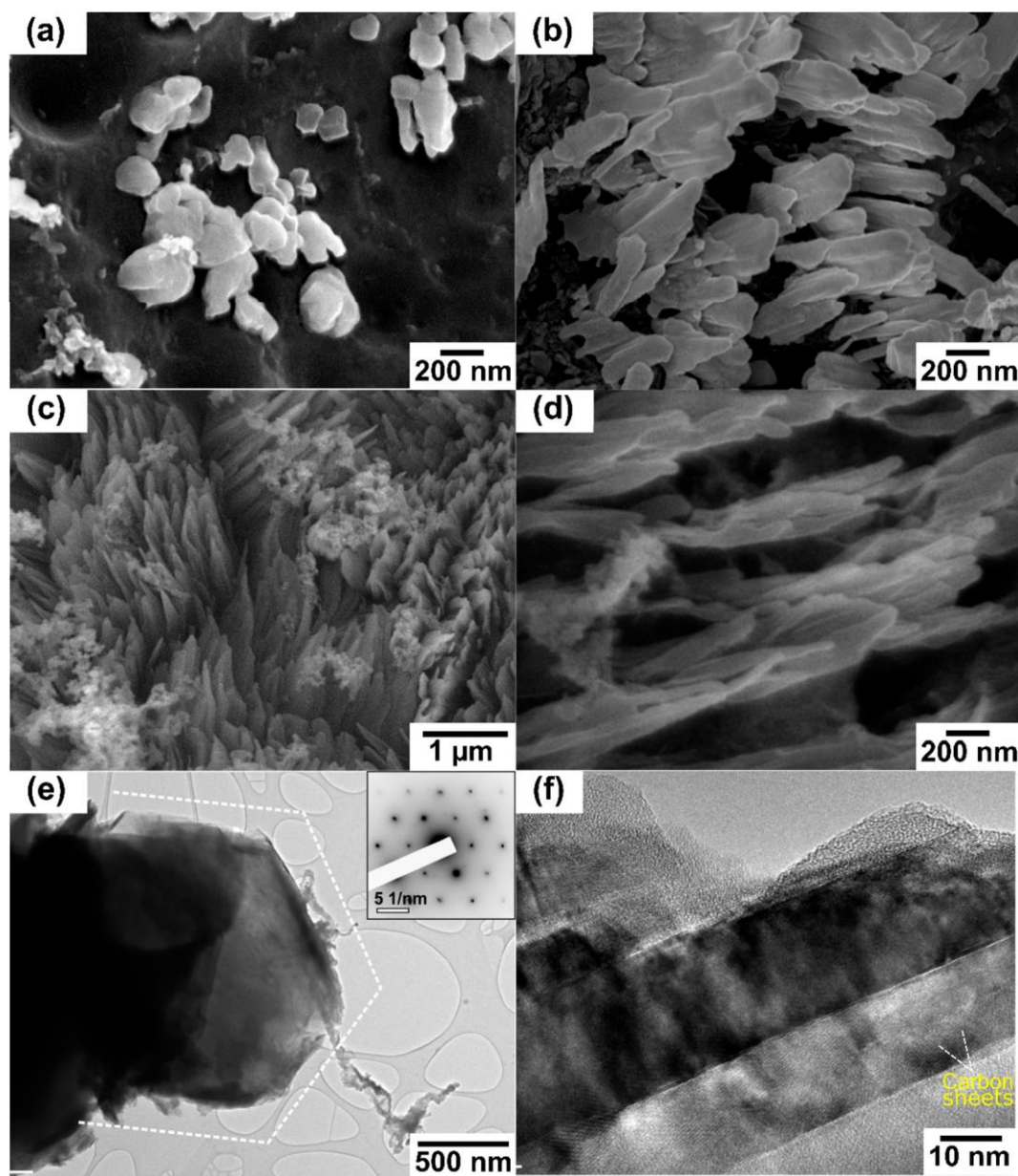


Figure 2. High-resolution SEM micrographs of the carbon nanostructure formation during the time-dependent growth at 250 W and 100:50 sccm after: (a) 3 min; (b) 5 min; (c) and (d) 8 min treatment; (e) overview TEM micrograph of individual graphite-like hexagonal flake (diffraction in inset), and (f) side-view of graphite-like flake, showing several stacks of well-crystalline carbon structures.

The phase composition and crystal structure of CN structures formed after 8 min plasma surface treatment was further investigated by TEM. The morphology of individual flake-like structure has a

characteristic hexagonal outline, as seen in Figure 2e. The selected area electron diffraction pattern (Figure 2e, inset) corresponds to the graphite viewed down the [0001] zone axis (c-axis), showing {10-10} and {1-100} reflections. When looked at from the side (down the a- or b- axis), at sufficiently high magnification, we can resolve individual highly-crystalline layers separated for about 3.4 Å, bonded together by Van der Waals bonds, as seen in Figure 2f. The thickness of such stacks is several tens of nanometers. Therefore, plasma surface treatment for 8 min at a power 250 W and Ar: H₂ flowrate 100:50 sccm was considered as the optimum condition for the synthesis of OCNs. Additionally, the change in chemical composition and improvement in structural quality during the time-dependent growth of OCNs were investigated to identify the characteristics of the deposited OCNs.

The evolution of the crystal structure of the plasma-treated samples was assessed by XRD (Figure 3a). The results show there are no clear diffraction peaks observed in 1 min and 3 min plasma-treated RF gel, and in the diffraction spectra, only broad and diffused scattered reflections can be observed, characteristic for amorphous or poorly-crystalline structures with only short-range ordering. In contrast, the samples that were treated 5 and 8 min exhibit sharp diffraction peak at $2\theta = 26^\circ$ corresponding to (0 0 2) lattice plane of graphite [38], which is typical for so-called graphitic structures where we have at least few graphene-like monolayers stacked in c-direction, resembling the graphite structure.

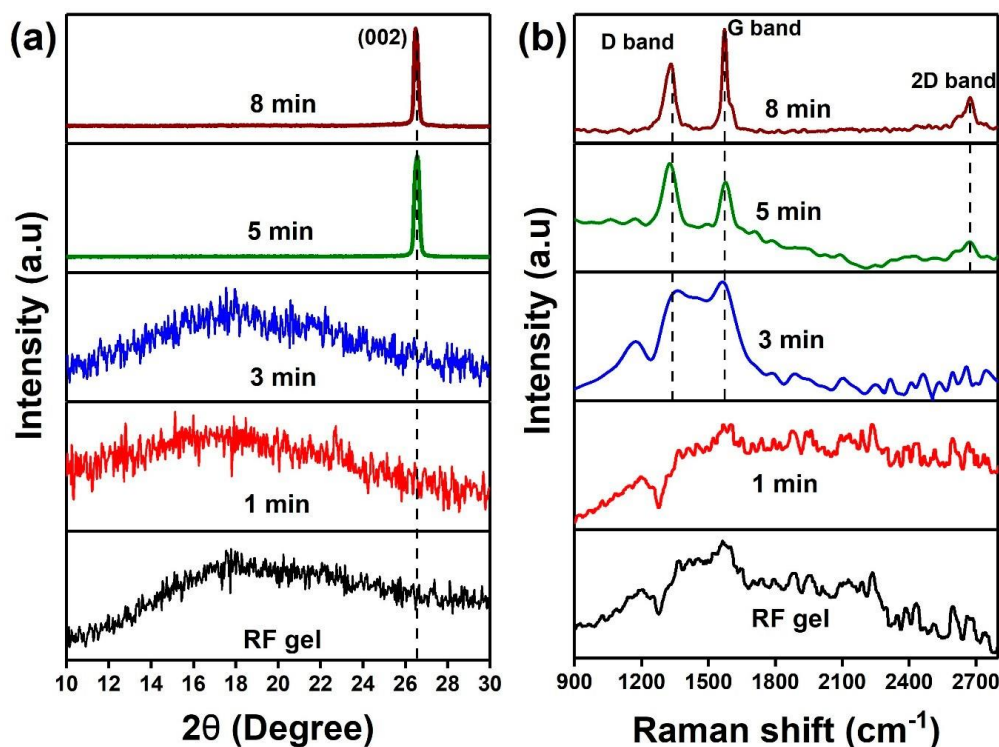


Figure 3. (a) XRD spectra and (b) Raman spectra of CNs obtained after the time-dependent plasma surface treatment on RF gel at 250 W and flow rate 100:50 sccm.

The chemical composition of the CNs produced during the time-dependent structural reformation of RF gel by plasma treatment was analyzed with surface analytical techniques. Raman spectra were used to investigate the structural organization of the samples (Figure 3b). A broad peak at 1350–1600 cm⁻¹ region is observed for the non-treated RF gel, and similar characteristics are observed in the sample after 1 min of plasma treatment. The peak can be ascribed to the presence of aromatic rings present in the polymer chain [44]. On the other hand, 3 min treated samples exhibit two broad peaks at 1362 and 1570 cm⁻¹ characteristic for the amorphous carbon species, while 5 and 8 min plasma-treated samples display an evolution of well-distinguished peaks at 1330, 1581 and 2700 cm⁻¹ that correspond to characteristic D, G and 2D peaks in defected graphitic carbon structures [45–47].

Detailed information on the peak positions is presented in Table S2. The results obtained from Raman and XRD analysis are confirming the graphitization of CNs after 5 and 8 min plasma treatment.

The changes in the functional entities upon the plasma treatment were further investigated by the FTIR analysis (Figure 4a). FTIR spectra of non-treated RF gel and 1–5 min treated samples indicates peaks at 3200–3410 cm^{-1} , 1620 cm^{-1} , 1460 cm^{-1} , and 1300 cm^{-1} corresponding to the vibrations from the hydroxyl group, aromatic group, CH_2 group, and alkyl-phenyl ether groups respectively [48–50]. Compared to this, all the chemical bond vibrations were diminished in the FTIR spectra of the OCNs formed after 8 min plasma treatment, which is confirming the graphitic characteristic of the OCNs [51]. This result suggests that the oxygen-containing functional groups are eliminated from the RF surface during the CNs formation.

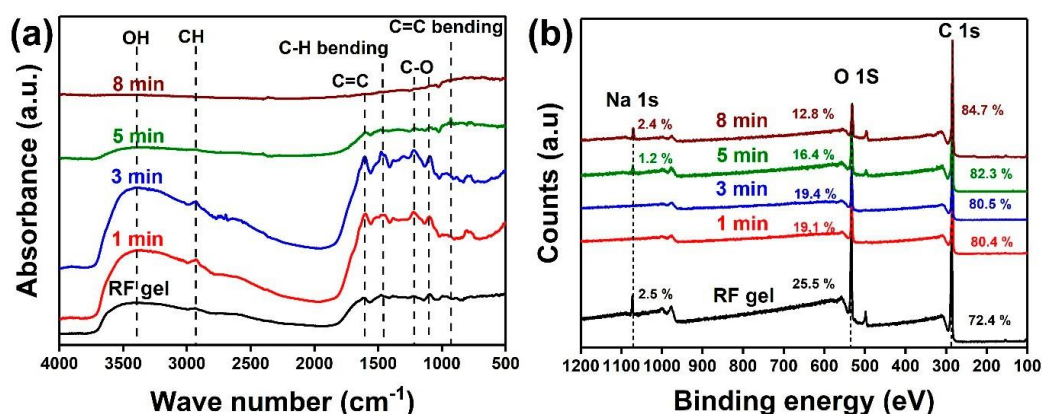


Figure 4. (a) FTIR spectra and (b) XPS survey spectra of OCNs obtained after the time-dependent plasma surface treatment on RF gel at a power:250 W, and flow rate:100:50 sccm.

To confirm the changes in functional entities during the CN formation, changes in the chemical composition of RF gel during each stage of time-dependent plasma treatment were studied by XPS analysis. The loss in the atomic concentration of the oxygen during the conversion of RF gel to OCNs is evident in Figure 4b. Interestingly, the peak observed for metallic Na is diminished after 1 and 3 min of plasma treatment. However, the peak from Na is observed in 5, and 8 min plasma treated samples, which can be due to the recombination of the functional entities on the surface during the reformation. The high-resolution C 1s spectra of the non-treated and 1, 3 and 5 min treated samples were deconvoluted to three main peaks located at 284.8, 286.3 and 288.3 eV, corresponding to C–C bonds, sp^3 C–C/carbon singly-bound to oxygen, and the carbon in carbonyl groups (Figure 5a–e) [52]. In addition to these peaks, the plasma-treated sample exhibited an additional peak at 290.8 eV, corresponding to the π - π^* shake-up satellite. Moreover, the area of C–O–C component after 5 min treatment is higher than the other samples, indicating that the initial CNs formation is occurred by the structural reformation of the C–O–C bonding and forming sp^3 C–C. Further plasma treatment enhances the removal of these sp^3 C–C components and improve the sp^2 C–C characteristics of the CNs and creates vacancy defects in the CNs, which is evident in the C 1s spectra of the 8 min plasma-treated sample. Detailed information on the deconvolution of the peaks, peak position, full width half maximum, and peak area are described in the Supplementary information file, Table S3. The reduction in the peak intensity of O 1s spectra after the plasma treatment also confirms the removal of oxygen functional groups upon the plasma treatment (Figure 5f). The changes observed in O 1s and C 1s spectra and evolution of a peak in the C 1s spectra corresponds to vacancy defect confirming the plasma-enabled formation of defect-rich graphitic OCNs from RF gel.

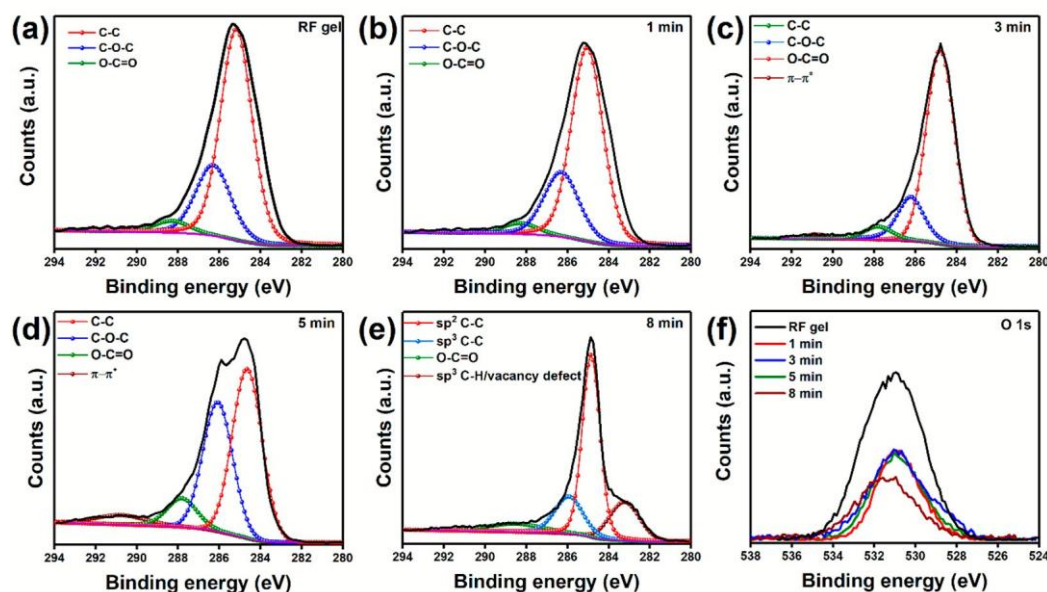


Figure 5. High-resolution C 1s spectra of RF gel and CNs obtained after the time-dependent plasma surface treatment at a power of 250 W and flow rate of 100:50 sccm: (a) RF gel (b) 1 min; (c) 3 min; (d) 5 min; (e) 8 min; and (f) O 1s spectra of RF gel and CNs after each stage of plasma surface treatment.

In thermal annealing methods, a substrate temperature above 600 °C is the key factor for the graphitization, and it could only decompose the carbon-containing precursors into carbonaceous building blocks [53]. In this study, the RF gel cast on the glass substrate directly interacted with the plasma generated species, and the substrate temperature during the process are comparatively lower than the thermal annealing methods, suggesting that temperature was not likely the determining factor of the transformation of the sample in plasma. Thus, the synthesis of OCNs could be explained as the plasma-enhanced etching and constructive interplay between the discharge gases. During the plasma surface treatment, argon and hydrogen are dissociated and form various species in plasma (Figure S4). H₂ is considered as a critical factor in the nucleation and growth of many carbon-based nanostructures [1,54], while Ar is considered as the amorphous etchant. As seen from the time-dependent changes on the surface morphology (Figure 2), at the initial stage, carbon building blocks are extracted from the top-layer of RF gel due to the ion bombardment and neutral radical interaction and re-form into hexagonal carbon rings, which is considered as the essential elements for the growth of OCNs [55]. The presence of reactive H atoms allows the diffusion of these building units on the surface through the recombination-mediated energy dissipation and facilitating the nucleation of CNs [32,56]. Further treatment is enhancing the extraction from these structures as well as seeds the nanostructures, and finally, CNs were formed by the continuous recombination of building units. These diffusions of building units and recombination are influenced by the different plasma discharge parameters and resulted in the various morphology of such obtained nanostructures. Based on the experimental observations, a possible mechanism of the plasma-enhanced surface reformation of RF gel to OCNs is illustrated in Figure 6.

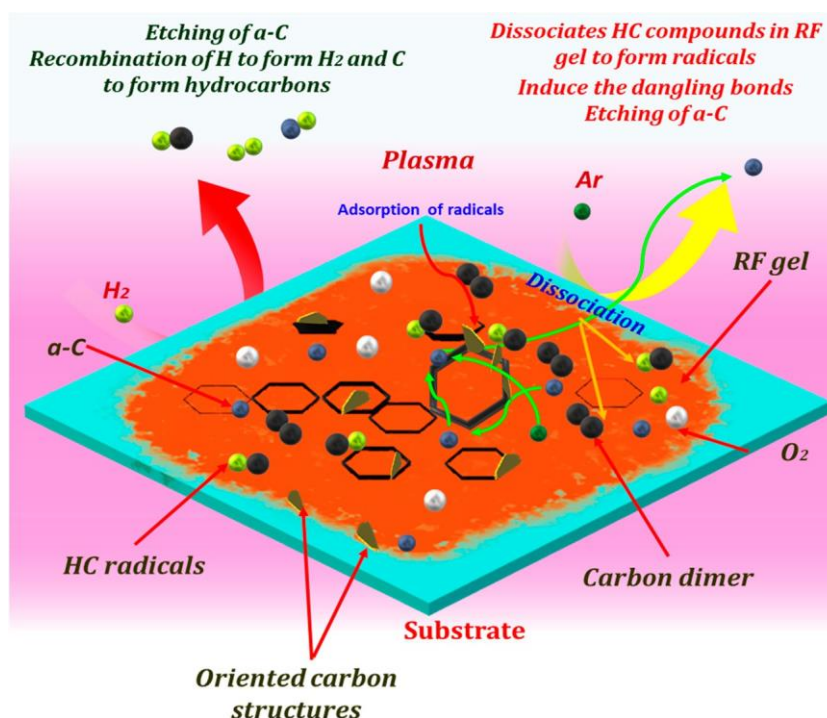


Figure 6. Schematic of the possible mechanism of the growth of OCNs by the plasma reformation of RF gel at the plasma discharge conditions power of 250 W, time of 8 min, and the flow rate of 100:50 sccm.

The graphitization of the carbon is enhanced by the removal of impurities and to form a continuous sp^2 carbon network by the H atoms present in plasma. However, the etching rate becomes dominant at higher power and gas flow rates, which can create more defects and structural damage [57]. On the other hand, insufficient etching and recombination at a low concentration of gases and low plasma power have resulted in the amorphous carbonaceous structures.

5. Gas Sensor Properties

Vertically oriented morphology and defect-rich graphitic characteristics of the CNs can enhance the adsorption of chemical species and change the electrical properties during the process. Thus, the OCNs obtained after 8 min of surface treatment at a power of 250 W and gas flow rate of 100:50 sccm were used for the gas sensing measurements. During the sensing measurement, the sensor was kept in an empty flask for 180 s and then placed into the ethanol environment for 180 s to detect the ethanol vapor. The sensor responses at room temperature and different heating temperatures are presented in Figure 7a, which indicates the increase in sensor response with the increase in ethanol vapor concentration. It has been seen that the OCNs significantly react with ethanol, even at room temperature, with a response value of 0.56 ± 0.02 . The response was increased to a value of 1.86 ± 0.06 at a heating temperature of 80°C , about three times higher than at room temperature. It is worth noting that the performance was repeatable and indicating the sensor did not lose the sensing capabilities after the initial response cycle (Figure 7b).

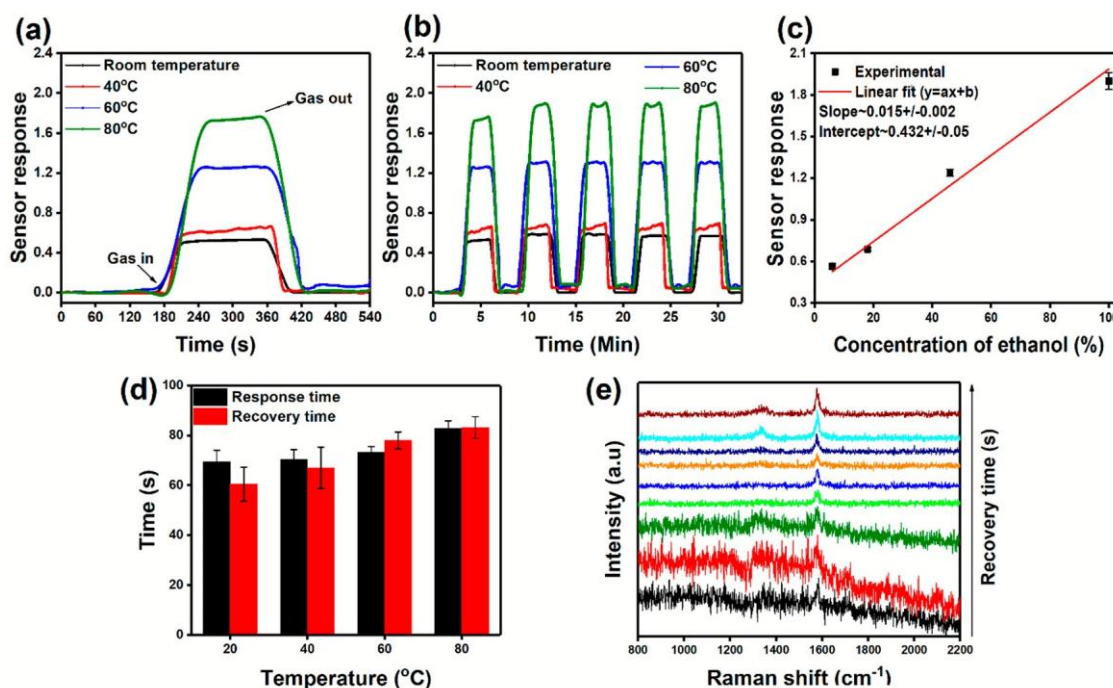


Figure 7. Gas sensor properties of OCNs prepared from RF gel: (a) sensor response to ethanol vapor at different heating temperatures, (b) repeatability of sensor response towards ethanol vapor; (c) sensor response towards the ethanol concentration as a function of heating temperature; (d) response and recovery time of OCN-based sensors towards ethanol at different heating temperature; and (e) ex-situ Raman spectra recorded on OCN sensor during the recovery of ethanol after sensor response at an acquisition time of 4 s with an interval of 6 s.

The sensor response towards the increase in ethanol concentration as a function of the heating temperature is presented in Figure 7c. The OCN-based sensor exhibits a linear increase in the response towards ethanol vapor with an increase in concentration. The linear fitting denoted as:

$$\text{Sensor response } S = 0.432 + (0.01 \times \text{Concentration of ethanol}) \quad (2)$$

A comparison between the response and recovery times of the sensor at room temperature and the different heating temperatures is represented in Figure 7d. The response time T_{res} was estimated as the time taken to achieve 90% of the maximum change in resistance. In contrast, recovery time T_{rec} was calculated as the time taken to recover down to 90% of the maximum resistance change. It is seen that the response and recovery times are increasing with the heating temperature. The sensor took 69 s for the initial response at room temperature, while it increased to 83 s at 80 °C. The sensor attains the initial resistance within 60 s at room temperature after the sensing cycle. On the other hand, the sensor took 84 s for the complete recovery after the sensing cycle at a heating temperature of 80 °C. Additionally, there is a slight change in baseline resistance observed after the first sensing cycle at heating temperatures of 60 and 80 °C. During the sensing cycle, ethanol molecules replace the oxygen on the surface, and during the recovery process, oxygen molecules are partly occupied at the surface and resulted in the change in baseline resistance and prolonged response and recovery time [58,59].

The repeatability of the sensing cycle, indicating that the sensor is not losing the sensing capabilities after the first sensing cycle, can be explained by the chemical stability of the sensor. To understand the chemical changes occurring during the sensing cycle, ex-situ Raman spectra were recorded on the OCN-based sensor after the sensor response and are presented in Figure 7e. The spectra were recorded at an acquisition time of 4 s from a single point with an interval of 6 s to understand the chemical changes that occurred after the maximum sensor response. The signal from the graphitic characteristics of OCNs is suppressed during the initial spectra, which could be due to the presence of the ethanol

vapors. Later, the well-defined Raman peaks are visible with the increase in recovery time, suggesting that the ethanol is completely desorbed from the surface, and there is no chemical modification takes place during the sensing measurements. These results are indicating that the OCN-based gas sensor shows excellent sensing capability towards ethanol molecules.

6. Conclusions

We synthesized graphitized OCNs using an environmentally benign radio-frequency plasma surface-treatment technique. Resorcinol-formaldehyde gel cast on a glass substrate was used as the precursor source for the synthesis of graphitized OCNs. The time-dependent evolution of the OCNs with vertical orientation and influence of plasma discharge parameters on the structure-controlled synthesis was studied in detail. The graphitic characteristics with structural defects were explored using various surface analytical techniques, such as SEM, TEM, XRD, XPS, and Raman analysis. Synthesized defect-rich OCN structures exhibit excellent gas sensing properties to ethanol at room temperature. The response of the sensor towards the increase in the concentration of ethanol was also explored. It is also to be noted that the sensor response, response time, and recovery time of the sensors were increasing with the ethanol concentration. Thus, with further optimization, these OCNs produced from polymer resources could potentially form the backbone of a novel sensing platform based on nanomaterials. Moreover, improving sensitivity and selectivity towards different gases needs to be investigated for the future applications of the OCN-based sensor.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-4991/10/9/1704/s1>, Figure S1. The progressive change in color of RF gel as a function of reaction time during the gelation process from clear (initial stage) to deep red (after complete gelation), Figure S2. Experimental setup for the rf-ICP system used for the synthesis of CNs from RF gel by plasma surface treatment, Figure S3. Experimental setup for the home-built sensing device for ethanol detection, where the sensor is placed to the saturated vapor above the liquid ethanol, Figure S4. Optical emission spectra of the Ar/H₂ plasma ignited at 250 W, and 100:50 sccm flow rate with all the species excited during the surface treatment process, Table S1. The concentration of ethanol at different temperatures calculated using Dalton's law, Table S2. Details of the peak positions observed in the Raman spectra of CNs obtained after 3, 5 and 8 min of plasma treatment, Table S3. Peak position, FWHM, and roughly estimated concentration of the peak components in XPS C 1S spectra of the time-dependent growth of carbon nanostructures.

Author Contributions: N.M.S. planned the experiments and contributed to the data curation, analysis of physical and chemical properties of the samples and manuscript preparation. A.V. contributed to experiments and manuscript preparation. A.J., J.Z. and G.F. contributed to the characterization techniques and reviewed the manuscript. U.C. planned the main conceptualization of the work and reviewed and edited the final manuscript. All authors have read and agreed to the published version of the manuscript.

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Supporting information

Oriented Carbon Nanostructures from Plasma Reformed Resorcinol-formaldehyde Polymer Gels for Gas Sensor Applications

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RF gel preparation

Resorcinol-formaldehyde gel was prepared using a simple polymer gelation method, reported elsewhere [1]. 1.28 g of resorcinol, 2 ml of formaldehyde and 0.04 g of sodium carbonate was dissolved in deionized water and kept in an oven at 85 ± 3 °C for 24–36 h. During the gelation period, the solution changes the colour from clear to yellow, then to orange, and deep red as a function of the reaction time. The solution was deep red after the complete gelation, as shown in Figure S1. In the next step, the gel was used for the synthesis of CNs using plasma surface treatment.



Figure S1. The progressive change in colour of RF gel as a function of reaction time during the gelation process from clear (initial stage) to deep red (after complete gelation).

Experimental set up of the rf-ICP system

The plasma-surface treatment was carried out in a radio-frequency plasma inductively coupled through a 9-turn copper antenna. RF gel cast on a glass substrate was placed in the centre of the coil, and the chamber pumped down to 3 Pa before the experiments. Argon and hydrogen were used as the discharge gases, which were inserted to the chamber from the sides. During the discharge, different flowrates and plasma power were used for surface treatment. Schematic diagram of the rf-ICP system for the plasma-surface treatment is presented in Figure S2.

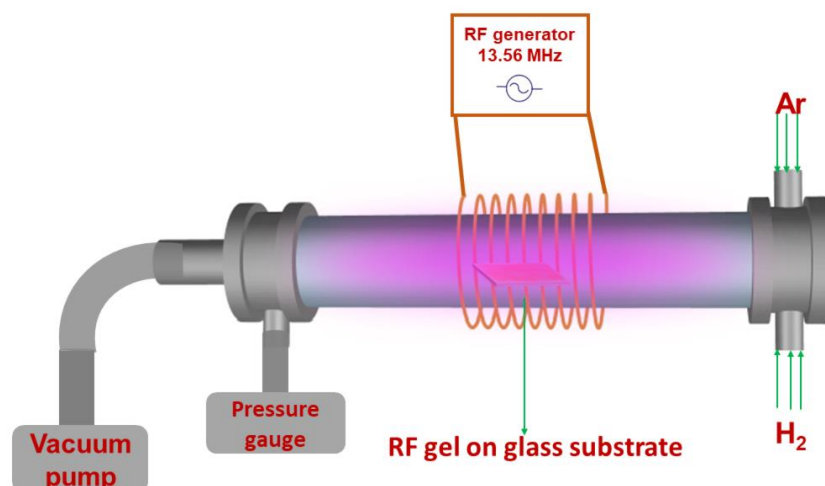


Figure S2. Experimental setup for the rf-ICP system used for the synthesis of CNs from RF gel by plasma surface treatment.

Experimental setup for sensing measurements

The OCN structure filtered on PU membrane was cut into a dimension of 1.5*1.5 cm placed on a sensing chip and connected to the source meter. Two identical 250 ml conical flasks were used as the sensing chamber during the experiment, and ethanol was used as the sensing gas. Ethanol was transferred to one flask, and the other flask was filled with the ambient air. During the sensing measurement, the sensor was moved manually from the “empty” flask to the flask with ethanol (gas on phase) and put the sensor to the saturated vapour above the ethanol surface. Later, the sensor was put back to the empty flask (gas off phase). The schematic of the experimental setup for the sensor measurements is presented in Figure S3.

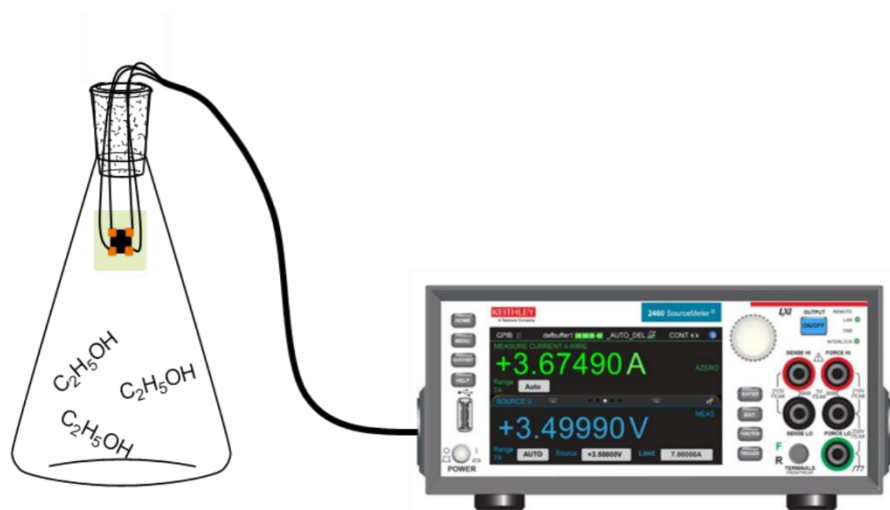


Figure S3. Experimental setup for the home-built sensing device for the ethanol detection, where the sensor placed to the saturated vapor above the liquid ethanol.

Calculation of ethanol concentration

The concentration C_{et} of ethanol inside the sensing, the chamber was controlled by heating the known volume of ethanol to different temperatures. Since the sensing chamber is filled with a mixture of gases (air and ethanol vapour), Dalton's law was used for the estimation of the volume-based concentration of ethanol as following:

$$p_{et} = p_{tot} C_{et}$$

where p_{et} is the vapour pressure of ethanol, p_{tot} is the atmospheric pressure (101.325 kPa) and C_{et} is the volume-based concentration of ethanol. The saturated vapour pressure of ethanol was obtained from the publicly available online databank (table footnote ^a). The calculated concentrations of ethanol are presented in Table S1.

Table S1. The concentration of ethanol at different temperature calculated using Dalton's law.

Temperature	Vapour pressure of ethanol (kPa)	Concentration of ethanol (%)
20 °C	5.82625	~5.75
40 °C	17.8258	~17.59
60 °C	46.7509	~46.14
80 °C	108.432	~107

^a <http://ddbonline.ddbst.com/AntoineCalculation/AntoineCalculationCGI.exe?component=Ethanol>

Raman analysis

The changes occurred in the structure quality of the CNs during the plasma treatment were evaluated by Raman spectroscopy. The peaks of the Raman spectra observed in the CNs after 3-8 min plasma treatment is showing the characteristic behaviour of the graphitic structure. The peak around 1330 cm^{-1} (D band) is ascribed to the A_{1g} breathing mode of six-atom rings in the 1st Brillouin zone boundary K or K' [2]. The G band observed at ~1581 cm^{-1} is assigned to the E_{2g} symmetry corresponds to the one-phonon Raman scattering process at the 1st Brillouin zone centre [3,4]. Evolution of peak at ~2700 cm^{-1} , corresponds to the second-order of zone boundary phonons and activated by the scattering of two phonons with opposite wave vectors.

Table S2. Details of the peak positions observed in the Raman spectra of CNs obtained after 3, 5 and 8 min of plasma treatment.

Sample condition	Peak 1 (cm^{-1})	Peak 2 (cm^{-1})	Peak 3 (cm^{-1})
3 min	1337	1577	
5 min	1328	1578	2662 (cm^{-1})
8 min	1330	1582	2665 (cm^{-1})

X-ray photoelectron spectroscopy (XPS) analysis

The chemical composition analysis of the prepared CNs was investigated by XPS. The C 1s spectra of the non-treated RF gel was deconvoluted to three main peaks located at 284.8, 286.3 and 288.3 eV, corresponding to C-C bonds, carbon singly-bound to oxygen, and the carbon in carbonyl groups [5]. C 1s spectra of the 1 min, 3 min and 5 min treated shows similar peak characteristics and exhibits an additional peak at 290.8 eV corresponding to the π - π^* shake-up satellite. Addition to this, the OCNs formed after the 8 min plasma treatment the peak observed at 283.2 eV corresponds to the sp^3 C-H/ vacancy defect and hence confirms the defected nature of CNs [6]. Compared to remaining samples, the peak observed at 284.8 eV is narrow with a full-width half-maximum of 1 eV, confirms the graphitic behaviour of the carbon nanostructures. Detailed information on the peak position and roughly estimated composition ratio (%) of the deconvoluted peaks of the high-resolution spectra are summarized in Table S1.

Table S3. Peak position, FWHM, and roughly estimated concentration of the peak components in XPS C 1S spectra of the time-dependent growth of carbon nanostructures.

Sample	Peak 1			Peak 2			Peak 3			Peak 4		
	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %
RF gel	284.8	1.7	66.3	286.3	2.0	22.7	288.3	2.0	11.0			
1 min	284.8	1.7	69.5	286.3	2.0	26.1	288.3	2.0	4.4			
3 min	284.8	1.6	74.4	286.3	1.5	18.5	288.1	1.8	5.3	290.8	1.5	1.6
5 min	284.8	1.6	48.9	286.1	1.5	37.3	287.9	1.8	9.0	290.8	2.1	4.7
8 min	284.8	1.0	56.0	285.9	1.5	18.4	288.4	2.2	7.5	283.2	1.7	18.7

The optical emission spectra (OES) analysis

The optical emission spectra (OES, broad range spectrometer LR1, ASEQ) was recorded every 30s during the plasma treatment of RF gel to observe the excited species during the process of CNs formation. The spectra were recorded for 8 min at plasma power 250 W and Ar: H₂ flowrate 100:50 sccm. In the beginning, only noise can be seen in the spectrum, which could be explained with plasma species going into fast chemical reactions with the RF gel so that the recombination of excited species is too fast to record with the used spectrometer. After 2 min we observed a formation of OH peak at 309 nm and H_α at 656 nm. After another minute, other species start to show – N and Ar lines become distinguishable along with the nitrogen continuum that is always observed inside low-pressure rf plasma. Even though Ar was a working gas, we observe OH in the spectrum; it can be because of the excitation of the top layer of RF gel during the surface reformation.

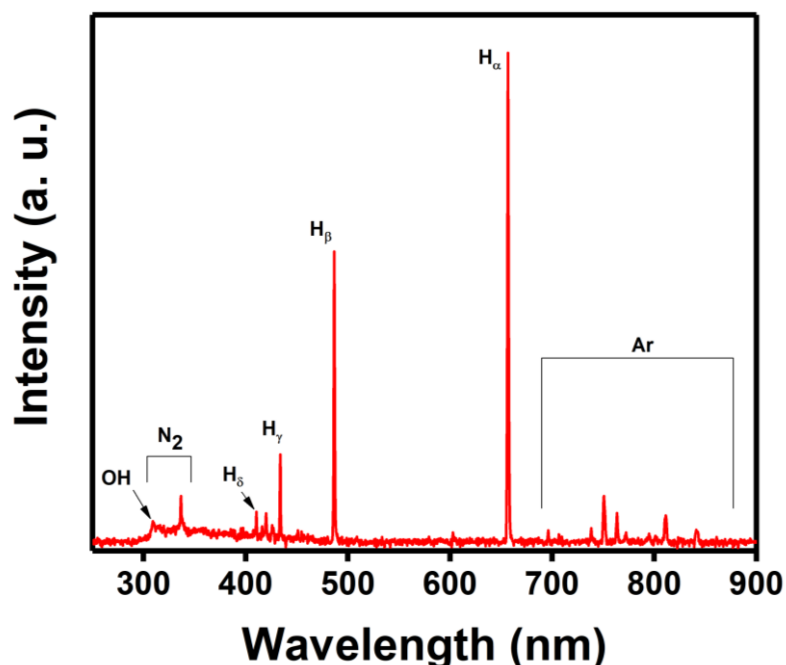


Figure S4. Optical emission spectra of the Ar/H₂ plasma ignited at 250 W, and 100:50 sccm flow rate with all the species excited during the surface treatment process.

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Chapter 3.2

Low-Pressure Plasma-Enabled Synthesis of Vertical Carbon Nanostructures

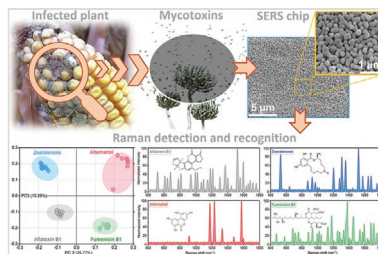
In Chapter 3.2, we developed our own radio-frequency inductively coupled plasma-enhanced chemical vapour deposition system for the deposition of carbon nanostructures. This chapter investigated the nucleation and initial growth of vertical carbon nanotubes and their transformation to carbon nanoforest on a catalytic solid surface (nickel foil) as the function of deposition time. The developed plasma approach provided a high growth rate and controllability over the morphology. We demonstrated that nanostructures synthesised with this technique revealed a high structural ordering and crystallinity, confirmed by Raman spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy. It was established that the developed plasma-enabled technique is fast, efficient, and easy compared to the other commonly used conventional techniques. During the surface imaging of the nanostructures, it was identified that the morphology would be favourable for use as a platform for plasmonic applications. The vertical orientation of carbon nanotubes, large surface area and the electromagnetic enhancement mechanism makes them a favourable geometry for plasmonic applications. Therefore, the plasma-designed carbon nanostructures were covered with plasmonic gold nanoparticles and then explored in the capabilities for the plasmonic detection of mycotoxins.

Regarding my contribution: I synthesised all the carbon nanostructures using plasma-enabled techniques and contributed to the surface and chemical composition analysis. I jointly wrote the paper with co-authors.

RESEARCH ARTICLES

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**Label-Free Mycotoxin Raman
Identification by High-Performing
Plasmonic Vertical Carbon
Nanostructures**



It is reported that plasmonic substrates consisting of vertical carbon nanotubes offer a unique option for immediate and accurate mycotoxin vibrational fingerprint detection. Plasma nanoengineering improves the surface morphology, enhancing the chip's sensitivity. Consequently, optical investigations of cancer-provoking biosphere entities are possible at ppb concentration levels, thus advancing existing food-quality inspection equipment.

Label-Free Mycotoxin Raman Identification by High-Performing Plasmonic Vertical Carbon Nanostructures

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Mycotoxins are widespread chemical entities in the agriculture and food industries that can induce cancer growth and immune deficiency, posing a serious health threat for humankind. These hazardous compounds are produced naturally by various molds (fungi) that contaminate different food products and can be detected in cereals, nuts, spices, and other food products. However, their detection, especially at minimally harmful concentrations, remains a serious analytical challenge. This research shows that high-performing plasmonic substrates ($AEF = 5 \times 10^7$) based on plasma-grown vertical hollow carbon nanotubes can be applied for immediate detection of the most toxic mycotoxins. Due to excellent sensitivity allowing operation at ppb concentrations, it is possible to collect vibrational fingerprints of aflatoxin B₁, zearalenone, alternariol, and fumonisin B₁, highlighting the key spectral differences between them using principal component analysis. Regarding time-consuming conventional methods, including thin-layer chromatography, gas chromatography, high-performance liquid chromatography, and enzyme-linked immunosorbent assay, the designed surface-enhanced Raman spectroscopy substrates provide a clear roadmap to reducing the detection time-scale of mycotoxins down to seconds.

starts with aflatoxins (AFs) where aflatoxin B₁ (AFB₁) occupies a leading position as the most potent natural carcinogen.^[1] The rest are considered less toxic; nevertheless, their ingestion can still lead to serious health-related complications, especially with long-term exposure and consequent accumulation in living organisms. Mycotoxins such as fumonisins, zearalenone (ZEN), trichothecenes, and alternate mycotoxins induce many different toxicities, including genotoxicity, mutagenicity, neurotoxicity, hepatotoxicity, immunosuppression, and endocrine disruption.^[2,3] Many mycotoxins induce toxicity at ppm levels, whereas AFs are already dangerous at ppb levels. Such low concentrations pose a problem as it is extremely challenging to detect and distinguish between different types of mycotoxins. Current analytical methods, such as different types of chromatography and enzyme-linked immunosorbent assay, are time consuming or require complex sample preparation, data collection, and analysis. A method possessing better analytical performance and providing reliable results within a short time is a “holy grail” dream in healthcare applications,^[4] but characteristic of plasmon-coupled Raman scattering. A spectroscopic tool is considered a cutting-edge method for biosensing applications, especially in the food industry, where product quality monitoring is of prior interest.

1. Introduction

Mycotoxins are toxic secondary metabolites produced by a variety of different filamentous fungal species. Their toxicity for humans has been unanimously proven and depends on the mycotoxin type. Presently, more than 300 structurally different mycotoxins have been identified. A list of the most dangerous

Surface-enhanced Raman spectroscopy (SERS) is closely associated with nanoengineering of nanorough plasmonic substrates, serving as an origin for photon scattering's electromagnetic enhancement.^[5] A prominent nanoroughness and a high aspect ratio at the atomic scale are the surface properties for customizing optically induced regions with strong electric field confinement, known as “hot spots.” Surface patterns composed of vertically standing, inclined pillar-like structures with rough sidewalls and developed tips, willing to provide excellent plasmonic media, are considered as substrates to build up high-performing SERS-active detectors. The superior analytical sensitivity, temporal stability, chemical inertness and reusability, of such templates are crucial for SERS sensing and directly linked to fabrication strategies. Recently, the large-scale production methodologies listing lithography related,^[6,7] oblique angle deposition techniques,^[8,9] and surface etching approaches^[10,11] have proved SERS usability of metallic, metal coated and nanometer-thick oxide-layer protected pillar-like substrates. Although,

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despite having a decent practical interest, the fabrication pathways frequently require to employ costly equipment or synthesis do not provide wide options for surface morphology fine-tuning.

From a nanoengineering perspective, carbon-related structures are considered to be a promising candidate for SERS applications as a skeleton template, due to a possibility of controllable morphology tailoring at the atomic scale. Synthesis of carbon nanomaterials is typically provided via chemical vapor deposition (CVD) processes. Conventional thermal CVD techniques enable the growth of carbon nanostructures, but synthesis is not a trivial process due to elevated fabrication temperatures varying within a range of 1000–1700 °C.^[12–14] Also, large-scale synthesis is problematic using custom thermal CVD techniques. A solution can be accessed by implementing an improved technique that relies on reactive gaseous plasma synthesis.^[15]

Plasma-enhanced chemical vapor deposition (PECVD) represents a faster, facile, and highly controllable method for deposition of the various carbon nanostructures on solid substrates by dissociating the precursor gases at relatively low temperatures. Additionally, the use of catalytic metals such as nickel (Ni), molybdenum (Mo), copper (Cu), and platinum (Pt) increases a variety of prominent surface morphologies, including vertical carbon nanotubes (CNTs), vertical nanoforests, carbon nanowalls, few-layer graphene sheets, graphene, carbon nanofibers, conical textures, etc.^[16–25] During PECVD, morphology and growth rate can be controlled by plasma discharge parameters (gas selection, power density, substrate material and temperature selection, substrate position, and treatment time).^[26,27] The presence of a metal catalyst and its nucleation during growth can determine CNT height and diameter.^[28–30] The PECVD method provides more room for nano-to-microstructure surface morphology transition and control. Additionally, certain plasma parameters and synthesis time can induce CNT clustering, resulting in the formation of forest-like structures with exceptional environmental stability over time. Decorating such textures with plasmonic materials like gold (Au), silver (Ag), or even bimetallic coatings (Au/Ag or Au/Pd) of different thicknesses and composition could improve the optical response significantly utilizing plasmon resonance frequency shift, opening more options for SERS features customization.^[31] In the real world, sensor surface functionalization layers are added, which help in making the nanostructures more stable over time.^[32]

Herein, we successfully employed a fast and facile radio-frequency (RF) PECVD approach and synthesized high-performing plasmonic substrates. Four developed nanostructures decorated with Au film were systematically characterized. A surface with the best optical response was utilized to collect Raman fingerprints of four different mycotoxins at the ppb level. Significant differences in vibrational spectra were detected to unanimously distinguish between AFB₁, ZEN, ALT, and FUMO-B₁ mycotoxins after applying a statistical dimensionality-reduction method.

2. Results and Discussion

2.1. Nanostructure Characterization

Plasma synthesis was conducted at 1, 2, 4, 10, and 30 min, to explore the growth mechanism. Surface color changes observed

in the Ni film can be attributed to the formation of carbon structures and content change across the surface during plasma treatment. Scanning electron microscopy (SEM) images were taken to monitor morphology alterations of the carbon structures. For the sake of clarity, samples were labeled as follows: S1 is a structure treated in plasma for 2 min, S2—4 min, S3—10 min, and S4—30 min. Initial seeding and formation of nanostructures with vertical orientation were perceived after 2 min as vertical carbon nanoseeds (S1, **Figure 1a**). Uniformly grown and densely packed vertically aligned tube-like nanostructures were observed after 4 min of deposition (S2, **Figure 1b**). A 10 min deposition resulted in increased density of these tube-like structures that tend to cluster together, forming bundled vertical nanostructures with the initiation of branches along different directions (S3, **Figure 1c**). When the growth time was increased to 30 min, these branched nanotubes were transformed smoothly to a nanoforests-like texture that continued to grow vertically with more intense pillar branching (S4, **Figure 1d**). Along with the morphology alterations, the height of vertical carbon nanostructures (VCNs) also changed with growth time following a simple exponential trend, as shown in **Figure 1e**. After 1 min of deposition, melted Ni with thin carbon layers was formed with thickness 70–80 nm. A nanoforest formed after 30 min and its height was ≈2 μm. In all cases, a building unit is a tube-like structure; thus, a detailed transmission electron microscopy (TEM) analysis was conducted to investigate the tubes' structure.

The TEM image of the nanotubes obtained after 4 min plasma deposition is exhibited in **Figure 1f**. The structures were composed of multiwalled CNTs (**Figure 2**), with an average diameter of 50 nm and terminated by faceted single crystal metallic Ni particle having a size of about 30 nm. Each carbon nanotube consists of more than ten carbon layers that form the walls. Since the Ni crystals were located at the tip of carbon tubes, it is proposed that the nanostructures were formed by the tip-growth mechanism as explained in refs. [28–30]. A well-known fact is that CNT catalytic growth is influenced by metallic nanoparticles forming during nucleation.^[33–35] If their size is <5 nm, CNT growth occurred by base growth, where the catalyst particle is situated at the structure's base. Once the nanoparticle's size is >5 nm, growth is promoted by the tip-mechanism, and CNTs are terminated with the catalytic nanoparticle.^[33–35]

Here we deal with the second mechanism, where several consequent steps of growth are observed (**Figure 1h**): i) formation of nickel nanoparticle, ii) nucleation and initial growth of VCNs, iii) elongation of VCNs by tip-enhanced growth and lift-off Ni nanoparticle, and iv) clustering and branching of VCN structures. During the PECVD process, hydrocarbon gas (methane) was ionized and dissociated into ions and radicals. These reactive plasma species induce Ni surface etching (by ion bombardment) forming point defects and dangling bonds, where carbon deposition is initiated. During the initial stage, i.e., after 1 min of plasma treatment, Ni was melted. It led to Ni nanoparticle nucleation on the foil surface and deposition of a thin layer of carbon underneath. The second stage began with the seeding of carbon nanostructures, which was followed by vertical growth. The particle size exceeded 5 nm threshold during the initial seeding process. Thus, reactive

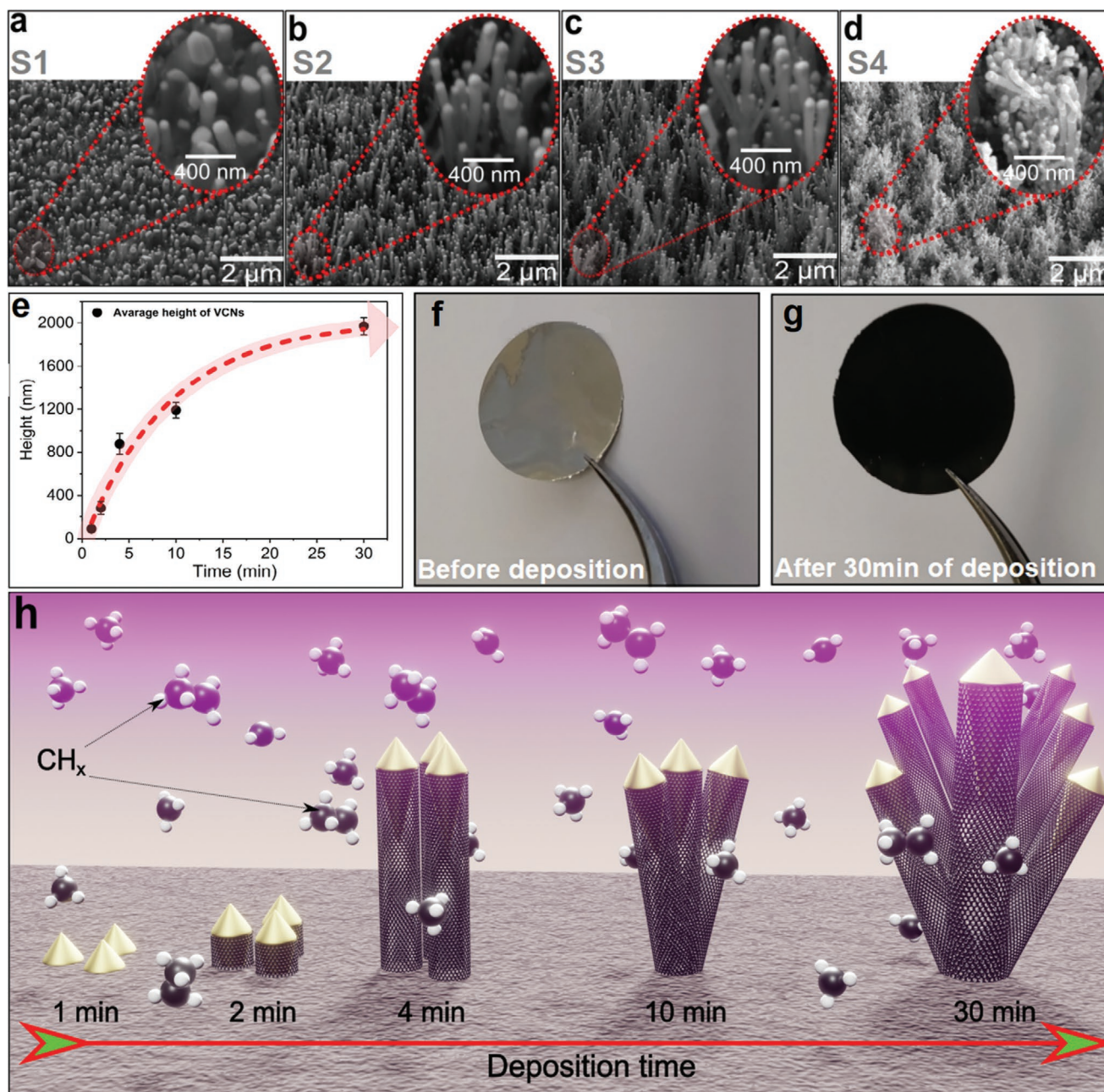


Figure 1. Surface morphology of the carbon nanostructures after time-dependent growth by SEM imaging: a) 2 min—S1, b) 4 min—S2, c) 10 min—S3, and d) 30 min—S4. e) The height of VCN structures synthesized at different growth time described by a simple exponential fit. f,g) Digital photos of Ni foil before and after plasma synthesis. h) Schematic roadmap of the VCN growth mechanism by plasma-assisted deposition.

species had a sufficient time for diffusion into the large catalyst particle before the formation of complete nanoislands/hemispherical cap. Simultaneously, the reticulated carbon chains merged with the metal surface, leading to its stabilization. Because of the higher aspect ratio and catalytic activity, the Ni nanoparticle was exposed to further carbon absorption, and elongation of the nanoparticle occurred along with carbon deposition. As a result, the Ni substrate and Ni nanoparticles separate during the nanostructure growth when nanoparticles were lifted. Hence, growth continued, where the carbon tubes elongated due to further absorption of carbon atoms, forming

a pillar-like structure. With an increase in growth time, these individual structures started to cluster together and branching began, caused by defect generation on the surface. After 30 min of treatment, this ended up forming densely packed tubes with increased vertical dimension.

To obtain more insights into the structure quality and its chemical composition, the samples were characterized by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) (Figures 3 and 4). After the former, all the samples exhibited characteristic peaks of graphene-like structures located at 1328–1331, 1610–1613, 1580–1583, and 2660–2668 cm^{-1} .^[36]

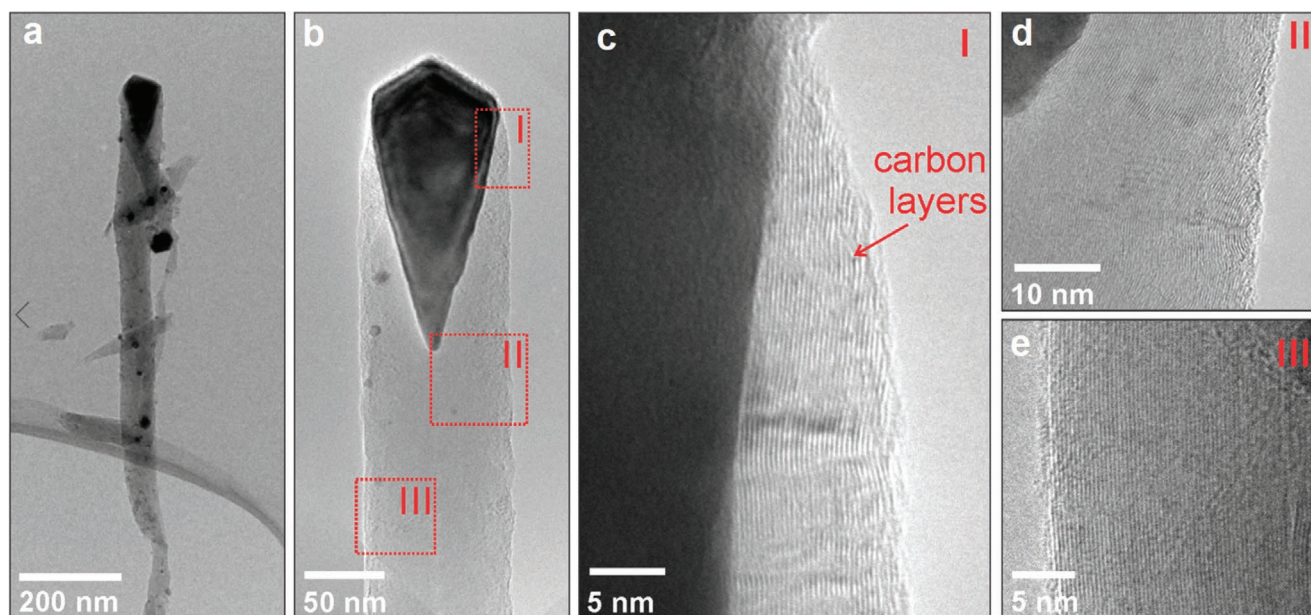


Figure 2. a,b) TEM and c,d) HRTEM images of multiwalled CNTs: a) overview image of individual nanotube topped by b) faceted Ni nanocrystal, c) HRTEM image of CNT to present multiple carbon layers, d) aligned around the nickel nanoparticle, and e) aligned in the carbon backbone.

The D (defect) peak observed at $1328\text{--}1331\text{ cm}^{-1}$ is ascribed to the A_{1g} breathing mode of six-atom rings in the 1st Brillouin zone boundary K or K' , activated only in the presence of defects. The G (graphitic) peak placed at $\approx 1580\text{--}1583\text{ cm}^{-1}$ occurs due to the collective in-plane bond stretching of sp^2 bonded carbon atoms and is assigned to the E_{2g} symmetry. It corresponded to the one-phonon Raman scattering process at the 1st Brillouin zone center. The D' band detected within a range $1610\text{--}1613\text{ cm}^{-1}$ is also associated with defects mainly due to the localized vibration of randomly distributed impurities in the graphitic edges. The G' or 2D (overtone of D) peak at $\approx 2660\text{--}2668\text{ cm}^{-1}$ was the

second order of zone-boundary phonons and is related to the scattering of two phonons with opposite wave vectors.^[37,38]

The level of disorder of the designed nanostructures can be characterized by the intensity ratio of D and G peaks (I_D/I_G). Comparison of the I_D/I_G ratio of S1–S4 structures is presented in Figure 3b. The I_D/I_G ratio increased with a longer growth time, which can be attributed to nanostructure branching and defect generation during plasma deposition. Moreover, the well-defined D' peak and $I_{D'}/I_G$ observed in all samples further supports the defect-rich nature of deposited textures related to the clustering of the individual vertical CNTs.

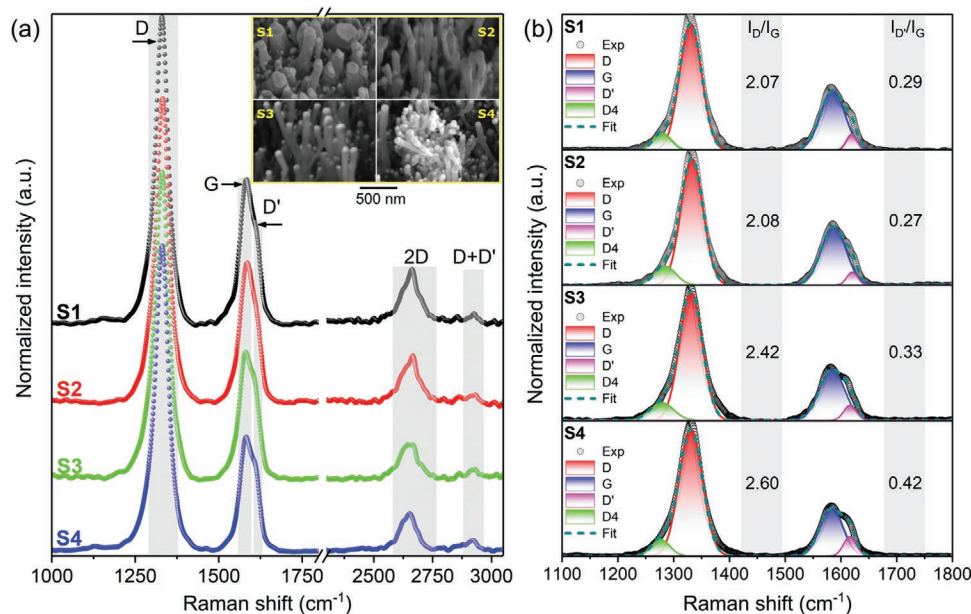


Figure 3. a) First- and second-order Raman spectra of as-prepared carbon nanostructures. b) Gaussian peak deconvolution analysis of the characteristic vibrational modes accompanied by I_D/I_G and $I_{D'}/I_G$ ratios as a function of growth time.

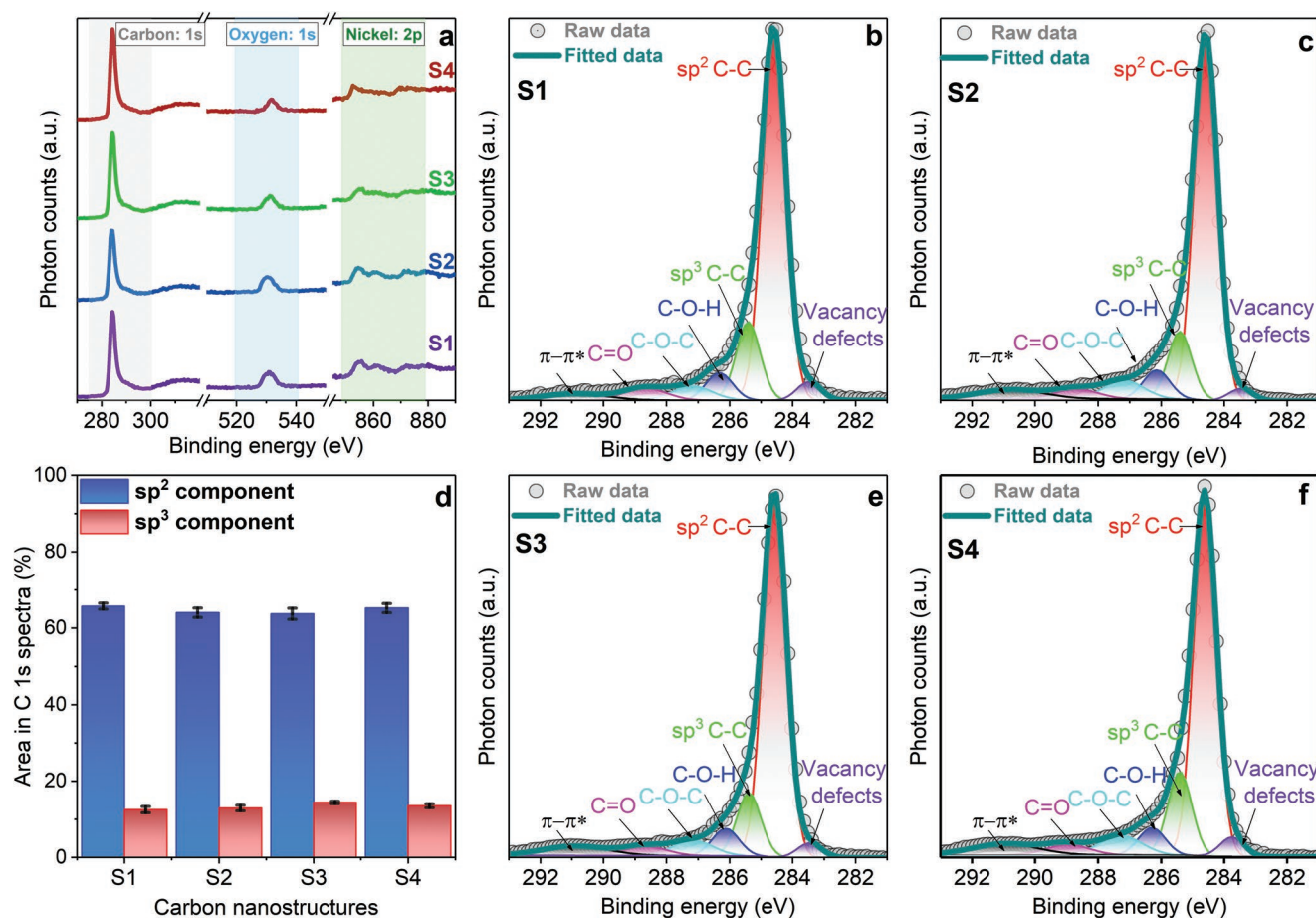


Figure 4. a) High-resolution XPS spectra of designed carbon nanostructures. b,c,e,f) Deconvoluted carbon peak reveals a contribution of binding surface components in S1–S4 nanostructures. d) Estimated contribution of sp^2 and sp^3 hybridized carbon atoms into structure formation.

XPS analysis investigated changes in chemical composition and the surface components concerning growth time. Long-range spectra of S1–S4 substrates consisted of the C, Ni, and O peaks located at around 284.6, 531.8, and 850.2 eV, respectively (Figure 4a). Naturally, carbon content rose with increasing growth time. All samples contained oxygen that was absorbed from the ambient air by the reactive carbon atoms. The carbon's bonding environment in all samples was evaluated by numerical deconvolution of high-resolution C 1s spectra (Figure 4b–f). Five main structure-related peaks located at 284.6, 285.5, 286.6, 288.5, and 290.4 eV were observed. The peaks were assigned to sp^2 C–C bond (graphitic-C), sp^3 -bonded carbon atoms, carbon singly bound to oxygen, the carbon in carbonyl groups, and the $\pi-\pi^*$ shake-up satellite, respectively.^[39]

2.2. Plasmonic and Optical Properties

Despite being plasmon-active nanomaterials themselves due to $\pi-\pi^*$ resonances, the designed carbon nanostructures play the role of a skeleton providing a solid basement for depositing more plasmonic gold. A specific morphology of carbon nanostructures with multiple hotspots might increase the optical response of the later one. To explore and compare the designed

nanopatterns' optical features, a 100 nm Au layer was placed on top of substrates S1–S4. As is known, Au is widely exploited in plasmonic biosensing due to its biocompatibility, high optical response in the red and near IR spectral range, and better resistance to environmental oxidation. After Au film deposition, the samples' surface morphology underwent slight alterations (Figure 5a–d). At the shortest synthesis time (Figure 5a), namely 2 min, the surface was composed of short densely packed CNTs encapsulated in Au film. With increased treatment time from 4–30 min, tubes tended to agglomerate into individual clusters, and the distance between them increased (Figure 5b–d).

The nanomaterials' plasmonic efficiency depends on the optical response, namely extinction coefficient, linked to a combination of scattering and optical absorption.^[40] These optical properties are strongly magnified due to electron cloud oscillations (plasmonic waves) near the metallic nanostructures. The color of the surface plasmonic scatterers can be estimated by dark field optical microscopy, as was shown recently.^[41] It was demonstrated that the prepared substrates scatter mostly green-red photons, which could be associated with frequencies of the localized surface plasmon resonances (Figure 5a1–d1). The red color dominated in each case and nanotube clustering induced an increase in the intensity of the scattered light (see bar graphs of R, G, B channels Figure 5a2–d2). It should be

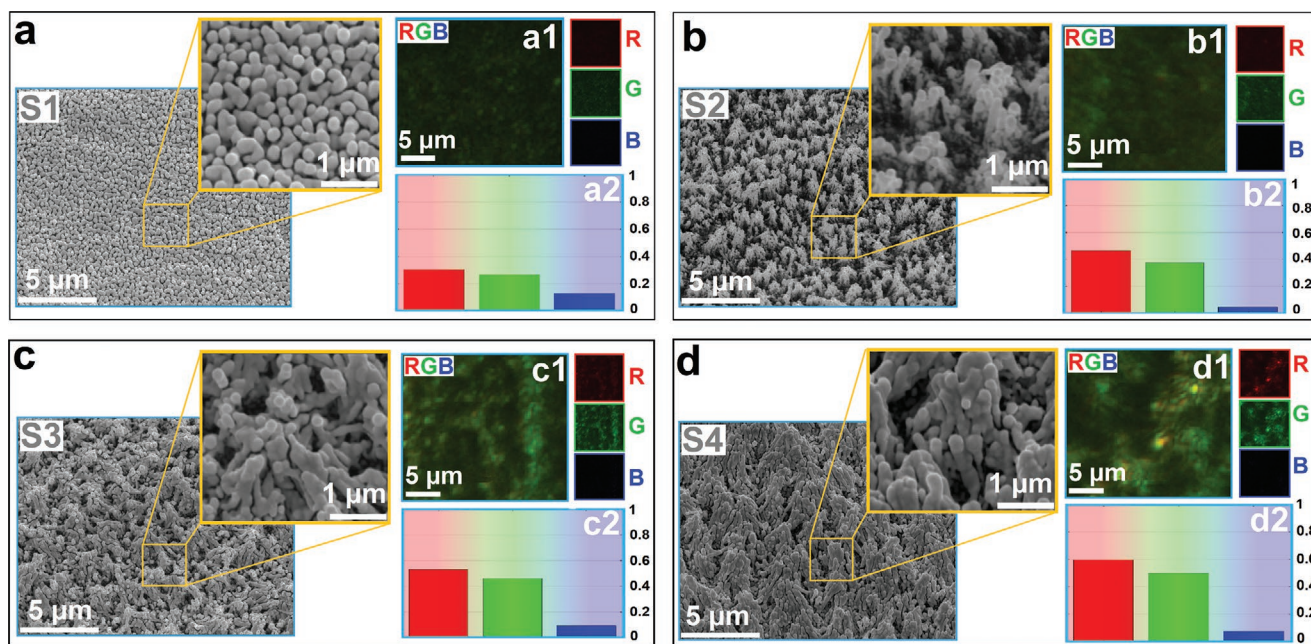


Figure 5. a–d) Tilted SEM images representing surface morphology of the nanostructures synthesized at a) 2 min, b) 4 min, c) 10 min, and d) 30 min after Au sputtering. a1–d1) Dark-field optical scattering of four Au-coated carbon nanostructures presented as an RGB picture of a selected area with accompanying decomposition into red, green, and blue components. a2–d2) A bar graph comparing relative scattering intensities from each R, G, B channel of the corresponding substrates.

noted that the area observed in the dark-field regime did not coincide with the real size but gave a photon scattering intensity estimation of a certain point on the surface. These results correlated with those obtained from total reflectance measurements (Figure 6a). The Au decorated carbon nanostructures reflect more in the red part of the visible spectrum and reflectance increases with sample preparation time.

Next, Au deposited substrates were tested regarding their Raman signal enhancement. A 1 μL drop of crystal violet (CV) diluted in water with a concentration of 1×10^{-6} M was pipetted on top of the substrates, dried at ambient conditions, and SERS measured. Figure 6b represents a vibrational fingerprint region of CV with distinct strong characteristic peaks ranging from 1700 to 600 cm^{-1} , starting with a double signal at 1620 and 1588 cm^{-1} typical of the $\nu(\text{C}-\text{C})_{\text{ring}}$. Peaks detected at wavenumbers 1369 and 1179 cm^{-1} belonged to the bonds' vibrations in $\nu(\text{C}_{\text{center}}-\text{C})_{\text{ring}}$ and in-plane $\sigma(\text{C}-\text{H})_{\text{ring}}$, respectively. The vibration observed at 915 cm^{-1} corresponded with asymmetric stretching of another $\nu(\text{C}-\text{C})_{\text{ring}}$. The mode placed at 808 cm^{-1} stands for out-plane bending motion $\sigma(\text{C}-\text{H})_{\text{ring}}$. Note that ν and σ indicate stretching and bending molecular motions.^[42]

The highest average signal intensity was observed in sample S1 with the shortest plasma synthesis duration. Longer synthesis times had progressively lower CV signals, reaching a fivefold lower SERS response for the sample treated at the longest time (30 min). Descending order of SERS activity (Figure 6b) showed an opposite behavior to that one observed at total reflectance (Figure 6a). These contradictory findings were a result of the different morphologies of the sample surfaces. A large height variation of CNTs for S2–S4 substrates posed a problem in capturing the objective's focus during measurements. Instead, plasmonic tips/dots of S1 were lying preferably

in a focal plane of the objective; thus, they produced an accumulative effect, summing up the Raman scattering from each point of the surface.

A limit of detection was estimated using the best performing substrate S1 and a set of different water-diluted concentrations of CV. Linear extrapolation of the most dominant Raman mode of CV described the experimental data well, revealing that the designed substrate deposited with Au can easily operate within a range of micro–nanomolar analyte concentrations. The intersect of a calculated line with a concentration axis was observed just below 5×10^{-9} M (Figure 6d), revealing the substrate's sensitivity threshold at the selected experimental conditions. Using the intensity of Raman reporter from glass substrate as a reference in combination with data obtained from S1, it is possible to estimate an analytical enhancement factor of the substrate via $\text{AEF} = \frac{I_{\text{SERS}} \times N_{\text{Raman}}}{N_{\text{SERS}} \times I_{\text{Raman}}} = \frac{I_{\text{SERS}} \times C_{\text{Raman}}}{C_{\text{SERS}} \times I_{\text{Raman}}}$. In the formula I_{SERS} and C_{SERS} are the photon scattering intensity and analyte's concentration during SERS measurements, and I_{Raman} and C_{Raman} are the vibrational mode intensity and concentration of the normal Raman analysis. Thus, the AEF of S1 reached a value around $\approx 5 \times 10^7$. The enhancement factor was reduced with plasma synthesis time. Taking AEF of sample S1 as a reference, the consecutive signal intensity of S2, S3, and S4 substrates decreased by 35%, 65%, and 80%, respectively.

After the SERS measurements, the S1 substrate was mildly dry-cleaned in oxygen-enriched plasma. Several rounds of CV (1×10^{-6} M) loading–decomposing were conducted (Figure 7a). As observed, a flat background (“out” curves) was obtained after each exposure to plasma of a total duration equal to 100 s. Consequently, the comparable Raman signal of CV was recorded after each CV deposition with insignificant intensity variations,

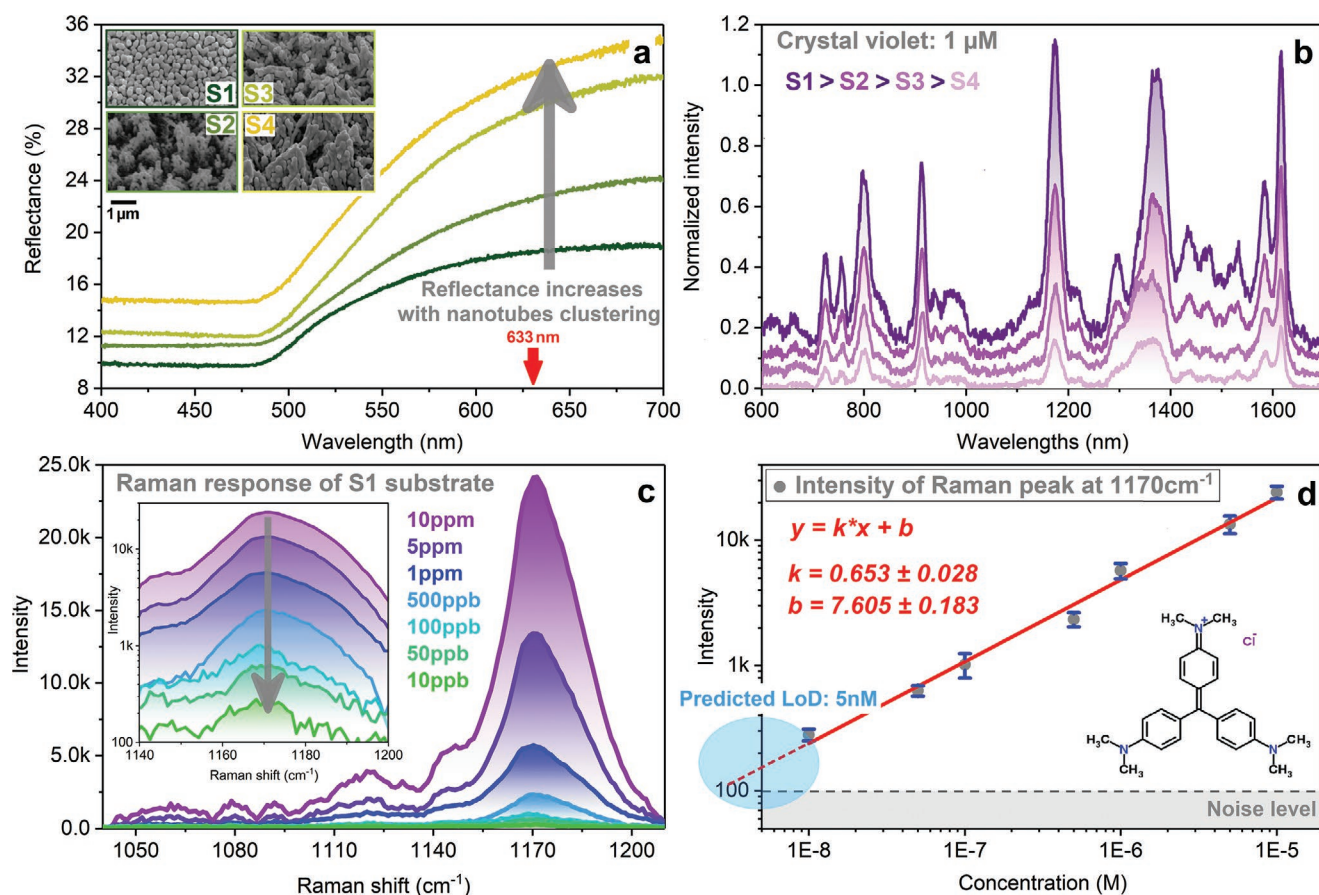


Figure 6. a) Total reflectance of the Au-coated carbon nanostructures in a visible spectral range; a red pointer indicates a monochromatic optical illumination used during the SERS study. b) SERS fingerprint of 1×10^{-6} M aqueous solution of crystal violet dye. c) Raman intensity of in-plane $\sigma(\text{C-H})_{\text{ring}}$ vibration in the molecular structure of crystal violet taken at different analyte concentrations from the S1 substrate. The inset is in logarithmic scale to better visualize peak intensities. d) Log-log graph representing average intensity of the corresponding mode versus analyte concentration. A red line is a linear fit for limit of detection estimation.

as confirmed by a standard deviation plot (Figure 7b). Importantly, plasma treatment at such low power (100 W) and short duration of exposure (10 s, ten times) did not influence the surface optical response. Thus, these results justify the presented plasmonic template as a robust technique, suitable for multiple purposes.

Plasma treatment is an effective approach for the rapid degradation of chemicals having multiple aromatic rings in their structure.^[43] For instance, Okeil et al. used a low-pressure Ar plasma to remove analyte residuals from granular and porous Ag films.^[44] Because of Au film's better oxidation resistance than Ag, we were able to use a combination of Ar and

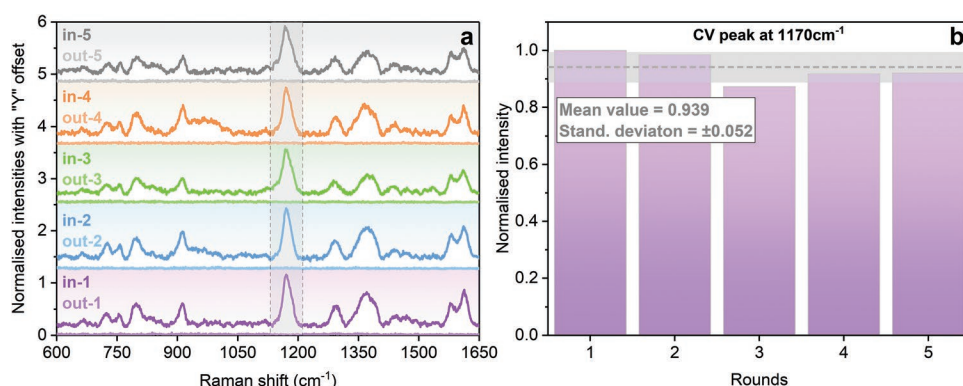


Figure 7. a) SERS signal recovery of 1×10^{-6} M crystal violet after dry-cleaning in plasma. b) Raman intensity of a peak enclosed within a light-gray box (1170 cm^{-1}) after each consequent deposition.

O₂ gases to obtain a synergetic effect of cleaning. Noble gas argon is known to act as a kinetic remover due to a preferable ion bombardment mechanism. Moreover, it contributed to increased oxygen radical concentration, which enabled more stable plasma ignition. In contrast, O₂ as a source of highly reactive species, led to plasma chemical interactions with the analyte, resulting in a breakdown of the important bonds between analyte and substrate. A combination of kinetic and chemical cleaning mechanisms takes much less time than observed for a single gas plasma reported by Okeil et al.^[44] and Liu et al.^[45]

The mechanism that causes the SERS enhancement factor to be largest for the S1 sample is most likely due to several geometrical parameters of the film that were found to be optimum in similar SERS substrates prepared by the glancing angle deposition technique called nanosculptured thin films (nSTFs):^[46,47]

- Thickness of around 300 nm, which is determined by the wavelength used and the carbon structure underneath
- Vertical columnar structure caused the formation of sharp Au needle heads after Au deposition
- Porosity around 30% was found, not only in nSTFs^[41] but also in other systems with a large number of hot spots to be the optimum, for example, Au nanoparticles spread on a substrate.^[48] The porosity effect is a result of compromise between the density of hot spots and the optimum gap between the nanostructures.

2.3. SERS Study of Mycotoxins and Spectra Elaboration

At this point, the best performing template is a label-free detection platform which is capable of providing unspecified raw spectra of chemical analytes beating a ppb sensing threshold. These analytical features were tested using real samples. A fully characterized S1 substrate was next employed to investigate vibrational features of different pure mycotoxins such as AFB₁, ZEN, ALT, and FB₁. An equal amount (500 ppb) of each analyte was added to a substrate, dried at room temperature, and analyzed with Raman spectroscopy. The spectra of mycotoxins were expected to be distinctive in a fingerprint region due to their structural differences. Data displayed in **Figure 8a** represent an example of a raw Raman spectrum obtained from AFB₁. The shape of the spectrum is complex, containing a large number of peaks accompanied by parasitic fluorescence background. Similar features were monitored for the rest of the mycotoxins (see the Supporting Information). To get a deep insight into obtained spectra, they were elaborated through multiple steps. First, the noise from experimental curves was eliminated by using a locally estimated scatterplot smoothing (LOESS) function based on one main parameter: window size (Figure 8a “red curve”). For each window, a parabolic fit was performed to bind the experimental points using standard least-squares regressions.^[49] The next step employed was baseline creation (Figure 8a “blue curve”) with its following subtraction from a noiseless curve. An asymmetric least-squares fitting was performed to complete this task. This mathematical function

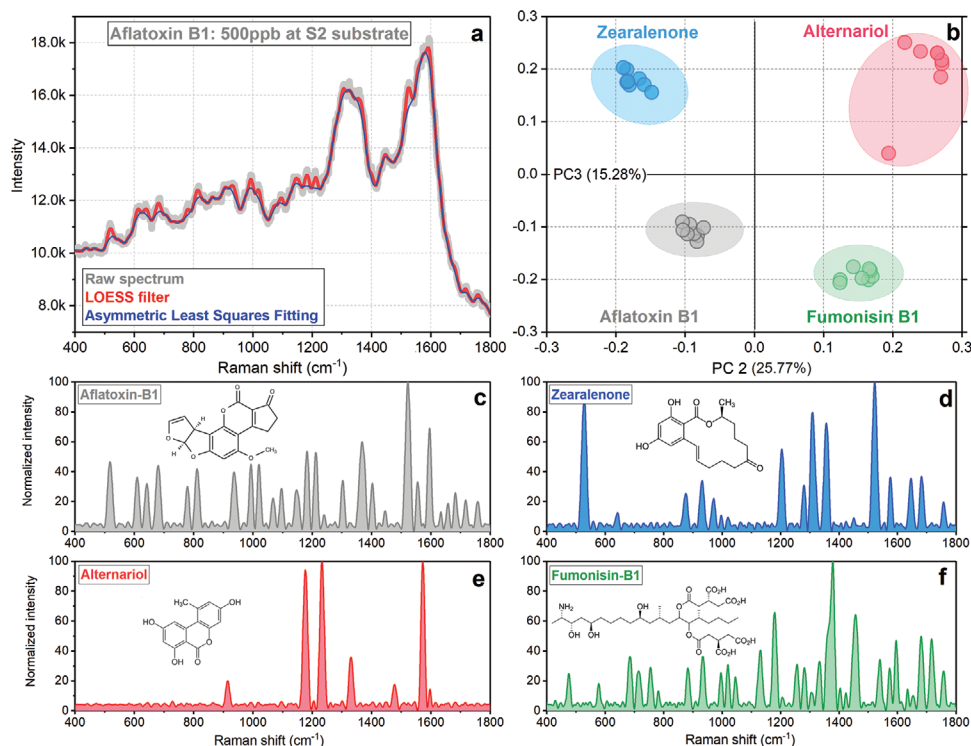


Figure 8. a) Raw Raman spectrum of AFB₁ deposited at S1 plasmonic gold-carbon template (gray line), smoothed curve after applying an LOESS function (red line), and baseline created by asymmetric least-squares fit (solid blue line). b) Principal component analysis of mathematically produced vibrational spectra of mycotoxins: c) AFB₁, d) ZEN, e) ALT, and f) FB₁.

is based on two main variables: λ and p . The first parameter defines a curvature penalization term and the other stands for the asymmetry in the least-squares iterations.^[50] Finally, the produced curves were normalized with respect to peak intensity from “0” to “100.”

The elaborated spectra of mycotoxins are displayed in Figure 8c–f. It should be noted that the total number of remaining peaks in fingerprint areas increased with the complexity of the mycotoxin structure. The least number of strong modes was observed for ALT, whose chemical configuration consists of the least number of aromatic rings (Figure 8c). At the same time, FB₁, whose molecular structure is the most complex produced many more vibrational modes (Figure 8f). The dominant vibrations modes (Figure 8c–f) that characterized each type of mycotoxin are similar to the ones reported elsewhere: AFB₁,^[51] ZEN,^[52] ALT,^[53] and FB₁.^[54] Possible small red and blueshifts of the published Raman modes compared to those detected in the current research can be attributed to a different wavelength of the incident illumination and the localized plasmon resonance's optical properties of the substrate.^[51,55] It should be noted that none of the existing publications presented Raman data of the analyte at concentrations within ppb levels, which is extremely important in the case of highly hazardous substances such as mycotoxins; in general, mycotoxins are harmful at ppm levels of uptake. Thus, it is a priority to develop an approach which can detect and differentiate mycotoxins at the lowest possible concentrations.

To classify spectral data of analytes possessing comparable features, it was not obligatory to identify all possible peaks, shifts, etc. Instead, general fingerprint signatures are sufficient. Therefore, a statistical was performed to reduce large datasets of similar spectral dimensionality. Proceeded vibrational spectra were elaborated using the orthogonal partial least squares function. This algorithm can provide reliable data distinguishing, focusing on the major differences in spectra. Instead of operating on a single variable (such as mode location, number of vibrational features, peak intensities.), it creates a linear correlation of the data massive to build separated spectral groups. After, it searches a line where the difference is the tiniest; then, values are projected to the line. The second one is selected to be perpendicular to the prior line. Known as PCA, this statistical approach clusters comparable spectra collected together. A place of original parameters (mode position, number of vibrations detected, scattering intensities) utilizes principal components as variables. This statistical approach was used previously for successful semi-quantitative SERS analysis of multiple chemical mixtures^[56] and compositional investigation of binary/ternary compounds of common dyes.^[57]

By forming separated spectral clusters based on parameters containing the greatest variance, the AFB₁, ZEN, ALT, and FB₁ mycotoxins can be differentiated. Based on the PCA report, two pairs of principal components PC1 versus PC2 and PC2 versus PC3 were compared. In the case of a PC2 versus PC3 plot, both components vary from “negative” to “positive” values leading to better data visualization (Figure 7b). On the contrary PC1 component was always “positive;” therefore, some cluster overlapping occurred (see the Supporting Information). Also, it is worth mentioning that the maximum variance of the PC1 component is much smaller than that of PC2 and PC3. The

extracted value $\Delta(PC1_{\max} - PC1_{\min}) = 0.13$ is about 3.5-fold lower than $\Delta(PC2_{\max} - PC2_{\min}) = 0.46$ and $\Delta(PC3_{\max} - PC3_{\min}) = 0.46$. Due to this reason, a loading plot comprised of a combination with higher components might be more favorable for visualizing data clusters. By observing a loading plot PC2 versus PC3 in Figure 7b, one can confidently state that all types of mycotoxins are separated clearly, taking their place within a particular coordination quadrant. From 32 collected spectra, four clusters are created with no overlap. Following the eigenvalues extracted, the cumulative discriminative percentage after PC1, PC2, and PC3 components was: 40.38%, 66.15%, and 81.43%, respectively.

Furthermore, looking closer to the PC3 axis, it could be said that the cluster's position is related to several detected Raman peaks. FB₁ and AFB₁ spectra contain on average more than 25 distinct Raman modes. Their corresponding “green” and “gray” clusters are located in a negative region of PC3 values. ALT and ZEN reveal less than 15 strong vibrational modes located in the upper part of the plot (positive PC3 values). Overall, the proposed algorithm is reliable and can detect, identify, and distinguish between different mycotoxins.

3. Conclusions

Using a facile and efficient plasma-deposition synthesis approach, we designed an advanced plasmonic template based on carbon nanostructures' catalytic growth. The best performing substrate was prepared at the shortest time of plasma treatment, leading to the highest AEF value (i.e., 5×10^7) having a thickness of around 300 nm, composed of vertically aligned nanorods with average porosity close to 30%. It allowed operating at nanomolar Raman reporter concentrations, showing a limit of detection between 4×10^{-9} and 5×10^{-9} M. The robustness of the plasmonic nanotemplate and its capability for multiple applications was demonstrated via applying a mild dry-cleaning in an oxygen-containing plasma environment. The Au-decorated substrate's high sensitivity was used for label-free detection and recognition of four different hazardous mycotoxins. With the help of a statistical PCA operator, all 32 recorded SERS spectra of AFB₁, ALT, ZEN, and FB₁ were clustered into well-separated spectral groups, indicating an excellent distinguishing ability of the method. Thus, a combination of plasmonic SERS sensing and statistical PCA opens an opportunity for alternative reliable and fast probing of mycotoxins at nanomolar concentrations.

4. Experimental Section

Synthesis of Carbon Nanostructures: Synthesis of carbon nanostructures was conducted in a RF inductively coupled plasma-enhanced CVD system operating at low pressure. A polycrystalline 0.25 μm thick Ni foil (thermal annealed 99 % metal basis, Alfa Aesar) was used as the substrate to synthesize carbon nanostructures. A cross-type glass tube with diameter 8 and 40 cm per arm was used as the plasma chamber. The RF generator (13.56 MHz) was coupled through a 14 cm long Nagoya type-III inductive coil, air-cooled externally. Before the experiments, the plasma system was pumped down to 10 Pa with a rotary pump and methane (CH₄) as the carbon precursor was inserted

into the chamber with a flow rate of 20 sccm to set a total pressure of 30 Pa. The Ni foil substrate was placed directly in the plasma discharge region in the coil's center using a stainless-steel holder and plasma was ignited with 800 W of RF power. There was no external substrate heating during the experiment and the substrate temperature was stabilized within a range of 750–800 °C due to plasma heating effects. Depositions were performed at different growth times from 1 to 30 min to investigate the carbon nanostructures' morphology evolution.

Characterization Techniques: Surface Morphology of the Carbon Nanostructures: All samples were characterized by a field-emission SEM (JSM 7600F, Jeol Inc.) operated at 5 kV. Chemical and phase composition of the samples were analyzed by a TEM (JEM-2100, Jeol Inc.) operating at 200 kV and additionally equipped with an energy-dispersive X-ray spectrometer. The images were recorded by a slow-scan CCD camera (Orius SC1000, Gatan).

Raman Investigations: Spectra of the samples were recorded using an NTEGRA confocal Raman spectrometer at an excitation wavelength of 633 nm with an incident power of ≈ 3 mW at a spot size of 10 μm focused by a $\times 20$ objective. The spectra were recorded at different spots of the sample and averaged to eliminate structural variations.

X-Ray Photoelectron Spectroscopy: Chemical composition analysis was done employing a PHI-TFA-XPS spectrometer (Physical Electronics Inc) equipped with Al-monochromatic source emitting photons at energy 1486.6 eV. The analyzed area was 0.4 mm in diameter. The XPS spectra were analyzed using MultiPak software and the spectra were deconvoluted by Gauss–Lorentz fitting considering Shirley-type background.

Deposition of the Gold Films: All substrates were decorated by 100 nm Au film deposited by a magnetron sputtering device (Quorum Q 150R, Quorum Technologies) with layer thickness monitoring for plasmonic purposes.

Optical Properties: The plasmonic color analysis of metallic surfaces was characterized by a dark-field reflection using a Leitz microscope LABORLUX 12 MES equipped with a $\times 100$ magnified objective and a tungsten bulb illuminating at 60 W. The observed true RGB color obtained by the 1.3-megapixel CMOS camera was corrected to PTFE white plate standard. Total reflectance was investigated by a double beam UV–vis spectrophotometer (Perkin Lambda 1050, PerkinElmer) equipped with an integrating sphere module (150 mm Spectralon Integrating Sphere, PerkinElmer).

SERS Measurements: Signal enhancement of all substrates was tested by recording and comparing Raman marker CV dye vibrational spectra. A water-diluted solution of concentration 10^{-6} M was prepared to accomplish the task. A set of concentrations ranging from 10 ppm to 10 ppb was used to estimate a limit of detection of the best performing plasmonic sample. All spectra were acquired under laser illumination of 3 s and accumulation of five times.

Plasma Cleaning: Inductively coupled RF plasma ignited at 13.56 MHz and operating power of 100 W was utilized for CV dye degradation. A gas mixture containing Ar and O₂ created a total flow of 200 sccm (Ar = 160 sccm, O₂ = 40 sccm) and stabilized a pressure inside the chamber at a value of about 30 Pa. The sample was placed on top of a glass slab in the center of a coil having nine inductive turns. Treatment was conducted as follows: ten cycles in a regime 10 s plasma “ON” followed by 10 s plasma “OFF.” At such conditions, the sample was not overheated.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

Keywords

mycotoxins detection, plasma-enhanced deposition, SERS substrate, vertical carbon nanostructures

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Chapter 3.3

Low-Temperature Low-Power PECVD Synthesis of Vertically Aligned Graphene

In this chapter, we partnered with the researchers from France and Germany to investigate a low-pressure capacitively coupled radio-frequency plasma system for designing carbon nanostructures, specifically 2D vertically aligned graphene nanosheets (VGNs). VGN structures are a variety of 2D carbon nanostructures in which the graphene layers are standing perpendicular to the substrate. Two different strategies were used for revealing the influential factors during the growth of VGNs. In the first strategy, we used substrates with and without a catalyst material (nickel). We identified that the presence of catalyst material enhanced the growth rate and structural quality of the VGNs. In the second strategy, we studied the effect of substrate temperature on the growth of VGNs. Here, we successfully demonstrated the growth of VGNs at 450 °C, one of the lowest temperatures reported for the VGN growth so far. Al so, we revealed that the structural quality and crystalline properties of the nanostructures improved with the increase in temperature. As we designed all the experiments at a low plasma power, we established the ability of developed technique to fabricate carbon nanostructures rapidly at low-energy consumption.

Regarding my contribution: I contributed to the surface analysis and chemical composition analysis of VGNs, and jointly wrote the paper with all the other co-authors.

Low-temperature low-power PECVD synthesis of vertically aligned graphene

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Abstract

The need for 2D vertical graphene nanosheets (VGNs) is driven by its great potential in diverse energy, electronics, and sensor applications, wherein many cases a low-temperature synthesis is preferred due to requirements of the manufacturing process. Unfortunately, most of today's known methods, including plasma, require either relatively high temperatures or high plasma powers. Herein, we report on a controllable synthesis of VGNs at a pushed down low-temperature boundary for synthesis, the low temperatures (450 °C) and low plasma powers (30 W) using capacitively coupled plasma (CCP) driven by radio-frequency power at 13.56 MHz. The strategies implemented also include unrevealing the role of Nickel (Ni) catalyst thin film on the substrates (Si/Al). It was found that the Ni catalyst on Si/Al initiates the nucleation/growth of VGNs at 450 °C in comparison to the substrates without Ni catalyst. With increasing temperature, the graphene nanosheets become bigger in size, well-structured and well separated. The role of Ni catalysts is hence to boost the growth rate, density, and quality of the growing VGNs. Furthermore, this CCP method can be used to synthesize VGNs at the lowest temperatures possible so far on a variety of substrates and provide new opportunities in the practical application of VGNs.

Keywords: VGNs, PECVD, Raman, XPS, NEXAFS

(Some figures may appear in colour only in the online journal)

1. Introduction

Vertical graphene nanosheets (VGNs), also referred to as vertically-oriented graphene nanosheets (VOGN) or carbon nanowalls (CNWs) are two-dimensional graphitic platelets which are typically oriented vertically on a substrate [1]. Rising interest in the synthesis and application of VGNs

emanates from their unique characteristics such as non-stacking morphology, high-aspect-ratio, sharp edges, and high-density reticular arrangement, etc [2–4]. Besides this, excellent electrical and mechanical properties of VGNs and their derivatives enabling their applicability in enormous fields, including supercapacitor, battery electrodes, power sources, field emitters, flexible electronics, gas sensors, and

catalyst supporters [5–10]. An individual VGN typically consist of few stacked graphene layers having a thickness of several few nanometres with lateral and vertical dimensions of hundreds of nanometres to tens of micrometres. With few exceptions where chemical vapour deposition (CVD), and sputtering techniques for the synthesis of VGNs are used, plasma-enhanced chemical vapour deposition (PECVD) methods are considered as the emerging techniques for building VGNs. Compared to other techniques, PECVD techniques offer a low-temperature synthesis of VGNs with controlled growth and morphology at a large scale. The structure and morphology of VGNs can be influenced by plasma sources and parameters such as substrate temperature, feedback gas type and composition, operating pressure and plasma power used for the synthesis process [11, 12].

In a PECVD system during the growth of VGNs, the precursor gas (generally hydrocarbons) undergo inelastic collisions with the electrons in the plasma to form different plasma species. It has been already reported that the VGNs can grow on the substrate without the presence of catalyst particles, which indicates that the precursor dissociation by plasma and interaction of plasma species to the substrate surface plays a key role for the growth of VGNs. Thus, several studies have been carried out for successfully synthesising VGNs using various plasma sources such as radiofrequency inductively coupled plasma (RFICP) [13], microwave plasma [14], DC plasma [15], RF capacitively coupled plasma (RFCCP) assisted by radical injection [16], helicon plasma, and electron beam excited plasma (EBEP). Generally, a higher concentration of hydrogen atoms and carbon dimers (C_2 radicals) are needed for the growth of VGNs [17]. Carbon dimers produced by the radical recombination and subsequent dissociation of CH_x ($x = 1, 2, 3$) radicals are playing a vital role in the nucleation of VGNs and hydrogen acts as the etching agent for the removal of amorphous carbon(a-C). It has been reported that microwave (MW) and ICP systems employed with CH_4/H_2 or $CH_4/H_2/Ar$ mixture have higher C_2 radical density for the direct nucleation for the VGN growth. On the other hand, a CCP plasma effectively generates CH_3 radicals from the carbon precursor, but because of the deficiency of H atoms, CCP plasma by itself is not suitable for the growth of VGNs [18, 19]. Thus, radical injection of H atoms and coupling of CCP with other plasma sources are used to provide sufficient H atoms for the growth of VGNs.>

In addition to the plasma source, the most direct and controllable parameters in the PECVD process that can influence the growth and morphology of VGNs are plasma power and substrate temperature [19, 20]. Several groups successfully synthesised VGNs by employing MW plasma with power in the range of 350 W–16 kW at a substrate temperature between 350 °C–700 °C [2, 21]. ICP plasmas with a power range from 400 W to 1000 W at substrate temperatures of 350 °C–1100 °C have also been used for synthesising VGNs [21, 22], as well as DC plasma and EBEP plasma sources by employing higher input power and temperature [23, 24]. Most of all the reported VGN growth by CCP was assisted either by an external hydrogen source or by other plasma sources at different power (250–700 W) and temperature (500 °C–700 °C)

[25–27]. The lowest temperature that has been used for the growth of VGNs so far is ~ 350 °C using an ICPECVD system, where an external bias was added for the VGN growth [22]. In all other cases, the VGN growth was observed at a temperature above 500 °C by employing higher plasma power. Also, it has been demonstrated that higher temperatures and higher plasma power can corrugate the morphology of VGNs [28]. Therefore, the synthesis of VGNs at lower temperatures and lower power without using any additional plasma source or bias is still considered as the main challenge in the research of oriented graphene structures.

Even though VGNs can grow on the substrate without any addition of a catalyst, several researchers have taken the effort to investigate the effect of catalysts (e.g. Ni) on the growth of VGNs [29–31]. It has been reported that the low-temperature plasma assisted treatment improve the catalyst substrate interaction, reduce the catalyst particles mobility and thus influence the growth of such 2D and 3D materials [32]. Also, during the annealing of the substrate, the application of plasma-pre-treatment readily transform the catalyst layer and reduces the size of the catalyst nanoparticles, which drastically improves the homogeneity [32]. Thus, the hydrogen plasma treatment is almost considered as a standard pre-treatment, and several morphologies have been documented by this method [33]. On the other hand, an argon plasma, which is more effective than hydrogen plasma for the cleaning or etching, is very rarely used for the pre-treatments. Therefore, revealing the effect of Ar plasma pre-treatment on the substrate surface for the growth of VGNs can be beneficial for future applications.

Herein we are reporting a successful application of a radio frequency capacitively coupled plasma-enhanced chemical vapour deposition (RFCCPECVD) system at lower power and lower temperature for the synthesis of VGNs without using any additional plasma source. VGNs were synthesised in a cold wall CCPECVD reactor using a very low power of 30 W at a substrate temperature of 450 °C to 620 °C. The influence of Ni thin film on the growth rate and structure quality of VGNs was also investigated. We have investigated the effect of substrate temperature on the structural quality of VGNs using Raman spectroscopy and chemical composition analysis. NEXAFS spectroscopy was used to obtain chemical, structural and orientation information of the nanoscale samples. To our knowledge, a successful application of capacitively coupled plasma to synthesis VGNs using low power and temperature has not been reported so far.

2. Experimental section

2.1. Synthesis of VGNs

The VGNs were synthesized using a cold-wall CVD by radio frequency capacitively coupled plasma (RFCCP) operated at 13.56 MHz RF power. The detailed scheme of experimental setup has been presented in our previous studies [33–37]. Silicon wafers covered with 200 nm thick aluminium (Al) are used as the substrate for synthesizing VGNs. A 10 nm thin Ni film was deposited by a precision etching coating system (PECS) onto the Si/Al to investigate the effect of catalytic

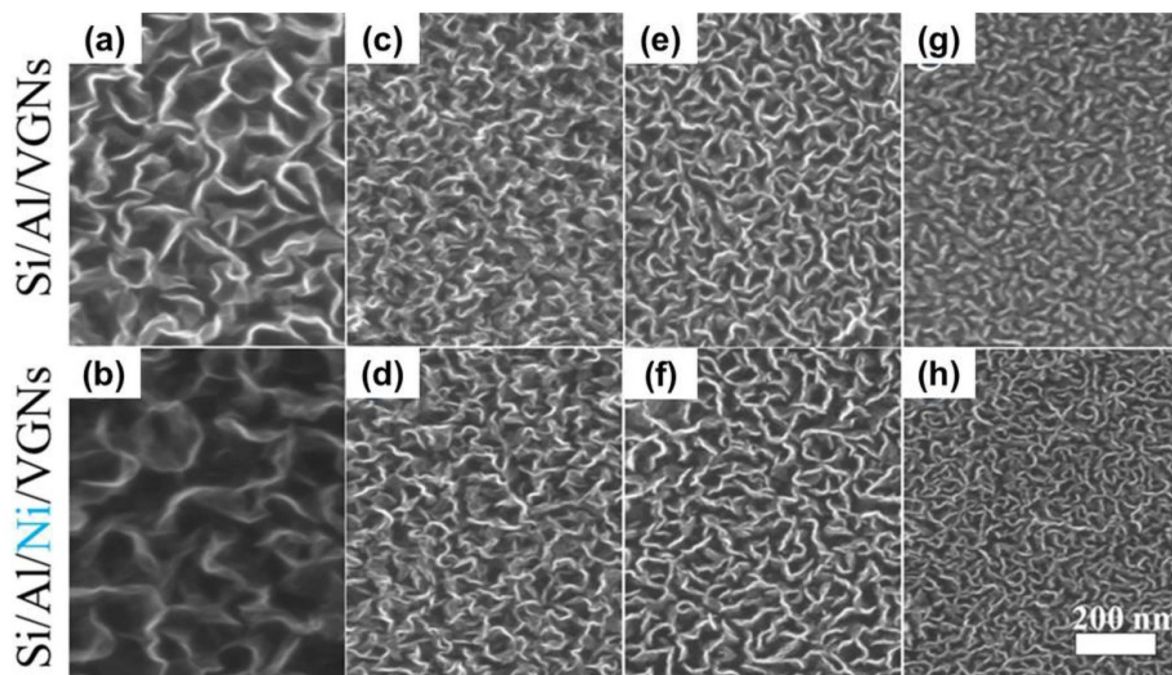


Figure 1. SEM images of VGNs obtained at 620 °C (a), (b), 550 °C (c), (d), 480 °C (e), (f), 450 °C (g), (h). scale bar is 200 nm for all figures.

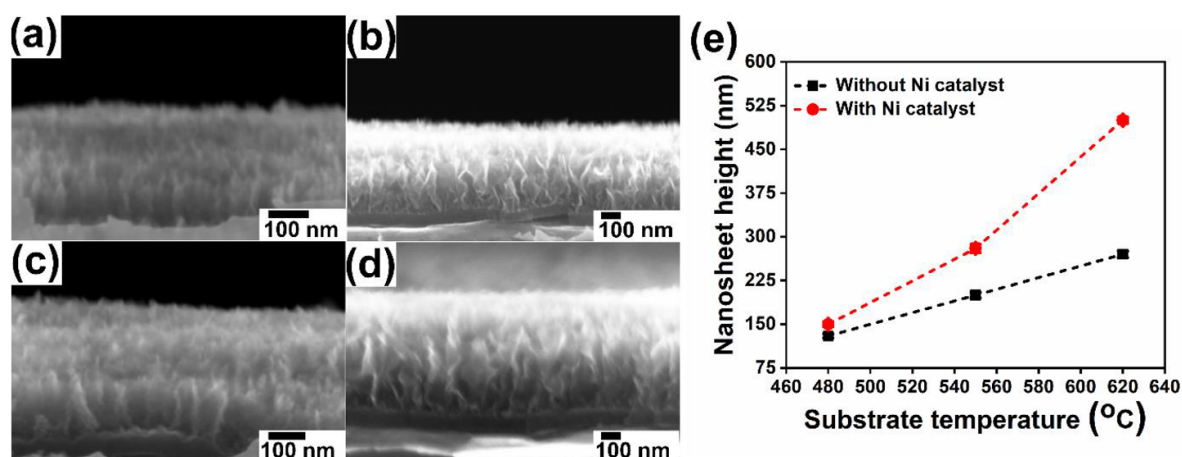


Figure 2. SEM images of VGNs height comparison on Si/Al {(a) at 480 °C, (b) at 620 °C}, on Si/Al/Ni {(c) at 480 °C, (d) at 620 °C}, (e) variation of VGNs height with respect to growth temperature.

materials on the growth of VGNs [31]. These values were chosen after several trial and error experiments and showed the best results. The substrate was transferred into the PECVD reactor, and the base pressure inside the reactor was kept below $4 \cdot 10^{-4}$ Pa. Substrates were pre-treated at different annealing temperatures (450 °C to 620 °C) with CCP plasma. Argon gas (10 sccm) was inserted to the chamber at a pressure of ~ 29 pa for the pre-treatment with a ramp time of (960 s to 1200 s) and held the conditions for 1800 s. Subsequently, a mixture of hydrogen (H_2) and ethylene (C_2H_4) with a flowrate of 40:20 sccm were introduced to the reactor at the pressure of ~ 100 pa and the growth of VGNs was performed for 900 s. For simplicity, the growth scheme of VGNs presented here is very similar to the growth of CNTs performed in previous studies [31, 36].

2.2. Characterization techniques

Scanning electron microscopy (SEM) by a Zeiss-Supra device was used to examine the morphology of VGNs. Raman spectra were recorded to study the structural organization of the synthesised VGNs using a Renishaw InVia Reflex Spectrometer at an excitation wavelength of 514.5 nm. The spectra were collected under a Leica DM2500 optical microscope ($\times 50$ objectives/N.A. = 0.75) and a grating of 1800 l mm^{-1} . The laser power in the sample was kept at around 0.5 mW to avoid any heating damage. The samples were analysed at three different spots. The elemental composition and orientation-dependent chemical properties of VGNs were analyzed by x-ray photoelectron spectroscopy (XPS) and Near Edge x-ray-absorption fine structure (NEXAFS) spectroscopy using the HE-SGM

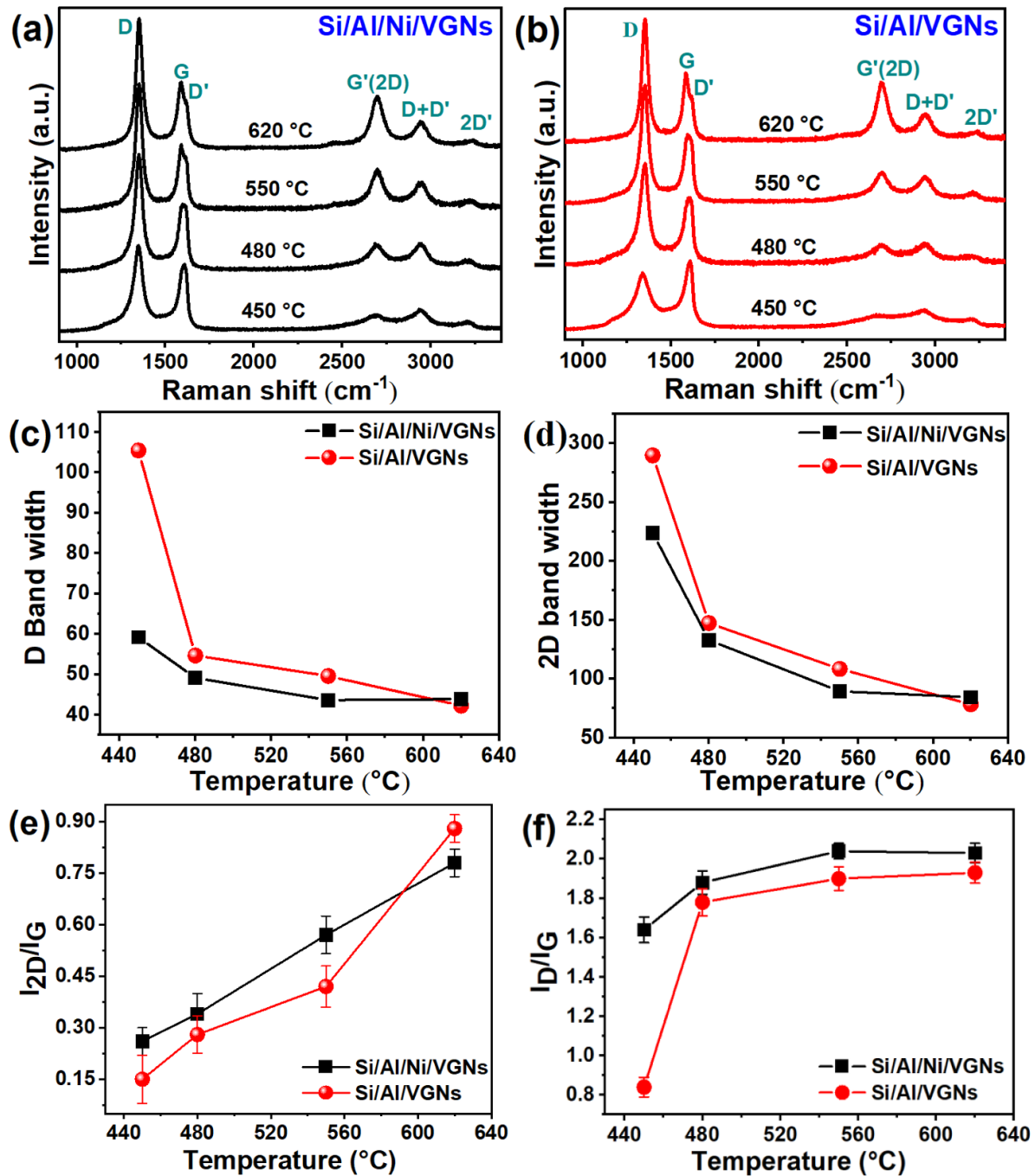


Figure 3. Raman spectra of VGNs grown at different temperatures (a) with Ni thin film (b) without Ni thin film, (c), (d) Full widths at half maximum FWHM(D) and FWHM(2D) for different growth temperatures (e), (f) Raman intensities comparison for different growth temperatures.

beam line with the PREVAC end station at the BESSY II electron storage ring in Berlin, Germany. The elemental depth information during the analysis was about 2 nm by measuring the high-resolution photoelectron lines of the different elements at the same constant kinetic energy [38].

3. Results and discussion

The SEM micrographs displayed in figure 1 indicate a vertically standing morphology and uniform growth of VGNs on

Si/Al and Si/Al/Ni substrates at different temperatures ranging from 450 to 620 °C. Even though the general morphology of VGNs is similar, the density, interlayer spacing, and thickness of VGNs are varying along with the temperature. A comparison between the growth of VGNs with and without the presence of a Ni catalyst suggests that the morphology of VGNs is different even for the same growth temperature. This could be related to differences in the nucleation steps evolving in the initial stages [31], where the nucleation of nanoislands during the growth of VGNs with Ni catalyst is faster than without Ni.

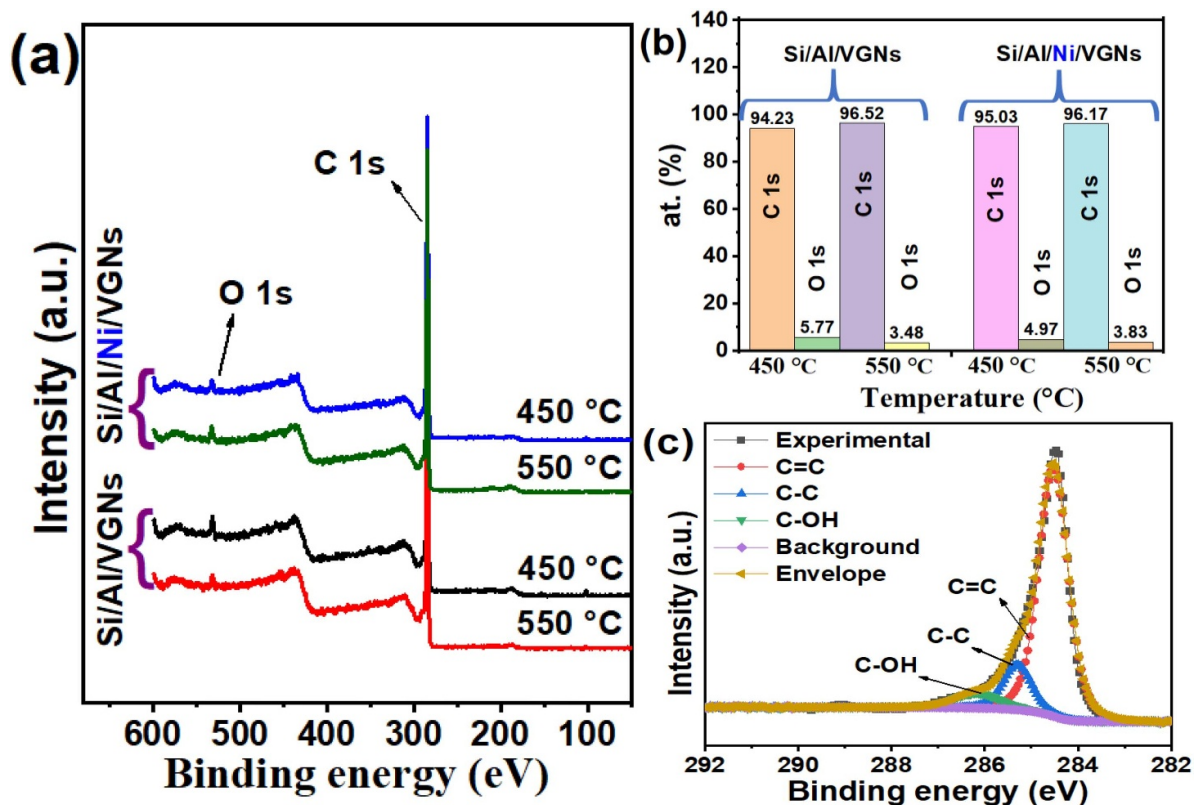


Figure 4. (a) Survey scan comparison of VGNs grown under different conditions (Excitation energy 700 eV), (b) plot of oxygen content in the near-surface region, (c) C 1s deconvoluted spectra of VGNs grown at 550 °C on Si/Al/Ni (excitation energy 385 eV).

Table 1. Percentage area of the different carbon species obtained from fits of XPS C 1s spectra.

	(°C)	284.5 eV (%)	285.2 eV (%)	286.1 eV (%)
Si/Al/VGNs	450	70.5	21.9	7.6
	550	80.1	13.3	6.6
Si/Al/Ni/VGNs	450	71.4	19.4	9.2
	550	78.9	13.6	7.5

At lower temperatures, nucleation and initial growth of densely packed nanosheets are occurring due to the longer surface residence time for the different plasma species; however, the possible migration of plasma species on the substrate surface at low temperature is lower than that at higher temperature and results in smaller lateral and vertical dimensions of VGNs at lower temperature. The lateral dimension of the individual nanosheets is increasing with the temperature and highly interconnected nanosheets are observed at higher temperatures.

Considering the fact that the density and interlayer spacing of the VGNs is varying with the growth temperature, the changes in the vertical dimension of the VGNs are also investigated. Figures 2(a)–(d) exhibits the cross-sectional images of the VGNs grown at different temperatures. The height of VGNs on Si/Al increases from 130 nm to 270 nm for temperatures 480 °C to 620 °C, respectively. The addition of Ni catalyst enhances the growth of VGNs as the height reaches 150 nm to 500 nm for temperatures 480 °C to 620 °C, as displayed in

figure 2(e). The growth of VGNs observed on the Si/Al and Si/Al/Ni substrates at the lower temperature (480 °C) is having an almost similar growth rate of 520–600 nm h⁻¹. Hence with the increase in temperature to 620 °C, the growth rate of VGNs on Si/Al/Ni substrates ($\sim 2 \mu\text{m h}^{-1}$) is two-times higher than on Si/Al ($\sim 1 \mu\text{m h}^{-1}$). Since the plasma power is very low and maintained constant during the experiments, the effect of plasma heating of the substrate can be neglected. Thus, the changes in growth rate can be explained as a combined effect of growth temperature and catalyst particle. At lower growth temperature, the plasma species has high surface residence time with low mobility of the surface atoms. On the other hand, at higher temperatures, the migration of plasma generated species on the substrate surface is higher and favours the formation of interconnected stable nanostructures by surface chemical reactions. This results in the formation of well-aligned highly interconnected VGNs at higher temperatures. The presence of the Ni catalyst is enhancing the surface diffusion of the hydrocarbon species on the surface for the initial growth of graphene layers and promotes a higher growth rate on the Si/Al/Ni substrates. In order to gain a better understanding of the influence of temperature and Ni catalyst on the structural organization and chemical composition of the VGNs, the samples were further analysed with different surface analytical techniques.

The inner structural arrangement of the VGNs synthesised on different substrates at different temperatures was analysed by Raman spectroscopy. Figures 3(a) and (b) displays

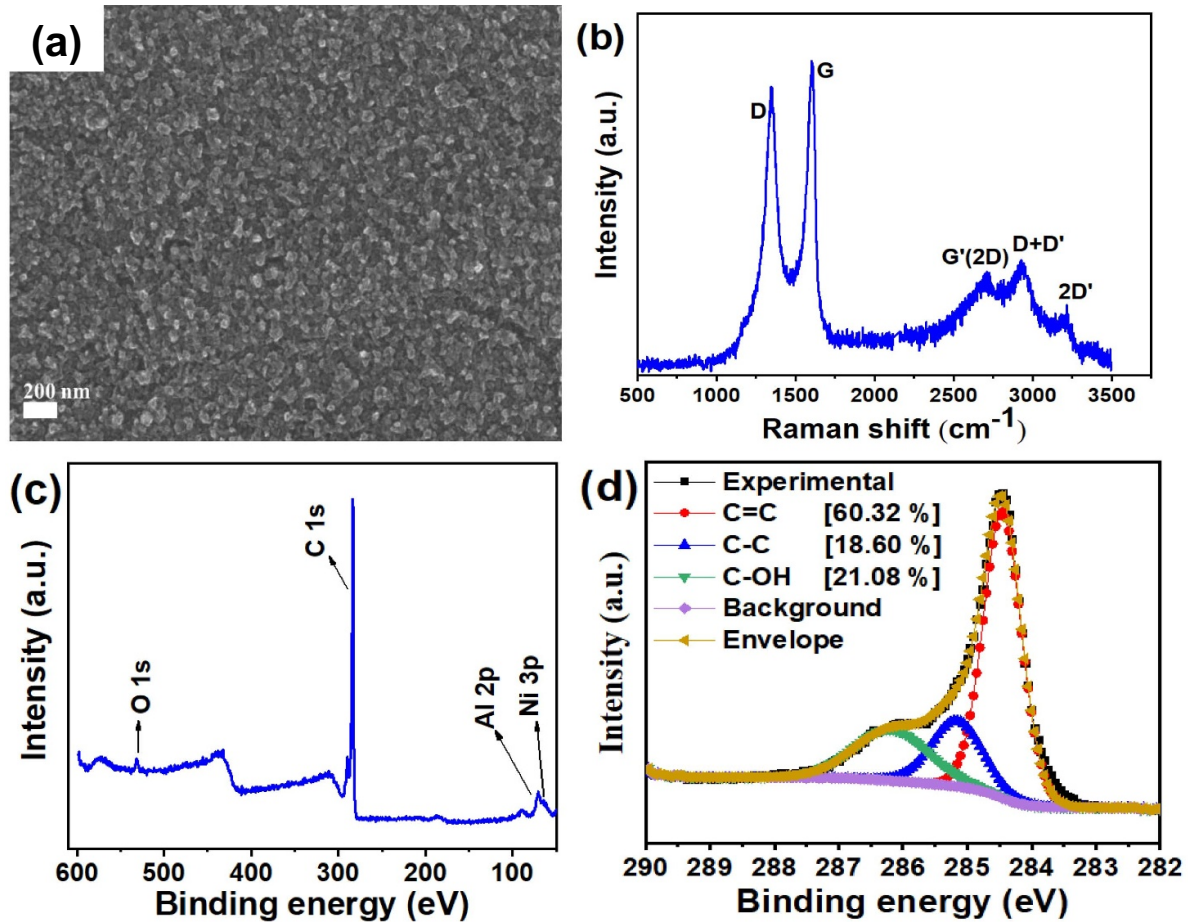


Figure 5. Carbon nanostructures grown at 410 °C on Si/Al/Ni, (a) SEM image, (b) Raman Spectra, (c) XPS survey scan, (d) C 1s deconvoluted spectra.

normalised Raman spectra of VGNs grown on substrates with and without Ni thin films at different temperatures. The spectra are composed of several bands; most importantly, the D band located at $\sim 1350 \text{ cm}^{-1}$ attributed to the A_{1g} breathing mode of six-atom rings at the 1st Brillouin zone boundary K or K'. Due to the conservation of momentum, it becomes active only in the presence of defects. The G band at $\sim 1581 \text{ cm}^{-1}$ corresponds to the one-phonon Raman scattering process at the 1st Brillouin zone centre and consists of the collective in-plane bond stretching of carbon atoms (E_{2g} symmetry) [39, 40]. The D' band at 1622 cm^{-1} is also a defect-induced phonon mode near the 1st Brillouin zone centre. The G'(2D) band at $\sim 2700 \text{ cm}^{-1}$ and the G'' (2D') band at $\sim 3240 \text{ cm}^{-1}$ are respectively the second orders of the D and D' bands originating from the scattering by two phonons with opposite wave vectors, and therefore they are always active by symmetry [41]. The D + D' band observed at $\sim 2940 \text{ cm}^{-1}$ corresponds to the combination of phonons and also requires defects for its activation [42].

As the growth temperature is increasing, the recorded Raman spectra undergo several changes, which indicates the structural modification of the resulting VGNs. Figures 3(c) and (d) display the evolution of the full width at half maximum FWHM of D and G'(2D) as a function of the growth temperature. Both parameters, which are the fundamental

characteristics of the local structural order, are decreasing with a temperature towards minimum values suggesting the increased structural ordering of VGNs with increased growth temperature. Figure 3(e) exhibits the changes in the I_{2D}/I_G ratio, which continuously increases with an increase in temperature. It is the characteristic behaviour for an increase in the concentration of polyaromatic carbons. Moreover, the G and D' bands are merged and seen as a single band located at $\sim 1600 \text{ cm}^{-1}$ for the VGNs grown at 450 °C and 480 °C, which is due to the lower structural order.

For higher growth temperatures (550 °C and 620 °C), the G band position undergoes a downshift towards lower wavenumbers leading to a clear distinction of D' band. All these variations are in good agreement with the literature regarding the characterization of sp^2 carbon-based materials with an increasing degree of ordering [19, 43, 44]. Figure 3(f) represents the variation of the I_D/I_G with the growth temperature, which varies with the type and concentration of the introduced defects [42, 45, 46] and exhibits opposite behaviour compared to what is usually seen in the literature [47]. In this specific range of structural ordering, this parameter is expected to continually decrease with the increase in growth temperature. Generally, defect density characterized by different geometries is quantified by Raman scattering via the number of active areas around

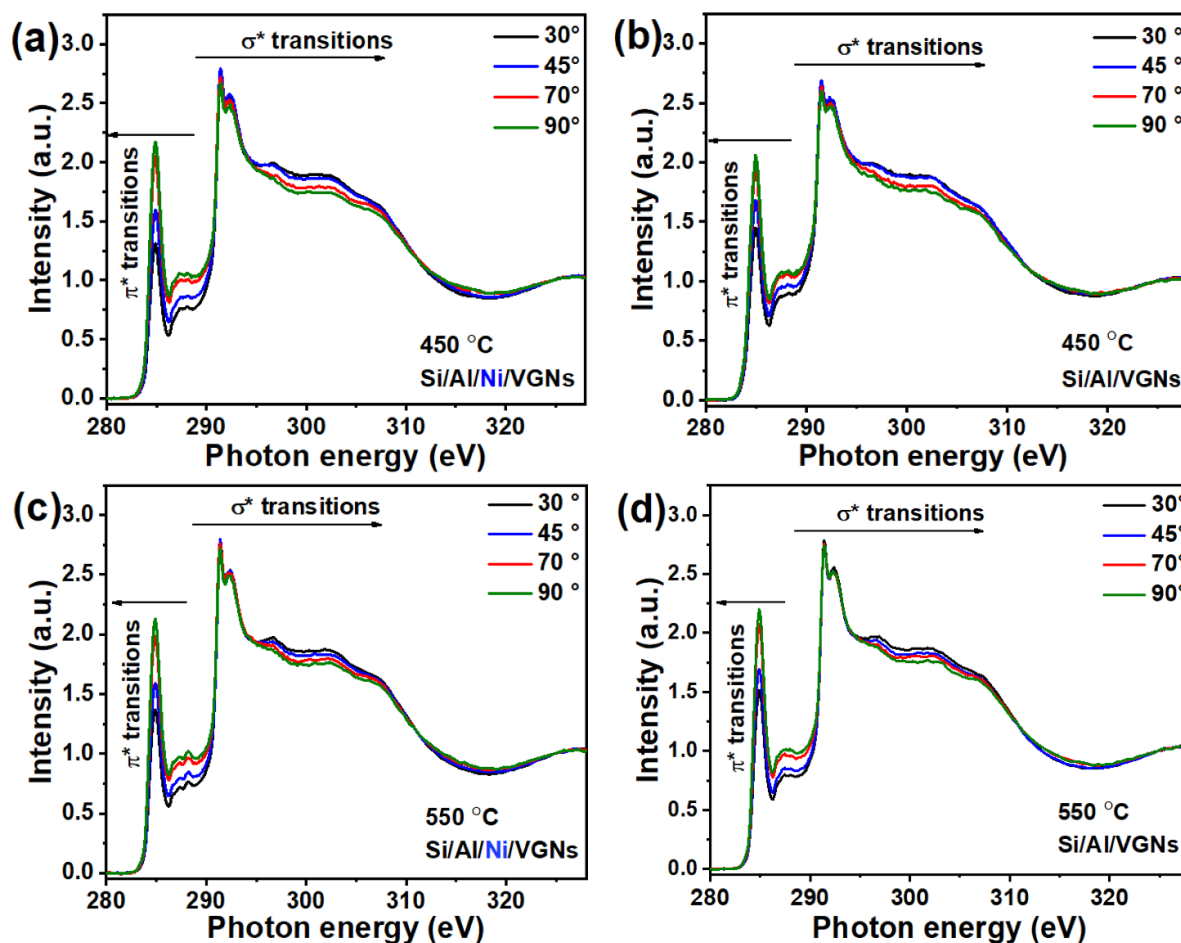


Figure 6. NEXAFS spectra of VGNs grown at 450 °C {(a) with and (b) without nickel as a catalyst}, at 550 °C {(c) With and (d) without nickel as a catalyst}. Angular dependence. All the spectra were normalized to an absorption edge jump setting the post-edge intensity at 325 eV to 1.

borders or point-like defects with respect to the total area of the laser spot. Therefore, the variation of I_D/I_G provides a measure of the crystallite size L_a or a determination of the average distance between point-like defects L_D . In the present work, there is a fundamental difference in the orientation (vertical growth) of the analysed graphene nanosheets. This configuration results in the exposure of the laser spot to a large number of graphene edges vertically aligned that satisfy the momentum conservation leading to the full activation of the D band. Therefore, since the D band is the breathing mode of polyaromatic carbon, increasing the ordering of graphene nanosheets with the growth temperature leads to an increase of its intensity similar to what could be observed for its second-order band $G'(2D)$ active by symmetry. Its asymptotic behaviour (or possible decrease) can be explained by the increase of the spacing between the walls in the area illuminated by the laser spot. One must, therefore, be careful about interpreting the Raman spectra based only on the I_D/I_G ratio. This also means that all the relationships found in literature allowing the determination of in-plane crystallite size (L_a or L_d) based on the I_D/I_G , should definitely not be used in the case of vertically aligned graphene nanosheets [48–50]. The SEM images and Raman analysis confirm that VGNs start to grow at the lowest

temperature of 450 °C and show a relatively well-organized structure at 550 °C when Ni catalyst has been used whereas without catalyst the growth starts at a temperature of about 480 °C and a well-organized structure is obtained at 620 °C.

Chemical compositions of the grown VGNs at different temperatures were investigated with XPS. Figure 4(a) shows XPS survey scans of the samples. The analysis suggests the existence of only two elements in VGNs, namely carbon and oxygen. Samples show different O 1s to C 1s ratios for VGNs grown without Ni catalyst and with Ni catalyst. In both cases, the appearance of O 1s lines is probably due to chemical reactions of structural defects and dangling bonds upon exposure to the ambient. The analysis also indicates the reduction of oxygen functional groups and an increase in carbon content with an increase in the growth temperature as represented in figure 4(b), possibly due to an increase of the crystallinity of the VGNs structure. Figure 4(c) shows the high resolution of deconvoluted C 1s spectra of VGNs grown with Ni catalyst at 550 °C. For the deconvolution of the C 1s line, the position at 284.5 eV was taken as a reference, which is assigned to regular graphitic carbon atoms [51, 52].

C 1s of all the samples were deconvoluted into three peaks, as summarized in table 1. The main peak at 284.5 ± 0.2 eV

corresponds to sp^2 -hybridized graphite-like carbon atoms ($C=C$), the peak centered at 285.20 ± 0.2 eV is an indication of sp^3 -hybridized carbon atoms ($C-C$) considered to originate from edges, bending, ($a-C$) absorbed on the graphene surface and the peak at 286.2 ± 0.2 eV is due to OH functional groups attached to carbon atoms ($C-OH$) [53, 54]. It was observed with an increase in growth temperature of VGNs, sp^2 content increases, and sp^3 decreased. These findings also support the interpretation of the results in the Raman analysis that the increase in the D band intensity is due to the boundary edges of graphene sheets and not from defects.

To investigate the growth of VGNs at very low temperatures, the experiment conducted at 410°C . There is no growth of VGNs observed at these experimental conditions. However, carbon nanoparticles with graphitic characteristics are deposited on the substrate, as observed by the SEM and Raman analysis (figures 5(a) and (b)). XPS analysis presented in figures 5(c), (d) indicates the significant presence of the nickel and substrate material along with the deposited carbon nanomaterial.

Near Edge x-ray Absorption Fine Structure spectroscopy (NEXAFS) is used to lighten up more detailed chemical, structural, and orientation information about VGNs. The spectra were obtained at the C K-edge, in a partial energy electron yield (PEY) mode, with only -20 V of retarding potential. Raw spectra were divided by the absorption spectra of a clean, freshly sputtered gold sample to correct for the photon flux [55]. The energy calibration was obtained by using an I_0 feature referenced to a C 1s $\rightarrow \pi^*$ resonance at 284.9 eV from a fresh surface of graphite foil standard sample [56]. Spectra are shown after normalization of the edge-step to one. The spectra were collected at different angles ($30-90^\circ$) of the incident linearly polarized synchrotron-light beam relative to the surface plane of the sample.

The C K edge NEXAFS spectra of the four samples (VGNs grown at two different temperatures 450°C and 550°C) are quite similar to each other and represented in figures 6(a)–(d). Figure (6) show three main absorption features for all the samples, a sharp resonance at about 285.2 eV and a double-structure resonance at around 292 eV. The feature at 285.2 eV is commonly assigned to C 1s to π^* transition of sp^2 carbons in a carbon-ring structure, and the features at 291.7 and 292.7 eV can be assigned to double resonances that come from excitonic and band-like contributions of graphitic carbon species, respectively [57–59]. Furthermore, when Ni is added as a catalyst, a small feature at around 288.5 eV becomes more prominent (figure 6(a)). This change can be attributed to defect states resulting from oxygenated groups and/or surface contaminations on VGNs, e.g. $\pi^*C=O$, σ^*C-H and $-(HO-\pi^*C=O)$ transitions [53, 55, 60–62] which is also confirmed by XPS analysis (see table 1).

For all four samples, there is a clear angular dependence of the C1s $\rightarrow \pi^*$ transition at around 285.2 eV. The differences are strongly correlated with the orientation of the transition dipole moments into the π^* orbitals relative to the surface and therefore support the synthesis of VGNs consisting of graphene sheets that grow preferentially perpendicular to the substrate. In this case, by looking to the spectra presented

in figure (6), the π^* orbitals deriving from p_z orbitals are preferentially oriented parallel to the substrate, and thus the σ^* orbitals (in-plane graphene bonds) are oriented perpendicular to the substrate. Therefore, as the angle between the incident beam and surface increases, the C1s $\rightarrow \pi^*$ resonance at 285.2 eV increases, which validates the SEM images of the respective samples, i.e. preferentially vertically oriented graphene nanosheets have been successfully synthesized.

Thus, comprehensive studies on all the aforementioned results suggesting that VGNs growth is initiated at the lowest temperature of 450°C and show a perfect structure with an increase in temperature. The presence of Ni catalyst enhances the growth rate and improves the interconnected feature of graphene nanosheets to perfectly orient on the substrate surface.

4. Conclusions

Vertical graphene nanosheets were deposited by radio frequency capacitively coupled plasma. SEM, Raman, XPS, and NEXAFS results affirm the growth of VGNs at the lowest substrate temperature of 450°C . The use of Ni catalyst on the substrate significantly reduced the nucleation temperature and raised the quality and growth rate of VGNs in comparison to the substrates without Ni. Moreover, the increase in I_D/I_G and I_{2D}/I_G ratios and the decrease of the band widths indicated the improvement in the structural order of graphene nanosheets with increase in synthesis temperature. Furthermore, the sp^2 to the sp^3 ratio increased with an increase in the synthesis temperature. These results are further supported by NEXAFS analysis which demonstrated that Ni catalyst facilitates the growth of 2D VGNs at lower temperatures, which opens new horizons for the direct growth of vertical graphene on different substrates at low temperatures with application-oriented properties.

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Chapter 4

Plasma-Enabled Approaches for the Surface Engineering of Carbon Nanostructures

Chapter 4 emphasises the ability of plasma techniques for the controlled surface engineering of carbon nanostructures, including heteroatom doping, atomic etching, and surface functionalisation. Heteroatom doping is one of the finest techniques to tune the electrical and electronic properties of carbon nanostructures for specific applications. Heteroatom doping is one of the finest techniques to tune the electrical and electronic properties of carbon nanostructures for specific applications. This doping process is influenced by the structural defects formed during the doping process. Thus, conventional thermal annealing and chemical doping methods are not ideal for controlling the configuration and concentration of heteroatoms in carbon lattice since these methods are not capable of providing sufficient defect regions for the doping. Alternatively, plasma is known to create defects in the structure and can thus be used to incorporate heteroatoms in the carbon structures simultaneously. Our research was focused on two distinct structure modifications: the possibility of plasma heteroatom doping and plasma restructuring and functionalisation of the surface. Based on this, Chapter 4 is also sorted into two sub-chapters. In the first sub-chapter, we demonstrate the effects of different nitrogen-containing low-pressure plasmas for nitrogen doping, the influence of plasma treatment time on the doping, and the role of structural defects for the sufficient doping of nitrogen atoms in carbon lattice. Based on our results and findings, we proposed a possible nitrogen incorporation mechanism and tried to bridge the gap between the existing experimental findings and theoretical predictions on the nitrogen doping process. In the second sub-chapter, we investigate the effects of plasma treatment using inert gases (argon and helium) at atmospheric conditions and the changes in the surface functionalities of carbon nanostructures. Therefore, in this research, we explored the ability of inert gas plasma treatment for tailoring the structural and electrical properties of carbon nanostructures. The effects of different plasma conditions and processes are evaluated by the following subchapters:

- 4.1. N-Graphene Nanowalls via Plasma Nitrogen Incorporation and Substitution: The Experimental Evidence
- 4.2. Improving sensing properties of entangled carbon nanotube-based gas sensors by atmospheric plasma surface treatment

This chapter addresses thesis Objectives 1, 2 and 3.

Chapter 4.1

N-Graphene Nanowalls via Plasma Nitrogen Incorporation and Substitution: The Experimental Evidence

Graphene nanowalls (or carbon nanowalls, or vertical graphene nanosheets) are the 2D form of graphene structures perpendicularly aligned on the substrate surface. Tailoring the electrical properties of graphene nanowalls by nitrogen doping has been widely investigated, and various techniques have been reported earlier for nitrogen doping in graphene lattice. Besides, several simulations have theoretically predicted the nitrogen incorporation mechanism. However, there is still a gap between the experimental results and predicted theoretical simulations. Therefore, in Chapter 4.1, we explained the effects of different nitrogen plasma conditions for nitrogen incorporation, identified the influence of structural defects on nitrogen incorporation, and establish a possible mechanism of nitrogen incorporation in graphene lattice. A low-pressure radio-frequency inductively coupled plasma with nitrogen and ammonia as active gases was used for the plasma treatment during the study. As a result, graphene nanowalls with a high concentration of $\sim 8\%$ (atomic concentration) were produced using nitrogen plasma treatment with desired nitrogen bonding configurations. Furthermore, the change in electrical conductivity upon different nitrogen concentrations was also investigated in this study. The outcomes of the study have set the base for the controlled synthesis of nitrogen-doped carbon-related materials with desired nitrogen concentration and configuration.

Regarding my contribution: I performed the plasma treatment processes, contributed to the structural and chemical analysis, identified the nitrogen incorporation mechanism and jointly wrote the paper with co-authors.



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N-Graphene Nanowalls via Plasma Nitrogen Incorporation and Substitution: The Experimental Evidence

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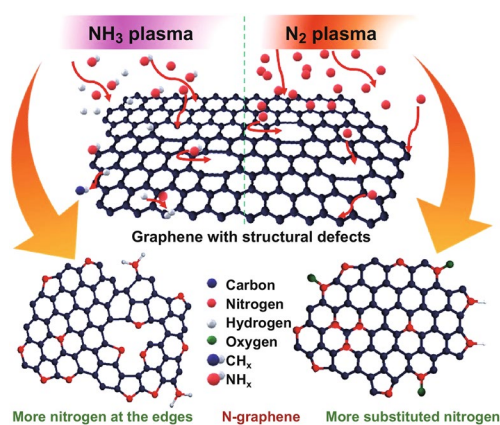
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HIGHLIGHTS

- Nitrogen was successfully incorporated in graphene nanowalls (CNWs) using cold gaseous plasma post-treatment and influence of nitrogen concentration and configuration in CNWs on electrical conductivity was demonstrated.
- The mechanism of nitrogen incorporation was systematically studied using different characterisation techniques to make a bridge between established DFT theories.

ABSTRACT Incorporating nitrogen (N) atom in graphene is considered a key technique for tuning its electrical properties. However, this is still a great challenge, and it is unclear how to build N-graphene with desired nitrogen configurations. There is a lack of experimental evidence to explain the influence and mechanism of structural defects for nitrogen incorporation into graphene compared to the derived DFT theories. Herein, this gap is bridged through a systematic study of different nitrogen-containing gaseous plasma post-treatments on graphene nanowalls (CNWs) to produce N-CNWs with incorporated and substituted nitrogen. The structural and morphological analyses describe a remarkable difference in the plasma–surface interaction, nitrogen concentration and nitrogen incorporation mechanism in CNWs by using different nitrogen-containing plasma. Electrical conductivity measurements revealed that the conductivity of the N-graphene is strongly influenced by the position and concentration of C–N bonding configurations. These findings open up a new pathway for the synthesis of N-graphene using plasma post-treatment to control the concentration and configuration of incorporated nitrogen for application-specific properties.

KEYWORDS Graphene; Graphene nanowalls; Plasma post-treatment; Nitrogen incorporation; Raman spectroscopy; Vacancy defects



1 Introduction

Carbon nanowalls (CNWs) or graphene nanowalls are considered as two-dimensional (2D) graphite sheet nanostructures composed of stacks of graphene sheets with open boundary edges standing vertically on the substrate and widely synthesised using the plasma-enhanced chemical vapour deposition [1–5]. The nucleation and growth of nano-sized structures on the substrate are influenced by temperature, plasma power and pressure, which are controlling the thickness of self-aligned nanowalls in the range of few nanometres to a few tens of nanometres with an interlayer spacing of few nanometres [6–9]. Catalyst-free synthesis, large surface area, sharp edges with open boundaries and ease of functionalisation of CNWs can be suitable for numerous applications such as field emission [10, 11], electrochemical and energy storage applications [12–18] and novel electronic devices [19, 20]. Thus, tailoring the electrical characteristics of CNWs/nanocarbons for achieving application-specific properties has attracted wide attention, specifically by incorporating a heterogeneous atom for controlling the surface properties [21], tuning the bandgap [22] and tailoring the electrical properties [23–25].

Among all the heterogeneous atom incorporation mechanisms, incorporation of nitrogen in the CNWs/graphene has potential research interests because of its ability to tune and modify the electrical properties of CNWs. Fabrication of nitrogen-incorporated CNWs (N-CNWs) can be done either by in situ method or by a post-treatment [26, 27]. In situ synthesis of N-CNWs occurs during the growth of CNWs, while in the post-treatment method, the pre-prepared CNWs are treated in a nitrogen-containing atmosphere to produce N-CNWs with homogenous incorporation of nitrogen. Post-treatment of CNWs with nitrogen precursors has been widely used for incorporating nitrogen on the surface of graphene-like structures with controlled nitrogen bonding, which is mainly done with thermal and plasma post-treatments [28]. Incorporated nitrogen concentration is low in the thermal treatment method due to the insufficient defect number in the graphene lattice and high annealing temperature [28–30]. Compared to the thermal treatment, when carbon materials are exposed to a nitrogen plasma atmosphere, carbon atoms will partly be replaced by the N-atoms and N-graphene with higher nitrogen concentration will be produced. This is mainly due to the creation of the excited nitrogen

species (either nitrogen-containing molecules, or atoms), reactive N-atoms or even ions and the defect generation on the graphene surface during plasma processing. These reactive species can influence the structure of CNWs through the crystallinity of the structure and nitrogen configurations or concentrations by controlling the plasma conditions and exposure time [26, 31–33]. Based on the position of incorporated nitrogen, the possible configurations of nitrogen in N-graphene such as pyridinic N (N-6, 398.1–399.3 eV), pyrrolic N (N-5, 399.8–401.2 eV), graphitic N/quaternary N (N-Q, 401.1–402.7 eV), amines (399.0–399.7 eV) and N-oxides of pyridinic-N (N-O, 403–405 eV) are presented in Fig. 1 [30, 34].

Pyridinic N bonds to two carbon atoms at the graphene edges and contributes one p-electron to the π system [33], and is weakly bonded to the graphene lattice due to the existence of dangling bonds [35]. Pyrrolic N has a five-membered ring structure, which contributes two p-electrons to the π system [36]. The N-atom substitutes one of the missing carbon atoms in the hexagonal ring to form graphitic N. Among these configurations, pyridinic N and graphitic N are sp^2 -hybridised [37], and pyrrolic N is sp^3 -hybridised [38]. Apart from these three common nitrogen configurations, amines have been observed at the carbon atoms situated at the edges and oxidised groups of N observed at pyridinic N.

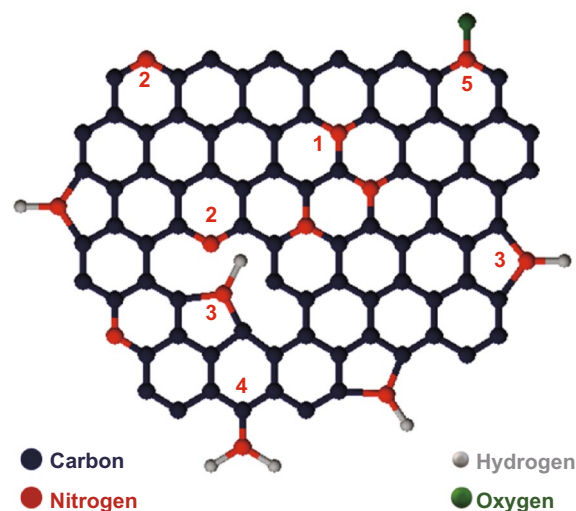


Fig. 1 Possible nitrogen configurations in graphene lattice, labelled as (1) graphitic N, (2) pyridinic N, (3) pyrrolic N, (4) amine, and (5) N-oxides of pyridinic N

High content of pyridinic N and pyrrolic N reduces the conductivity due to the existence of a large number of nanoholes and *p*-type doping [39]. Thus, graphitic N can be considered as the most promising nitrogen configuration for tuning the electrical properties due to the strong *n*-type doping effect without any significant defect generation [40].

Manipulation of structural defects is an effective approach for the intrinsic modification of graphene. Stone–Wales (SW), single or double vacancies (SV and DV), nanoholes and the edges of graphene are the active defect sites for the incorporation of a heterogeneous atom [41, 42]. Transformation of the four neighbouring hexagonal rings into two pentagons and two heptagons by the rotation of one of the carbon bonds causes SW defect. SV defect is formed due to the missing of a carbon atom in the hexagonal ring, which forms a five-membered and nine-membered ring structure known as “SV(5-9)”. DV can be formed either by the coalescence of two SV or by the removal of two neighbouring carbon atoms. The latter forms an energetically unstable structure with two pentagons and one octagon known as “DV (5-8-5)”. Thus, typically, one of the carbon atoms in “DV (5-8-5)” rotates for 90° and forms “DV (555-777)” with a ring structure having three pentagons and heptagons. These defects can be formed either during the growth of graphene-like structures or during the intrinsic modification. The interaction between these defects and heterogeneous atoms leads to the incorporation of nitrogen with different configurations.

Recent studies on the synthesis of N-CNWs using nitrogen-containing plasma treatment suggested that the structural defects are responsible for the formation of N-graphene with different N configurations [16, 43]. The reported DFT calculations based on different experimental conditions such as plasma exposure [16], thermal annealing [37, 44] and nitrogen ion implantation [45, 46] suggested that SV and DV (555–777) defects are the most favourable sites for the nitrogen incorporation, and SW and DV (5-8-5) defects are unlikely to trap N-atoms to form N-graphene [16]. Depending on the cooperative effect between the dopant and defects, pyridinic N in graphene lattice can be formed with an SV [45, 47], and pyrrolic N can be formed along with pyridinic N at DV [47]. Embedding of excited N-atom in the carbon vacancy and migration of carbon atom in the presence of a C-atom at an SV is the possible mechanism to form graphitic N by substituting the missing

C-atom using an N-atom, and this restores the hexagonal ring [16, 45, 48]. All these DFT calculations suggest that the interactions of nitrogen with the defect sites are the key to the efficient building of N-graphene. Here, one of the main challenges lies in the synthesis of N-CNWs/N-graphene with desired nitrogen configurations. However, there is a lack of experimental results to explain the mechanism of nitrogen incorporation in the structural defects of graphene and compare evidence with the proposed DFT theories.

Conjugating Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy with different characterisation techniques opens up the possibility to extract most of the chemical information of the graphene such as coordination environment, geometrical distortions and different defect types in graphene [49, 50]. To date, different groups confirmed theoretically that the formation of additional peaks in the “fingerprint” region (binding energy ~286–290 eV) of the graphene NEXAFS spectrum is mainly due to the structural defects [49, 50]. Significant variations in the NEXAFS “fingerprint” region due to the interaction of heterogeneous atoms with the structural defects are also reported elsewhere [51, 52]. Thus, comparing various established DFT calculations of the NEXAFS spectra with experimental results can enlighten the mechanism of interaction of nitrogen with the structural defects to form N-CNWs.

In this work, we demonstrate the effect of different nitrogen-containing plasma post-treatments for the incorporation of nitrogen into CNWs using ammonia (NH₃) and nitrogen (N₂) in an inductively coupled RF low-temperature plasma. Furthermore, we present a systematic study on the effect of plasma exposure time on the structure and morphology of CNWs using Raman spectroscopy and scanning electron microscopy (SEM). The time-dependent changes in the nitrogen configurations and concentrations are evaluated by X-ray photoelectron spectroscopy (XPS). NEXAFS spectroscopy is used to distinguish the structural changes and defect generation occurring during the plasma exposure time. Van der Pauw method is used to measure the electrical conductivity of the CNWs and N-CNWs and to understand the effect of nitrogen configuration on electrical conductivity. Finally, the obtained results are used to explain the effect of the plasma environment on the creation of defects in graphene and to unravel the mechanism of nitrogen incorporation into graphene when forming N-CNWs.



2 Experimental Section

2.1 Synthesis of N-CNWs

The CNWs were synthesised on a SiO₂ substrate using a double plasma device for CNWs deposition. The system consisted of a surface wave plasma (SWP) region driven by a 2.45 GHz microwave power supply to generate H-atoms and a capacitively coupled plasma (CCP) region generated by a 100 MHz power supply to fabricate nanowalls from CH₄ gas. The high-density H-atoms were generated at the top of the PECVD system by the SWP system, which was operated at 2.54 GHz and injected into the PECVD system. The CNWs were then grown on the substrate. The details are described elsewhere [53–55]. For the nitrogen doping and synthesis of N-CNWs, plasma post-treatment was carried out in an RFICP (radio-frequency inductively coupled plasma) system that consists of an 80-cm-long glass tube with a diameter of 4 cm. The RF generator was inductively coupled to the system by using a nine-turn water-cooled inductive coil. Ammonia (NH₃) and nitrogen (N₂) gases were used as the dopant gases at the flow rate of 100 sccm. The total pressure in the chamber before experiments was below 1 Pa, and during the experiments, it was not above 30 Pa. The sample was placed 10 cm away from the centre of glow discharge into the post-glow region. This was done in order to have low-temperature treatments of samples, where the surface temperature was never above 50 °C, typically even much less. Post-glow region also contained mostly the high densities of neutral reactive species and the negligible densities of ions. Plasma was generated at an RF power of 300 W. The plasma post-treatment was carried out in an incremental method, where the plasma was switched off during each treatment periodically to keep the surface temperature minimised. This was done typically in different steps of 4, 5 or 10 s and equal cooling periods. Depending on the aggressiveness of used nitrogen gases towards the samples and its consequent etching, the most optimal time treatments were selected. For the CNWs, the typical samples treated with NH₃ plasma in the post-glow region were 4, 8, 12 and 25 s with an incremental order of 4 or 5 s, and for N₂ plasma 10, 20, 30 and 40 s with an incremental order of 10 s. The schematic diagram of the posttreatment experimental setup is presented in Fig. S1.

2.2 Characterisation Techniques

The SEM characterisation of the samples was performed by a JEOL JSM-7600F, field emission scanning electron microscope using 5 kV electron acceleration voltage. The samples were placed on a double-sided carbon tape mounted on an aluminium stub. Raman spectra were recorded at different regions of the samples to study the structural properties of the CNWs and N-CNWs using NTEGRA confocal Raman spectrometer at an excitation wavelength of 633 nm with an incident power ~ 3 mW at a spot size of 50 µm. X-ray photoelectron spectroscopy (XPS) analyses were carried out on the PHI-TFA XPS spectrometer produced by Physical Electronics Inc. and equipped with Al monochromatic source emitting photons at the energy of 1486.6 eV. The analysed area was 0.4 mm in diameter with a takeoff angle (TOA) of 45°. The high-energy-resolution spectra were acquired with energy analyser operating at a resolution of 0.6 eV and a pass energy of 29 eV. The accuracy of binding energies was about ± 0.3 eV. Quantification of surface composition was performed from XPS peak intensities taking into account relative sensitivity factors provided by the instrument manufacturer [56]. The XPS spectra were analysed using MultiPak software, and Gauss–Lorentz method was used for the deconvolution of the peaks considering Shirley-type background deduction. Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy was performed at Helmholtz-Zentrum Berlin (BESSY II), at High Energy Spherical Grating Monochromator (HESGM) beam line in an ultrahigh vacuum chamber (PREVAC end station). NEXAFS measurements were performed at different incident angles (20°, 30°, 45°, 55°, 70° and 90°) relative to the substrate surface. NEXAFS data on the C K edge were obtained in the total electron yield mode (TEY) with an energy resolution of ~ 0.40 eV, 0.55 eV at the N K edge and 0.6 eV at O K edge using a home-built double-channel plate detector [57–59]. This mode enables a probing depth of about 10 nm. The further step was measurements in partial electron yield mode obtained at – 150 V (C K edge) or – 250 V (N K edge), giving information on the very surface of the material. All spectra were referenced against a peak at 284.9 eV in simultaneously recorded *I*₀ spectra of a carbon-contaminated Au grid, which

was previously referenced against the π^* resonance of highly oriented pyrolytic graphite at 285.38 eV. The raw NEXAFS spectra were normalised to the incident photon flux and corrected for the beamline transmission by division through a spectrum of a clean, freshly sputtered Au sample. Finally, the C K-edge spectra have been normalised to 1 at the energy of 325 eV. Van der Pauw method was used to measure the electrical conductivity of the samples. The measurements were done by using a TTIQL564P power supply as the current source, TENMA 72-7732A multimeter as the ammeter and an Agilent/Keysight 34970A data acquisition unit as the voltmeter.

3 Results and Discussion

The morphology of CNWs in Fig. 2a exhibits the uniform growth and characteristic morphology of the as-grown CNWs. The height of CNWs was about 600 ± 100 nm, with a thickness of approximately 10 nm (Fig. S2). The typical morphological characteristics of 10, 20, 30 and 40 s N_2 plasma-treated CNWs are presented in Fig. 2b–e. There was no noticeable change after the initial 10 s treatment. Another 10 s plasma treatment leads to the increase in roughness of nanowalls due to the etching of carbon atoms by plasma. The SEM images after 30 s and 40 s indicate that etching of nanowall structures increased with the plasma exposure time. Figure 2f–i exhibits

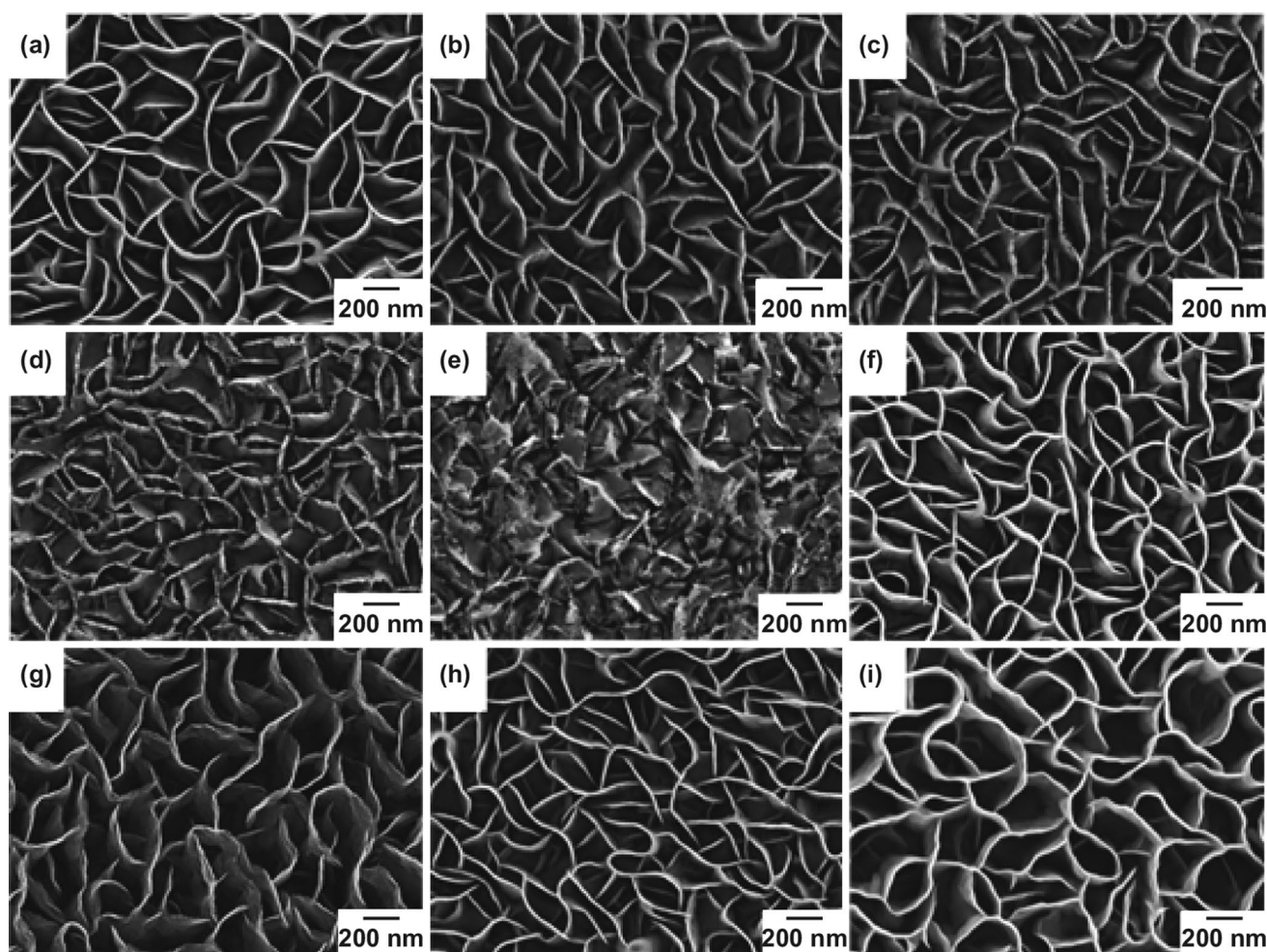


Fig. 2 SEM images of **a** nontreated CNWs, **b–e** 10 s, 20 s, 30 s, and 40 s of N_2 plasma-treated CNWs, **f–i** 4 s, 8 s, 12 s, and 25 s of NH_3 plasma-treated CNWs

the morphology of NH_3 plasma-treated CNWs. Compared to the N_2 plasma-treated samples, the morphology of NH_3 plasma-treated samples was not significantly changed during the plasma exposure. There were no observable changes in the edges of the nanowall or structure even after 25 s plasma treatment. This effect is due to the low concentration of incorporated nitrogen compared to N_2 plasma post-treatment. However, here it is worth noticing that also treatment periods were shortened due to the aggressiveness of NH_3 plasma.

Raman spectroscopy was further used to understand the structure and quality of graphene nanowalls. Typical Raman spectra of CNWs before and after N_2 and NH_3 plasma post-treatments are presented in Fig. 3a, b. The G-band peak is the first-order Raman band of the all sp^2 -hybridised carbon material, which corresponds to the six-membered ring structure of the graphene. The D band is the defect-activated band in the sp^2 -hybridised carbon and corresponds to the imperfection in the graphene lattice. There is a shoulder peak observed

along with G peak, known as D' peak, which is also a defect peak mainly due to the localised vibrational modes of randomly distributed impurities in the graphitic edges. The samples exhibit bands in the higher shift ranges ($> 2400 \text{ cm}^{-1}$), which are 2D (G') band and D + G band. The presence of the D band and a very weak 2D peak is the characteristic of multilayered graphene with a number of structural defects. The peak positions for all samples are almost similar and possess the main characteristic peaks of graphene [60]; D peak is observed in between 1330 and 1333 cm^{-1} , G peak at 1584 – 1587 cm^{-1} , D' peak at 1612 – 1618 cm^{-1} , 2D peak at 2360 – 2365 cm^{-1} and D + G peak at 2917 – 2919 cm^{-1} . The change in intensities of D and G peaks after plasma treatment is represented in Fig. S3. The quantitative analysis technique to estimate the degree of disorder in the graphene lattice is the ratio between the intensity of D and G bands (I_D/I_G) [61].

The evaluation of I_D/I_G ratios of CNWs before and after N_2 and NH_3 plasma treatments is delineated in Fig. 3c, d. It

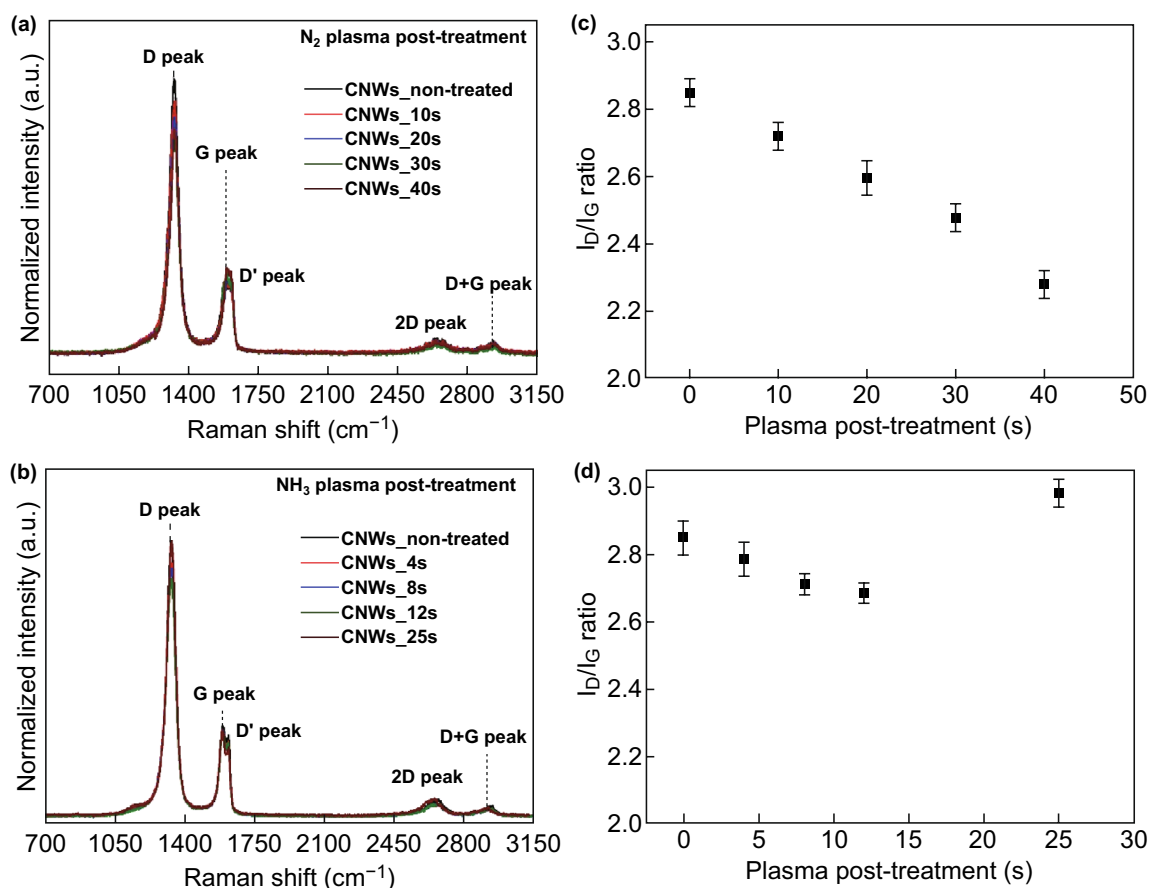


Fig. 3 a, b Raman spectra of CNWs before and after N_2 and NH_3 plasma post-treatments. c, d I_D/I_G ratio of CNWs before and after N_2 and NH_3 plasma post-treatments

is seen that the I_D/I_G ratio decreases to a certain minimum as the post-treatment time is increased. The I_D/I_G ratio of as-grown CNWs is 2.85, which decreases with N_2 plasma treatment and reaches a minimum of 2.28 after the 40 s of post-treatment. Compared to N_2 plasma, the I_D/I_G ratio of NH_3 plasma-treated CNWs exhibits very small changes with the initial plasma exposure and attains a minimum of 2.68 after 12 s treatment. Nevertheless, the prolonged plasma treatment for 25 s causes the increase of the I_D/I_G ratio to 3, which is higher than the initial nanowall condition. From the I_D/I_G ratio, in-plane crystallite size (L_a) of CNWs was calculated using the Tuinstra–Koenig relationship [62] and is presented in Table S1. The value of L_a for as-grown CNW is 13.53 nm, which increases to 16.90 nm after the 40 s of N_2 plasma treatment. On the other hand, for NH_3 plasma-treated CNWs, the highest L_a value of 14.36 nm was obtained after 12 s and a minimum of 12.93 nm was attained after 25 s. These L_a values after NH_3 plasma treatment do not have significant deviations from the initial L_a value (13.53 nm) of the CNWs. Considering L_a as average interdefects distance, an increase in L_a value indicates a lower defect concentration in the graphene lattice [30]. Thus, the defect sites were lowered after N_2 plasma treatment either by the substitution of nitrogen to the defect sites or by the etching of the amorphous carbon phase. These changes in Raman spectra illustrate that both plasma post-treatment methods can incorporate nitrogen and functionalise the surfaces without destroying the vertical alignment. However, the difference in surface morphology and the Raman behaviour of N-CNWs after different plasma exposures implies that the incorporation of nitrogen in the graphene lattice after N_2 and NH_3 plasma post-treatments occurs through different nitrogen bonding configurations.

XPS analysis was performed to determine the elemental composition and nitrogen configurations of the N-CNWs. The nontreated CNWs had two typical peaks in the spectra: around 284.6 eV for carbon and around 532.0 eV for some residual oxygen. A peak at about 400 eV in the XPS survey spectra of all the plasma-treated samples confirms the presence of incorporated nitrogen (Fig. S4) and increase in intensity of oxygen is due to the adsorption of oxygen from the air to the reactive carbon atoms at the edges [63]. A high concentration of incorporated nitrogen ($\sim 8.0\%$) was observed after 30 s of N_2 plasma treatment, while $\sim 2.8\%$ was the highest concentration after NH_3 plasma treatment (Fig. S5). The change in the chemical state of carbon due

to the nitrogen is a potential interest and investigated by acquiring the high-resolution XPS spectra of carbon and nitrogen. Since methane (CH_4) was used as the precursor for the synthesis of CNWs, the H-terminated structure of nanowall also influences the bonding configurations. Figure 4a, d represents the high-resolution C 1s XPS spectra of N_2 and NH_3 plasma-treated CNWs. The C 1s peak after both plasma-treated CNWs is deconvoluted into different components centred at 284.6, 285.1, 285.5, 286.2, 286.9, 288.2 and 290.0 eV. All the peak positions are assigned with an uncertainty of ± 0.3 eV. The main peak of CNWs at 284.6 eV corresponds to the graphite-like sp^2 C–C bond (graphitic-C) [64]. Other peaks observed at 285.1 eV are attributed to sp^2 C–N, the peaks centred 285.5 eV originate from the sp^3 -bonded carbon atoms, peak found at 286.9 eV is ascribed to sp^3 C–N bonds, carbon singly binds to oxygen at 286.9 eV and carbon in carbonyl groups at 288.2 eV. The broad peak centred at 290.0 eV represents the π – π^* shake-up satellite [65]. All the samples show similar peaks after plasma treatment, and the represented deconvoluted peaks belong to the N-CNWs with higher sp^2 -bonded nitrogen concentration after N_2 and NH_3 plasma treatments. Detailed deconvolution spectra of CNWs after each plasma treatment time are presented in Fig. S6, and it is seen that the concentration of sp^2 and sp^3 C–N bonds of N-CNWs after N_2 and NH_3 plasma treatments varies with the plasma exposure time. Information of the peak positions and roughly estimated composition ratio (%) of the deconvoluted peaks of the C 1s spectrum is summarised in Tables S2 and S3.

Detailed N 1s core-level spectra were analysed to understand the evolution of different peaks of C–N configurations in C 1s spectra during the plasma post-treatment. Figure 4b, e displays the N 1s XPS spectra of N_2 and NH_3 plasma-treated CNWs. The N 1s peaks in all the samples were fitted into three main components, namely sp^2 -bonded pyridinic N (398.9 eV), sp^3 -bonded pyrrolic N (400.1 eV) and sp^2 -bonded graphitic N (401.1 eV) [40, 66]. In the case of NH_3 plasma-treated CNWs, an additional peak is manifested at 399.5 eV, and it is ascribed to amine groups. However, in the samples treated with N_2 plasma, a minor peak is noticed at 402.3 eV due to the oxidation of pyridinic N by exposure to ambient air. Comparison of the deconvoluted N 1s peak intensities after different plasma and treatment time (Fig. S7) shows that the peak intensities are varying with each plasma treatment. Graphitic N and pyridinic N (sp^2 C–N) components are increasing with the initial N_2 plasma treatment.



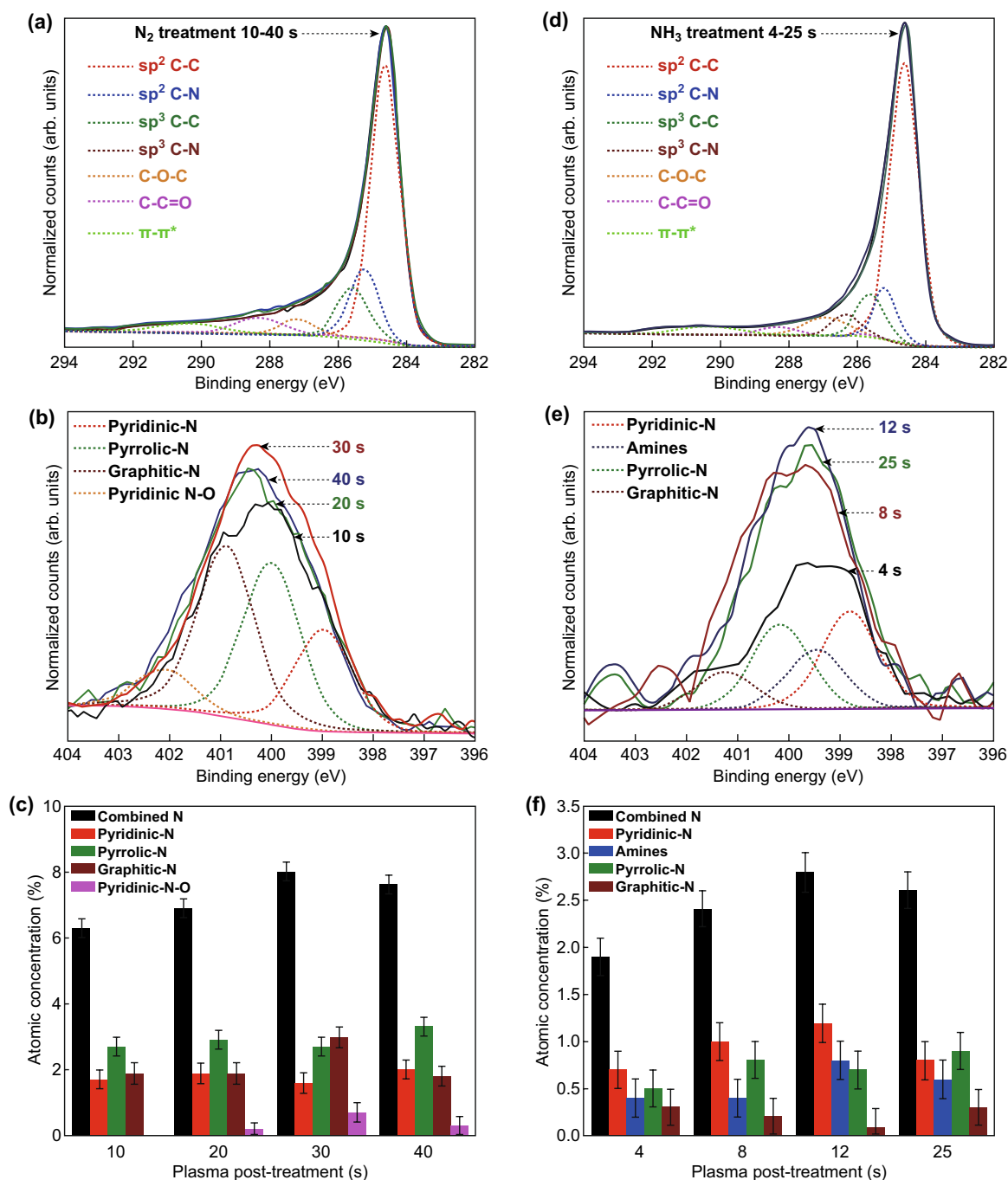


Fig. 4 **a** High-resolution C 1s spectra, **b** N 1s spectra, and **c** content distributions of nitrogen configurations after N₂ plasma post-treatment. **d** High-resolution C 1s spectra, **e** N 1s spectra and **f** content distributions of nitrogen configurations after NH₃ plasma post-treatment

On the other hand, pyridinic N and amine components are increasing with the initial NH₃ plasma treatment. Pyrrolic N component becomes dominant in both cases after longer plasma exposure, which is mainly because of the continuous loss of carbon atoms from graphene lattice due to the

plasma etching effect. Information of the peak positions and roughly estimated concentration (%) of all the fitted peaks is presented in Tables S4 and S5.

Roughly estimated content distribution of the different nitrogen components in N-CNWs after each plasma

post-treatment is represented in Fig. 4c, f. Nitrogen concentration in N_2 plasma-treated CNWs is above $\sim 6\%$ after all the treatment conditions. Initially, pyrrolic N has a higher concentration, and the concentrations of graphitic N and pyridinic N components are increasing upon increasing plasma exposure. The higher concentration of incorporated nitrogen can be due to the formation of multiple vacancy defects by higher etching of CNWs by N_2 plasma treatment [47]. However, the continuous loss of carbon will make the nitrogen incorporation more difficult; thus, the nitrogen concentration starts to drop and is mainly incorporated into the sp^3 C–N configurations, which eventually increases the concentration of pyrrolic N. On the other hand, the nitrogen concentration is lower in the case of NH_3 plasma-treated CNWs (Fig. 4f). The cause is likely due to the hydrogen radicals in NH_3 plasma. Hydrogen radicals can vividly etch amorphous carbon, which can remove a significant amount of the sp^3 -bonded carbon from the CNWs [67, 68]. Thus, the nitrogen is incorporated into the most favourable edges of graphene in pyridinic N form, which has a higher concentration during the initial plasma exposure (4–12 s). Nevertheless, the continuous loss of carbon atom makes the nitrogen incorporation more difficult and leads to the formation of more sp^3 C–N bonding and increases the concentration of pyrrolic N. The Raman studies on the in-plane crystallite sizes are strongly aligned with the XPS observations, where the crystallite size increases with the increase in sp^2 C components and decreases with the increase in sp^3 C concentrations. Thus,

more detailed investigations are needed to reveal the effect of plasma treatment on the graphene lattice concerning the incorporation of N-atoms through a different bonding.

NEXAFS studies were performed to gain further insight into the bonding environment of the adsorbing atom to identify the local bonding environment. Interpretation of NEXAFS signals can be used as the fingerprints to detect the sample defect fraction. C K edge spectra of the CNWs and N-CNWs after N_2 plasma treatment and NH_3 plasma treatment are shown in Fig. 5a, b. The spectra represented are recorded at an incident angle of 45° to avoid possible orientation effects. A characteristic sharp resonance is observed at 285.4 eV corresponding to a C $1s \rightarrow \pi^*$ transition. A double-structured resonance is observed at 292 eV corresponding to the C $1s \rightarrow \sigma^*$, which mainly arises due to the excitonic (~ 291.7 eV) and a band-like contributions (293.1 eV) [69, 70]. The significant changes observed in the C K edge spectrum are in the region between π^* and σ^* resonance in the energy range between 286 and 290 eV, known as “fingerprint” region [49], attributed to the structural defects and chemical modifications in graphene [49, 71]. Thus, the evolution of the peak around 288.0 eV can be attributed to either the plasma-enhanced defect formation or incorporation of nitrogen to the defects in graphene. The experimental investigations on the NEXAFS “fingerprint” database of defects on graphene are not described well yet. Thus, the several reported DFT calculations on the NEXAFS spectra from the structural defects in graphene are used to interpret the changes in graphene

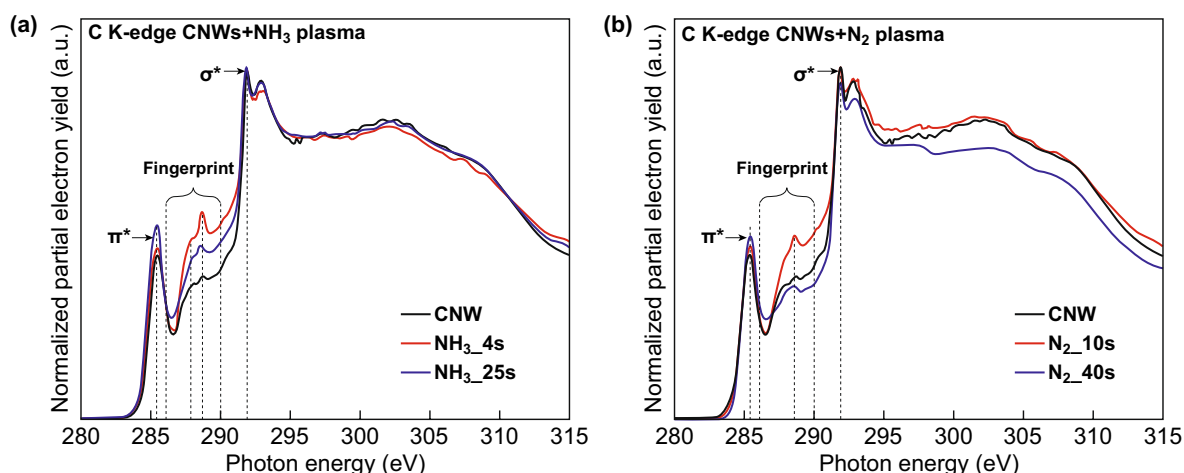


Fig. 5 C K-edge spectra of the CNWs and N-CNWs: **a** nontreated, 4 s and 25 s NH_3 plasma-treated CNWs, and **b** the nontreated, 10 s and 40 s N_2 plasma-treated CNWs

lattice after plasma treatment and to explain the nitrogen incorporation mechanism [50, 52].

The model proposed by Rojas et al. [52] suggested that the substitution of a single vacancy defect with N-atom does not affect the NEXAFS signal in the “fingerprint” region, but the adsorption of N-atoms to the graphene bridge distorts it. The calculations on the NEXAFS spectra obtained from the structural defects of graphene done by Ehlert et al. [49] demonstrate that the additional peak observed at the “fingerprint” region originates from the sp^3 -hybridised C-atom in SV (5-9) and carbon atoms near to the defect in DV (5-8-5). Hua et al. [50] suggested that the DV has a peak with a larger intensity at the “fingerprint” region slightly above 288 eV, and SV has a peak slightly below 288 eV with lower intensity. Comparing these results with our experimental NEXAFS results confirms that the changes observed in the “fingerprint” region are mainly due to the vacancy defects. As-grown CNWs have two low-intensity peaks in the “fingerprint” region around 288.2 and 287.5 eV. It is seen that the evolution of these peaks after 4 s NH_3 plasma treatment (Fig. 5a) and decreases the intensity with the longer plasma

exposure time (25 s). Considering the above-mentioned DFT calculations on the defect effects, these peaks at 288.2 and 287.5 eV can be assigned as the characteristics of DV (5-8-5) and SV (5-9), respectively. Compared to NH_3 plasma-treated samples, the noticeable change in the “fingerprint” region of C K-edge spectra of N_2 plasma-treated samples is the evolution of only one peak around 288.2 eV and is the characteristic of DV (5-8-5) (Fig. 5b).

Taking all these results into account suggests that building N-CNWs by plasma post-treatment has two stages: the plasma-enhanced defect generation and the incorporation of nitrogen into defects. Plasma-enhanced defect generation is mainly due to the removal of carbon atoms by the interaction of plasma species with the CNWs. The changes observed in the “fingerprint” region of NEXAFS spectra, the concentration of incorporated nitrogen and changes in the in-plane crystal size of N_2 and NH_3 plasma-treated samples are different, which indicates that the plasma-enhanced defect generation by the plasma species and nitrogen incorporation takes place differently. A typical NH_3 plasma contains excited species (NH_3^* and N_2^*), different kinds of ions

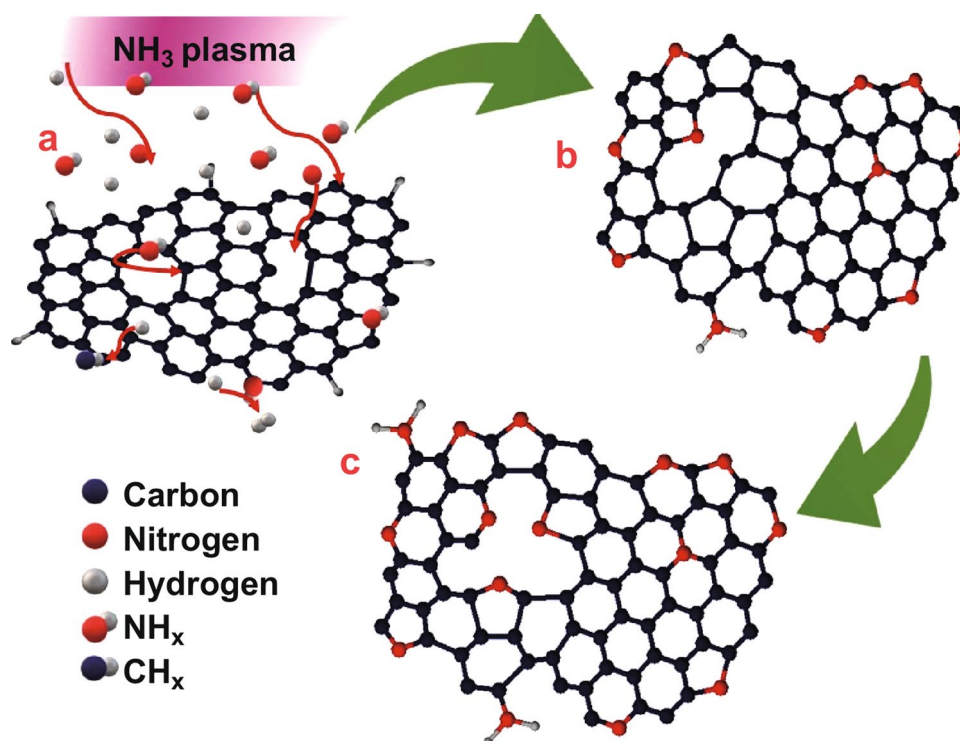


Fig. 6 Schematic diagram of the plausible mechanism of nitrogen incorporation in CNWs using NH_3 plasma post-treatment: **a** the interaction of plasma species with defects, **b** the substitution of N-atoms in the SV to form graphitic N and incorporating N at DV to form pyrrolic N, and **c** the transformation of pyrrolic N to form pyridinic N along with pyrrolic N at DV

and radical species (NH_2 , NH and H) [72], and N_2 plasma contains excited N_2 species, reactive N-atoms, N^{2+} and N^{4+} ions, which interact with H-terminated CNWs. The significant difference between NH_3 and N_2 plasma species is the presence of NH_x ($x = 1, 2, 3$) species and hydrogen species in the NH_3 plasma (Fig. S8). NH_x ($x = 1, 2, 3$) species can chemically functionalise the edges of carbon to the formation of amino groups that are observed in the XPS spectra. The capability of hydrogen to etch the carbon resulted in the creation of more structural defects. The active N-containing species in NH_3 plasma could react with the defects and incorporate nitrogen to the structure [73]. NEXAFS results propose that the defects formed during plasma treatment are DV (5-8-5) and SV (5-9). Transformation of DV (5-8-5) to stable DV (555-777) is well known [74, 75], can be made by the ion bombardment during the plasma exposure, which is the favourable site for nitrogen incorporation. Based on these findings, a plausible mechanism of nitrogen incorporation by NH_3 plasma in three stages is summarised in Fig. 6: (a) the plasma-enhanced defect generation and interaction of plasma species with the defects; (b) the interaction of

N-containing species at the SV defect site forms graphitic N, at DV defect forms pyrrolic N with an SV and at the edges forms amines, pyridinic N and pyrrolic N; and (c) the formation of pyridinic N by the transformation of pyrrolic N at DV after longer exposure. The increase in pyrrolic N in the graphene lattice decreases the in-plane crystalline size, which is evident from Raman.

In the case of N_2 plasma treatment, the nitrogen species interact with the H-terminated CNWs and form N-CNWs. There is no characteristic peak identified for SV defects in the NEXAFS spectrum after N_2 plasma treatment, which confirms that only DV defects are formed during the plasma exposure. XPS analysis and Raman analysis exhibit the improvement in sp^2 -components with an increase in the in-plane crystalline size which indicates the reduction of vacancy defect by forming graphitic N, where the position of N-atom is almost the same as the C-atom in graphene [37]. Thus, the plausible mechanism of nitrogen incorporation by nitrogen plasma is summarised in Fig. 7 and comprised of three stages: (a) the plasma-enhanced defect generation and interaction of plasma species with

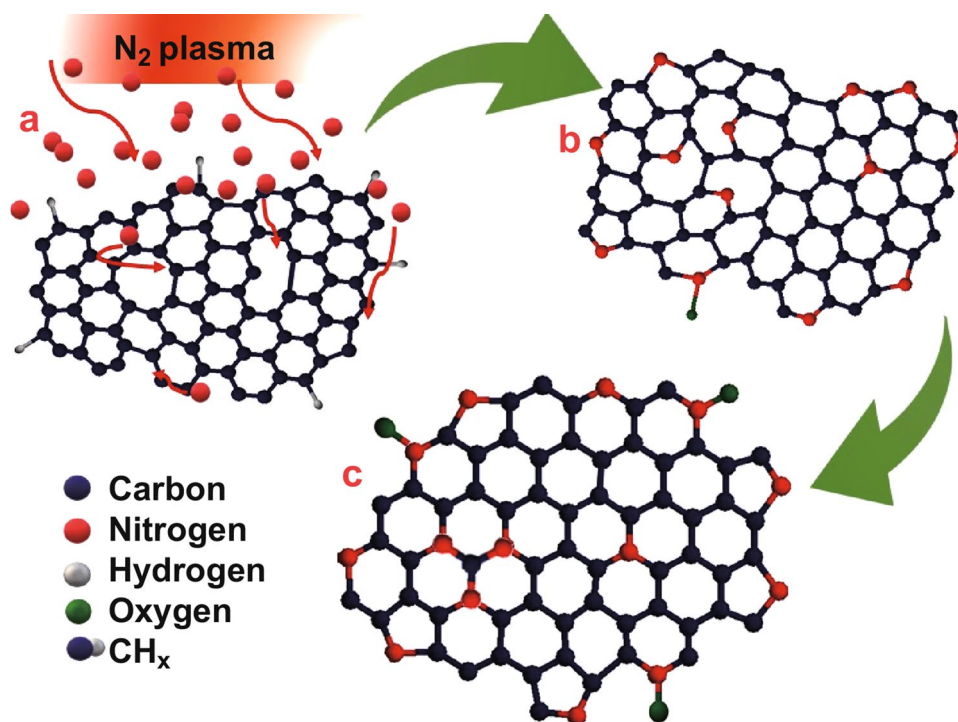


Fig. 7 Schematic diagram of the possible mechanism of nitrogen incorporation in CNWs by N_2 plasma post-treatment: **a** the interaction of plasma species with defects, **b** the substitution of N-atoms in the SV to form graphitic N and incorporating N at DV to form pyridinic N, and lastly **c** the transformation of pyridinic N to graphitic N by the bond rotation at DV and formation of oxidised pyridinic N groups by ex situ adsorption of oxygen

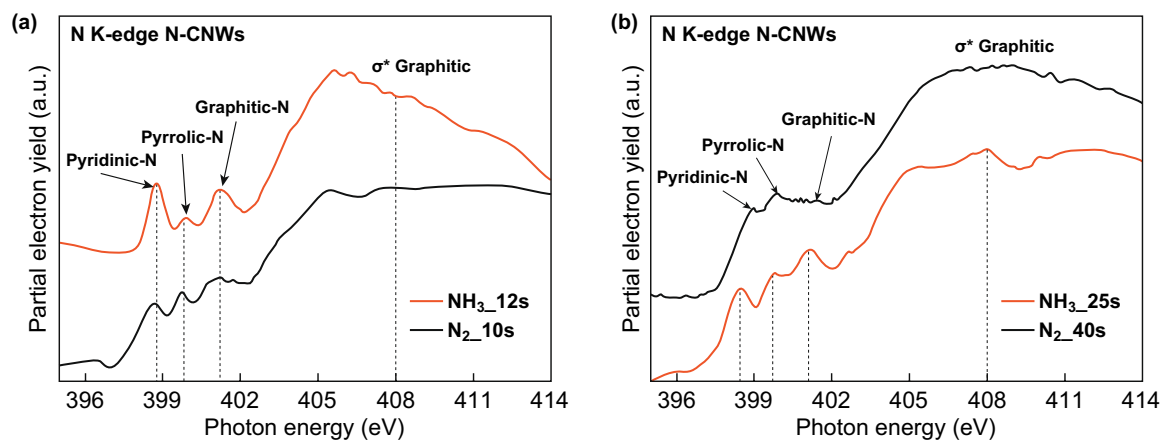


Fig. 8 N K-edge spectra of the NH_3 and N_2 plasma-treated CNWs at different plasma exposure times

the defects; (b) the interaction of N-containing species at the SV defect site forms graphitic N, at DV defect pyridinic N, and at edges pyridinic N, oxides of pyridinic N and pyrrolic N; and (c) the formation of more pyrrolic N at the edges and transformation of pyridinic N to graphitic N at DV sites by the defect migration [44, 48]. In both cases of plasma treatment, the structural defect generation in graphene and interaction of nitrogen with the structural defects play a key role in the formation of N-graphene/N-CNWs with different nitrogen configurations.

N K edges of N-CNWs after different plasma-treated conditions are observed and confirm the previously mentioned nitrogen incorporation mechanism. For the comparison, N K edge of 12 s NH_3 plasma-treated CNWs and 10 s N_2 plasma-treated CNWs is presented in Fig. 8a. The N K-edge spectra of N-CNWs after longer NH_3 and N_2 plasma post-treatment are shown in Fig. 8b. All of the samples possess three distinguished peaks in the π^* region. The peak observed at $\sim 398.5\text{--}399\text{ eV}$ falls into the pyridinic N behaviour of the N 1s core-level spectra. The appearance of a peak at $\sim 399.8\text{--}400.2\text{ eV}$ is assigned to the presence of pyrrolic N in the structure. The peak observed at $401.0\text{--}401.5\text{ eV}$ agrees on the existence of graphitic N in the graphene structure. The evolution of peaks above 405 eV can be associated with the σ^* resonance [40]. Observed results in the N K-edge spectra of N-CNWs have strong agreement with the features explained in the N 1s spectra (Fig. 4b, e). The peak intensity from graphitic N after 40 s N_2 plasma-treated samples is decreasing while

that for the prolonged NH_3 plasma treatment remains almost similar. This indicates that the prolonged N_2 plasma treatment leads to the formation of more pyrrolic N, which has a perfect agreement with the above-mentioned proposed nitrogen incorporation mechanism.

Four-point van der Pauw measurement was carried out to study the effect of nitrogen incorporation in CNWs on the electrical conductivity of N-CNWs at different temperatures, which is represented in Fig. 9. The conductivity of CNWs decreases with the initial plasma treatment in both cases. Compared to NH_3 plasma treatment, N-CNWs after N_2 plasma treatment have minimum conductivity. For N_2 plasma-treated CNWs, conductivity decreases with plasma exposure time. However, after NH_3 plasma treatment, the conductivity falls initially and increases with longer plasma exposure time. This result strongly agrees with the earlier studies based on Kubo-Greenwood approach done by Lherbier et al. [25], which suggest that the conductivity is only marginally affected when the N concentration is between 2 and 4%, and when the concentration is higher than 5%, the electron mobility of N-graphene largely decreases. Therefore, a higher concentration of nitrogen after N_2 plasma ($\sim 8\%$) leads to a decrease in the conductivity. In the case of NH_3 plasma-treated samples, conductivity decreases initially with the plasma exposure and increases with the concentration of substituted nitrogen increasing. The significant presence of oxygenated groups after the plasma treatment also causes the reduced conductivity.

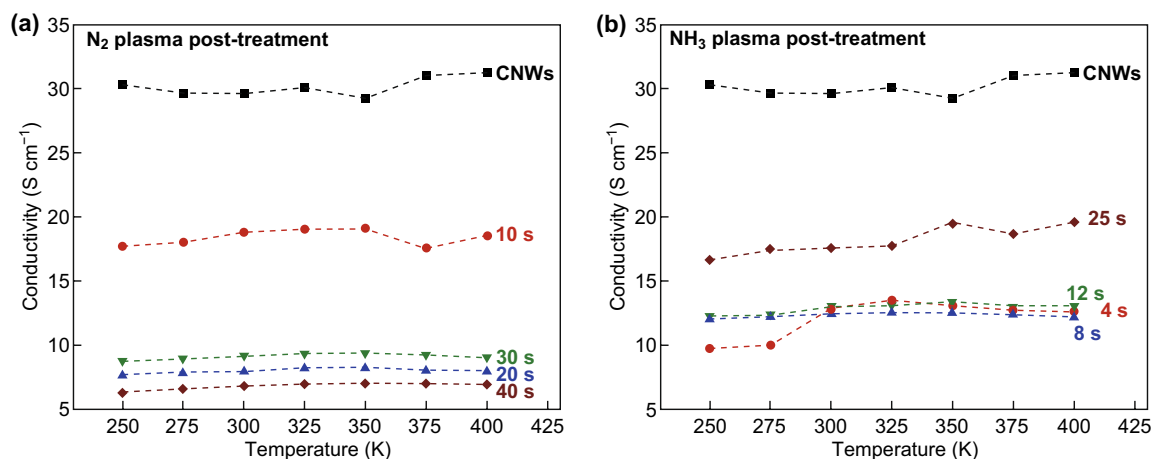


Fig. 9 **a, b** Temperature-dependent electrical conductivity of CNW and N-CNWs: **a** after N_2 , and **b** after NH_3 plasma treatment

4 Conclusions

Nitrogen-incorporated CNWs were successfully produced by the low-pressure RFICP system using N_2 and NH_3 cold-temperature plasma post-treatments. Mechanism of the incorporation and substitution of nitrogen in the CNWs and the influence of different plasma environments for controlling the concentration and configuration of nitrogen were successfully studied. The high concentrations of incorporated nitrogen $\sim 8\%$ after N_2 plasma post-treatment and $\sim 2.8\%$ after NH_3 plasma treatment give the possibility to control the nitrogen concentration using different plasma environments. Moreover, N_2 plasma treatment produces N-CNWs with higher graphitic N concentration, while NH_3 plasma treatment mainly produces N-CNWs with higher pyridinic N indicating the effective control of nitrogen configuration by choosing suitable plasma environments. Also, time-dependent plasma post-treatment studies give an insight into the change in the crystalline size of the nanowalls. Raman studies on the in-plane crystalline size explain that the crystalline order of graphene is improved by healing the vacancy defect by incorporating N-atom. Also, a better understanding of the defect generation and interaction of nitrogen with the bonding environments in nanowalls during the plasma post-treatment was obtained from NEXAFS analysis. All these experimental observations strongly corroborate the reported DFT calculations. Based on these findings, we propose a mechanism to explain the interaction of nitrogen with the defects in

CNWs for the incorporation and substitution of nitrogen in the graphene lattice. The electrical conductivity measurements also strongly support other reported studies, where the conductivity decreases with the higher nitrogen concentration and increases with optimum graphitic N content. To this end, our studies provide a rapid, cost-efficient and environment-friendly technique for the synthesis of N-CNWs via plasma post-treatment processes at low pressure. This strong agreement of experimental results with the existing theoretical calculations on the nitrogen incorporation mechanism will set the base for the controlled synthesis of N-CNWs/N-graphene with desired nitrogen concentration and configurations by choosing optimum plasma parameters for future electronic applications.

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Supporting Information for

N-Graphene Nanowalls Via Plasma Nitrogen Incorporation and Substitution: The Experimental Evidence

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Supplementary Figures and Tables

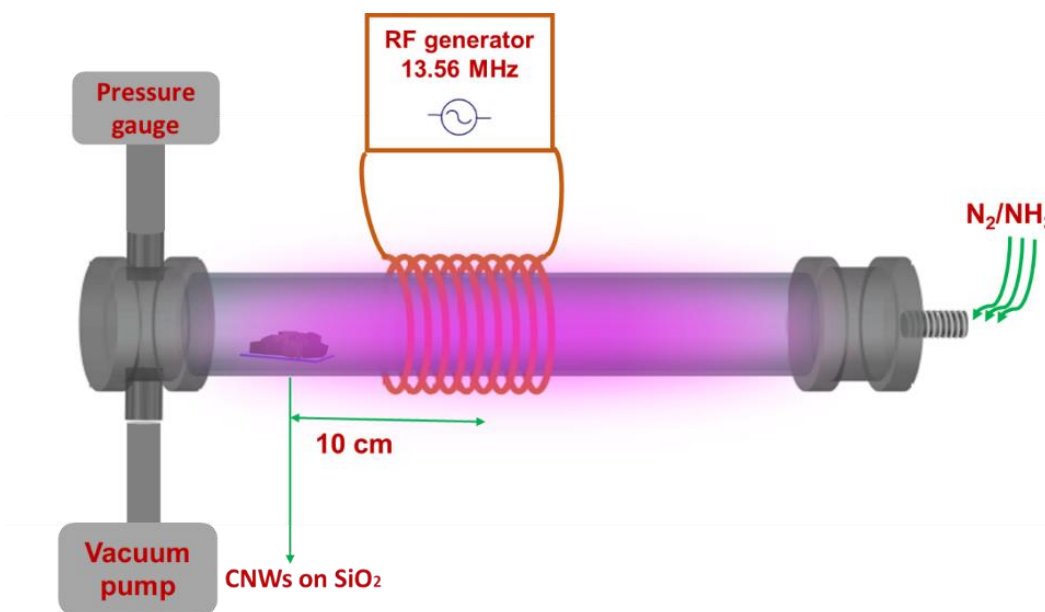


Fig. S1 Experimental setup of RFICP systems for producing N-CNWs

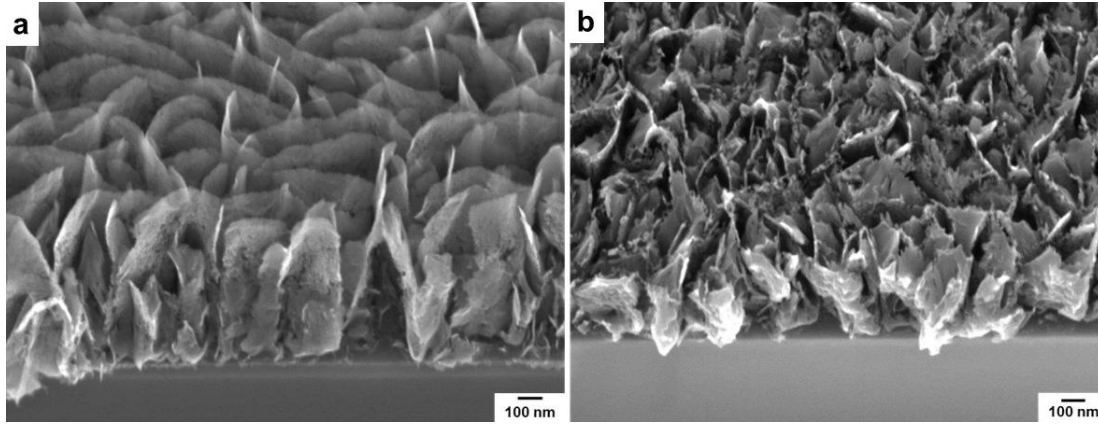


Fig. S2 **a** Tilted image of CNWs. **b** N-CNWs after 40s N₂ plasma exposure

Table S1 Peak position, I_D/I_G ratio, the in-plane crystallite size of CNWs and N-CNWs

NH ₃ plasma post-treatment					N ₂ plasma post-treatment				
Sample conditions	D peak (cm ⁻¹)	G peak (cm ⁻¹)	I _D /I _G ratio	L _a (nm)	Sample conditions	D peak (cm ⁻¹)	G peak (cm ⁻¹)	I _D /I _G ratio	L _a (nm)
0	1330	1586	2.85	13.53	0	1330	1586	2.85	13.53
4	1330	1586	2.78	13.84	10	1333	1587	2.72	14.17
8	1331	1585	2.71	14.21	20	1333	1587	2.59	14.88
12	1332	1584	2.68	14.36	30	1332	1585	2.48	15.54
25	1333	1587	2.98	12.93	40	1331	1585	2.28	16.90

Tuinstra-Koenig relationship to calculate in-plane crystallite size using I_D/I_G ratio:

$$L_a(\text{nm}) = 2.4 * 10^{-10} * \lambda^4 * (I_D/I_G)-1 \quad (\text{S1})$$

L_a is the in-plane crystallite size

λ is the Raman excitation wavelength (633 nm)

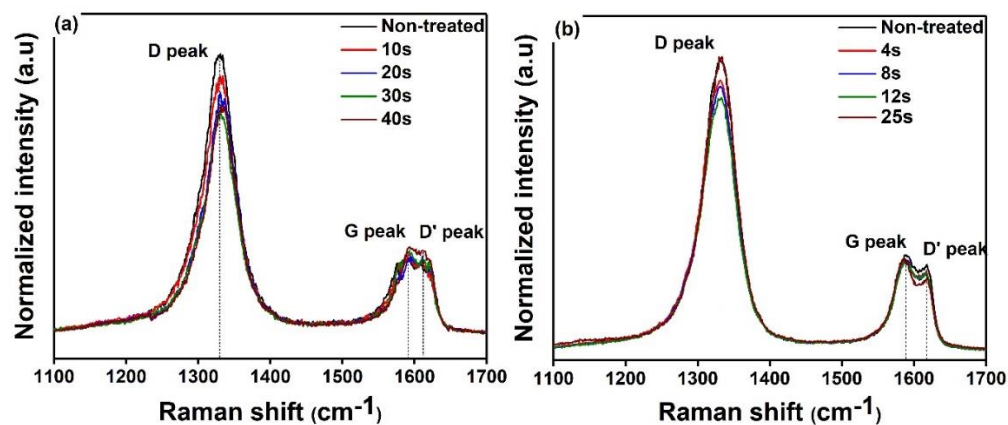


Fig. S3 Magnified region of D, G, and D' peak after **a** N_2 plasma post-treatment. **b** NH_3 plasma post-treatment

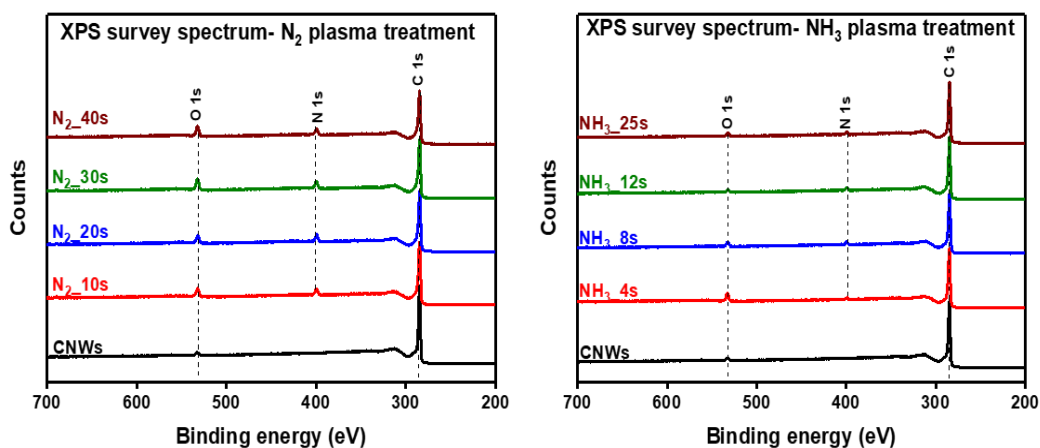


Fig. S4 XPS survey spectra of the samples before and after post-treatment. **a** N_2 plasma. **b** NH_3 plasma

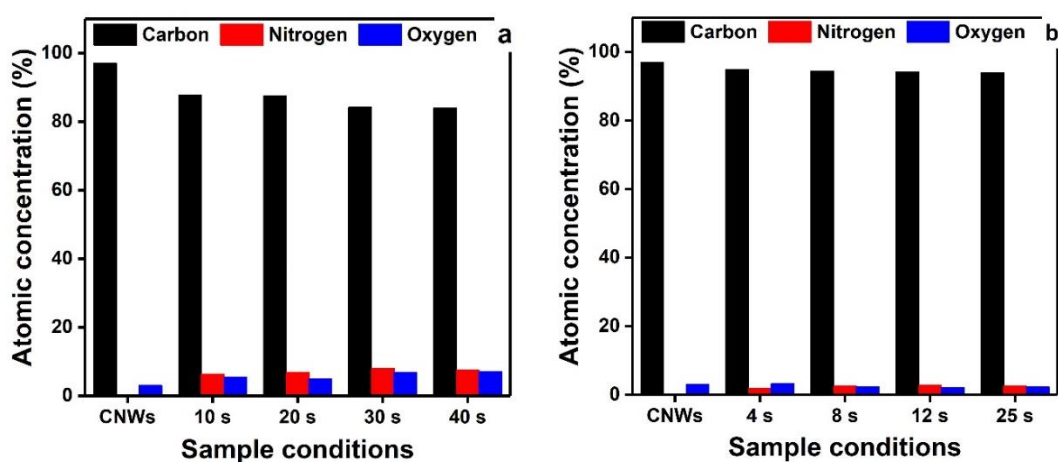


Fig. S5 The estimated atomic concentration of carbon, nitrogen, and oxygen after plasma treatment. **a** N_2 plasma. **b** NH_3 plasma

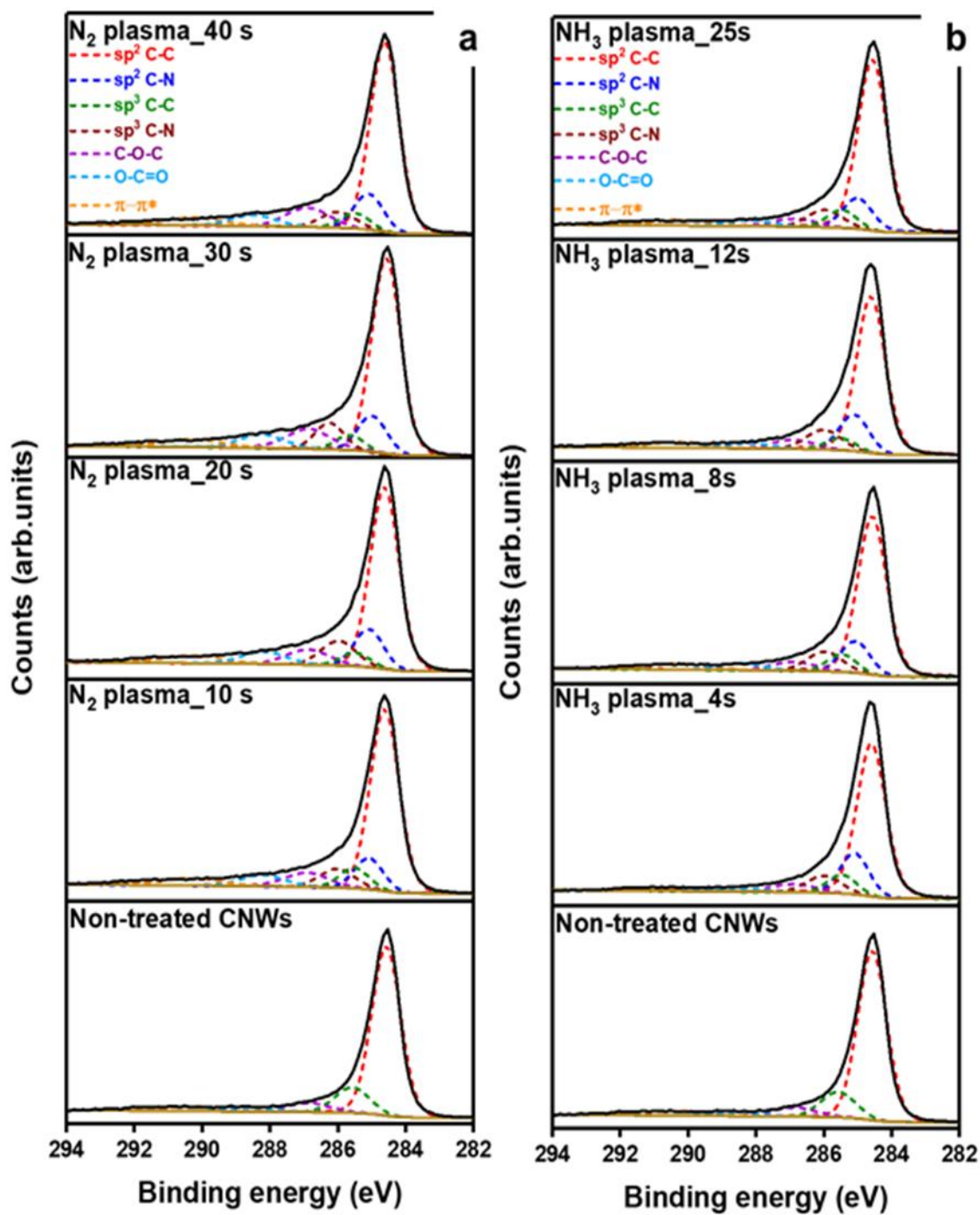


Fig. S6 Detailed C 1s region of the samples before and after **a** N₂ plasma post-treatment and **b** NH₃ plasma-treatment.

Table S2 Peak position, FWHM and roughly estimated concentration of the peak components in C 1s after N₂ plasma treatment

Peak position	CNWs		10 s		20 s		30 s		40 s	
	FWHM (eV)	Area %	FWHM (eV)	Area %	FWHM (eV)	Area %	FWHM (eV)	Area %	FWHM (eV)	Area %
284.6 eV (sp ² C-C)	1	74	1	66.5	1	62.5	1	61.5	1	59.4
285.1 eV (sp ² C-N)	1		1	7.2	1	11.4	1	13.2	1	15.7
285.5 eV (sp ³ C-C)	1.2	12.7	1.2	7.0	1.2	4.3	1.2	4.3	1.2	4.9
286.2 eV (sp ³ C-N)	1.2		1.2	5.6	1.2	8.5	1.2	8.5	1.2	6.1
286.9 eV (C-O-C)	1.5	6.1	1.5	5.8	1.5	4.7	1.5	4.7	1.5	4.7
288.2 eV (O-C=O)	1.5	2.8	1.5	4.8	1.5	3.6	1.5	2.8	1.5	4.8
290.3 eV (π - π^*)	2	4.2	2	3.1	2	4.6	2	4.6	2	4.0

Table S3 Peak position, FWHM and roughly estimated concentration of the peak components in C 1s after NH₃ plasma treatment

Peak position	CNWs		4 s		8 s		12 s		25 s	
	FWHM (eV)	Area %	FWHM (eV)	Area %	FWHM (eV)	Area %	FWHM (eV)	Area %	FWHM (eV)	Area %
284.6 eV (sp ² C-C)	1	74.0	1	59.9	1	59.9	1	58.7	1	58.8
285.1 eV (sp ² C-N)	1		1	8.9	1	8.0	1	9.8	1	8.4
285.5 eV (sp ³ C-C)	1.2	12.7	1.2	7.6	1.2	8.2	1.2	7.6	1.2	9.9
286.2 eV (sp ³ C-N)	1.2		1.2	4.4	1.2	9.2	1.2	7.0	1.2	9.7
286.9 eV (C-O-C)	1.5	6.1	1.5	7.9	1.5	7.1	1.5	7.2	1.5	4.4
288.2 eV (O-C=O)	1.5	2.8	1.5	5.9	1.5	6.1	1.5	4.1	1.5	4.3
290.3 eV (π - π^*)	2.0	4.2	2.0	5.0	2.0	5.1	2.0	5.3	2.0	4.4

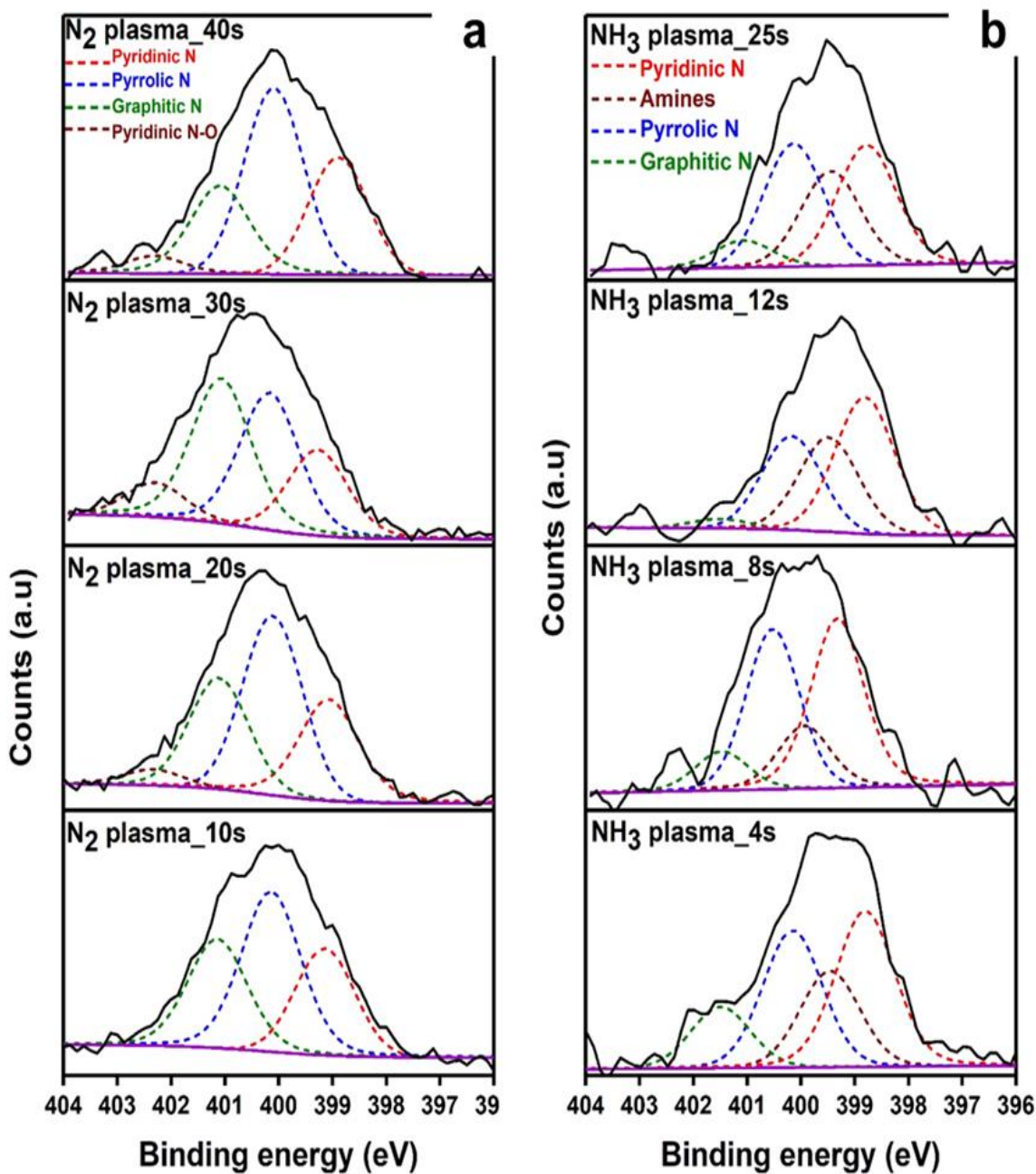


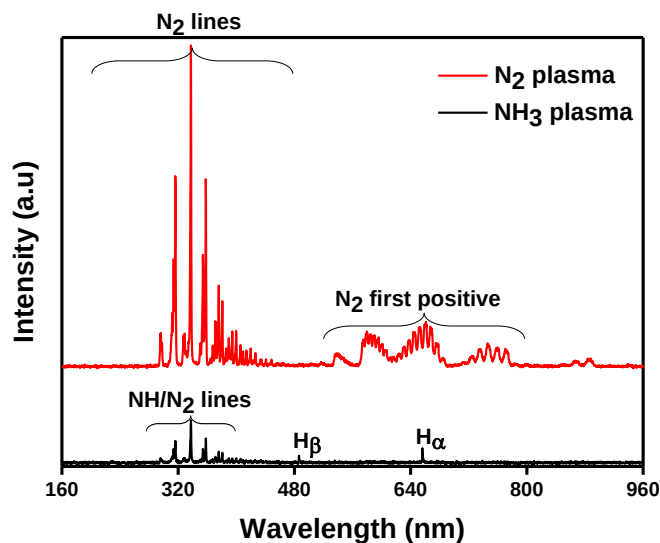
Fig. S7 Detailed XPS N 1s region of the samples before and after **a** N₂ plasma-treatment and **b** NH₃ plasma-treatment

Table S4 Peak position, FWHM and roughly estimated concentration of the peak components of N 1s after N₂ plasma treatment

Sample condition	Pyridinic N			Pyrrolic N			Graphitic N			Pyridinic N-O		
	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %
10s	398.9	1.3	26.5	400.1	1.3	43.7	401.1	1.3	29.8			
20s	399.1	1.3	27.1	400.1	1.3	41.8	401.1	1.3	27.1	402.4	1.3	4.0
30s	399.3	1.3	21.9	400.2	1.3	33.5	401.1	1.3	36.9	402.4	1.3	8.4
40s	398.9	1.3	27.7	400.1	1.3	43.7	401.1	1.3	23.7	402.4	1.3	4.9

Table S5 Peak position, FWHM and roughly estimated concentration of the peak components of N 1s after NH₃ plasma treatment

Sample condition	Pyridinic N			Amines			Pyrrolic N			Graphitic N		
	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %
4s	398.8	1.3	35.5	399.5	1.3	21.5	400.1	1.3	28.8	401.2	1.3	14.0
8s	398.8	1.3	40.7	399.5	1.3	15.1	400.2	1.3	35.2	401.3	1.3	8.9
12s	398.8	1.3	41.3	399.5	1.3	28.6	400.2	1.3	26.1	401.3	1.3	3.8
25s	398.8	1.3	30.4	399.5	1.3	26.3	400.2	1.3	32.6	401.2	1.3	11.8

**Fig. S8** The optical emission spectrum of the N₂ and NH₃ plasma in the RFICP system for an RF power of 300W

Chapter 4.2

Improving Sensing Properties of Entangled Carbon Nanotube-Based Gas Sensors by Atmospheric Plasma Surface Treatment

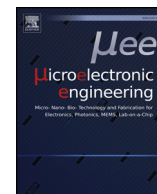
Chapter 4.2. focuses on the effect of atmospheric pressure plasma treatment on the surface of carbon nanostructures. Atmospheric pressure plasma surface treatment allows defect generation and surface functionalisation of carbon nanostructures simultaneously, controlled by the plasma-treatment conditions. In this study, we use d entangled carbon nanotubes as the carbon nanostructures, atmospheric pressure plasma jet as the plasma source, and inert gases (argon and helium) as the surface treatment gases. Here, we present a systematic study on the effect of plasma treatment on the electrical conductivity, surface properties and chemical functionalities of carbon nanostructures. It was identified that the atmospheric pressure plasma treatment using inert gases could improve the conductivity of carbon nanostructures. Furthermore, the plasma surface-treated entangled carbon nanotubes were used as a sensor platform to detect ethanol vapour. We have shown that sensors designed from the plasma-treated carbon nanostructures possess higher sensitivity than the non-treated materials. As we had not noticed any chemical changes from the functional characterisation of the material, we concluded that the defect formation after the plasma treatment leads to the enhanced sensing capabilities.

Regarding my contribution: I performed the plasma treatment processes, contributed to the structural and chemical analysis, tested the sensing properties and jointly wrote the paper with co-authors.



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Research paper

Improving sensing properties of entangled carbon nanotube-based gas sensors by atmospheric plasma surface treatment



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ABSTRACT

Entangled multi-walled carbon nanotubes (MWCNTs) on polyurethane (PUR) after Ar plasma-treatment and He plasma-treatment have been tested as gas sensors for ethanol sensing. It was found that plasma-treated sensors exhibit higher sensitivity compared to the non-treated samples along with different ethanol concentration. Non-treated sensors exhibit similar sensor response with the increase in ethanol concentration, while Ar plasma-treated sensors displays ~5 times improvement and He plasma-treated sensors show ~3 times improvement with an increase in ethanol concentration. The sensitivity of the plasma-treated sensors is also stable for following two-weeks after the preparation compared to the non-treated sensor. Entangled nanotube network exhibits a significant shift in the baseline resistance after both plasma-treatments. The response time of the sensor was increased after the plasma-treatment, while the recovery was rather quick. Surface analyses revealed that plasma-treatment did not make any significant morphological changes. Thus, the improvements in stability and sensitivity after plasma-treatment are attributed to the plasma-enhanced surface modification and formation of functional bonds on the surface of nanotubes, which are sensitive to the ethanol vapour.

1. Introduction

A gas sensor is a device that detects a particular concentration of gases in its environment. Fabrication of gas sensors mainly depends on the application, mostly on the type of gas that should be detected, its concentration and environment. In general, gas sensors should satisfy many requirements such as high stability, selectivity, good responsivity and quick recovery time [1]; at the same time the product should be low-cost, made from non-toxic and easy to use materials. Besides this, a sensor that operates at room/low temperatures is in high demand since heating of a sensor is more complex and expensive [2]. However, the main challenge for sensors operating at low temperatures remains due to their slow recovery after the sensor response. Along with the requirement for sensors operating at low temperatures, there is a continuous need for high sensitivity, which is dependent on the active surface that the sensing gas can occupy [1,3–7]. Recent studies exhibit that improving sensing performance at low temperatures can be done by using nanostructures [8–10], by layering materials [11–13] and by modifying surface or inducing hybrid structures [14–16]. Unique

properties of nanostructures such as gas adsorption capacity due to high surface-to-volume ratio, high structural and thermal stability, high modulation of the electrical charge upon gas exposure, and the possibility of changing the electrical properties by surface modifications can be used for improving the stability and sensitivity of the sensors [17]. Mostly, nanomaterial-based gas sensors are made of metal oxides, carbon nanotubes and graphene. Among them, CNTs possess quick response time, high sensitivity, good reversibility and stability [18].

CNTs are composed of graphene layers rolled into cylindrical geometry, which is classified as single-walled carbon nanotubes (SWCNT) composed of a single layer of graphene and multi-walled carbon nanotubes (MWCNT) composed of multiple layers of graphene with the same central axis [1]. Depending on the tube diameter and chirality, SWCNT can either be metallic or semiconducting in which case they are p-type semiconductors [17]. However, pure crystalline SWCNTs are inert to some volatile organic gases. In the case of MWCNT gas adsorption happens on the outer surface where a molecule connects with the sensor with Van der Waals forces. The molecule changes the electrical charge flow in the sensor, which can be measured as the change in

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the sensor resistivity [19]. In the case of adsorption of oxidising gas molecules on sensors surface, the electric resistance of CNT decreases with the number of adsorbed gas molecules, due to the creation of additional positive holes as an electric current carrier and *vice versa* [20]. Moreover, sensor response or other sensor properties can be improved by modifying the structure and morphology of the CNTs by combining with different nanostructures [17,21–23], by adding a transition metal [22], by plasma-treatment [19,24–27], etc. Compared to other surface modification techniques, plasma-treatment gives the possibility of defect generation and surface functionalisation of CNTs simultaneously, which can be controlled by plasma and treatment conditions. Research done with the plasma-enhanced surface modification of CNTs suggests that both, low and atmospheric pressure plasma can be used for the surface treatment to improve the stability and sensitivity. Depending on the sensor material, one can choose proper plasma type and plasma parameters for the surface modification. These treatment techniques allow changing the chemical composition of the CNT surface without destructing the morphology. Besides the functionalising gases, plasma generated by inert gases such as helium and argon provides higher ion bombardment and creates defects on the CNT surface due to the plasma-assisted etching. Furthermore, plasma-treatment can introduce free electrons to the sensor structure or creating free bonds inside the material, thus making them more sensitive when exposed to analyte vapours.

A variety of CNT based gas sensors are already reported to detect alcohols, where the sensing properties are improved by depositing metal oxides, metals and organic molecules. Among all the alcohol-based sensors, ethanol gas sensors are of considerable interest. Ethanol (C_2H_5OH) is a volatile, flammable, colourless organic compound (VOC) detrimental to the environment, plants, organisms and people [18,23]. Additionally, detection of ethanol fumes is essential in industries, alcohol storage facilities, fruit transportation, and many more. Ethanol is reductive, and when adsorbed on CNT surface, its electrons occupy positively charged holes and consequently increase the resistivity of the material [23,28–31], which results in the p-type sensor response.

In this work, we have designed a simple sensing device using entangled COOH-functionalised MWCNTs for the detection of ethanol at room temperature. Additionally, the effect of atmospheric pressure plasma-treatment on the CNTs using inert gases for improving the sensing properties were investigated. Also, we presented a systematic study on the changes in response and recovery time of the sensors by the effect of plasma-assisted surface modification. The gas sensors were prepared by simple vacuum filtration of MWCNTs on polyurethane (PUR) membrane to form entangled MWCNT sensor, and then they were treated with Ar or He plasma generated at atmospheric pressure. Changes in sensitivity of all sensors were measured by two-point electrical measurements while using ethanol vapours as the target gas. Stability of all prepared sensors was investigated by repeating all the measurements after two weeks. Structural and morphological analysis were obtained by Raman spectroscopy and scanning electron microscopy (SEM) analysis. Changes in the functional entities of the sensors were investigated using Fourier Transform Infrared (FTIR) spectroscopy. Finally, all the results were considered to explain the effect of inert gas plasma-treatment at atmospheric conditions on the sensing properties of entangled MWCNTs.

2. Experimental methods

2.1. Gas sensor preparation

Preparation of bucky paper (BP) was done by a vacuum filtration technique and reported elsewhere [32]. A surfactant solution of pH $\approx$ 10 was prepared with 46.2 g sodium dodecyl sulphate (Sigma-Aldrich), and 0.14 M water solution of pentanol (Alfa Aesar) in 300 ml deionised water. Separately, 0.8 g of 8% COOH-functionalised MWCNT (Sigma-Aldrich, average diameter $\times$ length is 9.5 nm $\times$ 1.5 μ m) was

weighed out and mixed with 250 ml deionised water. The above-prepared surfactant solution and MWCNT-water suspensions were mixed and sonicated for 1 h at room temperature to ensure the fine dispersion of MWCNTs. The suspension was vacuum filtrated through a PUR membrane (GSM 3 g/m², Pardam Nanotechnology, Czech Republic) to achieve a flat homogeneous sheet of entangled carbon nanotubes with a thickness of 0.03 ± 0.02 mm, also called the BP (Fig.S1 (a)). To remove the impurities, BP was washed several times with ethanol and distilled water. Prepared BP was left to dry overnight at room temperature. Finally cuts 1.5×1.5 cm from prepared BP to fabricate the gas sensors.

2.2. Plasma-treatment

Since the PUR membrane is a temperature-sensitive material, low-temperature atmospheric pressure plasma jet (APPJ) was used for the surface treatment to improve the sensitivity. APPJ system consisted of a single copper electrode without grounding and was powered by a kHz high-voltage signal source. This system allows smooth operation and produces low-temperature plasma, which is suitable for the temperature-sensitive sensors. Inert gases such as argon and helium were used to generate plasma. Compared to mono-functional specific grafting using specific gases like NH_3 , O_2 or N_2 ; atmospheric pressure plasma-treatment using inert gases allows the possibility of surface functionalisation by the functional groups present in the atmosphere [33,34]. Surface treatment was carried out with a gas flow rate of 100 sccm for a fixed time of 3 min. The distance between the sensor and the exit of the APPJ's orifice was fixed at 2.5 cm, meaning that the sensors were treated in the after-glow region of the plasma. Plasma dissipated over the surface, and uniform treatment is assumed.

2.3. Electrical and gas sensing characterisation

I-V characteristics of the sensors were measured by an easy two-point method. We forced a voltage (0–10 V) and measured the current. The gas sensor properties were determined by measuring the change in resistance of sensor during the sensing experiment by a two-point method using a Keithley 2460-high current source meter at a constant input current of 10 mA. Ethanol (ACS reagent for analysis) was used as the sensing gas for investigating the effect of plasma surface treatment on the gas sensor sensitivity. 5 ml volume of ethanol was measured and transferred to a conical flask of 250 ml capacity, and the rest of the flask was filled with ambient air. The sensor was placed to the saturated vapour above the ethanol liquid during the sensing cycle (gas in phase) and placed to an identical conical flask of 250 ml filled with air during the recovery process (gas off phase). The gas in and gas off during the sensing measurements were assigned with an interval of 180 s. The measurements were performed at different temperatures, starting from the room temperature (20 ± 2 °C), then at 35, 50 and 65 °C. The sensor response was calculated using the following equation:

$$\text{Sensor Response} = \frac{R_g - R_a}{R_a} \quad (1)$$

where R_g is the resistance of a sensor after inserting ethanol and R_a is the resistance of the sensor in air. The concentration C_{et} of ethanol, inside the sensing chamber was controlled by heating the ethanol volume to different temperatures. Since the sensing chamber is filled with a mixture of gases (air and ethanol vapour), Dalton's law was used for the estimation of volume-based concentration of ethanol as per the following equation:

$$p_{et} = p_{tot} c_{et} \quad (2)$$

where p_{et} is the vapour pressure of ethanol, p_{tot} is atmospheric pressure (101,325 kPa) and c_{et} is the volume-based concentration of ethanol. Calculation of ethanol vapour pressure is well researched, and the values for specific temperatures can be obtained from many databases. In

this study, we have used the vapour pressure described in Dortmund Data Bank (http://www.ddbst.com/en/EED/PCP/VAP_C11.php) for the calculation of ethanol concentration. The volume-based concentration of ethanol is estimated as 5.71% at 20 °C, 13.58% at 35 °C, 29.1% at 50 °C, and 57.68% at 65 °C. The concentration is increased by approximately 50% from room temperature to the highest temperature, which opens up an opportunity to explore the influence of ethanol concentration on the sensing measurements. Schematic diagram of the experimental setup was shown in Fig. S1(b). The stability of the prepared sensors was investigated by conducting all the measurements after two weeks.

2.4. Characterisation techniques

Surface morphology of the gas sensors was characterised by SEM analysis (JSM-7600F and JSM-5800, Jeol Inc.), operating at an acceleration voltage 10 kV. Chemical and phase composition of the samples were analysed by transmission electron microscope (TEM, JEM-2010F, Jeol Inc.) operating at 200 kV. The micrographs were recorded by a slow-scan CCD camera (Orius SC1000, Gatan). Raman spectra of the sensors were recorded using NTEGRA confocal Raman spectrometer at an excitation wavelength of 633 nm with an incident power ~ 3 mW and objective of $20\times$ at a spot size of $10\text{ }\mu\text{m}$. The spectrum was recorded at three different spots of each sensor to eliminate the variations and investigated the structural changes after the plasma-treatment. FTIR spectrum was recorded to analyse the changes in the functional entities of the sensors before and after plasma-treatment using Spectrum GX FTIR spectrometer by Perkin Elmer that was equipped with a photoacoustic detector with 64 scan runs average at 8 cm^{-1} . All the analysis was done right after the sensor preparation and repeated two weeks later to monitor the ageing effect.

3. Results and discussion

3.1. Resistance measurements

The resistance of the as-prepared sensor was measured as $(1041 \pm 5)\text{ }\Omega$. However, the resistance of the sensor is decreased to $(702 \pm 7)\text{ }\Omega$ after He plasma-treatment and to $(553 \pm 10)\text{ }\Omega$ after Ar plasma-treatment. In addition to the decrease in the resistance, the stability of the resistance after the plasma-treatment should also be noted. Fig. 1 (a) exhibits the steadiness of the resistance of both the non-treated and plasma-treated sensors at the room temperature

($20 \pm 2\text{ }^\circ\text{C}$). The significant change in the resistance might be due to the surface modification either by plasma-enhanced etching or by the functionalisation of CNT surface. Typical current-voltage (I-V) characteristics of the non-treated and plasma-treated sensors at room temperature are presented in Fig. 1 (b). The linear I-V relationship confirms the ohmic nature of the sensors.

The repeatability of the sensing cycle of the sensors was checked at different concentration of ethanol by heating at different temperatures as 20 °C, 35 °C, 50 °C and 65 °C, and the stability of the sensor was investigated by repeating all the measurements after two weeks. The sensor response measurements are presented in Fig. 2, which suggests that the plasma-treated sensors acquired more stable sensor response than the non-treated sensor. The non-treated sensor possesses an unstable response at room temperature, which slightly turns into a stable response with an increase in temperature. Nevertheless, the change in the sensor response with temperature is not significant. In the case of both plasma-treated sensors, the sensor response became stable and increased with the temperature. He plasma-treated sensors possess similar sensor response at low-temperature, which increases with the temperature and attained ~ 3 times improvement at 65 °C. Whereas Ar plasma-treated sensors exhibit a substantial improvement of sensor response (~ 5 times) even at low-temperature and increase with the temperature. A higher concentration of analyte after heating makes the sensor more stable during the sensing cycle. However, the stability studies after two weeks indicated that the maximum response of all the sensors were decreased, especially for non-treated and He plasma-treated sensors.

Average of maximum sensor response was calculated to understand more about the response and repeatability of the sensors changing with temperature. This response is presented in Fig. 3, where the average response of the sensors at different concentration of ethanol (at each temperature calculated using Eq. (2)) at as-prepared and two weeks later conditions. At higher concentrations of ethanol (increase with the elevation of temperature), plasma-treated sensors show better response than the non-treated sensor. Among all the tested sensors, the non-treated sensor exhibits a constant sensor response for all concentrations. For He plasma-treated samples, the response was almost similar to the non-treated sensor but slightly improved with higher concentrations. The highest sensor response was shown by Ar plasma-treated sensor, which could be attributed to the greater extent of surface modifications done by the Ar plasma. However, the stability studies on the average response after two weeks suggest that the maximum sensor response of all the sensors become lower than the as-prepared conditions. In the

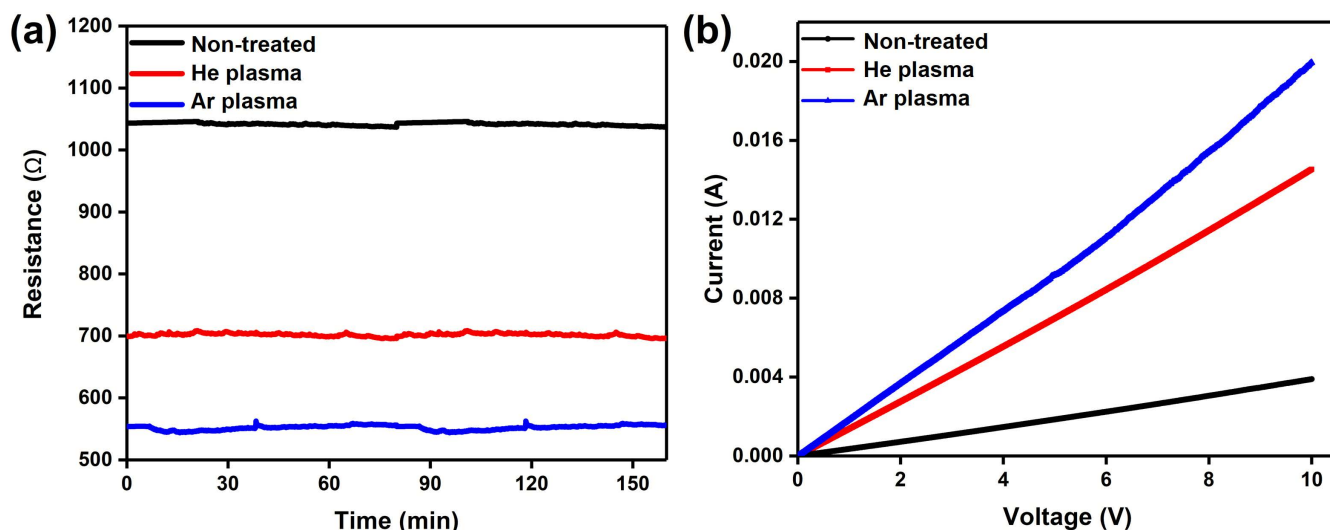


Fig. 1. (a) The stability of the resistance of the prepared sensors at room temperature, (b) I-V characteristics of the non-treated and plasma-treated sensors.

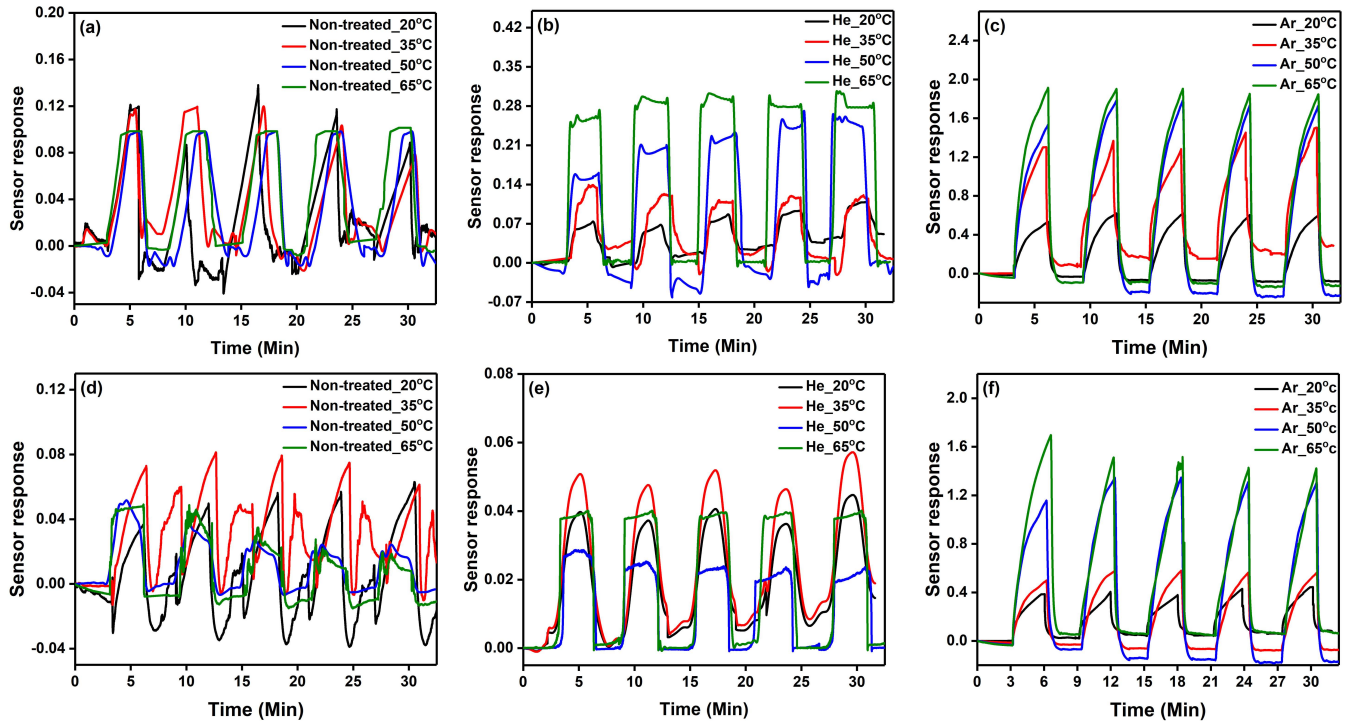


Fig. 2. The repeatability of vapour detection on (a) non-treated and (b) He plasma-treated and (c) Ar plasma-treated sensors; and corresponding measurements of stability in performance after two weeks for (d) non-treated, (e) He plasma-treated and (f) Ar plasma-treated sensors.

case of non-treated and He plasma-treated sensors, the sensor response was negligible after two weeks, even when the ethanol concentrations increased. On the other hand, Ar plasma-treated samples disclosed a stable response after two weeks and the sensor response increases with increasing the ethanol concentration.

The response and recovery curve of the sensors are presented in Fig. 4. The gas in and gas off during the sensor measurements are assigned with an interval of 180 s. The results show that the Ar plasma-treated sensors have higher sensor response, and the recovery to the initial resistance is quicker for the non-treated and He plasma-treated sensors. These results indicate that Ar plasma-treatment has made significant changes in the properties of sensor. Moreover, Ar plasma-treated sensors appear to be the most stable in both response and recovery even after two weeks. On the contrary, the non-treated sensor displays a behaviour where the response drops instantaneously to the value below the initial resistance and then recovers to the original value after the gas off. The response and recovery appear to be better after

two weeks, which could be explained by the surface interaction with the surroundings. However, He plasma-treated sensors have much longer recovery time than the response time. Since the change in sensor response is minimal, it implies that the capability of the sensor to adsorb ethanol vapour is comparatively low even after the plasma-treatment. During the recovery, the resistance falls below the original value and then recovered to the initial value similar to non-treated sensor. However, the response curves after two weeks displays similar behaviour as the initial response.

A comparison between the response and recovery times of all the sensors at the room temperature is given in Fig. 5. The response time T_{res} , of the sensors, was defined as the time taken to achieve 90% of the maximum change in resistance. In contrast, recovery time T_{rec} was calculated as the time taken to recover to 90% of the initial resistance from the maximum resistance change occurred during the sensing cycle. A schematic explanation for the calculation of T_{res} and T_{rec} from our results is shown in Fig. S2. It was observed that the as-prepared He

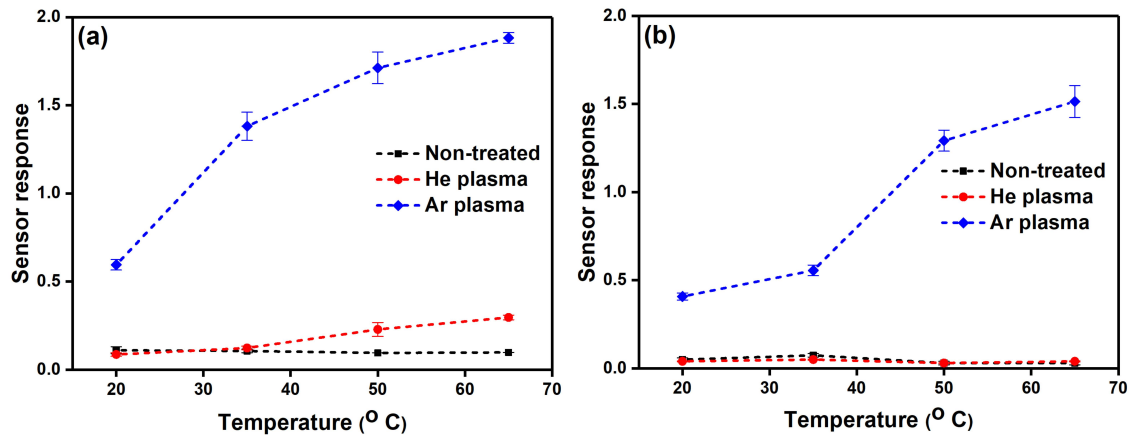


Fig. 3. The average sensor response compared to the concentration of ethanol for all the sensors (a) as-prepared and (b) two weeks later.

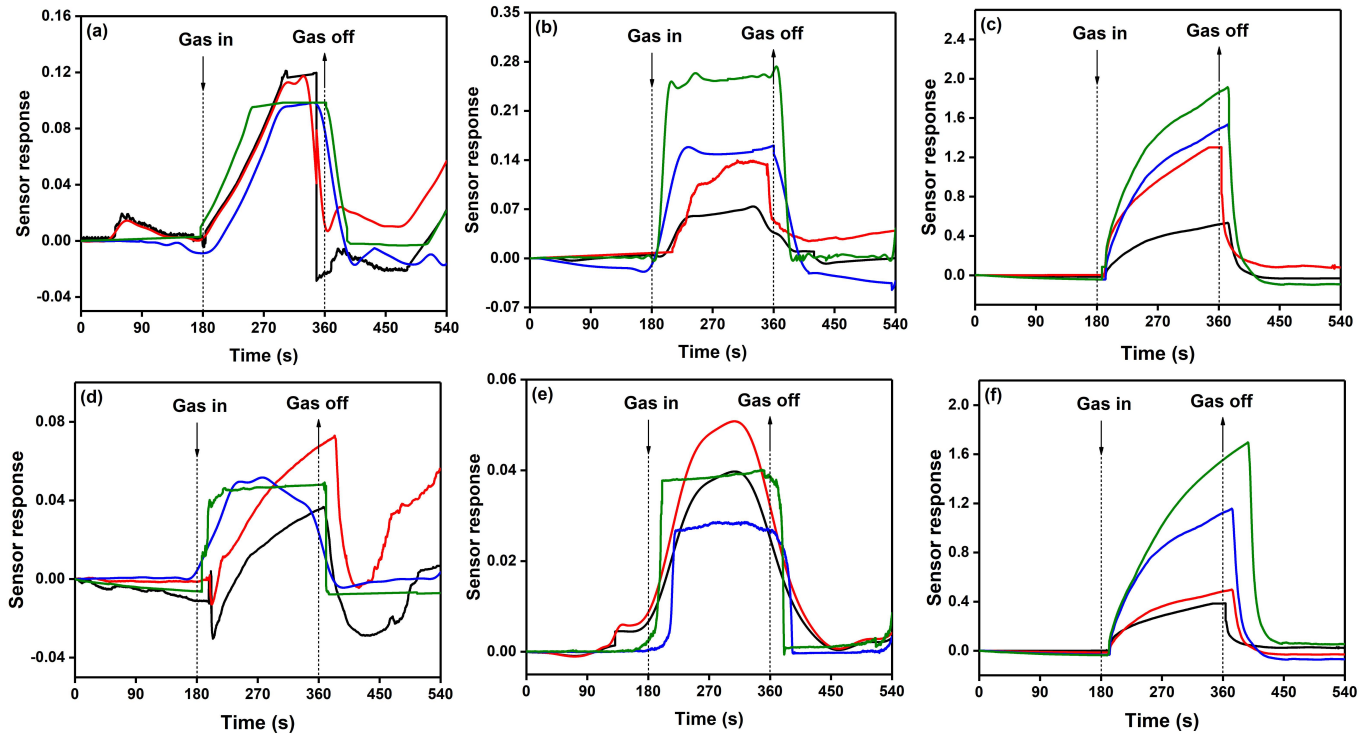


Fig. 4. The response curve for the first sensing cycle of the sensors at different temperatures: (a) non-treated, (b) He plasma-treated and (c) Ar plasma-treated; two weeks later: (d) non-treated, (e) He plasma-treated and (f) Ar plasma-treated sensors.

plasma-treated sensor had the fastest response time of 114 s, whereas the highest response time of 152 s was observed for Ar plasma-treated sensor. On the other hand, in the case of recovery, Ar plasma-treated sensor had the fastest recovery time of 40 s, where the non-treated sensor was displayed the slowest recovery time of 152 s. After two weeks, the non-treated sensors took the longest time to respond as well as to recover (156 s and 142 s respectively). He plasma-treated sensor had the fastest response of 88 s and Ar plasma-treated sensor demonstrates the fastest recovery time of 79 s. These results are indicating that the different plasma-treatments using inert gases are causing different effects on the surface of sensors, which allows tuning the gas sensing properties.

Since both the electrical resistance and sensing properties of the sensors change with plasma-treatment, which also varies after two

weeks of repeated measurements, sensors required a detailed investigation of the structural and morphological changes. Thus, the surface of sensors was analysed with different characterisation techniques to get a better insight into the effect of plasma surface treatment.

3.2. Morphology analysis

To analyse surface modifications of all non-treated and plasma-treated samples, SEM was used, and the results are presented in Fig. 6. Nanotubes did not seem to be affected by plasma, and no visual damages were observed on the entangled structure (Fig. S3 and S4), which means that the surface of sensors is the same before and after the plasma-treatment.

Detailed TEM and HR-TEM analysis were done to get an insight into

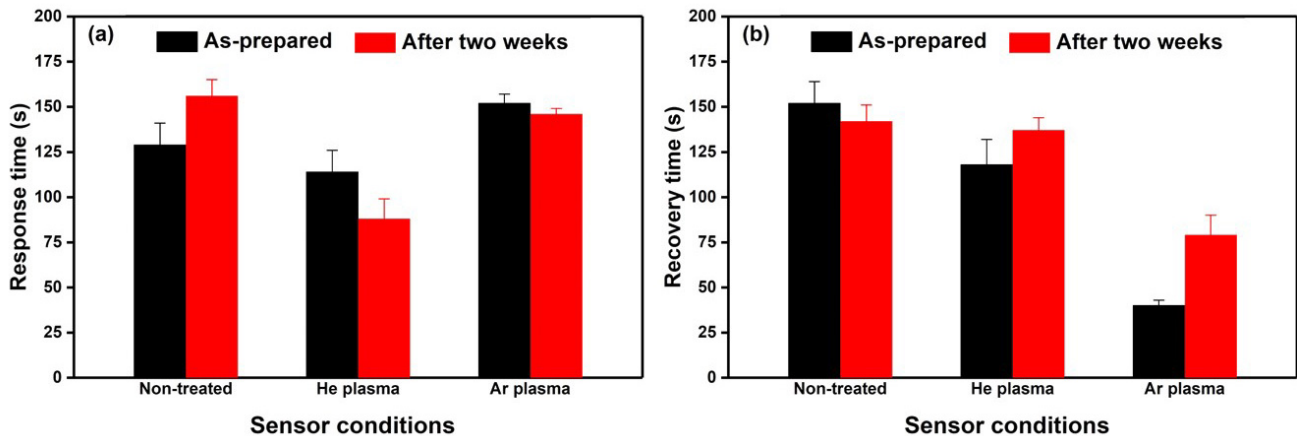


Fig. 5. Comparison of sensor (a) response time and (b) recovery time of non-treated, He plasma-treated and Ar plasma-treated sensors at the room temperature.

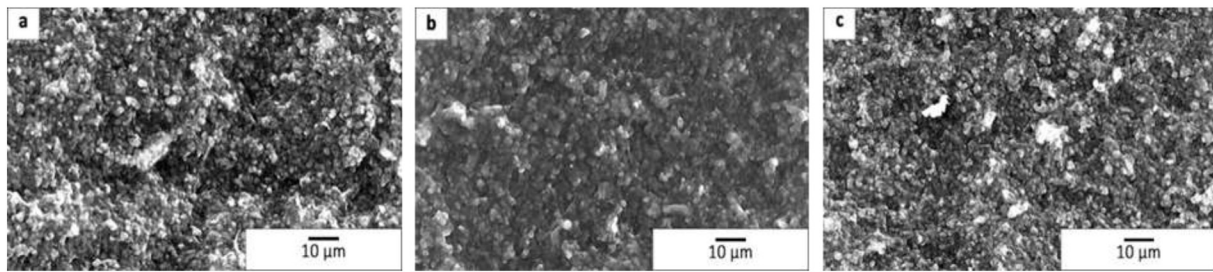


Fig. 6. Characteristic SEM micrographs of (a) non-treated, (b) He and (c) Ar plasma-treated sensor surface.

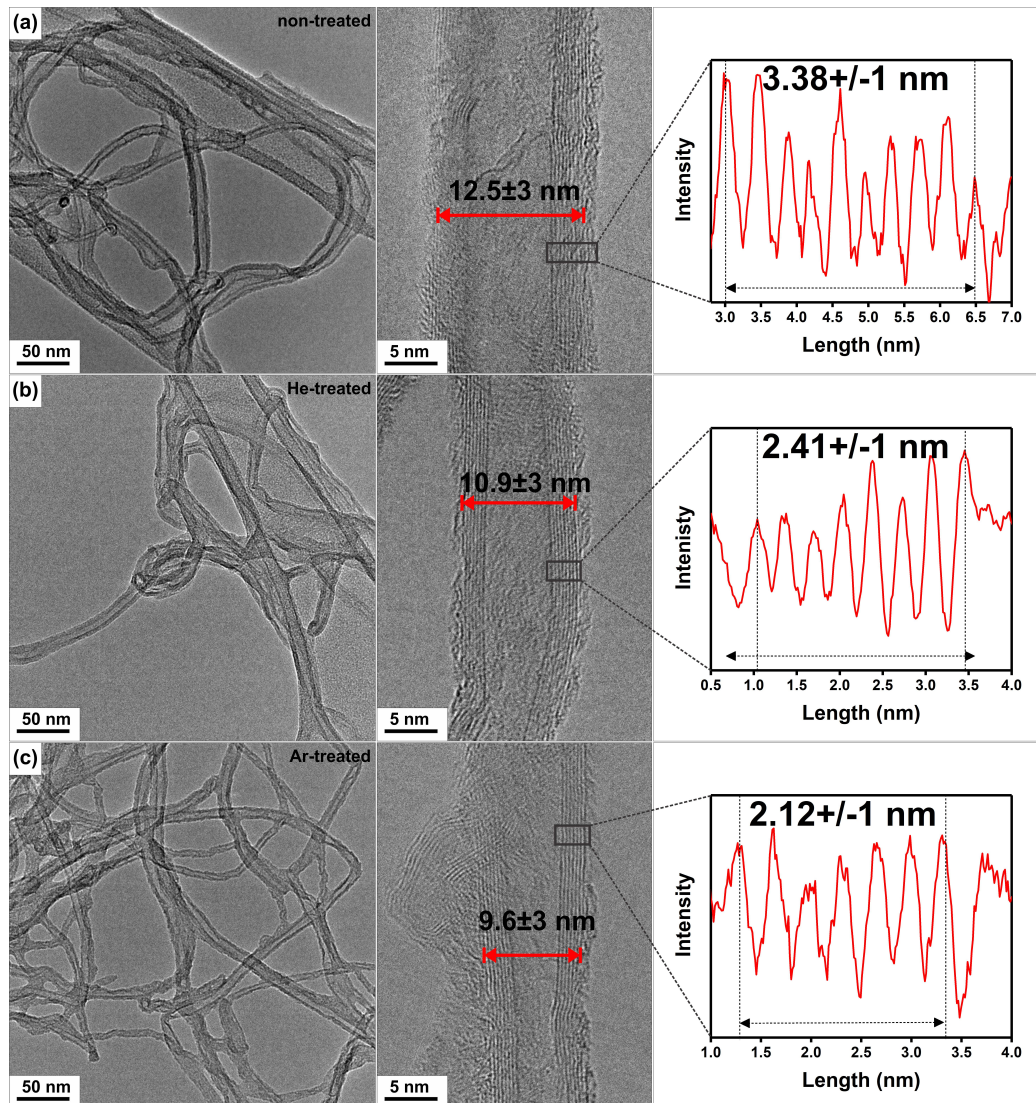


Fig. 7. Overview and high-resolution TEM micrographs of carbon nanostructures and intensity profile from the marked area of the (a) non-treated, (b) He-treated and (c) Ar treated sensor.

the changes that occurred on the surface of BPs after plasma-treatment (Fig. 7 (a–c)). The individual nanotubes are multi-walled with an average diameter of 10–15 nm. The surface of the nanotubes is covered with a wrinkled amorphous layer of carbon. The diameter of the nanotubes in the non-treated sensor was 12.57 ± 3 nm, and it was reduced to 10.9 ± 3 nm after He plasma-treatment and 9.6 ± 3 nm after Ar plasma-treatment. This slight reduction in the diameter can be ascribed to the plasma-enhanced etching effect, which also affects the thickness of the carbon layers. The intensity profile obtained from the

carbon layers (Fig. 7 (a–c)) is indicating that the layer thickness is also slightly decreasing with plasma-treatment, which can be due to the removal of the top layer. Additionally, the continuous amorphous wrinkled layer visible on the non-treated sensor is completely removed after He plasma-treatment and partially removed after the Ar plasma-treatment. These effects can improve the conductivity of the BPs after the plasma-treatment and enhance the interaction of the carbon layer with ethanol vapour during the sensor cycle, which in turn improve the response of the sensor.

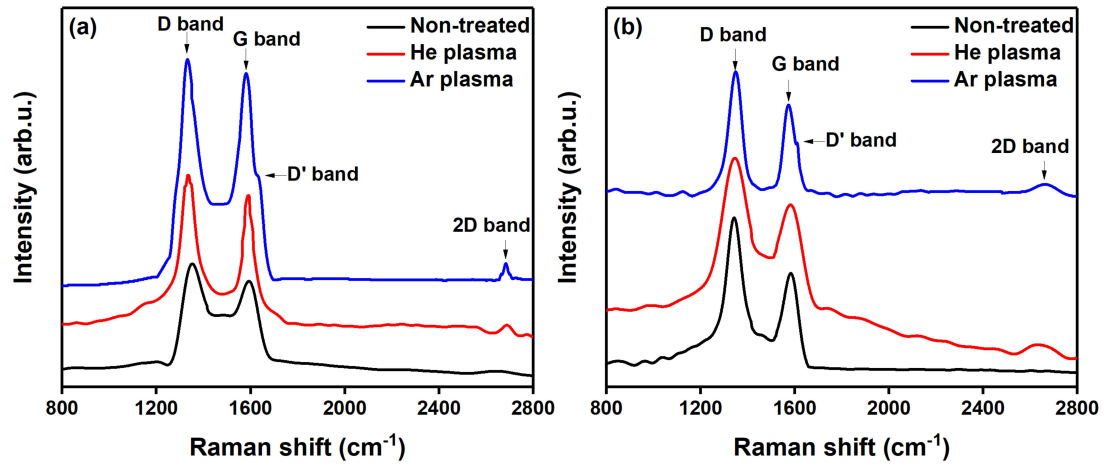


Fig. 8. Raman spectra of the non-treated, He and Ar plasma-treated sensors (a) as-prepared and (b) two weeks later.

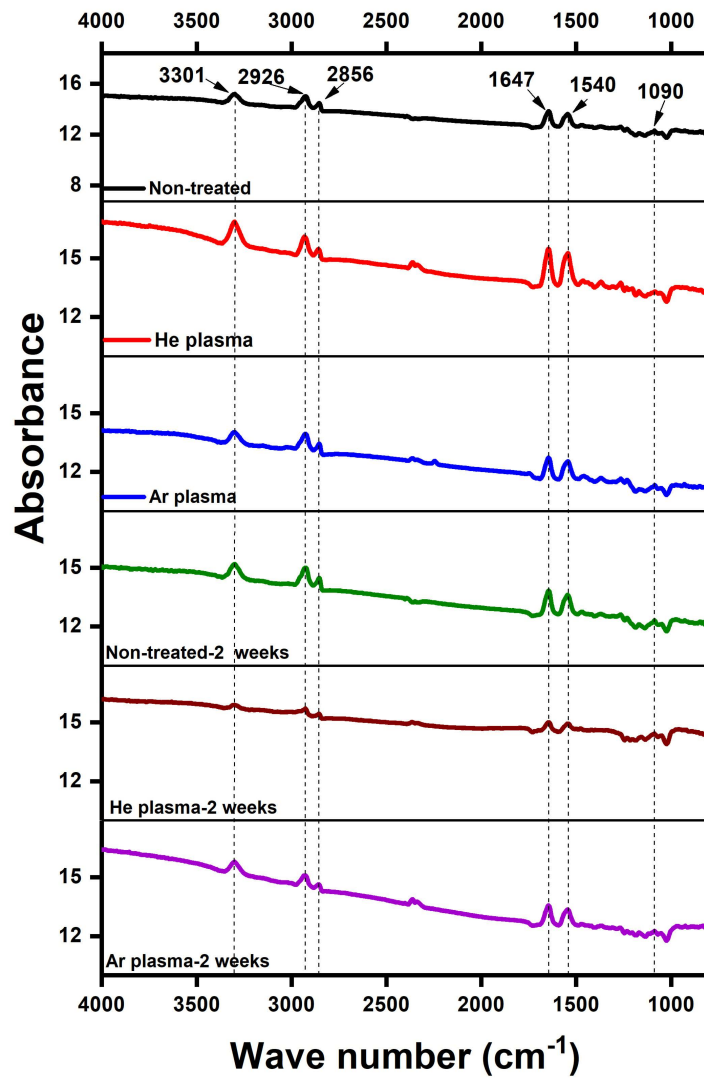


Fig. 9. FTIR spectra of the non-treated, He plasma-treated and Ar plasma-treated sensors

3.3. Raman spectroscopy

Raman spectroscopy was used for the qualitative characterisation of structural defects in CNTs, by comparing the ratio between the intensities of the defect and graphitic bands. The results of this analysis are presented in Fig. 8. The Raman spectra of the non-treated sensor display two well-distinguished peaks approximately at 1343 cm^{-1} and 1587 cm^{-1} , D and G peak, respectively, which are the typical characteristics of graphitic carbon. The D peak is induced by the disorder or defect due to the distortion of graphite lattice [35–37] and the G peak forms due to the crystallite graphite [38]. There was no 2D band (around 2675 cm^{-1}) observed in the Raman spectrum of the non-treated sensor, which is the second-order two-phonon process in a graphitic sp^2 material and indicates that the disordered graphene layers were overlapped with plenty of oxygenated functional groups. Lack of this peak indicates that the non-treated sensors possess more amorphous behaviour than the treated ones. The Raman characteristics of sensors were changed both with He and Ar plasma-treatments. The D peak is shifted to 1338 cm^{-1} and 1336 cm^{-1} after He and Ar plasma-treatment, respectively, which could be due to the formation of reactive edges on CNTs caused by plasma etching [39]. The evolution of a 2D band that was observed after He and Ar plasma-treatment around 2678 cm^{-1} and 2673 cm^{-1} indicates that the plasma-treatment causes the removal of amorphous carbon from the surface and progression of more graphitic behaviour. There was an additional shoulder peak observed along with the G peak at 1618 cm^{-1} after the Ar plasma-treatment, which is known as D' peak, a disorder peak frequently seen in microcrystalline graphite usually produced from the thin edges of graphitic layers.

Comparison of the I_D/I_G ratio of different sensors exhibits the change in structural quality. The I_D/I_G ratio for the as-prepared sensor was 1.1, which slightly decreases to 1.09 after He plasma-treatment and further decreases to 1.03 after Ar plasma-treatment. These results imply that the defect density of CNTs decreases with the plasma-treatment by the etching of disordered carbon atoms. There is no significant change observed in the Raman spectrum after two weeks, which means there is no substantial change in the structure of the sensors. Considering the changes observed in the TEM micrographs and Raman characteristics of the sensors, the improvement in sensor properties can be explained as the improvement in graphitic behaviour of sensors after the plasma-treatment.

3.4. Fourier-transform infrared spectroscopy

FTIR analysis was carried out to understand the effect of plasma-treatment on the functional entities (Fig. 9). All the spectra exhibit similar characteristic behaviour with akin vibrations of functional entities. The distinct peak around 3301 cm^{-1} refers to the O–H stretching of the hydroxyl group, that may arise from the oscillation of the carboxyl group. The peaks at 2926 cm^{-1} and 2856 cm^{-1} can be associated with the symmetric and asymmetric stretching of C–H group. The peak observed at 1647 cm^{-1} can be due to the stretching of the carbon nanotube backbone [40]. The peak signal formed at 1540 cm^{-1} was due to the stretching of C=C group in the CNTs [41]. A weak peak observed at 1090 cm^{-1} could be assigned to O–H bending deformation mode of the carboxyl groups [42]. The peak intensities of functional groups increased after the plasma-treatment, which indicates the increased surface functionalisation. Additionally, a peak at 2360 cm^{-1} was observed after the plasma-treatment, which corresponds to the stretching of carbon dioxide. A small peak at 2245 cm^{-1} appeared only in the Ar plasma-treated sensor and is attributed to the stretching of nitrile or alkynes groups. Also, the change of different weak peaks is observed in the range of $1500\text{--}1100\text{ cm}^{-1}$ for plasma-treated sensors that could arise because of the bending of alkane and aldehyde groups attached to the CNT network. However, the intensity of all the peaks from the He plasma-treated sensor decreased after two weeks, which shows that the

stability of the sensor changed with time. Whereas, the intensity of the Ar plasma-treated sensor did not change significantly, which implies its better stability. Since all the sensors show almost similar infrared spectrum, the difference observed in the sensor response after plasma-treatment is mostly associated with the vibrations of either improved graphitic behaviour or O-terminated and H-terminated functional groups, which can enhance the sensitivity of the prepared sensors.

4. Mechanism of ethanol sensing and the influence of plasma-treatment

The non-treated sensor shows a poor and irregular sensor response that improved and stabilised after the plasma-treatment, which may be due to the interaction of plasma-activated species with the surface of carbon nanotubes. Atmospheric pressure plasma surface treatment causes the removal of amorphous carbon, the formation of H/O-terminated groups and dangling bonds, all of which are improving the absorption of ethanol molecules to the surface of the sensor. No significant morphological changes observed from SEM images confirm the capability of plasma-treatment for improving the performance without any structural damage. Detailed analysis by TEM is suggesting that the plasma-treatment leads to the removal of amorphous wrinkled structures from the nanotube surface, which eventually improves the crystalline behaviour of the carbon nanostructures. Raman and FTIR spectra analysis are also confirming that the plasma-treatment mainly improves the graphitic behaviour of the CNTs rather than causing significant chemical modification. Improvement in the graphitic characteristics can be attributed to the plasma-enhanced etching by creating vacancies with the removal of amorphous carbon, which finally improves p-type conductivity of the sensor. Moreover, removal of the amorphous structures from the outer layer of the individual nanotube surface can enhance the adsorption of ethanol to the carbon nanotube and they donate electrons to the conduction state, which increases resistance. The removal of the amorphous structure is more prominent after Ar plasma-treated sensors, in which higher ethanol vapours were adsorbed to the nanotubes and shows higher response compared to other sensors. The other possible reason for the increase of resistance is the change of contact resistance between individual nanotubes and increases the macroscopic resistance of the sensor. The sensor performance after Ar and He plasma-treatment is vividly different and indicating that plasma surface modification using various inert gases at atmospheric conditions is also considerably different. Considering Ar and He as inert gases, the surface functionalisation is only carried out by the excitation of functional groups present in the atmospheric conditions. There is no considerable change in FTIR spectra, suggesting that state of functionalisation after the plasma-treatment is similar before and after plasma-treatment. Thus, the significant factor that influences the surface modification is the bombardment of plasma species on the CNT surface, which affect the electrical conductivity of the sensors. Compared to helium, argon is much heavier and carries more reactive species to the surface of the sensor and creates severe surface modifications by plasma-enhanced etching which results in the formation of more conductive channels. Also, the stability measurements of the sensors show that the changes made by Ar plasma-treatment are persistent even after two weeks but not in the case of He plasma-treatment. Based on the analysis of the experimental data, we can conclude that plasma-treatment makes the sensors more sensitive to the environment. Moreover, the stability of the sensors after plasma-treatment can be recognised as the formation of stable defect channels facilitating the ethanol vapours to access all parts of the sensor. In plasma-treated samples, the dangling bonds, which are formed by the plasma-treatment, might be responsible for the enhanced sensing properties.

5. Conclusion

It was found that the sensitivity to ethanol vapours of the entangled

COOH-functionalised MWCNTs networks was improved by the atmospheric pressure plasma-treatment using inert gases. The resistance of the sensors was decreased after the plasma-treatment. All the sensors were able to detect the ethanol vapour, whereas the non-treated sensor exhibits an inferior sensing ability. Sensor response and stability of the He plasma-treated samples were improved by 3 times, and that of Ar plasma-treated samples were improved by 5 times with an increase in ethanol concentration. Evaluation of response time and recovery time shows that the time of response increased after the plasma-treatment due to the higher sensor response while the time of recovery was fast. Surface morphology analysis confirms that the plasma-treatment did not destroy the tubular structure of CNTs. Raman spectra and TEM analysis confirm the improvement of graphitic behaviour after the plasma-treatment. Infrared spectrum suggests similar bond vibrations for all the sensors, but the presence of additional peaks after plasma-treated sensors indicates the improved functional entities in the CNT network. It is evident that the plasma-treatment improves the graphitic nature of nanotubes, the formation of defects, and the presence of functional groups of the sensors, which is enhancing the sensing properties. Exploring the selectivity of the prepared sensor towards different gases needs to be investigated for the future applications of the entangled carbon nanotube-based sensors.

Credit author statement

Neelakandan M Santhosh planned the experiments, contributed to the data curation, analysis of physical and chemical properties of the samples and manuscript preparation. Aswathy Vasudevan helped with the experiments and manuscript preparation. Andrea Jurov prepared the original draft of the manuscript and carried out the morphology analysis. Anja Korent helped with the morphology analysis and manuscript preparation. Petr Slobodian contributed to the editing of manuscript and proofreading. Janez Zavašnik carried out the TEM analysis of the samples and interpretation. Uroš Cvelbar planned the main conceptualization of the work, reviewing results and editing of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mee.2020.111403>.

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Supporting Information

Improving Sensing Properties of Entangled Carbon Nanotube-based Gas Sensors by Atmospheric Plasma Surface Treatment

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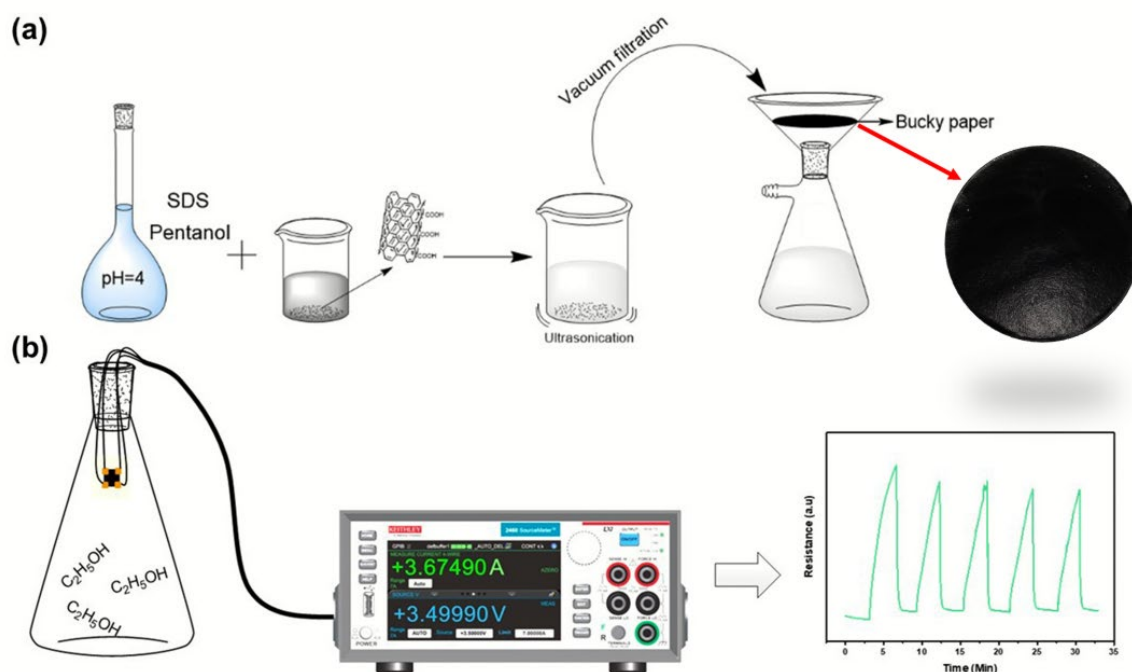


Fig. S1. (a) schematic diagram of preparation of buck paper and digital image of the prepared bucky paper. (b) Simple experimental set up for the gas-sensing measurements, where the sensor placed to the saturated vapor above the liquid ethanol.

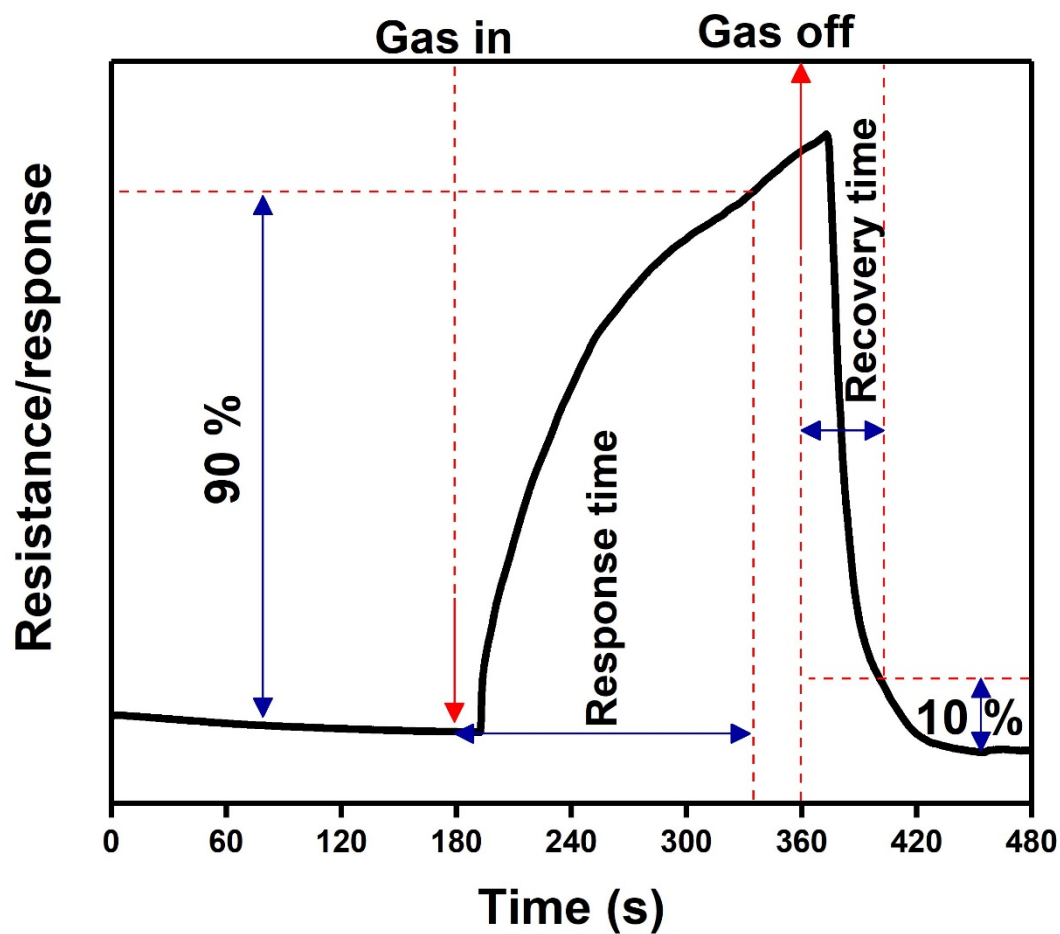


Fig. S2. Schematic of the calculation for time of response and time of recovery from sensor response curve. The recovery time is calculated as the time required for recovering 90 % of the original resistance; response time is calculated as the time taken to achieve 90 % of the ultimate change in resistance.

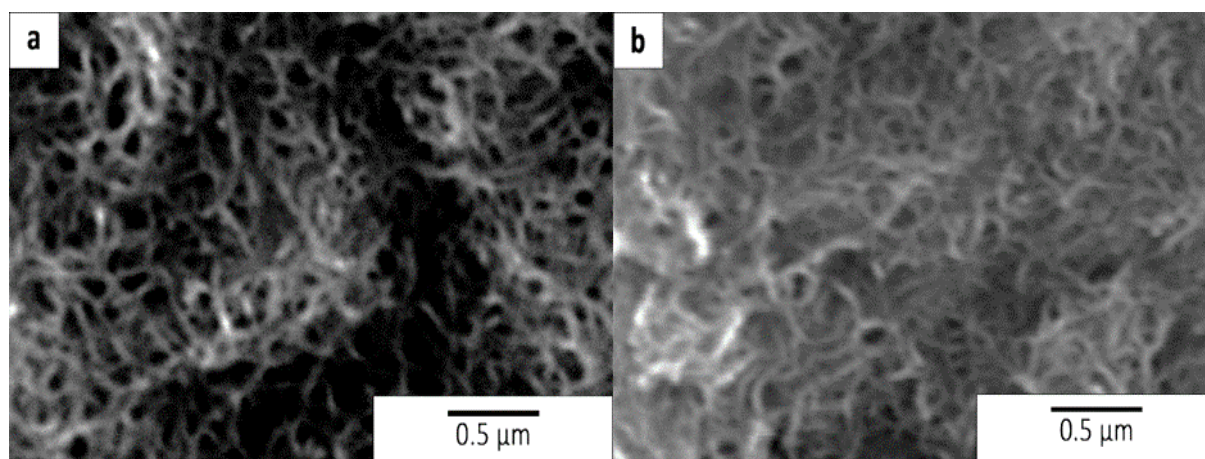


Fig. S3. SEM micrographs of the He and Ar plasma-treated sensors as-prepared conditions.

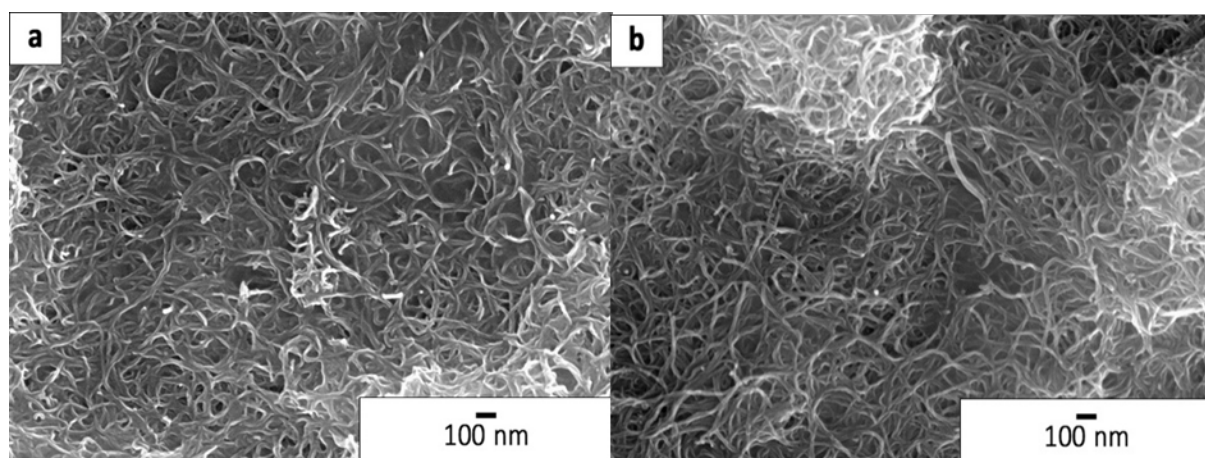


Fig. S4. SEM micrographs of the He and Ar plasma-treated sensors after two weeks.

Chapter 5

Plasma-Designed Hybrid Carbon Nanostructures for Energy Storage Applications

Chapter 5 describes our efforts to design high performing hybrid carbon nanostructures by plasma-enabled techniques and to reveal their energy storage capabilities. A potential material for energy storage application is expected to have three main features: high electrical conductivity and lower contact resistance, high surface area for the large electrolyte interaction, and excellent electrochemical stability. Plasma-enabled design of carbon materials ensures the lower contact resistance by direct deposition of active material on the current collector (substrate). Plasma techniques allow the designing of free-standing, vertical or hierarchical carbon nanostructures, which could enlarge the surface area due to the specific morphologies. Furthermore, carbon-based materials are electrically conductive, and their structural stability, which ensures electrochemical stability during energy storage reactions, is well-known. Additional electrical tuning can be achieved by heteroatom doping, e.g. with nitrogen. In the presenting research, the plasma-synthesised carbon platforms were used to design hybrid metal sulphide/carbon composite electrodes. Their energy storage performances for lithium-ion batteries and supercapacitors were investigated. For this reason, chapter 5 is divided into two sub-chapters, as follows:

- 5.1. Advanced Carbon-Nickel Sulfide Hybrid Nanostructures: Extending the Limits of Battery-Type Electrodes for Redox-Based Supercapacitor Applications
- 5.2. Vertically Aligned Hybrid Ni_3S_2 /Carbon-Based Nanostructures for Advanced Li-Ion Battery Electrodes

This chapter addresses thesis Objectives 1, 2, 3 and 4.

Chapter 5.1

Advanced Carbon-Nickel Sulfide Hybrid Nanostructures: Extending the Limits of Battery-Type Electrodes for Redox-Based Supercapacitor Applications

Chapter 5.1 emphasises the electrochemical energy storage performance of plasma-designed carbon material combined with nickel sulfide as an advanced electrode for redox-based supercapacitors. In this study, vertically aligned carbon nanotubes were directly deposited on nickel foil (current collector) using a low-pressure radio-frequency inductively coupled plasma system. The synthesised carbon nanotubes were terminated with a metallic nickel nanoparticle. After the plasma deposition, we subjected these carbon nanostructures to nitrogen plasma treatment to improve the electrical properties of the carbon nanostructure. After the nitrogen plasma treatment, a nitrogen-doped vertical carbon nanotubes were formed, and the top layer of metallic nickel nanoparticle was transformed into anatomically thin nickel nitride layer. As the final step, nitrogen-doped and vertical carbon nanotubes were thermally treated with H_2S gas at relatively low temperatures to design nickel sulfide/carbon composites. As a final product, we produced two different electrode materials: nickel sulphide/nickel/vertical carbon nanotubes and nickel sulfide/nickel nitride/nickel/nitrogen-doped vertical carbon nanotubes. In the first electrode of nickel sulfide was featured by poly crystalline structure, while the second was single-crystalline. As an electrode material, both electrodes exhibited battery-type electrochemical features, and nitrified nickel sulfide/carbon composites delivered almost double performance than the undoped electrode. The achieved electrochemical performance was one of the best performances in the battery-type electrode materials at the time of publishing, and extending the limits of battery-type electrodes for redox-based supercapacitor applications.

Regarding my contribution: I performed the experiments and designed plasma-fabricated carbon nanostructures, synthesised nickel sulfide/carbon composites, contributed to the surface and chemical composition analysis and jointly wrote the paper with co-authors.

Advanced Carbon–Nickel Sulfide Hybrid Nanostructures: Extending the Limits of Battery-Type Electrodes for Redox-Based Supercapacitor Applications

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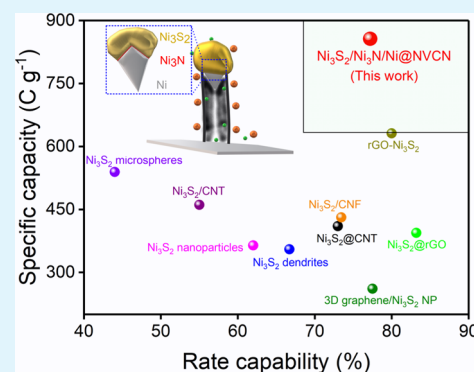
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Supporting Information

ABSTRACT: Transition-metal sulfides combined with conductive carbon nanostructures are considered promising electrode materials for redox-based supercapacitors due to their high specific capacity. However, the low rate capability of these electrodes, still considered “battery-type” electrodes, presents an obstacle for general use. In this work, we demonstrate a successful and fast fabrication process of metal sulfide–carbon nanostructures ideal for charge-storage electrodes with ultra-high capacity and outstanding rate capability. The novel hybrid binder-free electrode material consists of a vertically aligned carbon nanotube (VCN), terminated by a nanosized single-crystal metallic Ni grain; Ni is covered by a nickel nitride (Ni_3N) interlayer and topped by trinickel disulfide (Ni_3S_2 , heazlewoodite). Thus, the electrode is formed by a $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ architecture with a unique broccoli-like morphology. Electrochemical measurements show that these hybrid binder-free electrodes exhibit one of the best electrochemical performances compared to the other reported Ni_3S_2 -based electrodes, evidencing an ultra-high specific capacity (856.3 C g^{-1} at 3 A g^{-1}), outstanding rate capability (77.2% retention at 13 A g^{-1}), and excellent cycling stability (83% retention after 4000 cycles at 13 A g^{-1}). The remarkable electrochemical performance of the binder-free $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrodes is a significant step forward, improving rate capability and capacity for redox-based supercapacitor applications.

KEYWORDS: nickel sulfide, heazlewoodite Ni_3S_2 , vertical carbon nanostructure, redox-based supercapacitor, binder-free, plasma synthesis



INTRODUCTION

The increasing demand for power backup solutions and the use of renewable energy resources for fulfilling consumer requirements have prompted the development of advanced electrochemical energy storage devices such as batteries and supercapacitors.^{1–3} Supercapacitors have many practical applications and have attracted research attention due to their high power density, long cycle life, and fast charge–discharge rate properties.^{4,5} However, large-scale applications of supercapacitors are still limited due to their low energy density.^{6,7} To overcome these shortcomings, research has focused on the exploration of new electrochemically redox-active materials with higher specific capacity and new electrolytes to boost supercapacitor performance.^{8–10} Most current commercial electrolytes are organic and many are toxic, flammable, of high cost, and generally not environmentally friendly.¹¹ Hence, efforts are being made to develop hybrid high-performing electrode materials able to work in aqueous electrolytes.^{12,13}

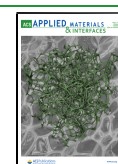
Materials for redox-based supercapacitor electrodes are expected to meet three criteria: first, the high electrical conductivity of the electrode material for the fast charge carrier

transport to the electrode interface from the electrolyte; second, high surface area because the capacity scales with the interfacial area; and third, excellent electrode electrochemical stability to avoid unwanted reactions with the electrolyte and decreased stability in long-term cycling. Thus, electrode materials need to be designed to withstand long-term cycling with enhanced electrochemical activity. In this aspect, novel electrode materials for supercapacitors can be classified according to their charge-storage process, which can be either non-Faradaic or Faradaic.^{14,15} In the former type, charge storage is induced by charge accumulation at the surface of the electrodes. In the second case, charge storage is achieved by Faradaic electron-charge transfer with fast and quasi-reversible redox processes that involve intercalation and electrosorption. Compared to non-Faradaic double-layer electrodes, the

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Faradaic type has the potential to deliver much higher capacity and energy density due to reversible redox reactions that are the main contributors to the charge storage.¹⁶ In the context of Faradaic supercapacitors, charge-storage mechanisms may be classified as pseudocapacitive, displaying a nearly linear galvanostatic charge–discharge (GCD) response, or as battery-like, in which the Faradaic process is explained by the Nernst equation featuring nonlinear GCDs, which can display one or more voltage plateaus.^{16,17} In this regard, materials with a noncapacitive Faradaic-type charge-storage mechanism are known as “battery-type” materials due to similarities with battery electrochemical responses.¹⁸ In general, materials that exhibit multiple redox valences, such as transition metals (e.g., Ni, Co, Mn, Ti, and Fe) and their compounds (oxides, hydroxides, and sulfides), have been proposed as materials for Faradaic electrodes.^{19–22} Additionally, electrochemical redox-active polymers are also considered as an important type of pseudocapacitive material.^{23,24} It is well known that many metal hydroxides and sulfides display a battery-type response. Compared to other transition-metal compounds, transition-metal sulfides appear particularly suitable for energy storage applications due to their good electrical conductivity, high redox activity, easy preparation, and low cost.^{25–28} Among them, nickel sulfides have the highest capacitance values.²⁹ Considering the varieties of nickel sulfides, such as NiS₂,^{30,31} Ni₃S₂,^{32–34} Ni₃S₄,^{28,35} Ni₇S₆,³⁶ and Ni₉S₈,³⁷ superior electrochemical performance has been reported for Ni₃S₂-based electrodes. Compared to other nickel sulfide phases, Ni₃S₂ structures possess high electrical conductivity, exceptional theoretical capacity, and excellent cyclic performance.^{38–40}

However, the use of nickel sulfide-based battery-type electrode materials for energy storage in commercial applications is still limited due to the poor electrical conductivity and structural stability compared to commercially available carbon-based nanostructures. These factors decrease the stability and rate performance of the electrode materials. An effective strategy to overcome this issue is compositing the nickel sulfide-based electrodes with a highly conductive and stable carbon matrix (e.g., graphene, carbon nanotubes, carbon nanofiber, and carbon nanowall).^{41–43} Direct growth/deposition of electrode materials on the current collector is considered the ideal strategy to provide free-standing hierarchical nanostructure-based electrodes with a large contact area to improve the electrochemical reaction. Additionally, this technique can eliminate resistivity-related issues due to the use of binders during electrochemical testing.^{44,45}

A feasible route to overcome the issues related to poor conductivity and other side effects of binders is the direct growth of a carbon matrix on the current collector, followed by compositing it with nickel sulfides. Direct growth of carbon-based nanostructures on different substrates and their processing has been performed in the past using different techniques. Commonly used techniques are chemical vapor deposition, arc-discharge method, electrochemical synthesis, and plasma-enhanced chemical vapor deposition (PECVD).^{46–48} Compared to other techniques, the PECVD technique allows the fastest controllable growth of various carbon nanostructures with different morphologies and orientations.^{47,49} The tip-growth mechanism is a well-known catalyst-assisted plasma deposition technique for the synthesis of vertical carbon nanotubes, resulting in each nanotube being terminated with the catalyst nanoparticle, which was also

successfully demonstrated for Ni.^{50–52} Combined with the possibility of post-synthesis alterations of the terminating Ni into nickel sulfide, the technique appears to be a highly promising approach to fabricate complex multiphase electrodes for energy storage applications. These nickel sulfide-carbon-based structures possess unique electrochemical properties compared to nickel sulfide and carbon when used individually as active materials. As a result, the composite provides a higher capacity, better cycling stability, and good rate capability, making it suitable for assembling high-capacity redox-based supercapacitors.

The electronic properties of carbon nanostructures can be tailored by chemical doping either by adsorption of foreign molecules on the carbon lattice or by substitutional doping by nitrogen, oxygen, or boron, which can either donate or withdraw free electrons.^{53,54} Among the varieties of heteroatoms, nitrogen is considered as a promising dopant since the presence of nitrogen also facilitates fast surface redox reactions, further improving the pseudocapacitive properties of the electrode materials.⁵⁵ Thus, the presence of additional nitrogen in the above-mentioned nickel sulfide-carbon nanostructure-based electrodes is expected to enhance electrochemical performance significantly.

This work proposes a fast and facile approach for the direct fabrication of a hybrid electrode material based on trinickel disulfide (Ni₃S₂) and vertically aligned carbon nanotubes (VCNs). The VCN structures are synthesized on Ni foil using an inductively coupled radio-frequency PECVD system. The VCN structures are terminated with a single-crystal metallic Ni nanoparticle at the tip, forming Ni@VCN. To improve the electronic properties of the carbon backbone, Ni@VCN structures are subjected to N-doping. Along with the N-doped VCN (NVCN), the exposed part of Ni in Ni@VCN is covered with an atomically thin layer of nickel nitride (Ni₃N), resulting in a Ni₃N/Ni@NVCN architecture. These structures are subjected to low-temperature annealing (125 °C) in the presence of H₂S gas to achieve the transformation to NiS. In the case of undoped Ni@VCN, the resulting Ni₃S₂ is polycrystalline with a broccoli-like morphology, while in the case of the N-doped samples with an intermediate Ni₃N layer, the process results in single-crystal Ni₃S₂ on top of Ni₃N/Ni@NVCN. The fabricated binder-free electrodes exhibit a Faradaic “battery-like” electrochemical response. Ni₃S₂/Ni₃N/Ni@NVCN electrodes show one of the highest discharge capacities among Ni₃S₂-based electrodes. Until now, one of the main challenges of translating these Faradaic materials into supercapacitor electrode applications has been poor rate capability. However, the fabricated Ni₃S₂/Ni₃N/Ni@NVCN retains 78% of the initial capacity at a higher current density of 13 A g^{−1}. The unique broccoli-like morphology of the hybrid vertical structures, the formation of defects in the crystalline structures during electrochemical reactions, and the direct contact between the current collector and active materials all contribute to boosting the electrochemical performance, capacity, and rate capability of the hybrid electrodes. Thus, this hybrid material is extremely promising as a basis for electrodes in supercapacitor applications.

■ RESULTS AND DISCUSSION

Nanostructure and Morphology Characterization.

The initial carbon nanostructures were deposited on Ni foil using a catalyst-assisted plasma-deposition technique (PECVD) reported similarly elsewhere^{50,51} and were grown

in the form of VCNs, capped by a single-crystal Ni nanoparticle. N-doping did not alter the samples significantly, and the VCN and NVCN both had an approximate height of $\sim 1\ \mu\text{m}$ (Figure S1a,b). Then, the samples were subjected to sulfur treatment and analyzed by scanning electron microscopy (SEM). The surface morphology of the uniformly grown and densely packed sulfur-treated VCN and NVCN is presented in Figure 1a,b. When comparing the VCN and NVCN, the tips of

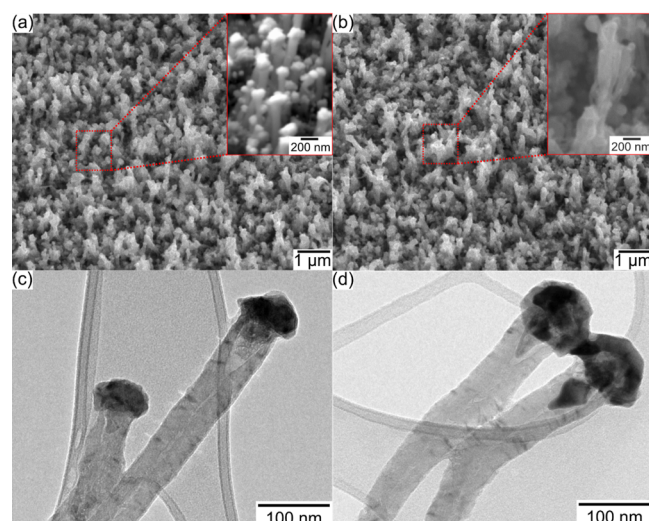


Figure 1. Secondary electron (SE) SEM images of nickel sulfide/carbon composites before and after N-doping. Tilted view of (a) nickel sulfide/carbon nanostructures and (b) nickel sulfide/N-doped carbon nanostructures. TEM micrograph of (c) nickel sulfide/carbon nanostructures and (d) nickel sulfide/N-doped carbon nanostructures.

the individual tubes became swollen after sulfur treatment, while the dimension and orientation of the nanotubes remained intact; apart from that, no other differences were

observed. Next, the structure and morphology of sulfur-treated VCN and NVCN were analyzed at the nanoscale by transmission electron microscopy (TEM; Figure 1c,d). In both cases, the metal tip of the VCN changed and expanded, corresponding to broccoli-like polycrystalline NiS for the VCN and to a single-crystal NiS for the NVCN.

To understand the formation and transformation of these sulfur phases, TEM and high-resolution TEM (HR-TEM) analyses were conducted on VCN and NVCN before and after sulfur treatment (Figure 2). The initial VCN was a multiwalled carbon nanotube, with an average diameter of 50 nm, terminated by a faceted, single-crystal metallic Ni nanoparticle (Figure 2a), forming a Ni@VCN structure. The NVCN showed similar features, with an additional nitride layer atop the exposed Ni (Figure 2b,e); the nitride phase formed an epitaxial layer, with a thickness of $\sim 5\ \text{nm}$ corresponding to Ni_3N (Figure S2). TEM micrographs of sulfur-treated VCN and NVCN are shown in Figure 2b,f, respectively. While neither N nor S treatment modified the carbon structures, and the sulfur neither damaged the vertical alignment, incorporated itself into the carbon backbone, nor deposited as elemental S on the nanostructure, both processes have a significant influence on the terminal Ni monocystal (Figure S3).

TEM results confirm that in both cases, a successful transformation of the capping single-crystal Ni to NiS was achieved. Sulfur reacted only with the exposed part of the Ni nanoparticle at the VCN tip and was locally converted into NiS, which was observed by SEM as an enlargement of the VCN tip. In both samples, remnants of metallic Ni can still be observed under NiS in the core of the VCN. HR-TEM studies on the hybrid $\text{NiS}/\text{Ni@VCN}$ and $\text{NiS}/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ structures are presented in Figure 2c,g. In the case of $\text{NiS}/\text{Ni@VCN}$ structures, NiS is polycrystalline (Figure 2c), with an individual domain size of 20–50 nm, firmly intergrown. In contrast, NiS formed on $\text{Ni}_3\text{N}/\text{Ni@NVCN}$ is a single crystal of size $\sim 50\text{--}100\ \text{nm}$. During the H_2S treatment of $\text{Ni}_3\text{N}/\text{Ni@NVCN}$, the exposed Ni faces were protected by a thin nitride

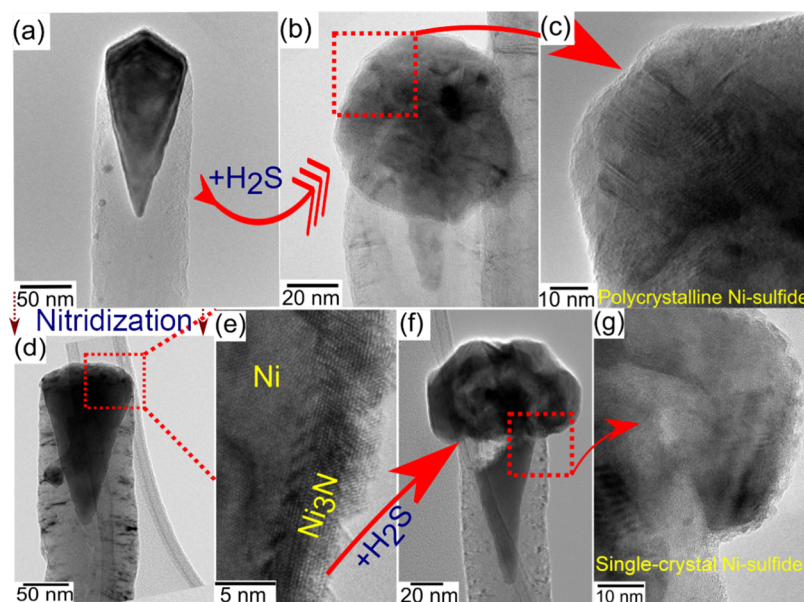


Figure 2. TEM micrograph of (a) Ni@VCN , (b) NiS grown at the Ni@VCN , (c) HR-TEM micrograph of polycrystalline nickel sulfide formed on Ni@VCN , (d) $\text{Ni}_3\text{N}/\text{Ni@NVCN}$, (e) HR-TEM micrograph of $\text{Ni}_3\text{N}/\text{Ni}$, (f) NiS grown at the top of $\text{Ni}_3\text{N}/\text{Ni@NVCN}$, and (g) HR-TEM micrograph of single-crystalline nickel sulfide formed on $\text{Ni}_3\text{N}/\text{Ni@NVCN}$.

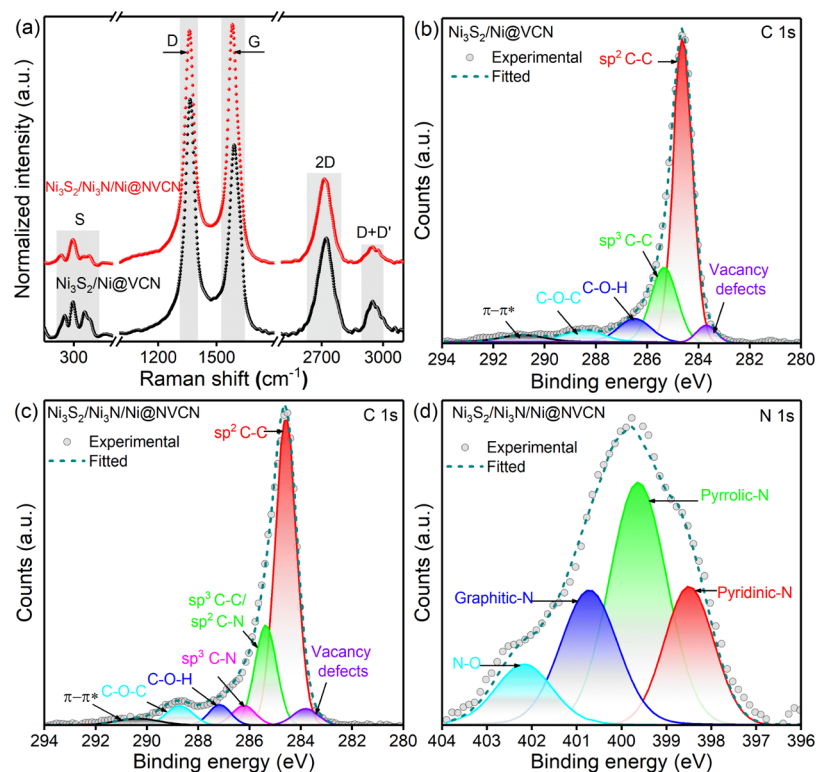


Figure 3. Structural and chemical analysis of the structures. (a) Raman spectra of Ni₃S₂/Ni@VCN and Ni₃S₂/Ni₃N/Ni@NVCN, (b) high-resolution C 1s XPS spectrum of Ni₃S₂/Ni@VCN, (c) high-resolution C 1s XPS spectrum, and (d) N 1s XPS spectrum of Ni₃S₂/Ni₃N/Ni@NVCN. The XPS spectra are also deconvoluted into different contributing peaks.

layer; thus, the sulfur had access to the metallic Ni only where the NVCN carbon layer and nitride layers met, leading to a slow in-diffusion of Ni, resulting in single-crystal NiS formation (Figure 2g). The process of Ni leaching may also explain the formation of a void observed in the Ni core in Ni₃N/Ni@NVCN, suggesting that no direct contact between Ni and NiS is needed for sulfide formation and that diffusion is only dictated by NVCN. As there are various abundant NiS phases, and their properties depend on the structure, selected area electron diffraction (SAED) was used to determine the NiS phase, identified as heazlewoodite Ni₃S₂ (Figure S4a,b) in both structures.^{44,56,57} In addition, Ni₃N phases were still preserved in the sulfur-treated Ni₃N/Ni@NVCN structures. Thus, the obtained results confirm that the broccoli-like morphology is a hybrid hierarchical structure of core-shell-type Ni–Ni₃S₂ on top of VCN structures (Ni₃S₂/Ni@VCN) and Ni₃N-encapsulated Ni₃S₂ nanostructures on NVCN structures (Ni₃S₂/Ni₃N/Ni@NVCN).

Chemical and Composition Characteristics. Chemical composition and lattice structure analyses of the Ni₃S₂/Ni@VCN and Ni₃S₂/Ni₃N/Ni@NVCN hybrid structures were conducted using different spectroscopy techniques. Structural features were characterized by Raman spectroscopy. The spectra of both samples are presented in Figure 3a and feature characteristic peaks of graphene-like structures at 1360 cm⁻¹ (D peak), 1581 cm⁻¹ (G peak), 2722 cm⁻¹ (2D peak), and 2943 cm⁻¹ (D + G peak).^{58,59} The presence of D and D + G peaks shows the defect-rich characteristics of the VCN backbone. Typically, the intensity ratio between the D and G bands (I_D/I_G) is used to examine the defect degree of carbon materials. The I_D/I_G values for Ni₃S₂/Ni@VCN and Ni₃S₂/Ni₃N/Ni@NVCN structures were calculated as 1.2 and 0.98,

respectively, which confirmed the presence of defects in the VCN backbone. Apart from the carbon-related peaks, both samples exhibited peaks at 200–400 cm⁻¹, which were assigned to peaks from Ni₃S₂, as reported in the literature.⁵⁷

Surface components and the chemical composition of the nanostructures were characterized by X-ray photoelectron spectroscopy (XPS) analysis. The presence of C, O, Ni, and S in the nanostructure was confirmed from the XPS survey spectra, which feature peaks at 284.6, 531.8, 850.2, and 162.2 eV, respectively (Figure S5). Besides these, a peak around 400 eV, indicating the presence of N in the structure, was observed in the survey spectrum of Ni₃S₂/Ni₃N/Ni@NVCN.^{60,61} High-resolution C 1s XPS spectra of Ni₃S₂/Ni@VCN and Ni₃S₂/Ni₃N/Ni@NVCN are presented in Figure 3b,c. Both spectra display an intense peak at 284.6 eV, which corresponds to sp² C–C bonds. A peak is observed around 285.4 eV in both samples that are assigned to sp³ C–C bonds. This peak becomes stronger in Ni₃S₂/Ni₃N/Ni@NVCN structures, which may be due to the presence of sp² C–N after N-doping. Peaks observed at 283.5, 286.7, 288.2, and 290.5 eV can be ascribed to the vacancy defects, the carbon singly bound to oxygen, the carbon in carbonyl groups, and the π–π* shake-up satellite, respectively.^{62,63} Additionally, a peak around 286.2 eV is observed in Ni₃S₂/Ni₃N/Ni@NVCN and attributed to the presence of sp³ C–N groups. High-resolution N 1s spectra of the Ni₃S₂/Ni₃N/Ni@NVCN structures have been deconvoluted into four peaks (Figure 3d), namely, pyridinic-N (398.5 eV), pyrrolic-N (399.6 eV), graphitic-N (400.7 eV), and oxides of pyridinic-N (402.2 eV).⁶⁴ Interestingly, there are no peaks from metal nitrides with corresponding lower binding energies (~397 eV) in N 1s spectra, indicating that the nickel nitride was fully encapsulated by the sulfide.

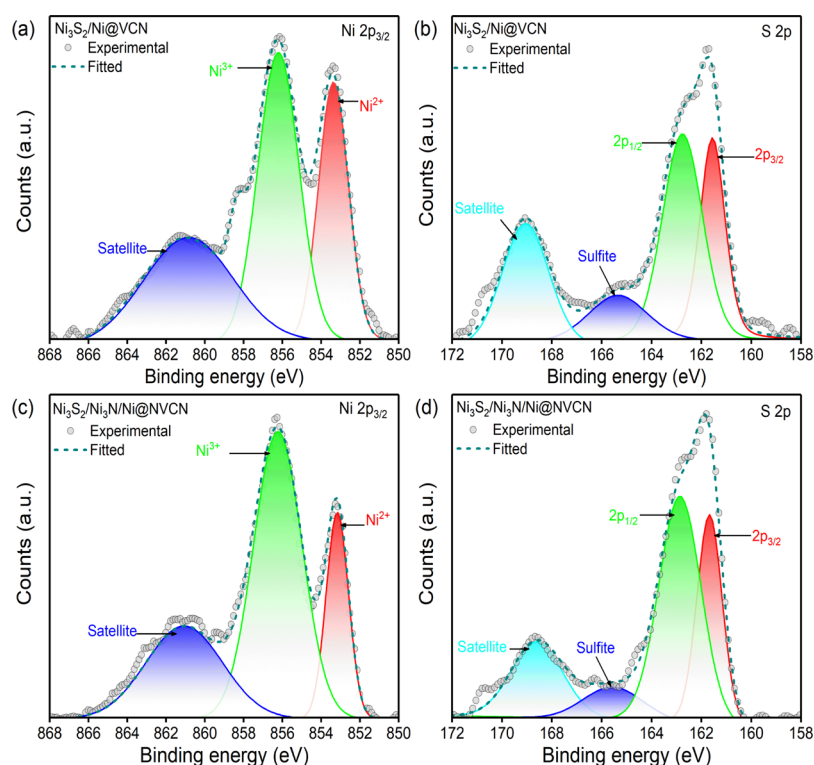


Figure 4. XPS chemical composition of the structures. High-resolution ionizations of (a) Ni 2p and (b) S 2p in $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$. High-resolution ionizations of (c) Ni 2p and (d) S 2p in $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@VCN}$.

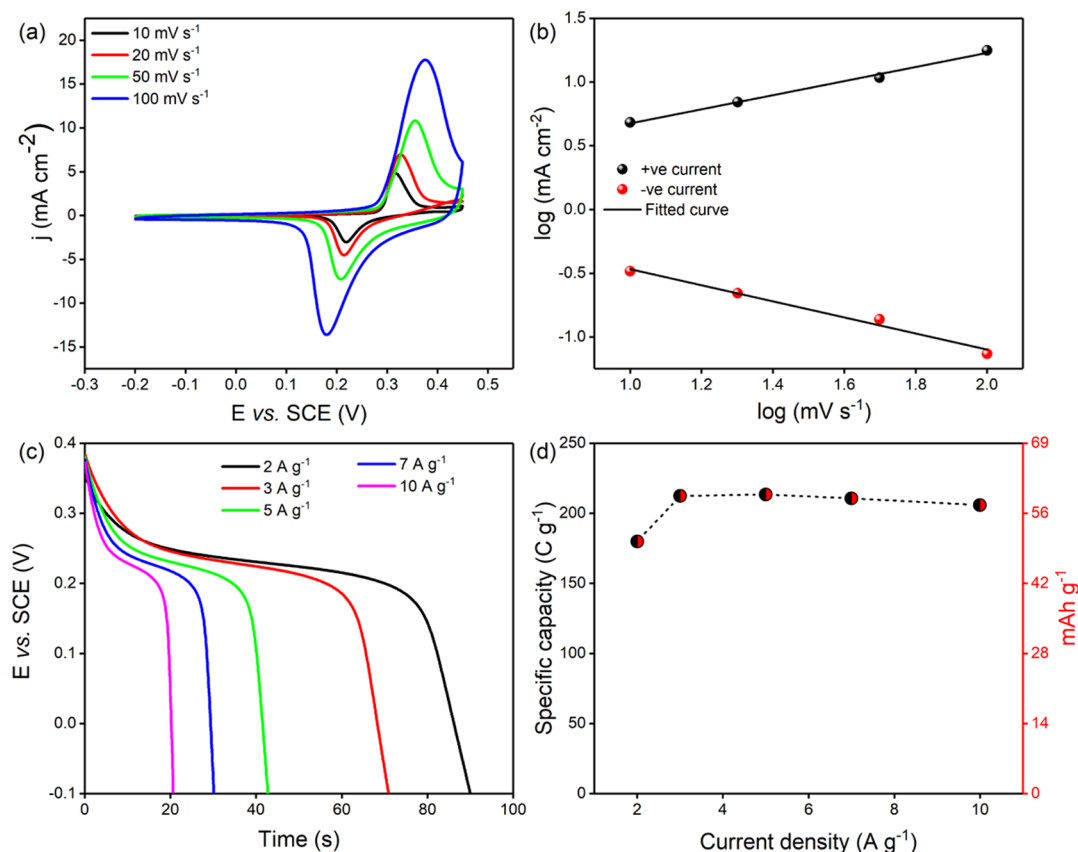


Figure 5. Initial performance of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrodes before cycling. (a) CV at different scan rates, (b) log (current density) vs log (scan rate), (c) GCD at different current densities, and (d) rate capability.

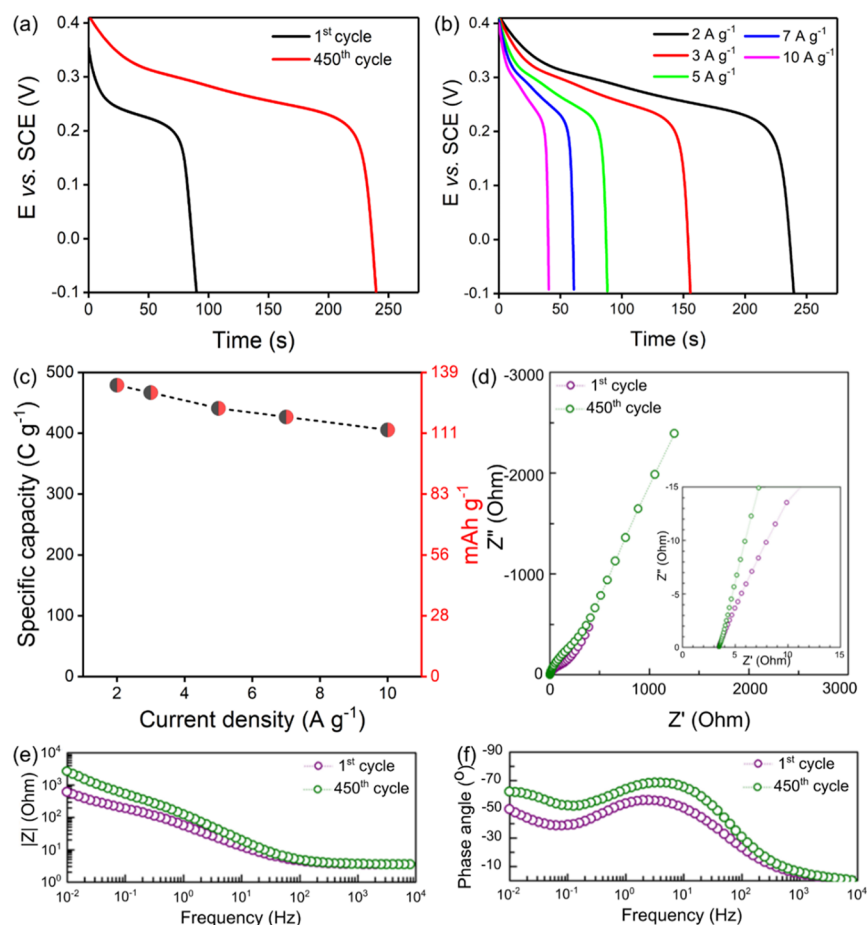


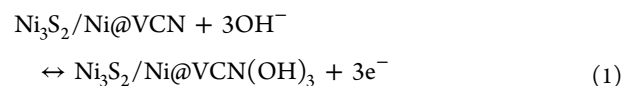
Figure 6. Electrochemical performance of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrodes after stabilization. (a) GCD comparison after the 1st and 450th cycles at 2 A g^{-1} , (b) GCD at different current densities after the 450th cycle, and (c) rate capability. EIS plot obtained after the 1st and 450th cycles: (d) Nyquist, (e) magnitude, and (f) phase angle plot.

In both samples, $\text{Ni } 2p_{3/2}$ ionizations are observed around 853.4, 856.2, and 861.0 eV. These can be ascribed to Ni^{2+} , Ni^{3+} , and the satellite peak, respectively (Figure 4a,c), which is usually observed in the $\text{Ni } 2p_{3/2}$ spectra of Ni_3S_2 .⁶⁵ The S 2p ionization of both samples features a spin–orbital doublet at 161.7 and 163.0 eV along with a satellite peak at 169.0 eV.⁶⁶ Ionizations are presented in Figure 4b,d. The S 2p ionizations with such doublets asymmetrically broadened to higher binding energies are S 2p characteristics in Ni_3S_2 structures.^{65,67} The Ni 2p and S 2p ionization of the N-doped sample and the nondoped sample shows similar spectral features, confirming that the chemical compositions are similar irrespective of the presence of N in $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@VCN}$.

Detailed information on the peak position and roughly estimated composition ratio (%) from the fitted photoionization of the high-resolution spectra of C 1s, Ni 2p, and S 2p is summarized in Tables S1, S2, and S3, respectively. All the interpretations suggest that sulfurization of Ni@VCN and Ni@NVCN at low temperatures promotes the formation of Ni_3S_2 -based hybrid structures. Also, the structural and morphological results give an insight into the synthesis of Ni_3S_2 with different crystallinities by protecting the exposed part of the Ni nanoparticle with a thin nitride layer. It is a well-known fact that Ni_3S_2 -based active materials have potential applications for energy storage devices due to their higher electrochemical activity compared to their corresponding oxides.

Electrochemical Characterization. The combination of Ni_3S_2 -based active materials with a conductive carbon matrix improves the electrical conductivity of the structure, enabling the easy penetration of electrolyte ions into the active material and facilitating charge transfer during electrochemical processes. Thus, both $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ and $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ materials were tested as electrodes for redox-based supercapacitors. Since the active materials were directly grown on Ni, these architectures were used as binder-free electrodes without any additional processing and considering Ni as the current collector. The electrochemical performance was studied in a three-electrode setup using the fabricated hybrid structures as the working electrode, Pt as the counter electrode, and saturated calomel as the reference electrode.

Electrochemical measurements of the $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrodes are presented in Figure 5. Cyclic voltammetry (CV) curves at different scan rates ranging from 10 to 100 mV s^{-1} show well-defined redox peaks and reversible current outputs on the reverse scan (Figure 5a). The anodic peak located around 0.37 V and the cathodic peak around 0.18 V are the evidence for the following proposed electrochemical reaction⁴⁴



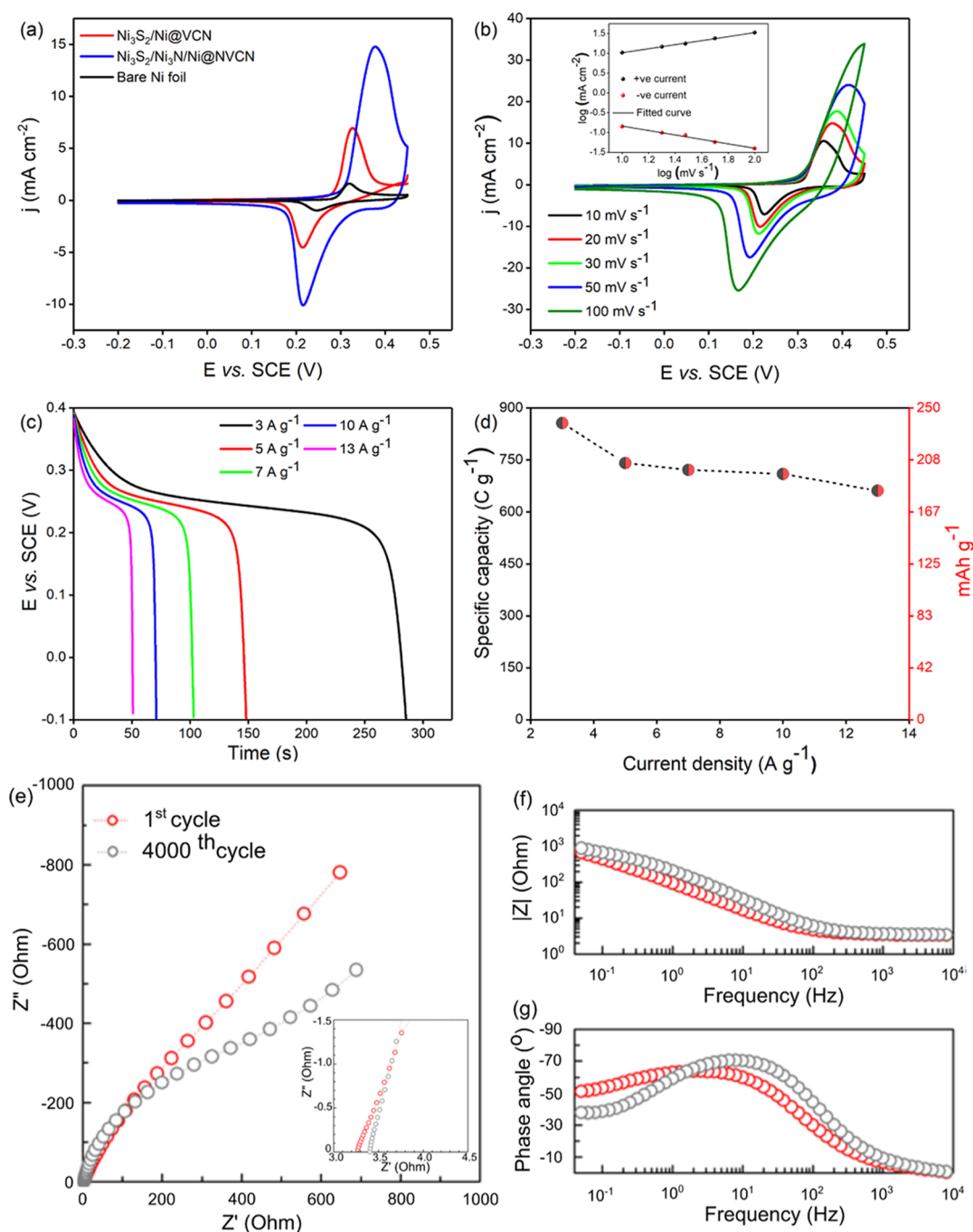


Figure 7. (a) CV comparison of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$, $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$, and bare Ni foil at 20 mV s^{-1} . (b) CV at different scan rates, with the inset showing $\log(\text{current density})$ vs $\log(\text{scan rate})$. (c) GCD at different current densities. (d) Rate capability of the $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrode. EIS comparison of $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ after 1st and 4000th cycles. (e) Nyquist plots, magnified view of Nyquist in the high-frequency region (inset), and (f,g) Bode plots.

Shape retention of the CV curves obtained at different scan rates suggests low internal resistance and quasi-reversibility of the electrode. The reaction kinetics of the electrochemical reaction was deduced from the CV curves using the power-law equation (eq 3).

Figure 5b highlights slopes of 0.55 and 0.63, respectively. This evidences the presence of diffusion-controlled charge-storage mechanisms.^{68,69} Specific capacity and rate capability of the electrodes were investigated by GCD measurements at different current densities, and the results are presented in Figure 5c. GCD curves show a clear plateau, confirming the

occurrence of Faradaic-based phenomena. Specific capacity and rate capability performance were calculated using the GCD data using eq 4 and are presented in Figure 5d. The maximum specific capacity of 180 C g^{-1} (50 mA h g^{-1}) was obtained at 2 A g^{-1} . It is worth noticing that the electrode delivered a specific capacity of 206 C g^{-1} (57.2 mA h g^{-1}) at a current density of 10 A g^{-1} . Electrodes delivering specific capacity over 100% when the applied current increases fivefold are very unusual and indicate that the electrochemical response was evolving and had not yet stabilized.

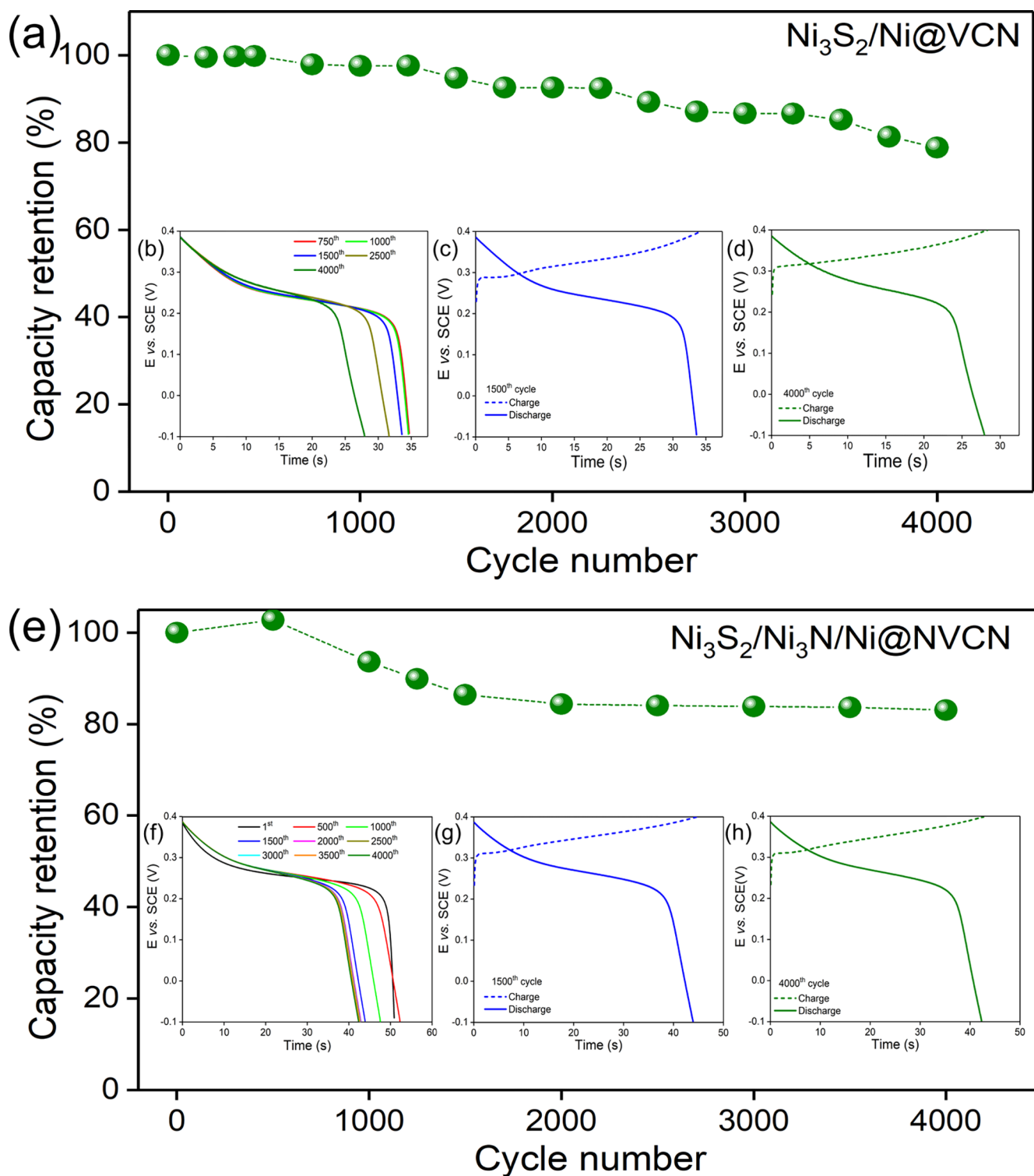


Figure 8. (a) Cyclic stability of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ up to 4000 cycles at 10 A g^{-1} . (b) Discharge plots (c) after 1500th cycle and (d) after 4000th cycle. (e) Cyclic stability of $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ up to 4000 cycles at 13 A g^{-1} . (f) Discharge plots (g) after 1500 cycles and (h) after 4000 cycles.

After this observation, the electrodes were subjected to cycling to study their electrochemical stability. Results evidenced a remarkable improvement in specific capacity after 450 charge–discharge cycles, as observed in the discharge curve comparison plot for the 1st and 450th cycles (Figure 6a). Specific capacity increased by almost 2.6 times the initial value after 450 cycles and attained 479 C g^{-1} at 2 A g^{-1} . More

importantly, after stabilization, the electrode retained 84% (405.5 C g^{-1}) of its initial capacity at a high current density of 10 A g^{-1} , as illustrated in Figure 6b,c. These results point to the good electrochemical performance of the directly grown $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ structures.

Electrochemical impedance spectroscopy (EIS) measurements were performed on the as-prepared electrode and after

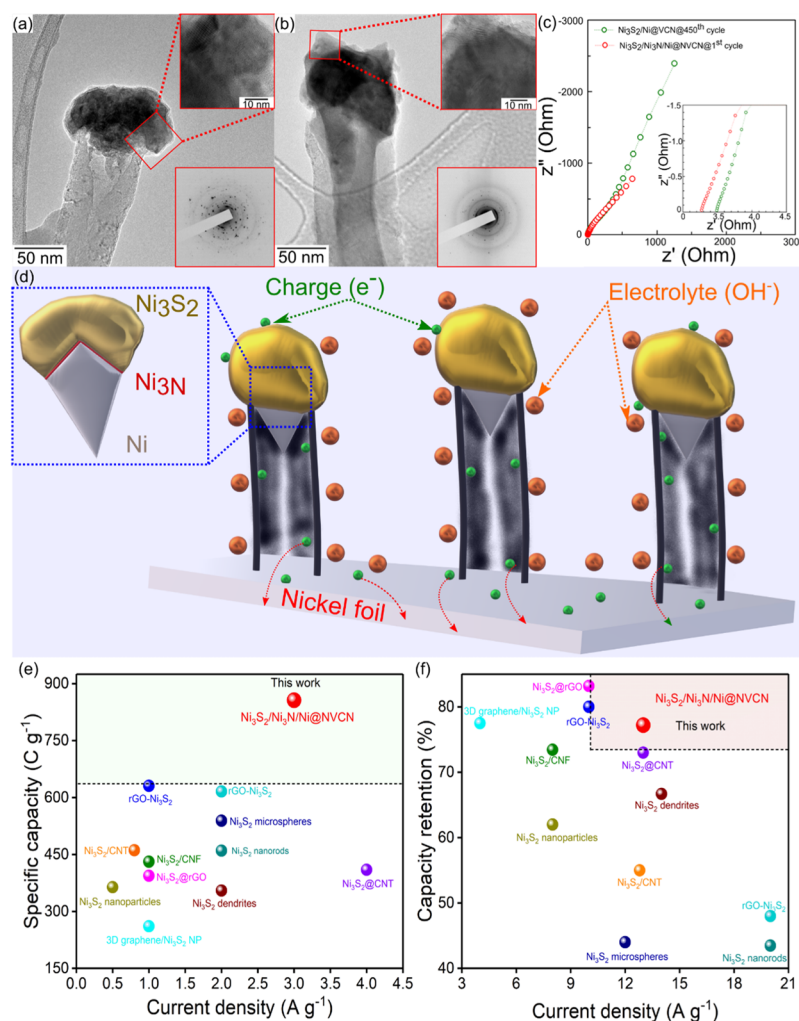
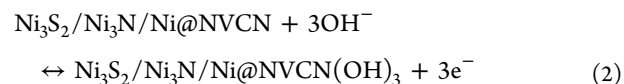


Figure 9. TEM and HR-TEM micrographs of (a) $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ and (b) $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrodes after 4000 cycles, with the SAED pattern (inverted intensity), recorded over numerous particulates presented as the inset. (c) EIS comparison plots for $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ after 450 cycles and the $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrode after the first cycle. (d) Schematic presentation of $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ as the electrode material for redox-based supercapacitors. (e) Comparison of specific capacity of Ni_3S_2 -based electrodes with $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$. (f) Comparison of rate capability performances of Ni_3S_2 -based electrodes with $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$.

450 cycles of charge–discharge to understand changes in internal resistance and the charge-transfer process. Nyquist plots are presented in Figure 6d–f. A magnified view of the Nyquist plot (Figure 6d) shows a higher slope for the spectrum taken after 450 cycles toward the imaginary axis that is the result of the enhanced capacitive response. This is confirmed in the phase angle plot (Figure 6f), where after 450 cycles, the electrode attained more negative phase angle values, around -60° in the low-frequency range, and also more negative phase angle values in the high–mid-frequency range. Overall, these results indicate enhanced electrochemical performance on cycling in terms of capacity and, interestingly, cycling seemed to attenuate diffusion limitations observed in the high–mid-frequency region.

To investigate the electrochemical responses induced by crystallinity changes and the presence of N in the active material, $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrodes were also studied through several electrochemical techniques. CV was performed on $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$, $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$, and bare Ni foil to understand the maximum current gains for different electrodes (Figure 7a). The effect of N-doping in $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ nanostructures is evident from the CV curves,

where the electrochemical performance increased almost twofold compared to $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ at a scan rate of 20 mV s^{-1} . Bare Ni foil delivered a minimal current response, showing that it has a negligible contribution to the overall current response. Furthermore, CV measurements performed on $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrodes at different scan rates (Figure 7b) show clear redox peaks with good reversibility, which can be explained by the following reaction at the interface



Logarithmic analysis of the anodic and cathodic peak current densities *versus* the scan rate based on the CV data (inset of Figure 7b) highlights slopes of 0.5 and 0.56, respectively. This strengthens the argument for the presence of diffusion-controlled charge-storage processes similar to the ones observed for the $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrode. Specific capacity and rate capability of the electrode were calculated from GCD measurements at different current densities ranging from 3 to 13 A g^{-1} , and results are shown in Figure 7c,d. The $\text{Ni}_3\text{S}_2/$

$\text{Ni}_3\text{S}_2/\text{Ni}@\text{NVCN}$ electrode delivered a specific capacity of 856.32 C g^{-1} ($240.3 \text{ mA h g}^{-1}$) at 3 A g^{-1} with a remarkable rate capability, retaining 77.2% of its initial capacity at 13 A g^{-1} . It is also worth noting that for the $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrode, cycling was not required to reach a stable electrochemical response. Additionally, it was observed that $\text{Ni}_3\text{S}_2/\text{Ni}@\text{VCN}$ electrodes were more hydrophobic compared to the $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ ones (Figure S6). This could also be a reason for the gradual improvement in the electrochemical performance of the $\text{Ni}_3\text{S}_2/\text{Ni}@\text{VCN}$ electrodes with cycling, which could be related to the slow and continuous impregnation of electrolytes throughout the active sites. EIS measurements were carried out for the $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrode after 4000 cycles, and results were compared to the data obtained on the fresh electrode before cycling (Figure 7e–g). There was a slight increase in the ESR value from 3.3 to 3.4Ω after cycling, as can be seen in the high-frequency region of the magnified Nyquist plot (inset). The phase angle plot (Figure 7g) has slightly more negative values in the high–mid-frequency range. Impedance studies did not reveal severe detrimental effects on the cycled electrodes from impedance analysis.

Cyclic stability is an essential feature for a material to be used in redox supercapacitor electrodes. Thus, GCD measurements of the $\text{Ni}_3\text{S}_2/\text{Ni}@\text{VCN}$ electrode were conducted up to 4000 cycles at 10 A g^{-1} , and results are presented in Figure 8a–d.

The $\text{Ni}_3\text{S}_2/\text{Ni}@\text{VCN}$ electrode retained a specific capacity of 78.8% after 4000 cycles. A decline in performance upon cycling can be seen in Figure 8b, which could be associated with partial morphological distortion and/or material oxidation. Despite reduced stability, the electrode had good Coulombic efficiencies (the ratio of discharge to charge time) of 98.3 and 98.6%, after 1500 and 4000 cycles, respectively (Figure 8c,d). The cyclic stability of the $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrode was also measured up to 4000 cycles at a current density of 13 A g^{-1} (Figure 8e). Results showed a slight improvement in capacity up to the initial 500 cycles, and then, the electrode retained 83% of its initial capacity after 4000 GCD cycles, even at higher current densities compared to the $\text{Ni}_3\text{S}_2/\text{Ni}@\text{VCN}$ electrode. The evolution of the discharge profile upon cycling is illustrated in Figure 8f. The charge–discharge profiles after 1500 and 4000 cycles are presented in Figure 8g,h. They show very good Coulombic efficiency (98%) after 1500 cycles, which further increased during cycling and attained almost 100% after 4000 cycles. These stabilities and Coulombic efficiency results highlight the good energy storage properties of the material with little interference of any parasitic reactions.

Surface and Structural Characterization of Cycled Electrodes and Discussion. The Ni_3S_2 -based electrodes fabricated in this work exhibited excellent electrochemical performance for Faradaic supercapacitor applications, with a high specific capacity, and excellent rate capability and cycling stability. Of the two different electrodes studied, $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ showed ultra-high specific capacity (almost double) and outstanding rate capability. Excellent structural stability and the formation of structural defects could be considered important factors for high energy storage performance. Thus, the *ex situ* TEM analysis of both electrodes after 4000 cycles was performed, and the results are presented in Figure 9a,b. The vertical broccoli-like morphology was intact in both structures, and we did not observe any strain and no

changes in the crystallinity or phase composition compared to the deposited structures before cycling. The SAED patterns of the electrodes after cycling are given in the insets. Additionally, a covering layer observed on both structures can be ascribed to the excellent intercalation with ions from the electrolyte, which seems dominant in $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$. HR-TEM images illustrate the formation of structural defects on both structures after electrochemical cycling. These structural defects can act as additional active sites for energy storage. Exposure to more active sites through the edges or structural vacancy defects can enhance the charge-storage mechanism of Ni_3S_2 . The presence of carbon, sulfur, nitrogen, and nickel, along with potassium in the XPS spectra of the cycled electrodes, is the evidence of the interaction between the electrode material and the electrolyte during the electrochemical reaction (Figure S7). Another possible reason for the higher capacity achieved by the $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrode could be the improvement in the electrical conductivity of the structure and the change in internal resistance. To understand this property, EIS measurements were conducted and compared with those of a fresh electrode of $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ and $\text{Ni}_3\text{S}_2/\text{Ni}@\text{VCN}$ after 450 cycles (Figure 9c). A magnified view of the Nyquist plot (Figure 9c) shows a lower ESR value for $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$. More importantly, the phase angle behavior of $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ in the mid–high-frequency range has a similar feature to $\text{Ni}_3\text{S}_2/\text{Ni}@\text{VCN}$ after 450 cycles (Figure S8). This means that fresh $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrodes, even without any prior cycling, have lower diffusion limitations, and therefore, cycling is not needed to attain a stable electrochemical response. Further evidence comes from the GCD and rate capability data, which did not rise above 100% (Figure 8c,d). This could be ascribed to the higher hydrophilicity offered by $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrodes due to N-doping, which helped electrolyte wetting at all the active material sites from early cycling.

Based on all these findings, a possible mechanism of charge storage in $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrodes is presented in Figure 9d. The N-doped VCN backbone not only acts as a support for the controlled growth of Ni_3S_2 but also enhances pseudocapacitance performance. Additionally, the vertical alignment of the N-doped VCN backbone can serve as a conductive framework to provide an efficient pathway for rapid electron transport and possibly OH^- ion diffusion. The free-standing structure of the N-doped VCN and the capped structure of Ni_3S_2 provide a large surface area to interact with the electrolyte during electrochemical reactions. Intimate contact between the Ni_3S_2 active material and the current collector eases charge-transfer reactions and enhances rate capability and capacity.

The $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrode developed in this work exhibits superior specific capacity even at a higher current density compared to other Ni_3S_2 -based electrodes (Figure 9e). In addition, the electrode possesses one of the best rate capability performances reported compared to other Ni_3S_2 -based electrodes (Figure 9f). A comparison of the electrochemical performance of various Ni_3S_2 -based electrodes and $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ is presented in Table S4, showing the potential of the material developed in this work for redox-based electrodes.

CONCLUSIONS

In summary, we fabricated metal sulfide–carbon nanostructure-based hierarchical battery-type electrodes for Faradaic

supercapacitor applications. One of the prepared hybrid binder-free electrodes consisted of trinickel disulfide (Ni_3S_2) on a single-crystal metallic Ni nanoparticle core terminated on VCNs in the form of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$. The other electrode consisted of the same components with a nickel nitride (Ni_3N) interlayer in the form of $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$. VCN structures were directly deposited on a conductive Ni substrate using plasma deposition. Later, the deposited Ni@VCN structures were subjected to nitrogen plasma post-treatment to fabricate $\text{Ni}_3\text{N}/\text{Ni@NVCN}$. In the last step, Ni@VCN and $\text{Ni}_3\text{N}/\text{Ni@NVCN}$ structures were thermally annealed at low temperature in the presence of H_2S gas to form nickel sulfide (Ni_3S_2), which was polycrystalline in Ni@VCN and single crystalline in $\text{Ni}_3\text{N}/\text{Ni@NVCN}$. Both structures possessed a unique broccoli-like hierarchical morphology.

The hybrid $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ - and $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ -structured materials were tested as binder-free electrodes for energy storage applications in redox supercapacitors. $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrodes delivered a capacity of 479 C g^{-1} with a good rate capability of 84% at 10 A g^{-1} . The $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrode delivered almost twice the capacity (856.3 C g^{-1}), one of the best values ever attained by Ni_3S_2 -based electrodes. Additionally, this electrode possessed an outstanding rate capability by retaining 77.2% of initial capacity even at a higher current density of 13 A g^{-1} . Both electrodes showed excellent cycling stability and retained above 80% initial capacity after 4000 cycles. The presence of nitrogen and defects in the VCN backbone, the hierarchical broccoli-like structure of nickel sulfide with a large surface area, the formation of additional defects in the active material during the electrochemical reaction, and the direct contact between the current collector and active material all contributed to enhanced electrochemical performance.

The electrode fabrication technique developed in this work is one of the fastest approaches for preparing Ni_3S_2 -based binder-free electrodes and produced Faradaic electrodes with enhanced electrochemical performance. The ultra-high capacity and outstanding rate capability of the prepared $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ structures represent a step change over current battery-type electrodes, which typically display high capacity and low rate capability. This work, therefore, addresses one of the main challenges in battery-type electrodes for redox-based supercapacitors and suggests that Faradaic supercapacitor performance can be dramatically improved in the near future.

■ EXPERIMENTAL SECTION

Synthesis of the Carbon Nanostructure. Synthesis of carbon nanostructures was carried out by PECVD in a radio-frequency (RF) inductively coupled plasma system at low pressure. The RF generator (13.56 MHz) was coupled through a Nagoya type III inductive coil (14 cm long with a diameter of 8.5 cm) to a cross-shaped glass tube. The diameter of the tube was 8 cm with a length of 40 cm on each arm, and the reactor was air-cooled externally. Polycrystalline $25 \mu\text{m}$ thick nickel foil (thermally annealed 99% metal basis, Alfa Aesar) with dimensions $2 \times 2 \text{ cm}^2$ was used as the substrate for the synthesis of the carbon nanostructures. The Ni-foil substrate was placed directly in the plasma discharge region in the center of the coil using a stainless-steel substrate holder, which was ground during the growth process. Methane (CH_4) at a flow rate of 20 sccm fed through a mass-flow controller was used as the carbon precursor. Before the experiment, the system was pumped down to 10 Pa with a rotary vacuum pump, and the total pressure of the system was kept at $\sim 30 \text{ Pa}$ during the experiment. Depositions were performed for 4 min at a plasma power

of 800 W to synthesize the carbon nanostructures on the Ni foil. The substrate temperature reached approximately $750\text{--}800^\circ\text{C}$ due to plasma heating effects.

Fabrication of N-Carbon Nanostructures. N-doped carbon nanostructures were fabricated using another RF inductively coupled plasma system at low pressure, as described in the literature.⁶⁴ The plasma system consisted of an 80 cm long horizontal glass tube with a diameter of 4 cm . The RF generator was inductively coupled to the system using a nine-turn water-cooled inductive coil. Nitrogen (N_2) was used as the dopant gas at a flow rate of 100 sccm . The system was pumped down to 1 Pa before the experiments using a two-stage rotary pump and maintained at 30 Pa during the experiments. The sample was placed 10 cm away from the center of the glow discharge into the post-glow region. Plasma was generated at an RF power of 300 W . Plasma post-treatment was carried out using an incremental method, where the plasma was switched off during each treatment periodically to keep the surface temperature minimized. This was done in three steps of 10 s (total 30 s) and equal cooling periods.

Synthesis of Nickel Sulfide. Nickel sulfide was formed on top of the nickel nanoparticle, which resided on the carbon nanostructure and was covered by nickel nitride. The nickel sulfide part of the composite was synthesized in an 80 cm long quartz tube furnace with a 45 cm heating zone (OTF-1200X-II, MTI Corp.). The carbon nanostructures and N-doped carbon nanostructures deposited on Ni foil were placed in the middle of the tube on a glass substrate. The tube was pumped-down with a rotary pump to $<1 \text{ Pa}$ before the experiment and then filled with H_2S gas to a pressure close to atmospheric pressure. The temperature of the chamber was elevated to 125°C at a rate of $6^\circ\text{C}/\text{min}$, and the samples were annealed for 3 h . Afterward, the furnace was left to cool down to room temperature, and H_2S gas was pumped out.

Characterization Techniques. Surface morphology of the samples was explored by a scanning electron microscope [Prisma E scanning electron microscope, Thermo Fisher Scientific Inc.], operated at 5 kV . The crystal structure and phase composition of the samples were analyzed with a transmission electron microscope (JEM-2100, Jeol Inc.) operating at 200 kV and additionally equipped with an energy-dispersive X-ray spectrometer (EX-24063JGT, Jeol Inc.). Micrographs were recorded by a slow-scan CCD camera (Orios SC1000, Gatan). Structural properties of the prepared structures were investigated by Raman spectra recorded using an NTEGRA confocal Raman spectrometer at an excitation wavelength of 488 nm . The Raman spectra were recorded at four different spots on the samples. XPS (PHI-TFA XPS spectrometer, Physical Electronics Inc) analysis was employed to evaluate the surface composition and bonding environment of the samples using an Al-monochromatic X-ray source at an energy of 1486.6 eV .

Electrochemical Measurements. Nickel sulfide/carbon nanostructures directly grown on Ni foil were used as binder-free working electrodes without using any conductive carbon and a polymeric binder. All the samples were subjected to electrochemical measurements without any further treatment. Electrochemical measurements were performed in a three-electrode setup using Pt as a counter electrode and saturated calomel as a reference electrode. CV was scanned in the potential window from -0.2 to 0.45 V and GCD from -0.1 to 0.4 V in a freshly prepared 2 M KOH electrolyte. EIS was conducted at an open-circuit potential (OCP) in the frequency range of $10^5\text{--}10^{-2} \text{ Hz}$ at an RMS amplitude of 10 mV . Gamry interface 5000E was used for all the measurements.

The power-law equation used for analyzing the diffusional processes from CV data is given by

$$i = a\nu^b \quad (3)$$

where i is the current (mA cm^{-2}), a and b are the variable parameters, and ν is the scan rate (mV s^{-1}).

The specific capacity of the electrodes was calculated using the equation^{55,70}

$$C = I\Delta t \quad (4)$$

where C is the specific capacity (C g^{-1} ; the values are also presented in mA h g^{-1}), I is the current density (A g^{-1}), and Δt is the discharge time (s).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.1c03053>.

SEM micrograph of VCN and NVCN; TEM micrograph of NVCN; EDS elemental mapping of the individual $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ structure; SAED patterns of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ and $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$; XPS survey spectra of nanostructures; XPS deconvolution details of $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$; water contact angle measurements of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ and $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrodes; XPS survey spectra of cycled electrodes; comparison of the specific capacity and rate capabilities of Ni_3S_2 -based electrodes; and EIS Bode plot comparison of electrodes (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Supporting Information

Advanced Carbon-Nickel Sulfide Hybrid Nanostructures: Extending the Limits of Battery-Type Electrodes for Redox-Based Supercapacitor Applications

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Vertically aligned carbon nanotube (VCN) structures with an approximate height of $\sim 1\ \mu\text{m}$ were used for N-doping and sulfur treatment. Vertical alignment and uniform growth of VCN structures are shown in **Figure S1a**. There was no structural damage observed after N-doping and the surface morphology after N-doping is presented in **Figure S1b**.

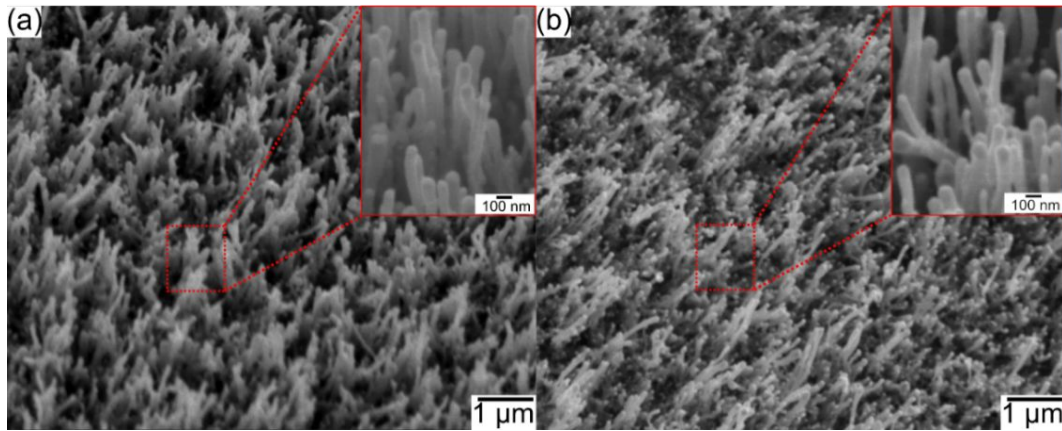


Figure S1. SEM secondary electrons (SE) micrograph of vertical carbon nanostructures: (a) VCN before N-doping and (b) VCN after N-doping.

After N-doping, there were no detectable changes observed in the morphology of the VCN structures. However, by HR-TEM observation of the terminal Ni monocrystal, a nitride layer is observed around the exposed part of the Ni in N-VCN. The Ni-nitride phase forms as an epitaxial layer with a thickness of $\sim 5\ \text{nm}$ on all free Ni surfaces, while not on those protected, even partially, by carbon layers from VCN. From the FFT of the HR-TEM image, the phase was determined to be Ni_3N , epitaxially grown on the single-crystal Ni (**Figure S2**).

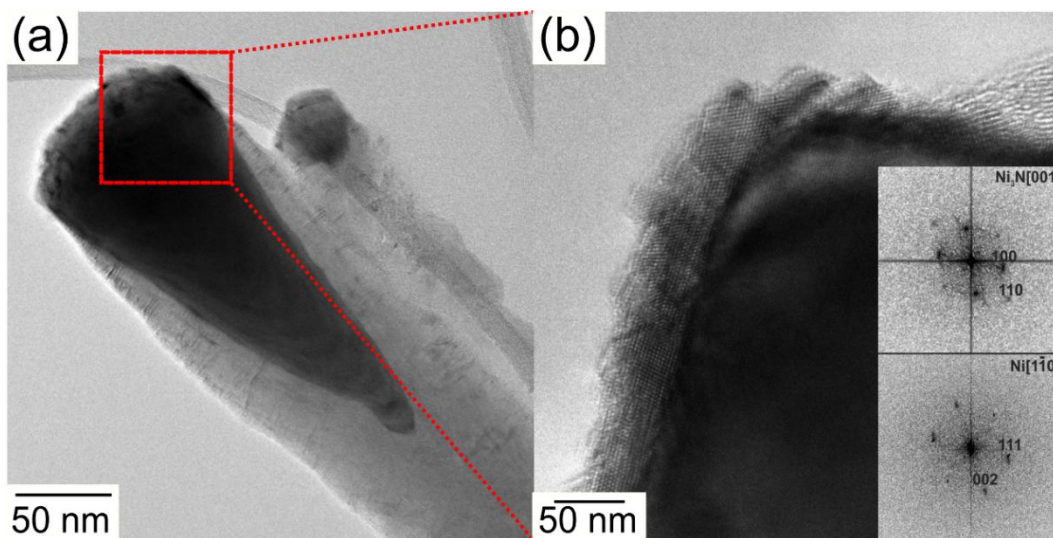


Figure S2. (a) TEM micrograph of N-doped VCN, capped by faceted Ni monocrystal covered by Ni₃N, (b) HR-TEM micrograph of epitaxial Ni₃N layer with a thickness of ~5 nm, grown atop of the single-crystal Ni. FFT patterns in the inset are indexed for Ni₃N (surface layer) and Ni (bulk).

The elemental analysis of the individual Ni₃S₂/Ni@VCN structure has been done by EDX. It is evident that after the sulfur treatment, the sulfur neither damaged the vertical alignment, incorporated itself into the carbon backbone, nor deposited as elemental S on the nanostructure. Processes have only made significant changes at the Ni monocrystal terminal (**Figure S3**).

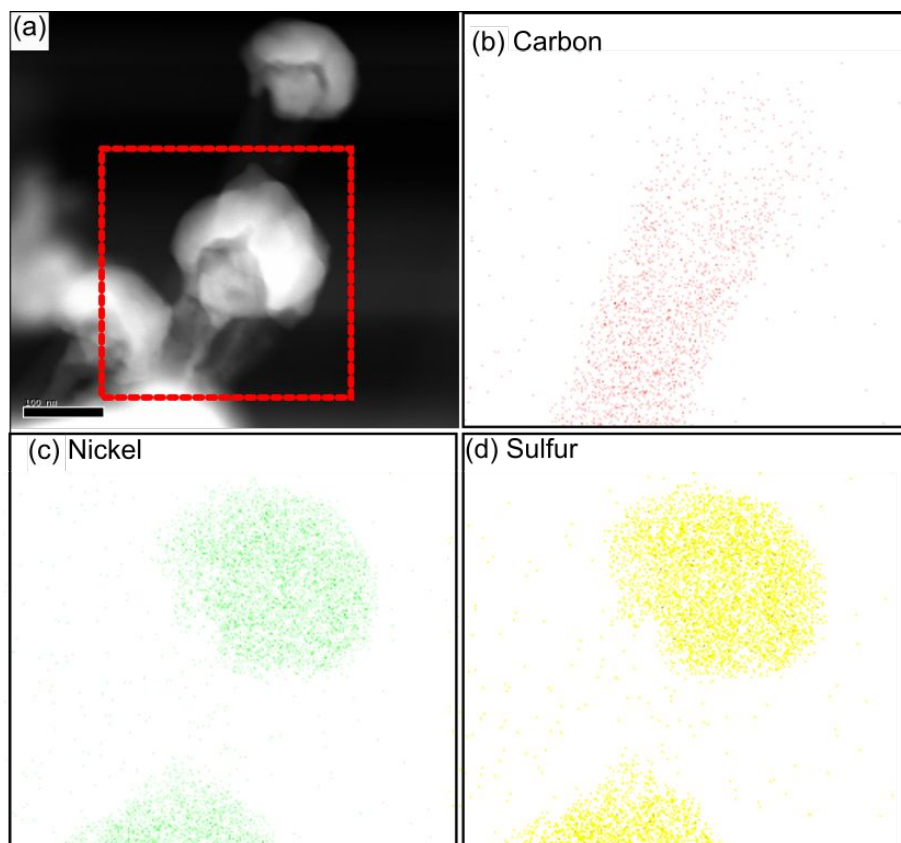


Figure S3. a) HAADF-STEM; corresponding EDS elemental mapping of individual Ni₃S₂/Ni@VCN structure b-d).

The SAED patterns of nickel sulfides confirm that the fabricated nickel sulfides possess the Ni₃S₂ phase (Heazlewoodite). The diffraction from the Ni₃N layer is also observed from N-doped VCN structures confirms that Ni₃N is protected even after the sulfur treatment. Experimental and simulated SAED pattern for Ni₃S₂, Ni₃N, Ni and VCN is presented in **Figure S4**.

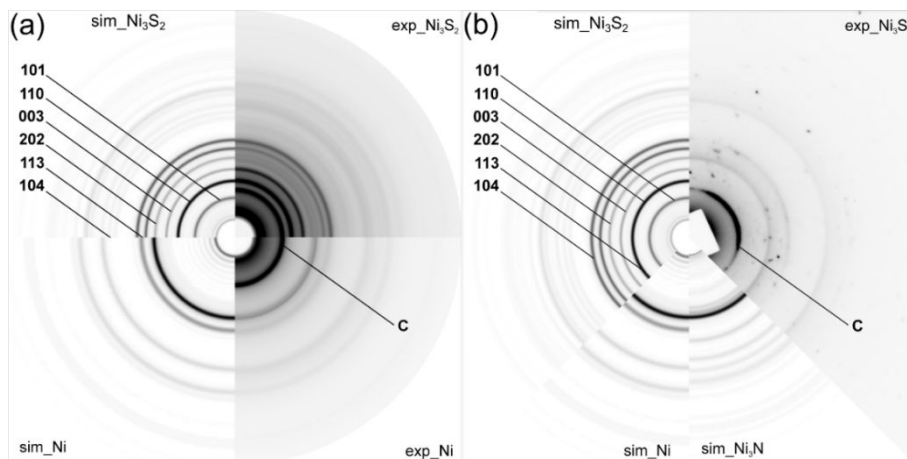


Figure S4. Phase composition analysis of nickel sulfides: (a) experimental SAED pattern for Ni_3S_2 , Ni , and VCN , and corresponding simulated patterns for Ni_3S_2 , Ni , and C in $\text{Ni}_3\text{S}_2/\text{Ni}@VCN$; (b) experimental SAED pattern for Ni_3S_2 , Ni_3N , Ni , and VCN , and corresponding simulated patterns for Ni_3S_2 , Ni , Ni_3N , and C in $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@NVCN$.

Surface components and the chemical composition of the prepared nanostructures were characterized by XPS analysis. Peaks at 284.6, 531.8, 850.2, and 162.2 eV confirm the presence of C, O, Ni, and S in the nanostructure as presented in **Figure S5**. A peak around 400 eV confirms the presence of nitrogen in the $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@NVCN$ structures.

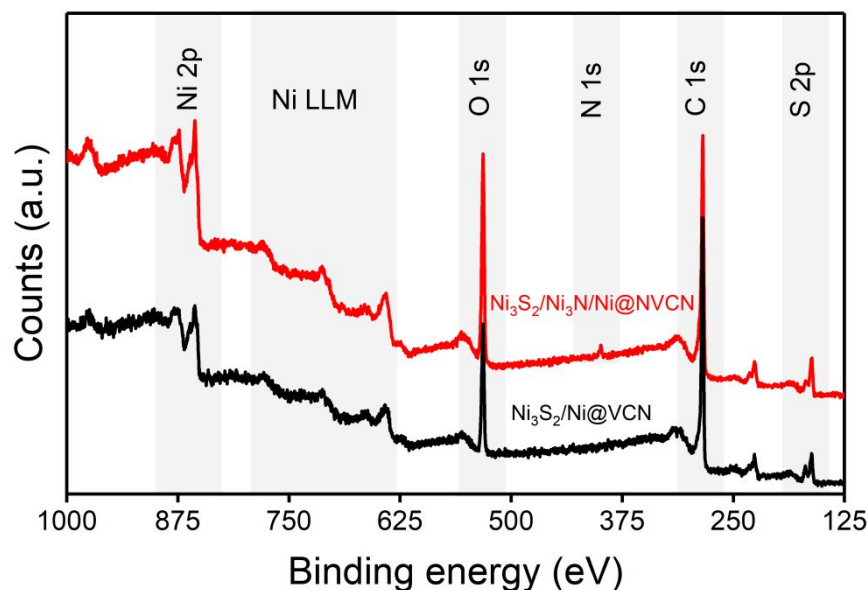


Figure S5. XPS survey spectra of the prepared nanostructures and elemental analysis.

Detailed information on the peak position and area of the deconvoluted peaks in the high-resolution XPS data of the carbon, sulfur, and nickel peaks of the samples are described in Tables S1, S2, and S3. The high-resolution XPS peaks were deconvoluted using the Gauss–Lorentz method considering Shirley-type background deduction.

Table S1. Peak position, FWHM, and area under the curve of the peak components in C 1s spectra of Ni₃S₂/Ni@VCN and Ni₃S₂/ Ni₃N/Ni@NVCN.

Deconvoluted peaks	Ni ₃ S ₂ /Ni@VCN			Ni ₃ S ₂ / Ni ₃ N/Ni@NVCN		
	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %
Peak 1	283.5	1	3.7	283.5	1	3.1
Peak 2	284.6	1	59.5	284.6	1	58.2
Peak 3	285.4	1.2	20.7	285.4	1.2	23.4
Peak 4	286.7	1.5	8.0	286.2	1.5	4.5
Peak 5	288.2	1.8	4.8	286.7	1.5	3.8
Peak 6	290.5	2.0	3.0	288.2	1.8	4.1
Peak 7				290.5	2.0	2.8

Table S2. Peak position, FWHM, and roughly estimated concentration of the peak components in S 2p spectra of Ni₃S₂/Ni@VCN and Ni₃S₂/ Ni₃N/Ni@NVCN.

Deconvoluted peaks	Ni ₃ S ₂ /Ni@VCN			Ni ₃ S ₂ / Ni ₃ N/Ni@NVCN		
	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %
Peak 1	161.7	1.2	24.6	161.7	1.2	25.9
Peak 2	163.0	1.9	37.1	163.0	2.0	45.9
Peak 3	165.4	2.5	12.3	165.4	2.5	9.0
Peak 4	169.0	2.2	25.8	169.0	2.4	19.1

Table S3. Peak position, FWHM, and area under the curve of the peak components in Ni 2p spectra of Ni₃S₂/Ni@VCN and Ni₃S₂/ Ni₃N/Ni@NVCN.

Deconvoluted peaks	Ni@VCNs			Ni ₃ S ₂ /Ni@VCNs		
	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %
Peak 1	853.4	1	27.7	853.4	1.3	18.1
Peak 2	856.2	2.5	40.4	856.2	2.8	55.5
Peak 3	861.0	5.4	31.7	861.0	5.0	26.2

Both the $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ and $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrodes were shown hydrophobic nature during the electrochemical reaction. However, $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrodes' characteristics were more hydrophobic. Thus, contact angle measurements were performed to analyze the surface properties. $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrodes ($125\pm3^\circ$) exhibit a more hydrophobic nature than the $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrodes ($108\pm5^\circ$), which indicates that the affinity towards the water was increased after the nitrogen plasma treatment. Hence, the treatment resulted in improved electrochemical performance.

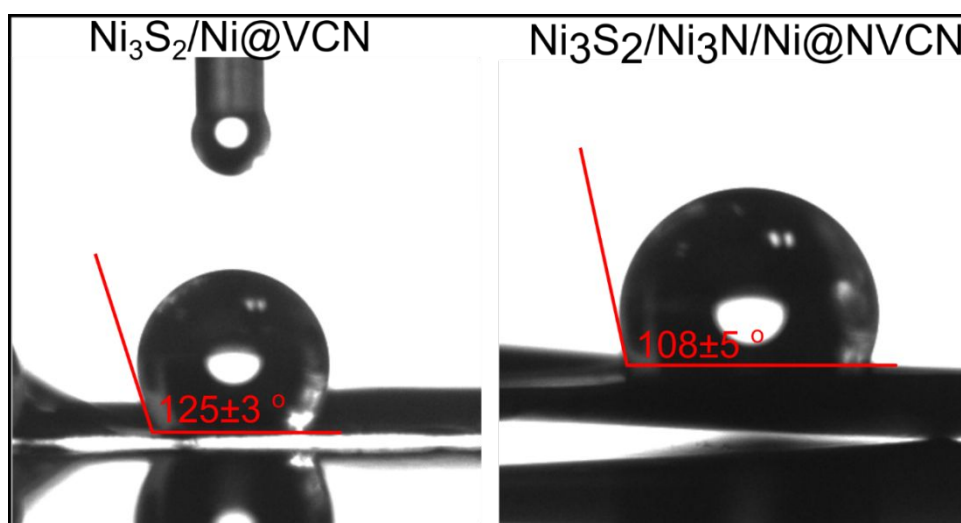


Figure S6. Water contact angle measurements of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ and $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrodes.

Electrodes were characterized by XPS analysis again after 4000 cycles to investigate the loss of elements after cycling. XPS survey spectra of the cycled electrodes are shown in **Figure S7**. Along with the electrode elements, a small peak in the spectra corresponding to the presence of potassium could be a result of excellent intercalation of electrode materials with the electrolyte. However, there is no structural damage or phase change observed from the TEM images, suggesting excellent chemical stability of the electrode material.

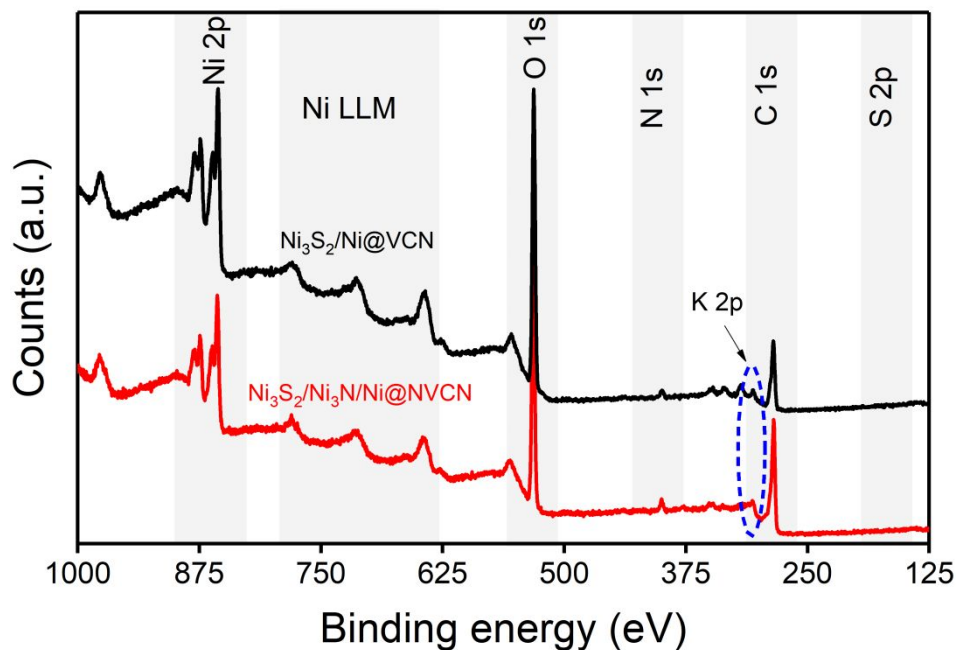


Figure S7. XPS survey spectra of the cycled electrodes and elemental analysis.

Phase angle behavior of $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ after 1st cycle and $\text{Ni}_3\text{S}_2/\text{Ni}@\text{VCN}$ after 450th cycle (after electrochemical stabilization) is presented in Figure S8.

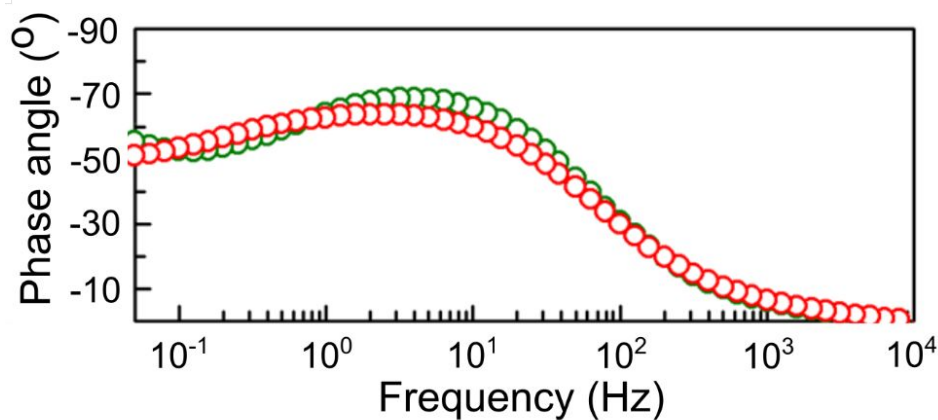


Figure S8. EIS Bode plot comparison of $\text{Ni}_3\text{S}_2/\text{Ni}@\text{VCN}$ after 450th cycle (green) and $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrode after 1st cycle (red).

$\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrode has a similar feature to $\text{Ni}_3\text{S}_2/\text{Ni}@\text{VCN}$ after 450 cycles in the mid-high frequency range. This indicates that fresh $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni}@\text{NVCN}$ electrodes, even

without any prior cycling, have lower diffusion limitations, and therefore cycling is not needed to attain a stable electrochemical response.

A comparison of the supercapacitor performances of Ni₃S₂-based battery-type electrodes has presented in Table S4. The comparison confirms that the electrode fabricated in this work, Ni₃S₂/Ni₃N/Ni@NVCN-based electrodes, has shown one of the best specific capacity and rate capability among the other varieties.

Table S4. Comparison of the specific capacity and rate capabilities of Ni₃S₂-based electrodes.

Electrode	Voltage (V)	Specific capacity (C g ⁻¹)	Current density (A g ⁻¹)	Capacity retention (%) @ current density (A g ⁻¹)	Number of cycles @ current density (A g ⁻¹)	Retention (%)	Ref
Ni ₃ S ₂ @CNT	-0.15-0.55	410 (586 F g ⁻¹)	4	73@13	1500@5.3	88	[1]
Ni ₃ S ₂ @rGO	0.1-0.55	394 (875 F g ⁻¹)	1	83.2@10	1000@5	91.3	[2]
Ni ₃ S ₂ dendrites	0-0.5	355 (710 F g ⁻¹)	2	66.7@14	2000@5	100	[3]
Ni ₃ S ₂ microspheres	-0.1-0.45	539 (982 F g ⁻¹)	2	44@12	1000@2	96.9	[4]
Ni ₃ S ₂ nanoparticles	0-0.4	364 (911 F g ⁻¹)	0.5	62@8	1000@0.5	90	[5]
rGO-Ni ₃ S ₂	0-0.48	631 (1315 F g ⁻¹)	1	80@10	1000@1	115	[6]
Ni ₃ S ₂ /CNT	0-0.45	461 (1024 F g ⁻¹)	0.8	46.24@25.6 (55@12.8)	1000@3.2	80	[7]
Ni ₃ S ₂ /CNF	0-0.45	431 (957 F g ⁻¹)	1	73.45@8	1000@4	83.5	[8]
3D graphene/Ni ₃ S ₂ NP	1.15-1.55	261 (652.5 F g ⁻¹)	1	77.5@4	2000@1	93	[9]
3D porous graphene/Ni ₃ S ₂	0-0.75	444.7 (593 F g ⁻¹)	0.5	33.7@50	5000@20	92.3	[10]
rGO-Ni ₃ S ₂	0-0.45	616 (1368 F g ⁻¹)	1	48@20	5000@5	92.7	[11]
Ni ₃ S ₂ /Ni	0-0.45	581.85 (1293 F g ⁻¹)	5 mA cm ⁻²	52.82@25 mA cm ⁻²	1000@25 mA cm ⁻²	69	[12]
Ni ₃ S ₂ nanorods	0-0.45	460 (1022.2 F g ⁻¹)	2	43.48@20	3000@2.4	93.1	[13]
Ni ₃ S ₂ nanowire	0-0.5	5.8 F cm ⁻²	5 mA cm ⁻²	50@30 mA cm ⁻²	5000@70 mA cm ⁻²	83.7	[14]
Ni ₃ S ₂ @Ni	0-0.5	1980 mF cm ⁻²	5 mA cm ⁻²	68.5@20 mA cm ⁻²	4000@20 mA cm ⁻²	100	[15]
Ni ₃ S ₂ @Ni	0-0.5	845 (1691 F g ⁻¹)	1.43	56.91@17.15	5000@10 mA cm ⁻²	106	[16]
Ni ₃ S ₂	0-0.55	3.42 F cm ⁻²	1 mA cm ⁻²	45.32@10 mA cm ⁻²	4250@7 mA cm ⁻²	102	[17]
Ni ₃ S ₂ @Ni ₃ N/Ni@VCN	-0.1-0.4	856.3	3	77.2@13	4000@13	83	This Work

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Chapter 5.2

Vertically Aligned Hybrid Ni_3S_2 /Carbon-Based Nanostructures for Advanced Li-Ion Battery Electrodes

Chapter 5.2 presents the electrochemical energy storage performance of plasma-designed vertically aligned nickel sulphide/carbon-based nanostructures as an advanced anode material for lithium-ion batteries. This study demonstrates a fast and facile two-step approach to fabricate a hybrid carbon-nickel sulphide-based electrode material. Here we deposited the vertical carbon nanotubes on a poly-crystalline nickel foil by a low-pressure radio-frequency plasma system. The nanotubes were terminated with a Ni nanoparticle faceted at the tip. Afterwards, a simple annealing in the presence of H_2S gas at low temperature was used for in-situ conversion of the outer layer of Ni to nickel sulphide. This two-step approach has yielded polycrystalline nickel sulphide nanostructures capping the tip of the nanotube, forming a “broccoli-like” morphology. Since the active material has grown directly on the current collector (nickel foil), we have used the hybrid structures directly as a binder-free electrode for lithium-ion battery. We found that the hybrid nanostructures largely contributed towards capacitive-type charge storage mechanism rather than diffusion-type charge storage during the electrochemical reaction. The unique “broccoli-like” structure and vertical morphology of the hybrid composites significantly increased both the active electrochemical area contacting the electrolyte material and the stability of the electrode. Additionally, direct contact between the nickel foil and nanotube structures reduced the contact resistance. The combined effect of all these factors resulted in outstanding electrochemical characteristics, and delivered one of the best lithium-storage performances among the nickel sulphide/carbon-based composites at the time of manuscript submission.

Regarding my contribution: I produced all plasma-enabled carbon nanostructures, fabricated nickel sulfide/carbon composites, contributed to the surface and chemical composition analysis and jointly wrote the paper with co-authors.

Vertically Aligned Hybrid Ni₃S₂/Carbon-Based Nanostructures for Advanced Li-Ion Battery Electrodes

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Abstract

Conversion-reaction induced charge storage mechanism of transition metal sulfides have received considerable interest in designing high-capacity electrodes for electrochemical energy storage devices. However, their low conductivity and structural degradation during cycling limit their applications as energy storage devices. A combination of different nickel sulfide phases tailored with carbon nanostructures is suggested to address these limitations. Herein, a facile, two-step approach is demonstrated for fabricating a hybrid electrode, consisting of trinickel disulfide (Ni₃S₂) formed on a metallic Ni nanoparticle supported by vertical carbon nanotubes (VCN) backbone in the form Ni₃S₂/Ni@VCN. Ni₃S₂/Ni@VCN electrodes tested as anode for lithium-ion batteries and the electrode featured with outstanding lithium-storage capabilities with a high reversible capacity (1113 mAh g⁻¹ after 100 cycles at 100 mA g⁻¹), excellent long-term cycling stability (770 mAh g⁻¹ after 500 cycles at 200 mA g⁻¹), and good rate capability. The resulting electrode performance is one among the best Li-ion storage capabilities in the Ni₃S₂-type anode materials described so far. A unique “broccoli-like” structure of polycrystalline Ni₃S₂ capped on conductive VCN backbone helps the interface storage process and boosts lithium storage performance.

Keywords: Ni₃S₂, Vertical carbon nanostructures, Hierarchical structures, Binder-free electrode, Lithium-ion batteries

Introduction

The need for high-performance energy storage devices is intensifying due to the exhaustion of non-renewable energy sources and the increase of ecological unbalances produced by the continuous consumption of fossil fuels. Enormous efforts are being made to develop environmentally friendly energy storage devices and fulfill societal energy needs beyond consumer electronics and electric vehicles [1–3]. Amid available battery technologies, lithium-ion batteries (LIBs) have high specific energy and power density, long cycle life, no memory effect, and high load capabilities [4–6]. However, these features have to be further modified for advanced applications [7,8].

The electrochemical performance of LIBs is mostly decisive by the capacity of the employed electrode material. Designing novel electrode materials is essential to address the challenges related to high energy/power density, safety, higher performance, and long lifespan. Ideal characteristics of such electrodes include high electrical conductivity, chemical inertness, mechanical resistance, large electrochemically active area, large surface area, and low cost. Graphite is a popular commercially available anode for LIBs. However, its low theoretical capacity (372 mAh g^{-1}) is still challenging to use for high energy density applications [9,10]. Thus, the performance of LIBs can be significantly improved by replacing graphite electrodes with advanced functional electrodes with improved specific capacity and steady electrochemical characteristics [11].

Endeavors to find alternative anode materials have resulted in several potential candidates with excellent electrochemical properties, i.e. carbon, transition metal oxides, and metal sulfides [12–16]. Among these, transition metal sulfides offer a larger capacity over traditional graphite anodes through the conversion and alloying reaction [17,18]. Moreover, transition metal sulfides (TMS) offer better reversibility and smaller volume/structure change during the electrochemical reaction, and higher conductivity than metal oxides, providing favorable conversion reaction kinetics and better performance [17]. Considering different TMSs, nickel sulfides (NiS , Ni_3S_4 , NiS_2 , Ni_3S_2 , and Ni_9S_8) have been reported as potential electrodes for future LIBs, considering their high theoretical capacity in the range of $446\text{--}870 \text{ mAh g}^{-1}$ [3,19–21]. Considering various nickel sulfide phases, heazlewoodite (Ni_3S_2) is the most promising variety for LIB applications due to its smaller volume change during lithium storage compared to other varieties. However, the poor electrical conductivity of such structures degrades cycling performance and rate capabilities [22,23]. To overcome these drawbacks, varieties of nickel sulfide electrodes have been combined with conductive carbon-related materials such as black carbon, graphite, nanotubes, nanofibers, and graphene to improve electrical conductivity and rate capability [24–28]. As a potential material to combine with nickel sulfide-based materials for energy storage applications, carbon nanotubes (CNTs) have revealed exceptional affinity due to its large surface area, excellent mechanical properties, and electrical conductivity.

In addition to the approaches mentioned above, the direct deposition of electroactive materials on current collectors has been developed as a new concept for fabricating binder-free electrodes. This method allows easy designing of electrode material with large electrochemical active area, high electrical conductivity, low contact resistance, and easy electrolyte penetration [21,29,30]. Direct growth of CNTs and other carbon-based structures and their processing on various substrates can be performed by chemical vapor deposition, electrochemical synthesis, mechanical exfoliation, sintering, arc-discharge, sintering, and plasma assisted vapor deposition (PECVD) [31–36]. Amid these techniques, PECVD techniques offer a rapid growth and processing of carbon nanostructures with different properties at low temperatures in controlled manner [32,33,37,38]. There are several works that have been reported regarding the plasma-assisted synthesis of individual, free-standing, vertical carbon nanostructures [31,39]. It is extensively recognized that the growth of vertical carbon nanotubes (VCN) by plasma is facilitated by the presence of a metal catalyst (e.g. nickel), which is critical to determine the height and diameter of such grown VCNs [40–42].

The growth of VCN depends on the diffusion of carbon in the nickel substrate, which is influenced by the substrate temperature and plasma parameters. Depending on the size of the nickel nanoparticle formed at the nucleation stage, the nanotube grow from the substrate with Ni nanoparticles either at the top or the bottom of VCN [33,43]. Thus, the growth of VCN with Ni nanoparticles on top, combined with the development of a facile approach to convert nickel catalyst particles to nickel sulfides with VCN backbones is highly promising and desirable. A hybrid composite of nickel sulfide and carbon nanostructures possess exceptional electrochemical properties compared to the individual performance of nickel sulfide and VCN, such as high discharge capacity, cycling stability, and rate capability, meeting the requirements for high energy density LIBs [44,45].

Herein, we demonstrate a fast and facile two-step approach to fabricate a hybrid carbon-nickel sulfide-based electrode material. The composite consists of trinickel disulfide (Ni₃S₂), metallic Ni nanoparticle and a VCN backbone with a structure of Ni₃S₂/Ni@VCN. The VCN structures are deposited on a polycrystalline nickel foil by a low-pressure radio-frequency plasma system and methane as the precursor gas. Due to the catalytic characteristics of nickel foil, the VCN structures deposited by tip-growth mechanism with a Ni nanoparticle faceted at the tip in the form Ni@VCN. A simple annealing technique at low-temperature in the presence of H₂S gas is used for *in-situ* conversion of the outer layer of Ni in Ni@VCN to Ni₃S₂, resulting in the formation of Ni₃S₂/Ni@VCN hybrid structure. This two-step approach yields polycrystalline Ni₃S₂ nanostructures capping the Ni@VCN, forming a “broccoli-like” morphology. We have further tested this hybrid hierarchical structure deposited on nickel foil as a binder-free electrode for LIBs. The fabricated binder-free Ni₃S₂/Ni@VCN electrode delivered outstanding lithium storage capabilities with a high discharge capacity (1113 mAh g⁻¹ after 100 cycles at 100 mA g⁻¹), long-term cycling stability (770 mAh g⁻¹ after 500 cycles at 200 mA g⁻¹), and good rate capability. The hybrid nanostructure is largely contributed towards capacitive charge storage mechanism than diffusion contribution. The unique “broccoli-like” structure and vertical morphology of the Ni₃S₂/Ni@VCN composites significantly increase both the active electrochemical area contacting the electrolyte material and the stability of the Ni₃S₂ nanostructure. Additionally, direct contact between the nickel foil and VCN structures reduce contact resistance. The combined effect of all these factors resulted in outstanding electrochemical characteristics. To the best of our knowledge, such a unique structure has never been reported as a binder-free anode material. The Ni₃S₂/Ni@VCN electrode exhibits one of the greatest Li-ion storage capabilities for LIBs up to now.

Experimental Section/Methods

Deposition of Carbon Nanostructures

Deposition of carbon nanostructures on nickel foil was performed using a low-pressure radio-frequency plasma system. The glass tube used as plasma system have a geometry of a cross-type, and the dimensions were: diameter of 8 cm and arm length of 40 cm. A Nagoya type III coil was used to couple the RF generator (13.56 MHz) with the system, which was coiled around the top arm of the reactor air-cooled externally. A schematic diagram of the plasma-deposition system is given in **Fig. S1a**. A 25 μ m thick nickel disc with a diameter of 14 mm was used as the substrate for deposition. Methane (CH₄) was used as the carbon source and fed to the system with a flow rate 20 sccm. The system was evacuated to 10 Pa prior to the experiment, and the total pressure was maintained as 30 Pa for the deposition. The substrate was directly placed on a stainless-steel substrate holder positioned at the plasma discharge region. Plasma was ignited with 800 W RF power. VCN structures were deposited for 4 min. The substrate holder was grounded during the deposition. The substrate temperature estimated as 750–800 °C due to plasma heating effects.

Sulfurization Process

Plasma-deposited carbon nanostructures were placed in a tube furnace (OTF-1200X-II, MTI Corp.) for the sulfur treatment. The quartz tube used was 80 cm long with 8 cm in diameter with a heating zone of 45 cm. The plasma deposited carbon structures on Ni foil were positioned in the heating zone of the furnace. The tube was vacuum sealed and evacuated to <1 Pa before sulfur treatment. Then, H_2S gas fed into the system and elevate the pressure to atmospheric conditions inside the tube. Sulfurization was carried out a temperature of 125°C and treated for 3 h. The H_2S gas was pumped out after the tube cools down to room temperature. A graphic presentation of the sulfurization chamber is presented in **Fig. S1b**.

Characterization Techniques

Surface morphologies of the as-grown carbon nanostructures and sulfur-treated nanostructures were analyzed by a field-emission scanning electron microscope (SEM, JSM 7600F, Jeol Inc.) operated at 5 kV. The cross-section analysis was done by dual-beam SEM - focused ion beam microscope (FIB-SEM, Helios NanoLab 650i, FEI). The initial cutting was done by 30 keV Ga^+ ions, while during final polishing the accelerating voltage was decreased to 5 keV to mitigate the re-deposition and damage of the sample. Before cutting, the surface of the sample was first magnetron-sputtered by thick Au layer (SCD-050, Balzers), followed by in-situ ion-beam deposited Pt protective layer, to protect the fine surface structures during cutting. Chemical and phase configuration of the structures were examined by a transmission electron microscope (TEM, JEM-2100, Jeol Inc.) operating at 200 kV. A slow-scan CCD camera (Orius SC1000, Gatan) was used to obtain micrographs. The crystalline properties of the samples were assessed by X-ray diffractometer (BRUKER AXS D4 ENDEAVOR), employing K-Alpha radiation operating at 30 mA, 40 kV. The spectra were recorded with a step size of $0.04^\circ 2\theta$ in characteristic range of 20 – $100^\circ 2\theta$. Structural features of the samples were evaluated by Raman spectra (NTEGRA confocal Raman spectrometer). The spectra recorded at four different points on samples before and after sulfur treatment using a blue laser (488 nm) with incident power ~ 5.8 mW and spot size of $50\ \mu\text{m}$ was used for the measurement. Surface composition and chemical bonding of nanostructures were analyzed by X-ray photoelectron spectroscopy (XPS PHI-TFA XPS spectrometer, Physical Electronics Inc.) equipped with an Al-monochromatic X-ray source at energy 1486.6 eV.

2.4. Electrochemical Measurements

The as-prepared carbon nanostructures and sulfur-treated nanostructures deposited on Ni foil were used as binder-free anodes. CR2032-type coin cells were assembled in an argon-filled glove box. The carbon-nickel sulfide electrode was assigned as anode, lithium-metal as the counter/reference electrode, and the separator was porous tri-layer Celgard PE/PP/PE (polyethylene/polypropylene/polyethylene) film. The composition of the used electrolyte solution was 1 M LiPF_6 dissolved in a blend of ethylene carbonate (EC) and diethyl carbonate (DEC, by 1:1 volume ratio). To test the electrochemical properties of the electrodes as battery anodes, galvanostatic cycling was recorded between 0.01 and 3.0 V versus Li/Li^+ with an electrochemical cyler (Battery Tester 05001, HTC) and the discharge capacity and cycling stability was measured. Further electrochemical properties were studied through cyclic voltammetry (CV) tested in a voltage range of 0.01–3.0 V by a multichannel electrochemical analyzer (COMPACTSTAT, IVIUM Technologies). Impedance properties of the electrode were analyzed using EIS measurements performed on a multichannel electrochemical analyzer (COMPACTSTAT, IVIUM Technologies) in the frequency range 0.01 Hz–100 kHz by fixing a bias voltage and AC amplitude of 5 mV.

Results and Discussion

Nanostructures and Morphology Characterization

A carbon nanostructure was successfully deposited on a metallic nickel foil using a plasma-assisted deposition technique, and sulfurization was achieved by a low-temperature annealing method. The substrate was uniformly covered with carbon after 4 min plasma deposition.

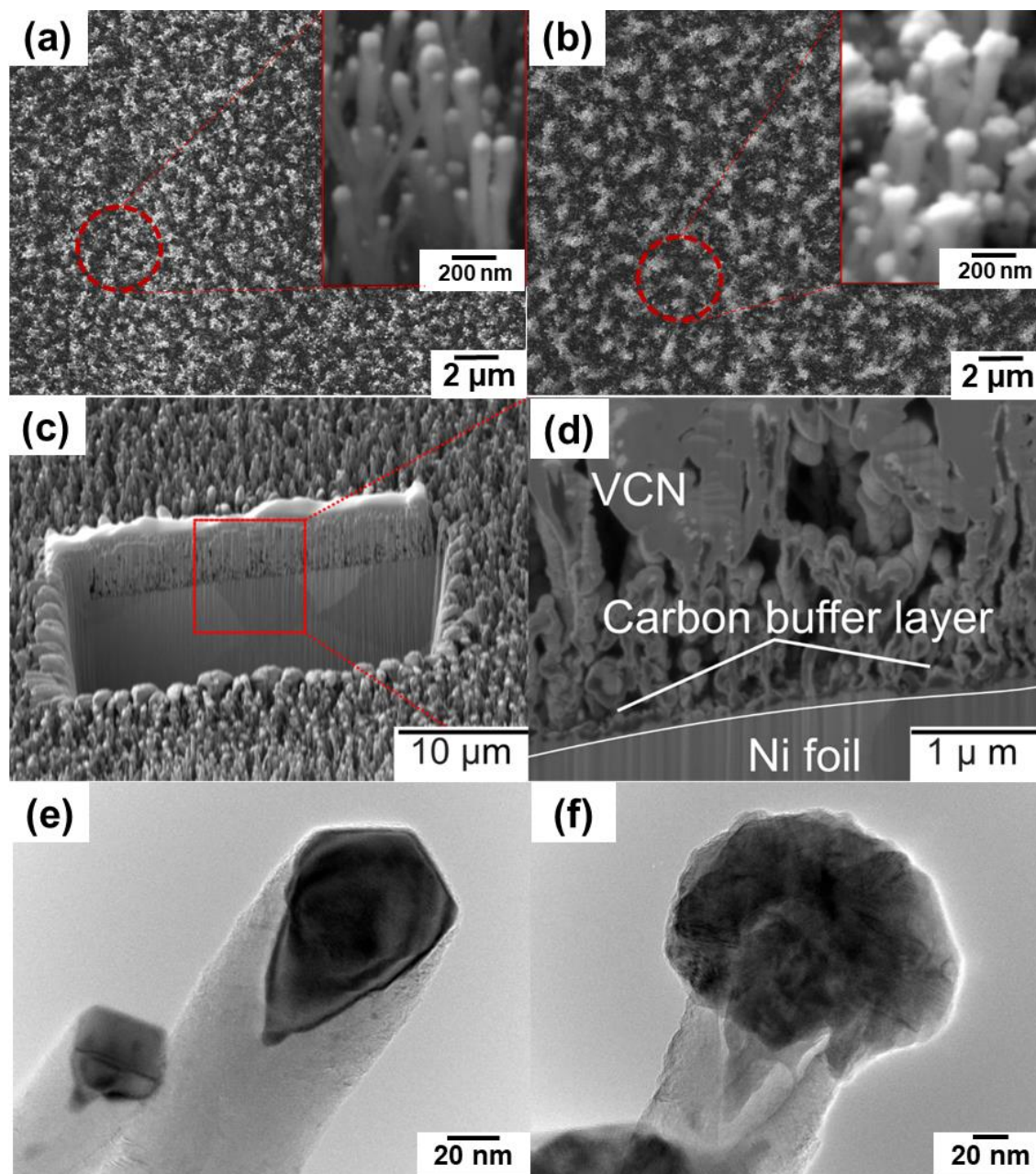


Fig. 1. Surface morphology of carbon structures before and after sulfur treatment. Top-view SEM micrographs of (a) plasma-deposited carbon structures and (b) carbon structures after sulfur treatment (tilted-view in the inset). (c, d) cross-sectional FIBSEM analysis of VCN to confirm the presence of carbon buffer layer. TEM micrograph of (e) as-grown Ni@VCN and (f) nickel sulfide@VCN.

After sulfur treatment, a slight yellow hue is visually observed on the surface, suggesting the presence of sulfur. The as-grown and sulfur-treated carbon structures were examined by SEM analysis to explore surface features. The homogeneously grown and closely packed tube-like structures of as-grown carbon nanostructures are presented in **Fig. 1a**. These nanotube-

like structures are vertically aligned on the nickel foil with a height of $\sim 1\ \mu\text{m}$, forming VCN. However, brighter spots at the tips of individual tubes suggest the presence of foreign elements on the structures. The change in surface morphology after sulfur treatment is presented in **Fig. 1b**. The difference observed in the morphology is the expansion of the VCN tip, while the length and orientation of the CNTs remain intact. In order to confirm that the substrate under the VCN structures is not sulfurized, the samples subjected to focused ion beam (FIB) cutting and carried out the cross-section analysis. As observed from the cross-section of the VCN samples (**Fig. 1c-d**), the substrate is protected with a carbon buffer layer, and thus the substrate is protected from sulfurization. The cross-section SEM image and corresponding EDX mapping of the sulfurized samples (**Fig. S2**) confirms that the sulfurization occurs only at the top of the carbon nanostructures. Therefore, to obtain further insights into the structure and morphology of the as-grown and sulfur-treated nanostructures, detailed TEM analysis was carried out, and the results are presented in **Fig. 1e, f**. The VCN is multi-walled having a diameter of 50 nm, and terminated by Ni nanoparticle (**Fig. 1e**) to form Ni@VCN structure. The Ni nanoparticle is single crystalline and faceted at the tip of the VCN backbone. This observation suggests that the tip-growth mechanism results in the formation of VCN structures due to the catalytic properties of nickel [40–42]. The TEM image of the sulfur-treated Ni@VCN is represented in **Fig. 1d**. The tip of the VCN is composed of polycrystalline nickel sulfide, forming a “broccoli-like” structure. In the core of the Ni-S, the remains of the original Ni nanocrystal can be observed. This indicates that the expansion at the tips of sulfur-treated Ni@VCN observed in **Fig. 1b** can be attributed to the formation of nickel sulfide on the Ni@VCN. Moreover, it is noticeable that the sulfur is attached only to the uncovered part of the metallic Ni nanoparticle and transforms into nickel sulfide in a controlled manner. Also, the sulfur neither distorts the orientation of structure, incorporated to the nanotube, nor deposits as an elemental S on the backbone. As there are numerous nickel sulfides in existence, and the properties of those vary with the crystallinity of the structure, proper phase determination of the formed nickel sulfides is critical for practical applications.

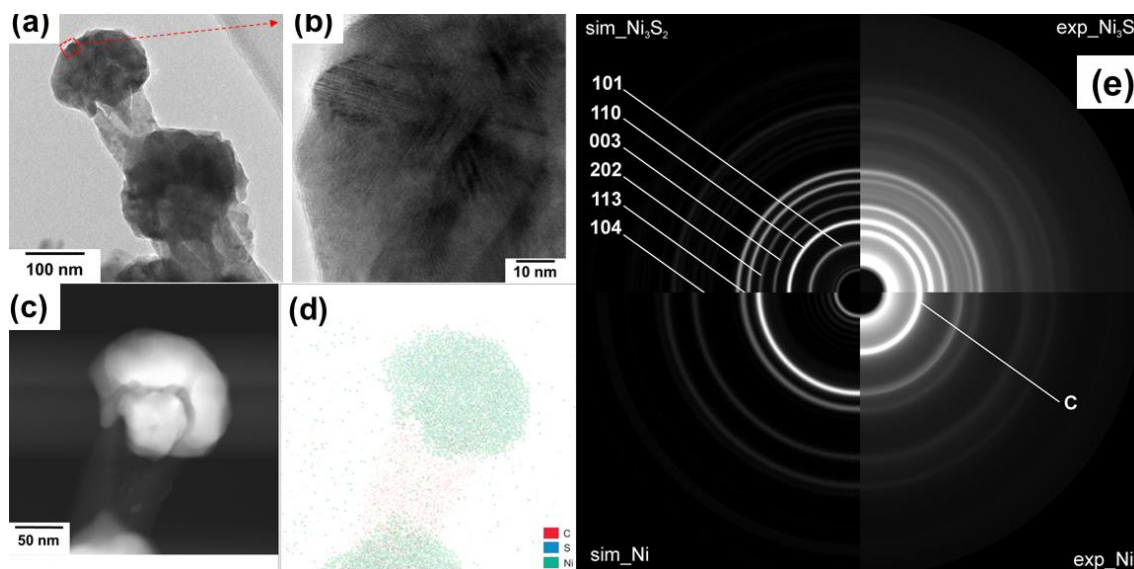


Fig. 2. TEM micrograph of (a, b) Ni-sulfide grown at the top of Ni crystal, supported by VCN. (c) HAADF-STEM and (d) EDS mapping of individual Ni_3S_2 -Ni-VCN structure. (e) Experimental SAED pattern for Ni_3S_2 , Ni, and VCN, and corresponding simulated patterns for Ni_3S_2 , Ni, and C.

Detailed TEM and high-resolution TEM (HR-TEM) studies on the hybrid sulfur-treated structures confirm nickel sulfide is formed on Ni crystal supported by the VCN, and that Ni is still preserved at the core. The synthesized nickel sulfide is polycrystalline (**Fig. 2a, b**), with individual crystallite sizes of 15–20 nm, firmly intergrown. Therefore, we have analyzed the

nanostructures using XRD to identify the crystal structure. Since the nanostructure is directly grown on the nickel foil, the fine structures deposited on nickel foil collected and concentrated on an adhesive polyamide tape to avoid the influence of nickel foil. As seen from the TEM images, the crystallites of the Ni₃S₂ phase are even smaller than Ni particles, with a maximum size up to 15-20 nm, most of the reflections are coincides with the nickel peaks, which could be from the remains of metallic Ni particle situated at the tip of VCN. The obtained results from XRD analysis is presented in the supplementary file, **Fig. S3**. Therefore, we have exploited the possibility of selected-area electron diffraction (SAED) method, which is especially suitable for phase identification of the nano-scaled materials. The diffractions obtained from the SAED pattern corresponding to heazlewoodite Ni₃S₂ (**Fig. 2e**) [3,46]. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) combined with energy-dispersive X-ray spectrometry (EDS) mapping (**Fig. 2c, d**) shows that there is no residual sulfur or sulfur contamination on the carbon structures besides Ni₃S₂ formed at the tip. Thus, the obtained “broccoli-type” structure is confirmed to be a hybrid structure of core-shell type functional Ni-Ni₃S₂ on top of vertically oriented carbon nanotube-like structures (Ni₃S₂/Ni@VCN).

Structural and Chemical Composition Characteristics

In order to gain a better understanding of the geometric structure and chemical composition of Ni@VCN and Ni₃S₂/Ni@VCN, the samples were studied with additional surface characterization techniques. The structural organization of Ni@VCN and Ni₃S₂/Ni@VCN were identified by Raman spectroscopy, and the results are presented in **Fig. 3a**. The as-grown Ni@VCN and Ni₃S₂/Ni@VCN structures exhibit features of graphene-like structures at 1358 (D band), 1583 (G band), and 2718 (2D band) cm⁻¹ [47]. The defect degree of carbon materials could be evaluated by the intensity ratio of D band to G band (I_D/I_G). The defect ratio calculated by I_D/I_G values and determined as 1.06 and 0.96 for Ni@VCN and Ni₃S₂/Ni@VCN, respectively. These values indicating the defect-rich characteristics of the VCN structure. Addition to carbon-related peaks, Ni₃S₂/Ni@VCN exhibits peaks at 221, 285, 330, 375 cm⁻¹, which infers that the Ni-S structure is Ni₃S₂, as reported in the literature [20,48].

Surface constituents and nanostructure chemical composition were investigated by XPS techniques in addition to structural organization characteristics. XPS survey spectra of the Ni@VCN and Ni₃S₂/Ni@VCN feature peaks of C, O, and Ni at around 284.6, 531.8, and 850.2 eV, respectively (**Fig. 3b**). Also, a peak observed at 162.2 eV in survey spectra of Ni₃S₂/Ni@VCN confirms the presence of sulfur. The presence of oxygen in both samples is due to air exposure to the plasma-activated reactive atoms and is not an intrinsic part of the structure [34,49]. **Fig. 3c** presents high-resolution C 1s spectra of Ni@VCN and Ni₃S₂/Ni@VCN. There are no obvious changes observed in the deconvoluted spectra before and after sulfur treatment. The main peaks are located at 284.6, 285.5, 286.7, 288.2, and 290.5 eV. They can be attributed to the sp² C-C bond (graphitic-C), sp³-bonded carbon atoms, C-O groups, C=O groups, and the π-π* shake-up satellite, respectively [34]. The peaks observed in the Ni 2p_{3/2} spectrum of Ni@VCN at 853.9, 855.6, and 861.3 eV can be ascribed to Ni³⁺, Ni²⁺, and the satellite peak (**Fig. 3d**) [50].

Similarly, three peaks are observed in the deconvoluted Ni 2p_{3/2} spectrum of Ni₃S₂/Ni@VCN (**Fig. 3e**), ascribed to Ni³⁺ (853.5 eV), Ni²⁺ (856.1 eV), and satellite (861.0 eV). The S 2p spectrum of Ni₃S₂/Ni@VCN was deconvoluted into a spin-orbital doublet, which are positioned at 161.7 and 163.0 eV. A satellite peak is also observed at 169.0 eV (**Fig. 3f**). Such doublets with peaks asymmetrically expanded to a higher binding energy region are characteristic of Ni₃S₂ [51,52]. Comprehensive details on the position and composition ratio (area %) of the deconvoluted peaks of C 1s and Ni 2p are summarized in Tables S1 and S2. All findings confirm that sulfurization of Ni@VCN at low temperature resulted in the formation of a unique Ni₃S₂/Ni@VCN hybrid structure.

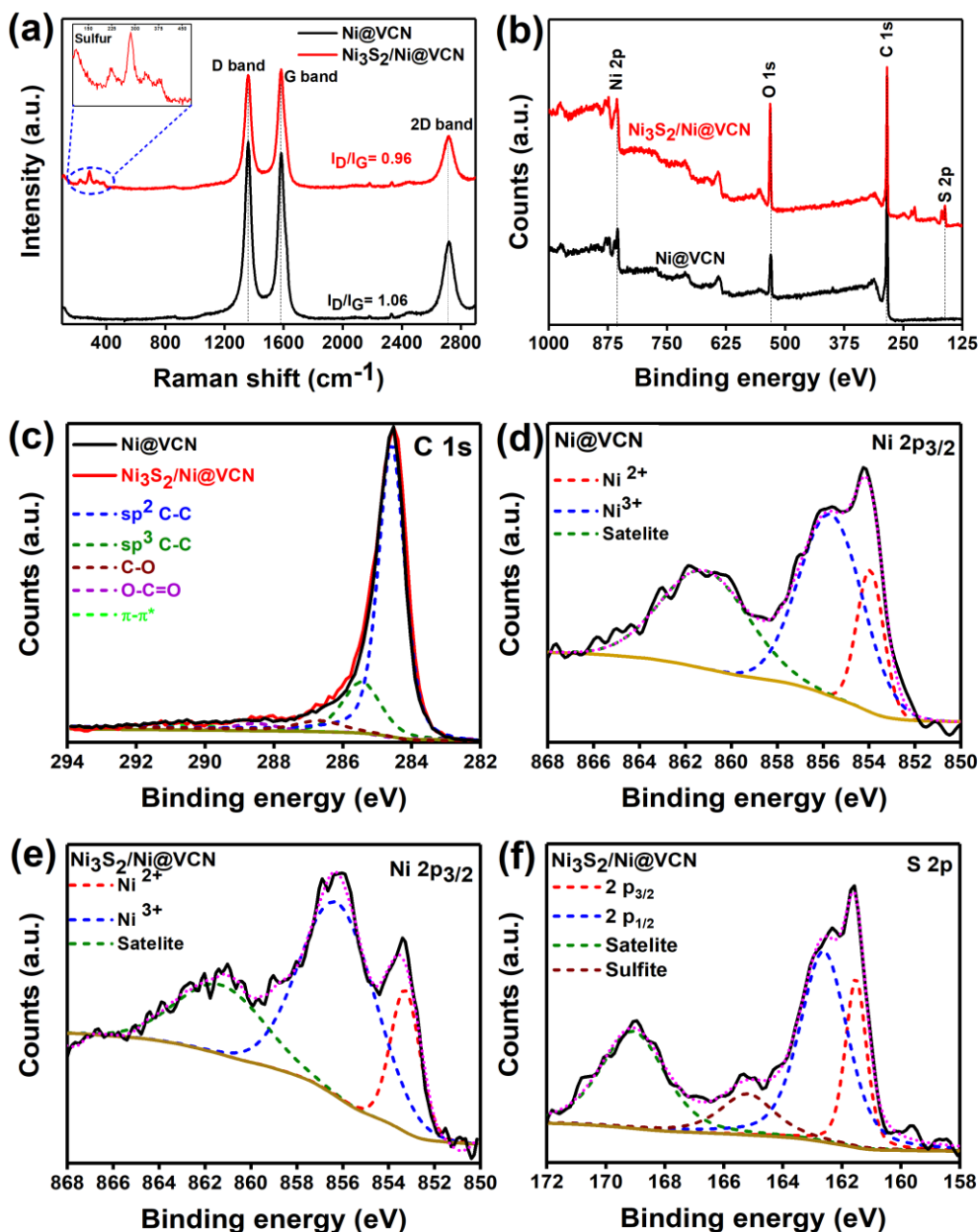


Fig. 3. Structural and chemical composition analysis of Ni@VCN and Ni₃S₂/Ni@VCN. (a) Raman spectra, (b) XPS survey spectra, high-resolution (c) C 1s and (d) Ni 2p_{3/2} of Ni@VCN, and (e) Ni 2p_{3/2} and (f) S 2p spectra of Ni₃S₂/Ni@VCN.

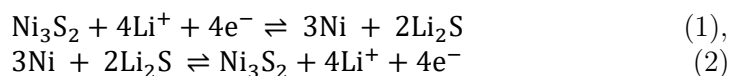
Electrochemical Characterization

The presence of carbonaceous materials in nickel sulfide-based active materials can increase conductivity, and simplify the electrolyte diffusion and charge transfer during the electrochemical performance. Thus, we have tested Ni@VCN and Ni₃S₂/Ni@VCN as electrode materials for LIBs. The prepared nanostructures were used as binder-free anodes for LIB applications, and electrochemical performance was investigated. The lithium storage performance of the Ni@VCN binder-free electrode was investigated by its galvanostatic discharge/charge profile in the voltage range 0.01–3.0 V and at a current density 100 mA g⁻¹, as presented in **Fig. 4a, b**. The electrode delivered an initial discharge capacity of 222 mAh g⁻¹ and a corresponding charging capacity of 168 mAh g⁻¹ with an initial coulombic efficiency of 75.8%. Later, the discharge capacity increased to 240 mAh g⁻¹ after 100 cycles and preserved a coulombic efficiency of above 96% during cycling. This could be ascribed to

the defect-rich carbon-nickel features, which could enhance the pseudocapacitive characteristics during the electrochemical reaction and increase the capacity with cycles. However, the identified lithium storage of Ni@VCN electrode was comparatively low, considering other carbon-based electrodes already reported [53].

The lithium storage performance of the Ni₃S₂/Ni@VCN binder-free anode for LIBs is presented in **Fig. 4 c–e**. The galvanostatic discharge/charge profile performed in the voltage range 0.01–3.0 V and at a current density 100 mA g^{−1} (**Fig. 4c**). The initial specific discharge capacity delivered is 657 mAh g^{−1} with a corresponding specific charge capacity of 610 mAh g^{−1}, giving an initial coulombic efficiency of 92.8%. Notably, the initial coulombic efficiency of Ni₃S₂/Ni@VCN is higher than that of Ni@VCN, which can be ascribed to the lower contact of Li ions to the irreversible sites of carbon in Ni₃S₂/Ni@VCN upon the first charge/discharge cycle. In the discharge curve, two potential plateaus are observed at 1.4 V and 1.8 V, and during the charging process the plateaus appear at 1.9 V and 2.2 V. To elucidate the electrochemical characteristics of the electrode, differential capacity versus voltage analysis was investigated between 0.01 and 3.0 V (**Fig. S4a**).

Two reduction peaks is observed in the first scan at 1.4 and 1.8 V that could be ascribed to the conversion-based reactions of Ni₃S₂ induced by the lithium-ion insertion, which could have accompanied by the electrolyte decomposition and solid electrolyte interface (SEI) formation. In the oxidation region, one sharp peak at 1.88 V, accompanied by a narrow peak at 2.22 V, is observed and ascribed to lithium-ion extraction. The well-overlapped peaks after the cell cycles are confirming the remarkable reversibility of the Ni₃S₂/Ni@VCN electrode. Also, the voltage plateaus noticed in the charge/discharge profiles corresponds to the oxidation and reduction peaks observed in the differential capacity versus voltage curve. Based on these findings, the overall electrochemical reaction can be written as



Furthermore, the Ni₃S₂/Ni@VCN electrode delivered a higher capacity, which increases with cell cycling (**Fig. 4d**). The electrode delivered an ultra-high reversible capacity of 1113 mAh g^{−1} at a current density of 100 mA g^{−1} after 100 cycles, which leave behind most of the Ni₃S₂-based functional electrodes described in the literature so far [20,21,54–56]. After the initial cycles, the coulombic efficiency of the Ni₃S₂/Ni@VCN electrode was maintained at nearly 100%, which highlights the excellent reversibility of the cell. A comparison of performance for various Ni₃S₂-based electrodes described in the literature is given in Table S3. The longstanding cycling stability of the Ni₃S₂/Ni@VCN anode is displayed in **Fig. 4e**. A reversible capacity of 450 mAh g^{−1} at 200 mA g^{−1} is obtained after the first cycle, which increased to 730 mAh g^{−1} after 220 cycles. After 500 cycles, the reversible capacity is maintained as 770 mAh g^{−1}. This lithium storage performance is believed to be one of the best in Ni₃S₂-based binder-free electrodes. Such outstanding electrochemical performance can be ascribed to the novel “broccoli-like” morphology of the active material and the synergistic effect of Ni₃S₂/Ni and VCN. Based on all the observations and findings, increased capacity and stability could be ascribed to the following aspects [3,53]: (1) combined electrochemical contributions from VCN and the polycrystalline Ni₃S₂ phase enhances lithium storage activity; (2) the nickel-sulfide crystal interface and the structural defects can enhance the charge storage capability (**Fig. S5**); (3) defects provide more space for the intercalation reaction and ensure sufficient space within and between each crystallite to balance the stresses caused by volume expansion during the electrochemical reaction and protect the structural integrity; and (4) direct contacts between Ni₃S₂/Ni to VCN and VCN to Ni foil (current collector) ensures that each of the VCN maintains electrical continuity to the current collector and takes part in the improved cycling stability.

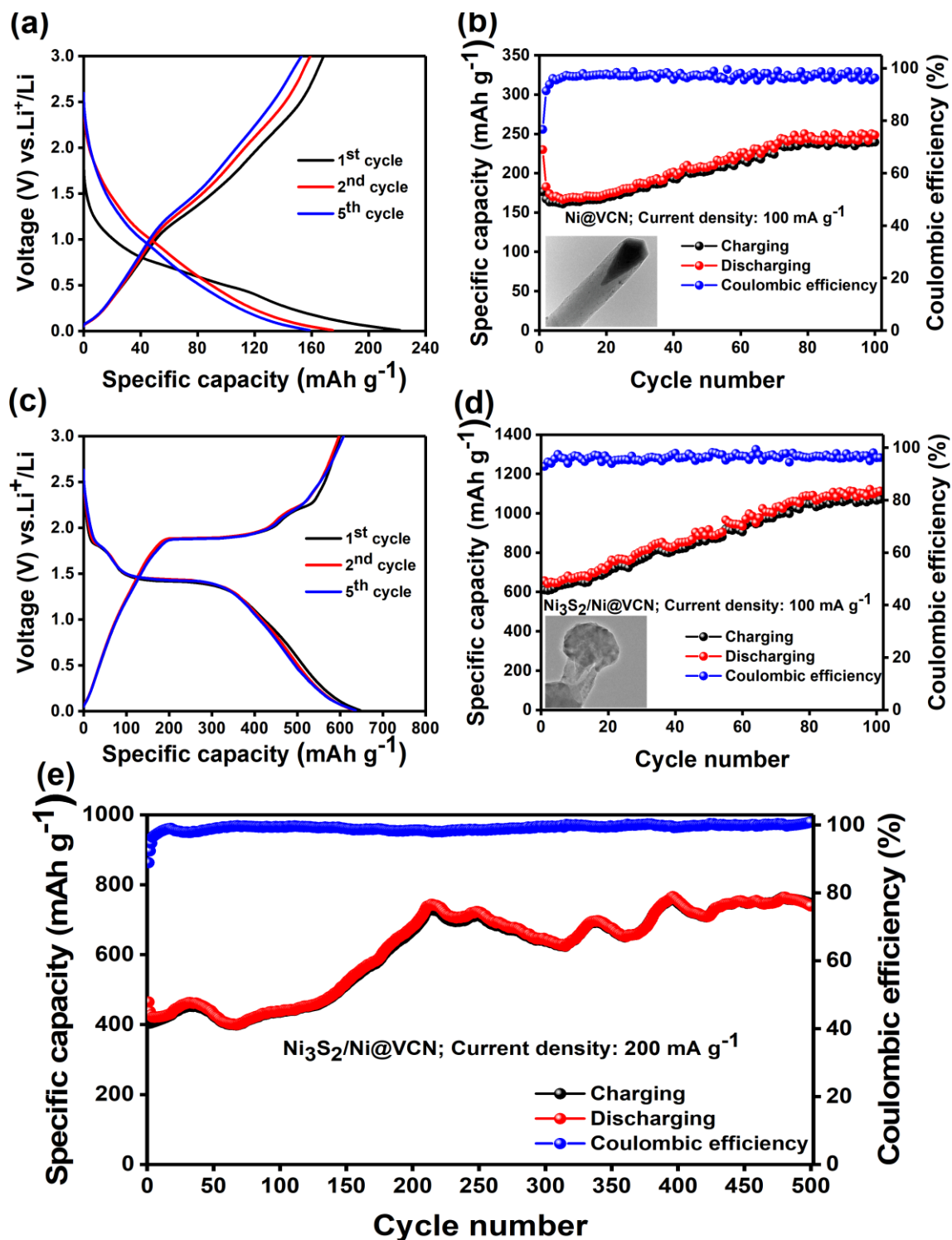


Figure 4. Electrochemical performance of Ni@VCN electrodes: (a) Discharge-charge profile, and (b) cycling performance at a current density 100 mA g⁻¹. Electrochemical performance of Ni₃S₂/Ni@VCN electrode: (c) discharge-charge profile and (d) cycling performance at a current density 100 mA g⁻¹, and (e) long-term cycling performance at a current density 200 mA g⁻¹.

Besides ultra-high capacity and longstanding stability, the Ni₃S₂/Ni@VCN anode displays a good rate capability. Charge-discharge rates were measured at current densities of 50, 100,

200, 400, 800, 1600, and 3200 mA g⁻¹. The electrode delivered specific discharge capacities of 706, 656, 631, 570, 489, 404, and 293 mAh g⁻¹, respectively, at these current densities (**Fig. 5a**). At lower current densities, Li-ion diffusion is more favorable; thus, the specific capacity is higher. The diffusion of Li ions is hindered and mainly occurs at the surfaces at higher current densities, and the specific capacity of the electrode decreases [57]. However, the specific capacity does not fade drastically during cycling at different current densities (**Fig. S4b**), which confirms the excellent structural stability and reversibility of the electrode.

To further elucidate the charge storage mechanism and electrochemical kinetics of the Ni₃S₂/Ni@VCN anode, cyclic voltammetry (CV) analysis was conducted. CV scans were performed at rates from 0.2 to 1.0 mV s⁻¹, and presented in **Fig. 5b**. The CV curves exhibit a strong reduction peak at 1.2 V and a distinct oxidation peak at 2.0 V, related to the intercalation and conversion of Ni₃S₂ with lithium ions. The charge storage mechanism in an electrode can be ascribed to the combination of a diffusion component and capacitive component. The diffusion component is because of the diffusion and intercalation of Li ions to the electrode material. The capacitive component is related to the non-faradaic double layer effect and faradaic charge transfer. Monolayer adsorption of ions can induce faradaic charge transfer at an electrode surface by the surface atoms (pseudocapacitance) [58]. The peak current in a scan, and corresponding scan rate in sweep voltammetry is following a relation according to Power-law, and the dominant component in charge storage can be assessed by the following equation [3,59]:

$$i = av^b \quad (3),$$

here i is assigned to current density, a is constant, and the scan rate is assigned as v . Charge storage kinetics in the electrode can be explained by the power coefficient b , which can be evaluated by plotting $\log(i)$ vs. $\log(v)$. The value of b approaches 0.5, indicating the ionic diffusion dominated electrochemical reaction. On the other hand, b value approaching 1 would indicate that the capacitive component dominates the electrochemical reaction [60]. The fitted values of b for anode and cathode reactions are 0.71 and 0.84 (**Fig. 5c**), respectively, indicating a mixed electrochemical reaction of the capacitive and diffusion process. The high specific capacity of the electrode is ascribed to the diffusion of Li ions by the intercalation, and a subsequent conversion reaction takes place in the Ni₃S₂/Ni@VCN electrodes. The capacitive component facilitates fast charge transfer in the electrode and improves the stability of the cycling performance. The capacitive and diffusion components are quantified using the relation [61,62]:

$$i_{(v)} = k_1v + k_2v^{1/2} \quad (4),$$

k_1 and k_2 are constants at a fixed value of voltage, k_1v and $k_2v^{1/2}$ correspond to the charge contributions from the capacitive-type and diffusion-type components and $i_{(v)}$ is the peak current of the scan rate. k_1 is determined as the slope of the linear fitting of $i_{(v)}/v^{1/2}$ vs $v^{1/2}$ plot and therefore the capacitive and diffusion contributions are able to calculate using equation (4), as previously demonstrated [3,63,64]. k_1 is determined as 0.78 from the linear fitting of $i_{(v)}/v^{1/2}$ vs $v^{1/2}$ curve (**Fig. 5d**). The capacitive and diffusion contributions at various scan rates are calculated using equation (5) and presented in **Fig. 5e**. The contribution from capacitive component is calculated as 55.7% at scan rate 0.2 mV s⁻¹, which steadily increases to 70.1% with scan rate approaches to 1 mV s⁻¹; confirming that during the electrochemical process, half of the charge storage contribution comes from the capacitive component. This can be ascribed to the polycrystalline Ni₃S₂ nanostructure's large electrochemical active area, and the direct contact between the VCN and the current collector. The larger contribution from the capacitive component at higher scan rates contributes to the stable cycling process and good rate capability

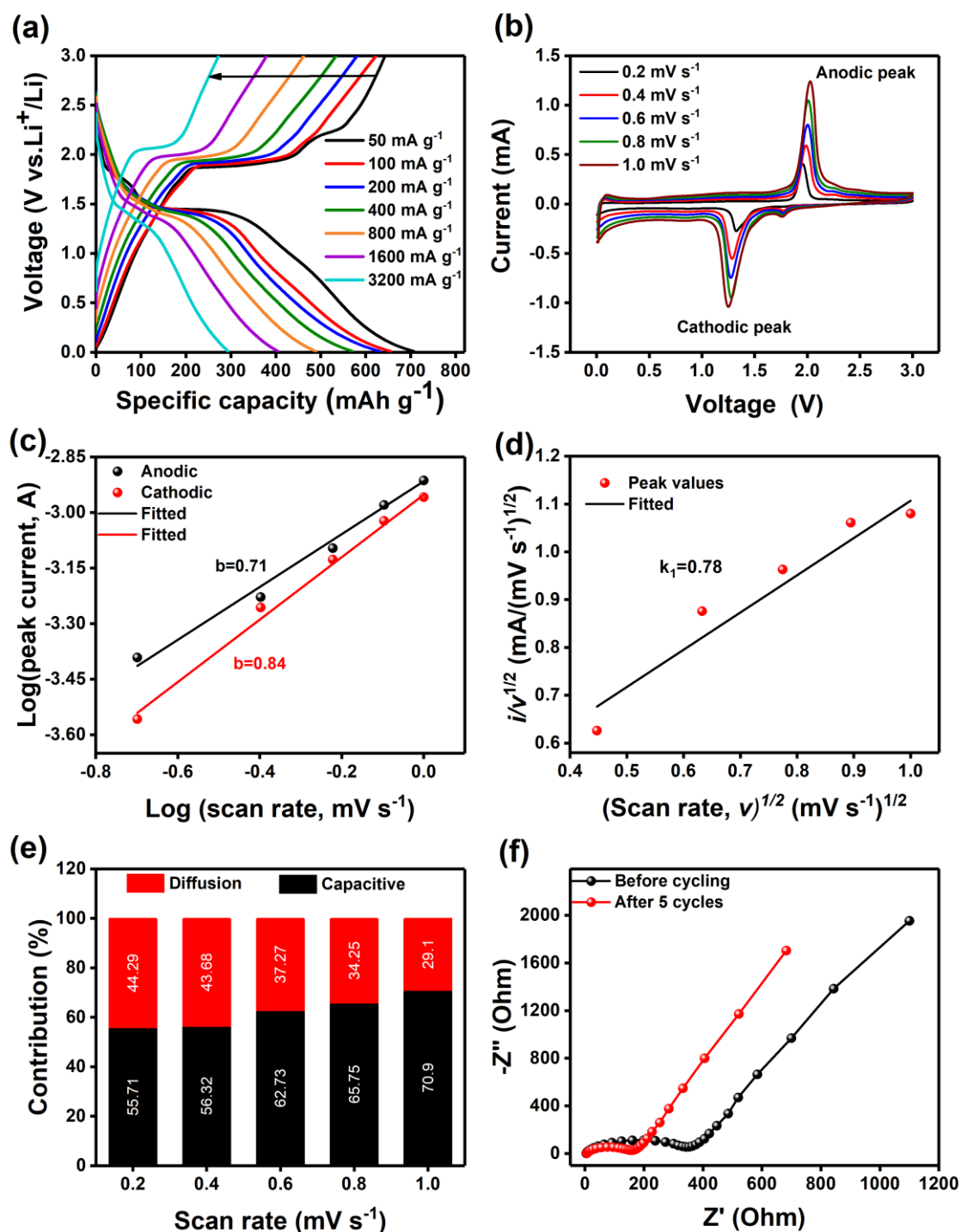


Fig. 5. (a) Galvanostatic discharge-charge profile of the $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrode at different current densities, (b) CV curve of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ at a scan rate of 0.2-1 mV s^{-1} , (c) $\log(i)$ vs. $\log(v)$ plots, (d) $i/v^{1/2}$ vs. $v^{1/2}$ plot, (e) charge contributions from capacitive and diffusion process during electrochemical reaction, and (f) impedance spectra of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ before cycling and after five cycles at a current density 100 mA g^{-1} .

To confirm the enhanced electrochemical characteristics of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ anodes, electrochemical impedance spectroscopy (EIS) tests were performed. EIS plots before cycling and after five cycles. EIS was carried on the electrode cycled at a current density of 100 mA g^{-1} and the results are presented in **Fig. 5f**. EIS spectra at high frequencies show a semicircle

corresponding to charge transfer resistance (R_{ct}), and a linear behavior observed from the lower-frequency region called Warburg impedance. The R_{ct} value of the electrode before the galvanostatic cycling test is observed to be 359 Ω , and that of the cycled electrode is 159 Ω . A comparison of impedance spectra before and after cycling suggests a reduction in the diameter of the semicircle for the cycled electrode, indicating higher conductivity and better electrolyte-electrode contact by improving the wettability of the cycled electrode. This could facilitate the easy diffusion of Li ions through the electrode material, thus improving electrochemical performance.

Characterization of Cycled Samples

To further understand the changes in the electrode after the electrochemical reaction, the electrode was re-investigated by *ex-situ* TEM after the cycling experiment. TEM micrographs of the electrode after the first cycle at a current density of 100 mA g⁻¹ are presented in **Fig. 6a, b** and show that the structure and morphology of “broccoli-type” Ni₃S₂/Ni@VCN composite after cycling are preserved. The SAED ring pattern recorded over the larger crystal agglomeration corresponds to pure Ni₃S₂ and graphene, without any other crystalline phases (**Fig. 6c**). This indicates no structural or phase modification of the initial materials, and it confirms the excellent electrochemical reversibility of the electrode. In addition, we have examined the change in the interplanar distance of Ni₃S₂ after the first cycle and it is evident that the interplanar distance have an increase (~ 10%) compared to the reference values. This effect could improve the intercalation capabilities of the Ni₃S₂ material and further improve the capacity of the electrode material during the cycling. Detailed comparison of the interplanar distances of the Ni₃S₂ structures is presented in **Fig. S6** and **Table S4**. The chemical composition of the electrode was again investigated by XPS analysis after 100 cycles cycled at a current density 100 mA g⁻¹. Peaks observed in the XPS survey spectrum confirm the presence of C, Ni, S, O, Li, P, and F (**Fig. S7a**). The presence of Li, P, and F in the electrode indicates the excellent interaction of electrode and electrolyte during the reaction. High-resolution spectra of C 1s, Ni 2p_{3/2}, and S 2p are presented in **Fig. S7b–d** to examine the bonding configuration of the elements after cycling. TEM and XPS analyses of the cycled electrodes confirm the nanostructure’s excellent reversibility without forming any new compounds during the electrochemical reaction. All the aforementioned results suggest that hybrid, hierarchal “broccoli-like” structured Ni₃S₂/Ni@VCN binder-free electrodes exhibit outstanding lithium storage performance with an ultra-high specific capacity, outstanding long-term stability, and good rate capability.

The unique structural feature of polycrystalline Ni₃S₂ supported by conductive CNTs and direct contact of VCN to the current collector in the electrodes enhance ionic and electronic conductivity, fast charge transfers, and structural stability. A higher capacitive contribution during the electrochemical charge-discharge reaction helps to improve long-standing cycling stability and rate capability. Additionally, the defect-rich VCN support provides additional reactive sites for lithium storage and enhances the total electrochemical performance. Based on these findings, we can conclude a possible mechanism of lithium insertion during the electrochemical reaction. As displayed in **Fig. 6d**, the direct contact of the current collector to Ni₃S₂ through VCN support enhances electronic and ionic conductivity. Polycrystalline Ni₃S₂ provides a platform that can be easily penetrated by the electrolyte. Moreover, lithium ions can interact with the defect sites in the VCN support and contribute to lithium storage. All these factors help to shorten the diffusion pathways for lithium ions and contribute to enhancing the lithium storage performance. A comparison between the specific capacity performances of Ni₃S₂-based binder-free electrodes reported in the literature with this unique “broccoli-like” Ni₃S₂/Ni@VCN electrode is presented in **Fig. 6e**. The figure shows that the performance of the Ni₃S₂/Ni@VCN electrode is one of the best in Ni₃S₂-based binder-free electrodes.

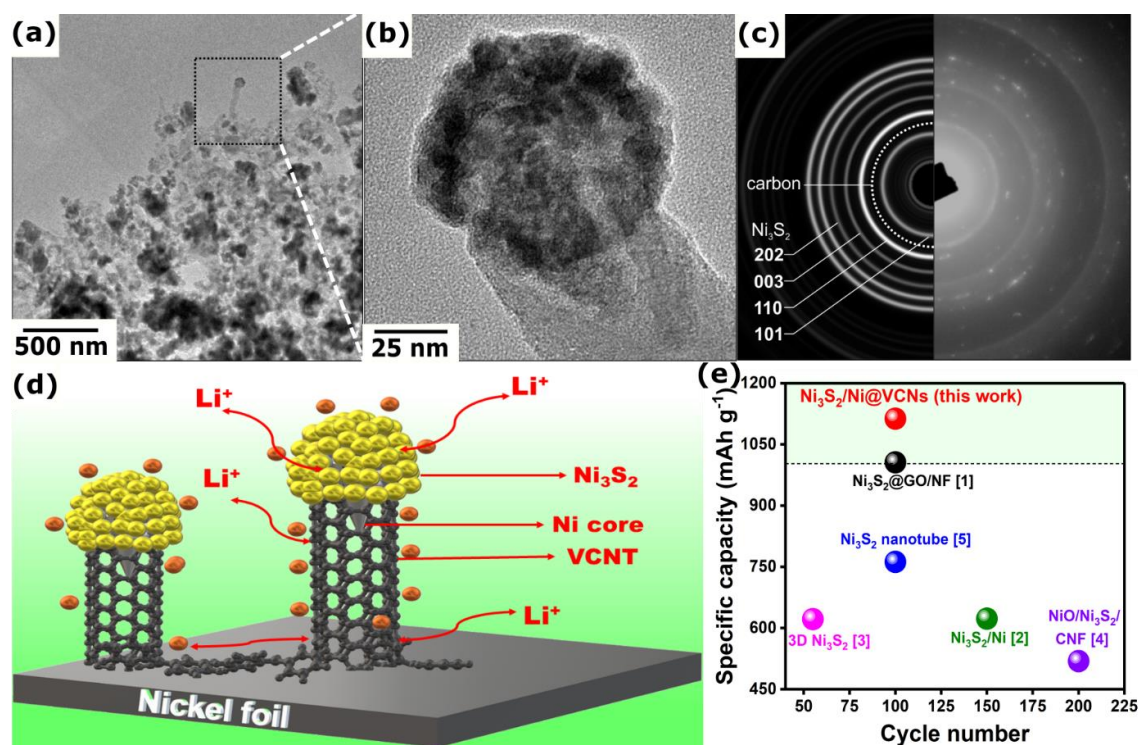


Fig. 6. (a, b) Overview and high-resolution TEM micrograph of Ni₃S₂/Ni@VCN electrode after the first cycle at 100 mA g⁻¹. (c) Experimental and simulated SAED pattern for Ni₃S₂, Ni, and C of Ni₃S₂/Ni@VCN electrode after the first cycle at 100 mA g⁻¹. (d) Illustration of possible lithium-ion pathways on Ni₃S₂/Ni@VCN electrode during electrochemical reaction. (e) Comparison of specific capacities reported for Ni₃S₂-based binder-free electrodes in the literature with this work (references correspond to the data presented in Table S3).

Conclusion

In summary, we fabricated a unique Ni₃S₂/Ni@VCN hybrid nanostructure by a facile two-step synthesis approach. In the first step, Ni nanoparticle terminated vertically aligned carbon nanotube structures (Ni@VCN) were deposited on a nickel foil using a PECVD system. Later, low-temperature thermal annealing in the presence of H₂S gas was used for fabricating the hybrid Ni₃S₂/Ni@VCN structure. The created sulfide structure had a unique “broccoli-like” hierarchical morphology with polycrystalline Ni₃S₂ phase, which is confirmed by TEM, SAED, SEM, XPS, and Raman analysis.

The synthesized hybrid Ni₃S₂/Ni@VCN structured material was tested as a binder-free anode material for LIBs. As an anode for LIBs, Ni₃S₂/Ni@VCN electrodes exhibit a high reversible capacity of 1113 mAh g⁻¹ after 100 cycles at 100 mA g⁻¹ and long-term cycling stability with a reversible capacity of 770 mAh g⁻¹ after 500 cycles at 200 mA g⁻¹, which is one of the best Li storage capabilities obtained by Ni₃S₂-based electrodes, up to now. A combined effect from the defect-rich VCN backbone structure and polycrystalline “broccoli-like” nickel sulfide, direct contact between the current collector and active material, and the large surface area of the active Ni₃S₂/Ni region, enhance the capacitive type of electrochemical charging/discharging and provides outstanding Li storage performance.

The electrode fabrication technique employed is one of the fastest approaches to the fabrication of high performing Ni₃S₂-based binder-free electrodes. Since this was a scientific investigation of the synthesis technique, there are still plenty of engineering optimization options to explore, providing a path towards the next-generation energy storage devices of the future.

CRedit Authorship Contribution Statement

N. M. Santhosh: Conceptualization, Methodology, Formal analysis, Writing original draft, Validation. **N. Shaji:** Data curation, Formal analysis, Writing. **P. Stražar:** Methodology, Formal analysis. **J. Zavašnik:** Formal analysis, Writing-review & editing. **G. Filipič:** Formal analysis, Writing-review & editing. **M. Nanthagopal:** Formal analysis. **C. W. Ho:** Formal analysis. **C.W. Lee:** Supervision, Resources, Validation, Writing - review and editing. **U. Cvelbar:** Conceptualization, Supervision, Validation, Resources, Writing-review & editing.

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Supplementary Information Supplementary data to this article can be found online.

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Supporting Information

Vertically Aligned Hybrid Ni_3S_2 /Carbon-Based Nanostructures for Advanced Li-Ion Battery Electrodes

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Synthesis of vertical carbon nanostructures (VCN) was carried out in a radio-frequency inductively coupled plasma-enhanced chemical vapor deposition system at low pressure in a cross-type plasma device, as shown in **Fig. S1 (a)**. Growth of nickel sulfide on the VCN structures was achieved by a thermal treatment system in the presence of H_2S gas at 125 °C, as described in **Fig. S1(b)**.

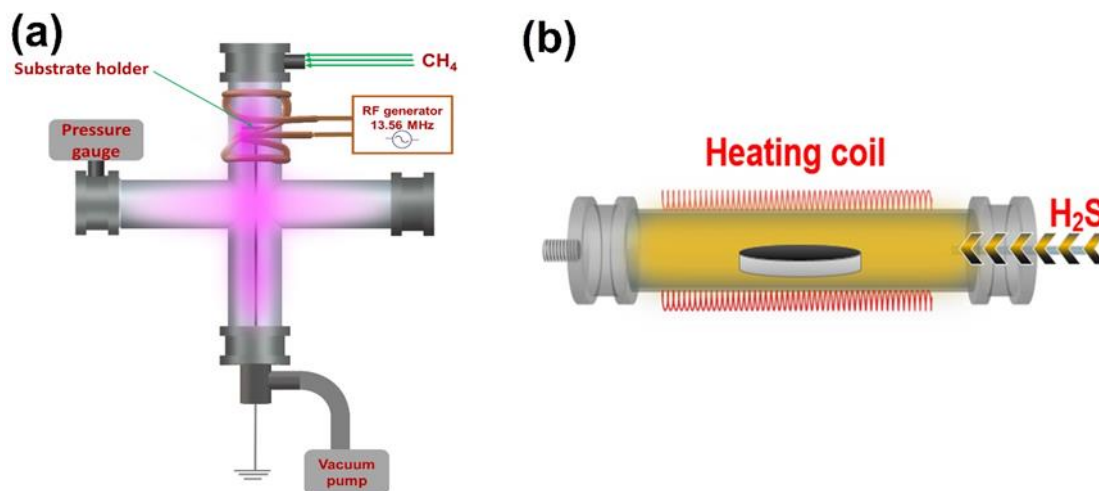


Fig. S1. Schematics of the experimental setup for (a) plasma-enhanced synthesis of carbon nanostructures on Ni foil and (b) synthesis of nickel sulfides on carbon nanostructures by thermal annealing in the presence of H_2S .

The presence of the carbon buffer layer is visible from the cross-section image of VCN (**Fig1 (c, d)**) and sulfurized VCN samples (**Fig. S2**). Therefore, the diffusion of the sulphur to the nickel substrate is prevented by this thin carbon layer, and the nickel substrate is not being sulfurized during the sulfurization process. To confirm and validate our results, we have carried out the cross-section analysis of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ and presented it in Fig. S2. The existence of the carbon buffer layer is still visible in the cross-section image indicates that the nickel substrate is protected from the sulfurization process. The EDS elemental mapping and spatial distribution of the samples are confirming that the nickel sulphide is formed only on

the nickel situated at the VCN tip. Thus, the chances for the sulfurization of nickel substrate is limited according to our synthesis technique.

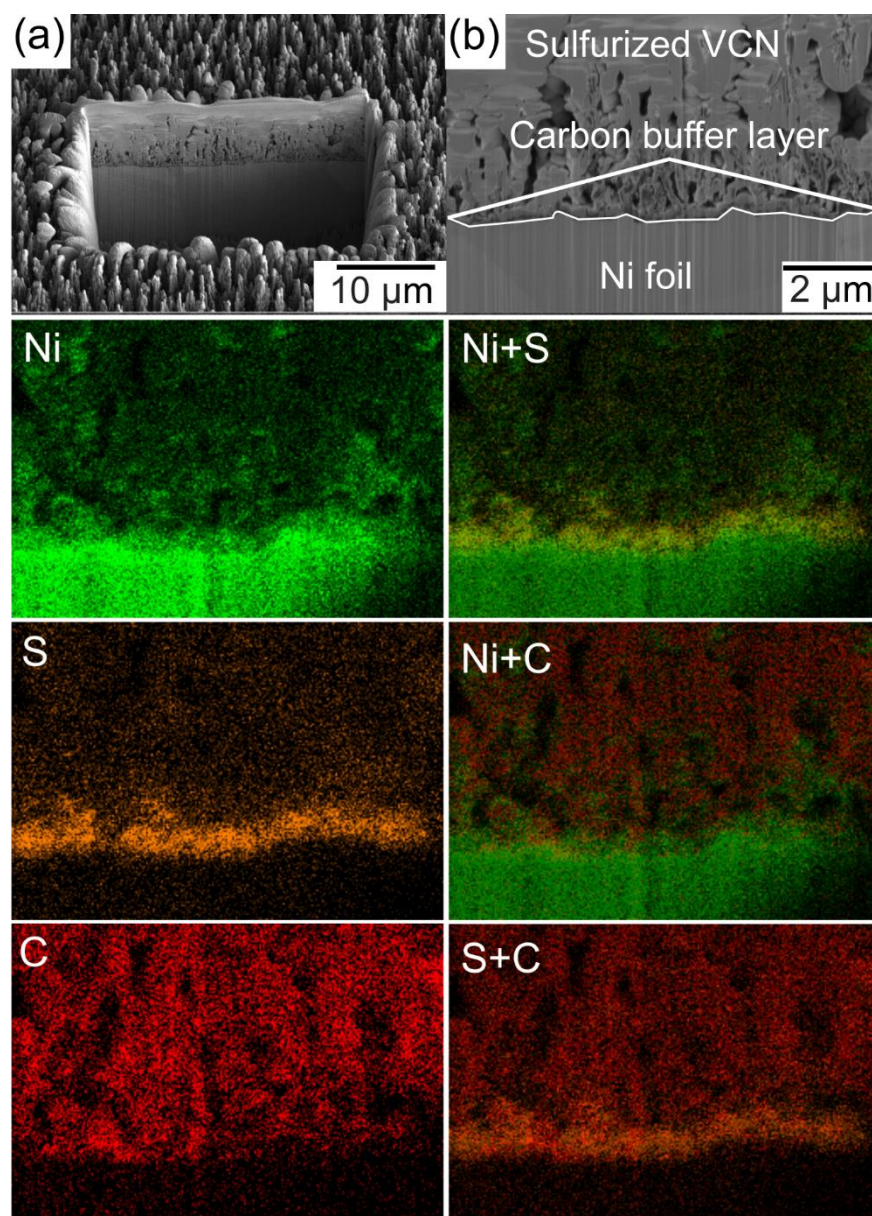


Fig.S2 (a, b). cross-section FIB-SEM image of Ni₃S₂/Ni@VCN to confirm the presence of carbon buffer layer between VCN and nickel substrate and the corresponding EDS elemental mapping and their spatial distribution in the sample.

All of the XRD patterns from Ni, and Ni₃S₂ experiments show a broad and diffused peak at about 20°2θ, originating from poorly-crystalline carbon species of nano-sizes. It is noted based on our TEM observations that all of the Ni nanoparticles are preferentially oriented in <001>, which will also reflect on the XRD pattern – the strongest (111) peak will be suppressed, and (002) peak becomes more pronounced, an effect we can observe on the **Fig. S3a**, and in detail in Fig. S3. Due to the high background, strong signal from carbon species, and low intensity of the Ni-phases reflection peaks, a small (111) peak can be observed at ~44° 2θ, and an additional (200) peak detected at ~52° 2θ, coinciding with the reported data for pure Ni, hence the metallic Ni at the tip of carbon nanostructures can be confirmed.

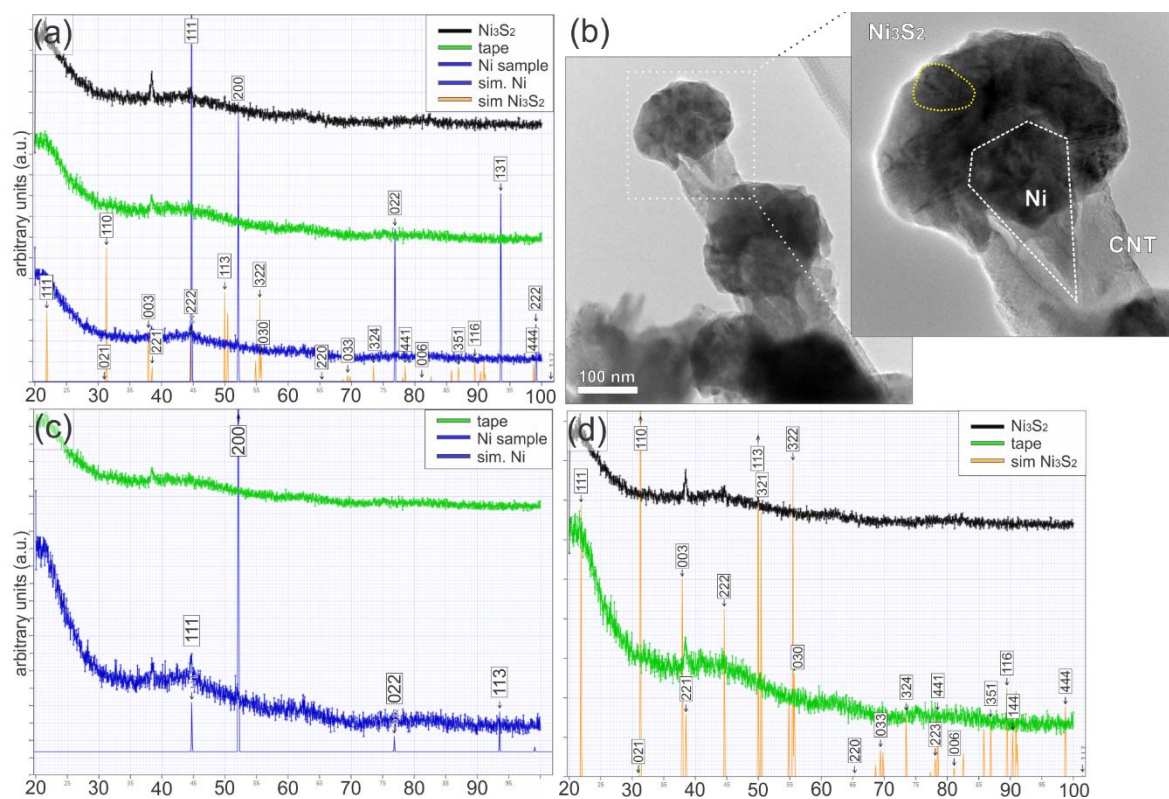


Fig. S3. (a) Experimental XRD spectra of Ni_3S_2 sample (black line), self-adhesive tape (background, green line) and Ni sample before Sulphur treatment (blue line), with simulated diffraction peaks for pure Ni (blue line) and Ni_3S_2 (orange line). (b) TEM micrograph of nickel-sulfide samples. (c) Experimental XRD spectra of Ni (blue) and substrate/tape (green), and (d) Ni_3S_2 (black) and substrate/tape (green)

For the Ni_3S_2 sample, the Ni(111) peak at $\sim 44^\circ$ 2 θ is still visible, which is in agreement with the TEM observations where remains of the Ni core were detected under the Ni_3S_2 crystallites as sketched on **Fig. S3a**. On the other hand, the crystallites of the Ni_3S_2 phase are even smaller than Ni particles –such crystallite is encircled by the yellow line on **Fig. S3b** and was identified from the phase-contrast (HR-TEM) images. From several TEM observations at the atomic scale, it is safe to say that majority of the Ni_3S_2 crystallites are smaller than 10 nm, with a maximum size of up to 15-20 nm. In the experimental XRD pattern, the strongest peak of Ni_3S_2 is (111) at $\sim 22^\circ$ 2 θ , while (222) at $\sim 44^\circ$ 2 θ coincides with Ni(111) peak. The reflection at $\sim 50^\circ$ 2 θ coincides again with the (113) peak of the Ni_3S_2 phase, while others are not detectable. While we can confirm that the observed XRD results partially coincide with the reported data for Ni_3S_2 , the preferential orientation of Ni_3S_2 grown atop preferentially oriented Ni is a matter of debate. Therefore, in our manuscript, we exploited the selected-area electron diffraction (SAED) method, which is especially suitable for phase identification of the nano-scaled materials.

Detailed information on the peak position and area of the deconvoluted peaks in the high-resolution XPS data of the carbon and nickel peaks of the samples are described in Table S1 and S2. The high-resolution XPS peaks were deconvoluted using the Gauss-Lorentz method considering Shirley-type background deduction.

Table S1. Peak position, FWHM, and roughly estimated concentration of the peak components in C 1s spectra of Ni@VCNs and Ni₃S₂/Ni@VCNs.

Deconvoluted peaks	Ni@VCNs			Ni ₃ S ₂ /Ni@VCNs		
	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %
Peak 1	284.6	1.0	73.1	284.6	1.0	66.3
Peak 2	285.5	1.2	13.1	285.5	1.2	18.8
Peak 3	286.7	1.5	5.4	286.9	1.5	7.1
Peak 4	288.2	1.5	2.7	288.3	1.5	3.3
Peak 5	290.5	2.4	5.5	290.5	2.4	6.7

Table S2. Peak position, FWHM, and roughly estimated concentration of the peak components in Ni 2p_{3/2} spectra Ni@VCNs and Ni₃S₂/Ni@VCNs.

Deconvoluted peaks	Ni@VCNs			Ni ₃ S ₂ /Ni@VCNs		
	Position (eV)	FWHM (eV)	Area %	Position (eV)	FWHM (eV)	Area %
Peak 1	853.9	1.4	13.3	853.5	1.4	18.0
Peak 2	855.6	3.2	48.6	856.1	3.2	50.5
Peak 3	861.3	1.4	38.1	861.0	4.5	31.4

Differential capacity versus voltage analysis was carried out between 0.01 and 3.0 V (**Fig. S4(a)**). The two reduction peaks observed near 1.4 and 1.8 V in the first scan could be attributed to the conversion reaction induced by lithium-ion insertion, which is accompanied by decomposition of the electrolyte and formation of the solid electrolyte interface (SEI). The sharp peak observed in the oxidation region at 1.88 V, accompanied by a narrow peak at 2.22 V, could be ascribed to lithium-ion extraction. The well-overlapped peaks after cell cycles reveal the excellent reversibility of the Ni₃S₂/Ni@VCNs electrode. The rate performance of the cell at different current densities is presented in **Fig. S4(b)**.

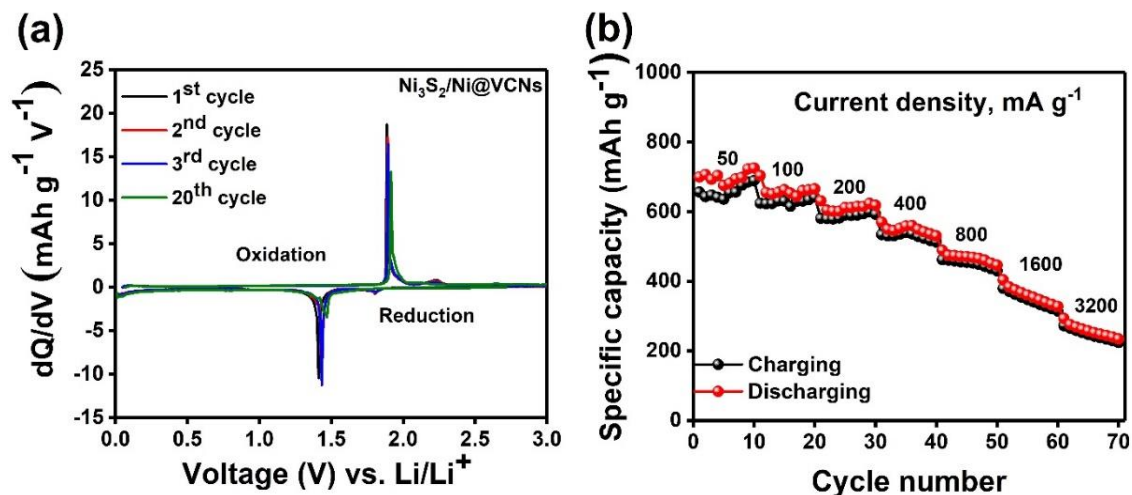


Fig. S4. (a) Differential capacity vs. voltage graphs of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrode at a current density 100 mA g^{-1} and (b) rate capability of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrode at different current densities.

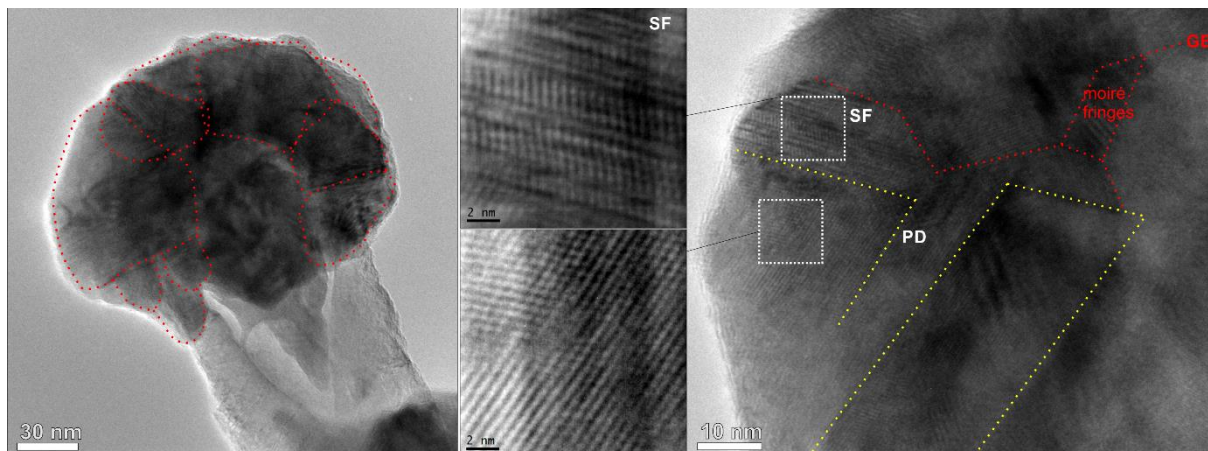


Fig.S5. Structural defects of the polycrystalline Ni_3S_2 nanostructure. (left) low magnification overview TEM micrograph, and right: HR-TEM micrograph of internal structures of Ni_3S_2 crystallites. In inset are average-background subtraction filtered HR-TEM images of respective regions marked on the main image. SF = stacking fault, GB = grain boundary, PD = planar defect.

Table S3. Comparison of lithium storage performance of $\text{Ni}_3\text{S}_2/\text{Ni@VCNs}$ in this work and Ni_3S_2 -based electrodes reported in the literature.

Sample	Electrode type	Current density (mA g^{-1})	Number of cycles	Discharge capacity (mAh g^{-1})	Ref.
$\text{Ni}_3\text{S}_2@\text{GO}/\text{NF}$	Binder-free	200	100	1006	[1]
$\text{Ni}_3\text{S}_2/\text{Ni}$	Binder-free	100	150	623	[2]
3D porous Ni_3S_2	Binder-free	150	55	622	[3]
$\text{NiO}/\text{Ni}_3\text{S}_2/\text{CNF}$	Binder-free	500	200	519	[4]
Ni_3S_2 nanotube array	Binder-free	100	100	762	[5]
$\text{Ni}_3\text{S}_2@\text{C}/\text{rGO}$	With binder	200	100	820	[6]
Ni_3S_2 nanoflakes	With binder	400	60	861	[7]
$\text{Ni}_3\text{S}_2@\text{C}-\text{RGO}$	With binder	100	100	560	[8]
$\text{Ni}_3\text{S}_2-\text{rGO}$	With binder	230	500	443	[9]
$\text{Ni}_3\text{S}_2@\text{N-doped rGO}$	With binder	50	150	809	[10]
$\text{Ni}_3\text{S}_2@\text{3D-CNTF}$	With binder	200	100	968	[11]
$\text{Ni}_3\text{S}_2/\text{Ni@VCN}$	Binder-free	100	100	1113	This work

To understand the changes in the interplanar distance of the Ni₃S₂ structures, which can enhance the intercalation of lithium ions, we have used Fast Fourier Transformation method for the calculations. The interplanar distances, measured from the phase contrast micrographs (HR-TEM images), for the sample after the cycling (**Fig. S6**) show slightly expanded unit cell (Table S4).

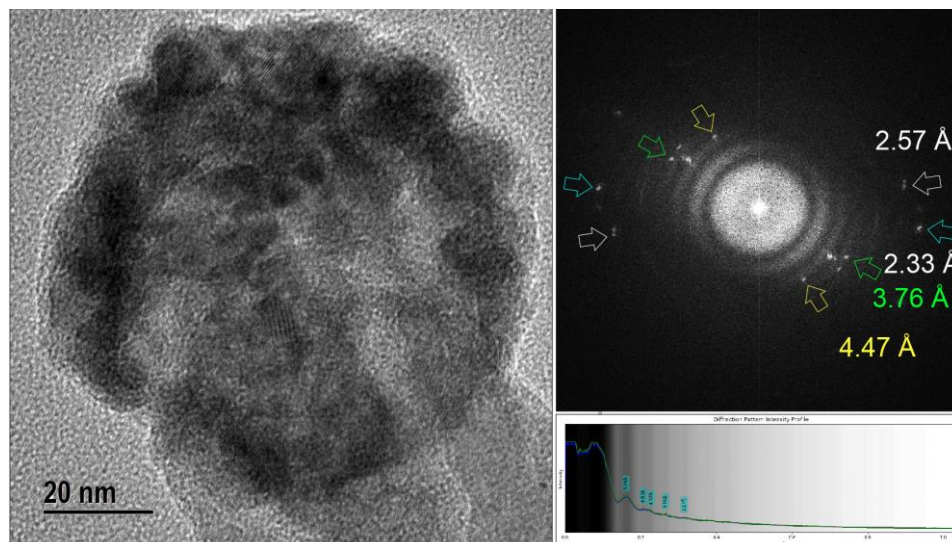


Fig. S6. HR-TEM micrograph and from calibrated image calculated Fast Fourier Transformation, with marked, measured and recalculated reflections.

Table S4: reference values for Ni₃S₂ and experimentally measured interplanar distances for Ni₃S₂ sample after the cycling.

	ref. plane	ref. values [Å]	experimental [Å]	mismatch [Å]
1.	101	4.05941	4.47	+ 0.41
2.	002	3.55475	3.76	+ 0.21
3.	003	2.36983	2.57	+ 0.20
4.	022	2.02970	2.33	+ 0.30

XPS of Ni₃S₂/Ni@VCN electrode after 100 cycles cycled at a current density of 100 mA g⁻¹ was carried out using X-ray photoelectron spectroscopy (XPS, MultiLab2000, Thermo VG Scientific System) utilizing a monochromatic Al X-ray source (Al-K α line: 1,486.6 eV). The peaks observed in the XPS survey spectra confirm the presence of C, Ni, S, O, Li, P, and F (**Fig.S7(a)**). High-resolution core-level XPS spectra of C 1s and Ni 2p_{3/2} are presented in **Fig. S7(b, c)**. The C 1s spectra are deconvoluted to four main peaks centered at 284.7, 286.4, 288.5, 290.0 eV corresponding to sp² C-C, sp³ C-C/C-O, C=O, and π π^* shake-up satellite. The deconvoluted peaks at 856, 858.6, and 862.4 eV in the Ni 2p core-level spectra corresponds to Ni 2p_{3/2}. The presence of sulfur in the survey spectra and the peak observed at 169.2 eV in the core level spectra suggest metal-sulfur bonds in the structure (**Fig. S7(d)**).

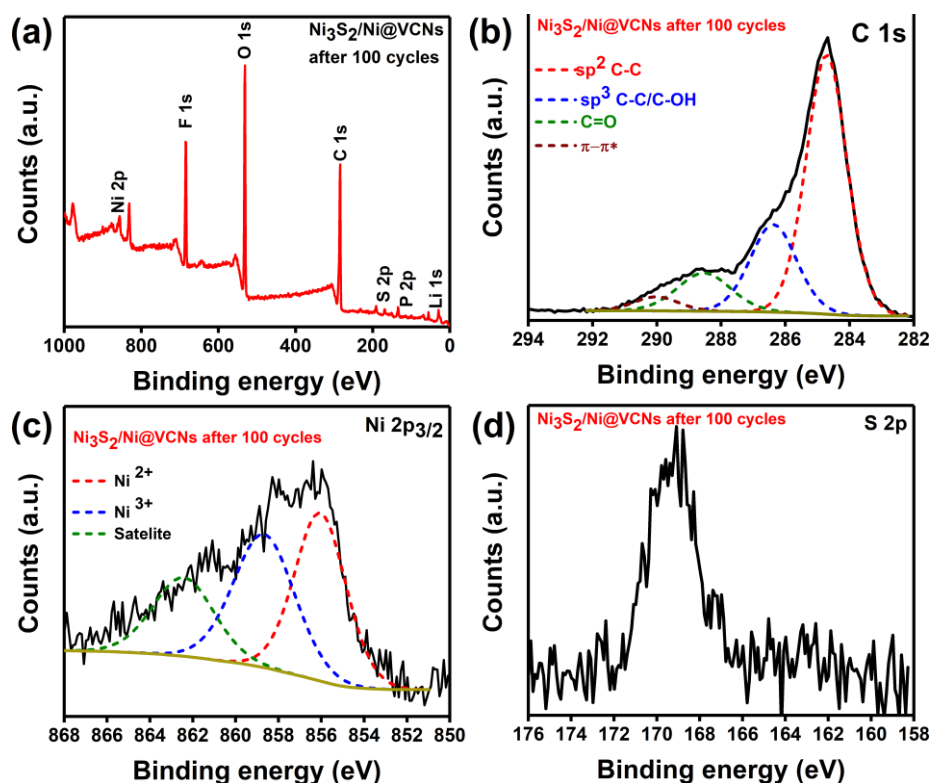


Fig. S7. XPS spectra of the $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrodes after 100 cycles: (a) survey spectra, (b) high-resolution C 1s spectra, (c) high-resolution Ni 2p spectra, and (d) high-resolution S 2p spectra.

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Chapter 6

Conclusions and Future Outlook

The experimental results presented in this dissertation demonstrate that low-pressure plasma-enabled techniques can be used for synthesising, processing and designing hybrid carbon-based nanostructures. The environmentally friendly features with rapid growth and higher controllability make plasma-enabled techniques efficient alternative methods to fabricate carbon nanostructures. Moreover, the ability of plasma-enabled techniques to control the morphology, dimension and orientation of nanostructures is confirmed to be multi-beneficial for various applications, especially for energy storage applications. In addition, it is found that plasma-enabled techniques open up new pathways for the controlled surface modification of carbon nanostructures either with heteroatom doping or with surface functional groups.

Further discussions regarding the results are concluded by each stated objective:

Objective 1: Exploration of low-pressure plasma-enabled green approaches for the direct growth of carbon nanostructures on solid substrates and optimisation of the growth conditions.

Different low-pressure plasma-enabled techniques were used to synthesise various carbon nanostructures. We fabricated vertically-oriented 1D carbon nanotubes and 3D carbon nanoforests on a nickel foil using a radio-frequency inductively coupled plasma deposition system. During the synthesis process, the growth mechanism of carbon nanotubes was identified, and the transformation of nanotubes to nanoforests was unravelled. It was found that the growth of carbon nanotube was facilitated by the catalytic nickel nanoparticle formed on the nickel foil and followed a 'tip-growth' mechanism during the nucleation and growth process. We found that the height and density of nanotubes could be controlled by the growth time and other plasma discharge parameters. In another approach, a radio-frequency capacitively coupled plasma deposition system was used to synthesise 2D vertical graphene nanosheets on silicon substrates at low plasma power and low temperature ~ 450 °C, one of the lowest temperatures reported so far for the growth of vertical graphene nanosheets. We deposited nanosheets using a catalyst-free method and using nickel as the catalyst, and revealed that the presence of nickel catalyst facilitates the growth and structural quality of the nanosheets. Additionally, we verified the improvement of the structural order of graphene nanosheets with the increase in the substrate temperature. We tested plasma-enabled surface reformation of polymer gels for designing oriented carbon nanostructures as an alternative approach. We confirmed that the proposed plasma surface reformation techniques can synthesise vertically oriented carbon nanostructures by the surface reformation of resorcinol-formaldehyde polymer gels using a low-pressure radio-frequency inductively coupled plasma. We studied the influence of plasma discharge parameters (power, pressure and treatment time) on the morphology, structural quality and functional entities of the carbon nanostructures. For all plasma-enabled approaches, we proposed a growth mechanism of carbon nanostructures concerning the plasma discharge conditions. Besides the growth process,

we identified the potential of these plasma-designed carbon nanostructures for different applications, such as gas sensors, bio-molecule detection and SERS applications.

Therefore, Objective 1 was addressed, and the goal to use plasma as an alternative tool to design advanced carbon nanostructures was achieved in Chapters 2 and 3.

Objective 2: Designing surface-engineered carbon nanostructures using plasma-enabled heteroatom doping and plasma surface functionalisation.

Both low-pressure and atmospheric pressure plasma post-treatment techniques were used for the surface engineering of carbon nanostructures. In the first approach, a low-pressure radio-frequency inductively coupled plasma with ammonia or nitrogen as the reactive gases were used for the surface engineering of vertical carbon nanowalls. The goal was to incorporate nitrogen in the carbon nanowalls and understand the incorporation mechanism. The concentration of incorporated nitrogen and configuration of nitrogen bonds was evaluated regarding the plasma treatment time. We discovered that carbon nanowalls with ~8 % (atomic concentration) incorporated nitrogen could be produced after the nitrogen plasma post-treatment. We identified that nitrogen plasma is better than ammonia plasma for attaining a higher concentration of incorporated nitrogen. The systematic experimental approach and employed characterisation techniques revealed that the structural defects in carbon nanowalls formed during the growth and post-treatment process significantly affect the nitrogen incorporation mechanism. All the findings observed in this work were compared with the already reported theoretical predictions, and a possible mechanism of nitrogen incorporation in graphene lattice was established.

An atmospheric pressure plasma jet system was implemented in the second approach for the surface engineering of entangled carbon nanotubes. Inert gases like argon and helium were used for the surface treatment process. As a result, we realised that the surface-treated entangled carbon nanotubes showed higher electrical conductivity than the non-treated ones. The surface and chemical composition analysis confirmed that surface treatment improves the structural quality of the nanostructures. For application-oriented purposes, plasma surface treated and non-treated nanocarbons were tested as gas sensors towards ethanol detection, and the treated nanostructures exhibited higher sensing capabilities.

Therefore, Objective 2 was addressed, and the goal to fabricate surface-engineered carbon nanostructures was achieved as described in Chapter 4.

Objective 3: Design hybrid electrodes by tailoring plasma-designed carbon nanostructures with pseudocapacitive materials.

We fabricated hybrid electrodes by tailoring plasma-designed carbon nanostructures with pseudocapacitive materials. The hybrid electrode comprised of vertical carbon nanotubes and trinickel disulphide (Ni_3S_2). For the electrode fabrication, we followed two different approaches; in both cases, plasma-designed vertical carbon nanotubes were synthesised in the first stage, and used as the backbone for designing the composites. The carbon nanotubes were deposited on a nickel foil using a low-pressure inductively coupled plasma deposition system. The tips of the nanotubes were terminated with a faceted nickel nanoparticle. In the first approach, we followed a three-stage process, where the synthesised nanotubes were subjected to a nitrogen plasma treatment in a low-pressure inductively coupled plasma. In the final stage, nitrogen plasma-treated vertical carbon nanotubes were treated with H_2S gas at low temperature (~125 °C). A two-stage process was used in the second approach, where the plasma-deposited carbon nanotubes were directly treated with H_2S gas, and the nitrogen plasma treatment process was eliminated. In both cases, the resulting nickel sulphide was identified as Ni_3S_2 capped on the nickel particle situated at the tip of the vertical carbon nanotubes. The hybrid structure possesses a "broccoli-

like" morphology. The Ni_3S_2 formed on nitrogen plasma-treated vertical carbon nanotubes had a single crystalline phase, while in the other case, Ni_3S_2 was polycrystalline.

In the three-stage approach, a protective layer of nickel nitride is formed on the outer side of nickel nanoparticles situated at the tip of vertical carbon nanotubes after the nitrogen treatment. We have found that the presence of this nickel nitride was the reason for the crystallinity changes. This atomically thin nickel nitride layer prevents the diffusion of sulphur directly to the exposed parts of nickel nanoparticles. Therefore, sulphide formation was initiated only at one nanoparticle site and grown as a single crystal particle. While in the case of the two-stage approach, sulphur was directly diffused with all the available active sites on the exposed parts of nickel nanoparticles and formed numerous crystalline structures with polycrystalline structures. The electrode prepared after the three-stage approach had the structure $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$, and the electrode prepared after the two-stage approach had the structure $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$. Structural, morphological and chemical composition analyses confirmed that the carbon backbones were intact after the sulphur treatments. Compared to other conventional techniques to design carbon-based electrodes, plasma-enabled techniques are faster to design high-quality carbon-based hybrid electrode materials.

Objective 3 was addressed and the goal to design hybrid carbon nanostructure-based electrodes was achieved in Chapters 2, 3, 4 and 5.

Objective 4: Exploring the energy storage performances of the designed carbon nanostructure-based hybrid electrodes.

In order to investigate the energy storage performances of prepared hybrid carbon/trinickel disulphide nanostructures, the hybrids were tested as active electrodes for supercapacitors and batteries. Since the nanostructures were directly deposited on the nickel foil, the designed hybrid electrodes are used as binder-free electrodes for energy storage applications.

The electrodes prepared via both three-stage ($\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$) and two-stage ($\text{Ni}_3\text{S}_2/\text{Ni@VCN}$) approaches (vertical carbon nanotube deposition/sulphur treatment) were used for the supercapacitor applications. Both electrodes showed redox-type electrochemical performances with battery-type features. The $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ electrode exhibited superior performances compared to the $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrode with double the specific capacity, higher rate capability and cycling stability. In addition, the electrochemical performance of $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{N}/\text{Ni@NVCN}$ was identified as one of the best supercapacitor performances among the Ni_3S_2 -based electrodes. Furthermore, both of these electrodes displayed excellent rate capability even at high current densities. Thus, we addressed one of the main challenges associated with the battery-type electrodes, which is the poor-rate capability of the battery-type electrodes for redox-based electrodes supercapacitors. Therefore, it was suggested that the Faradaic supercapacitor performance could be dramatically improved by using these types of hybrid electrodes in the near future. In another approach, the electrodes prepared via a two-stage approach ($\text{Ni}_3\text{S}_2/\text{Ni@VCN}$) were used as a binder-free electrode for lithium-battery (LIB) applications. As an anode in LIB, $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrodes delivered ultra-high capacity, good rate capability and excellent cycling stability. During the electrochemical cycling, the capacity of the electrode was increased with the cycling, which is attributed to the pseudocapacitive features of the electrodes. Detailed electro-kinetic studies revealed that the $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ electrodes demonstrated both diffusive and capacitive type reactions during the electrochemical process, leading to the electrode's ultra-high capacity. In addition, the electrochemical performance of $\text{Ni}_3\text{S}_2/\text{Ni@VCN}$ was identified as one of the best lithium-storage performances among the Ni_3S_2 -based electrodes.

In both applications, the unique morphology and structural properties of hybrid electrodes made them attain outstanding energy storage performances. In both cases, a combined effect from the defect-rich nanotube backbone structure, defect formation in the Ni_3S_2 phases during the

electrochemical reaction, direct contact between the current collector and active material, and the large surface area of the active $\text{Ni}_3\text{S}_2/\text{Ni}$ region enhances the electrochemical charging/discharging and provides outstanding charge storage performance. In addition, plasma-enabled direct designing of carbon nanostructures on current collectors eliminates the problems due to the polymeric binders and lowers internal resistance. All these findings obtained in this dissertation confirm the potential of plasma-enabled techniques for designing carbon-based hybrid electrodes for energy storage applications.

Objective 4 was addressed and the goal to explore the energy storage performances of plasma-designed hybrid electrodes was achieved in Chapter 5.

6.1. Conclusions and Propositions for Future Work

The dissertation work hypothesised that the cold low-pressure plasma could be used for the precise structure-controlled synthesis and the doping of different 1D, 2D or 3D carbon nanostructures, resulting in carbon hybrid nanostructures. These could be used as advanced electrodes for energy storage, such as supercapacitors and batteries. The major findings and discussions in this dissertation confirmed our hypothesis, and plasma-enabled techniques were identified as a feasible approach for synthesising and processing carbon nanostructures and designing hybrid carbon nanostructures.

The first part of the hypothesis is the possibility of plasma-enabled techniques for carbon nanostructure synthesis. We proposed different plasma-enabled techniques for synthesising carbon nanostructures with different morphology and dimensions. Additionally, we proposed an alternative plasma-enabled technique to produce carbon nanostructures from solid precursors. The second part of the hypothesis is about the potential of plasma for the surface engineering of carbon nanostructures via doping or functionalisation. We established a technique for the controlled nitrogen doping of carbon nanostructures with desired concentration and nitrogen bonding configuration. The last aspect of the hypothesis are plasma-designed carbon nanostructures used as potential electrodes for energy storage applications. We proposed two different approaches to design hybrid electrodes comprised of plasma-designed carbon nanostructures and pseudocapacitive material. Both approaches confirmed that plasma-designed carbon nanostructures could be used as a potential platform for the improvisation and resulted in remarkable energy storage performances for supercapacitors and lithium-ion batteries. This dissertation offers an insight into the fundamentals of cold low-pressure plasma, which can design and process advanced carbon nanostructures for multi-beneficial applications. Even though the primary focus of this dissertation is to design advanced electrodes for energy storage applications, the current state of our research suggests that the fabricated nanostructures also have a high potential for gas sensors, bio-material detections, and SERS applications. Additionally, the ability of plasma-enabled techniques to control the growth rate/thickness of deposition and control the surface functionalities during the process could be beneficial for extending the limits of currently available nanostructures for energy applications. One of the main applications could be using advanced nanocarbon platforms for high-frequency filtering applications, for filtering high-frequency alternating current to direct current using the supercapacitors. Designing nanocarbons with several micron thicknesses and a large surface area is critical for high-frequency filtering applications. In addition, the ability of plasma to deposit carbon materials directly on conductive substrates could lower the internal resistance of the nanostructure during the filtering applications. In another aspect, the improvisation of plasma techniques will help to dope more than one heteroatom simultaneously into carbon lattice. Dual-atom doped carbon nanostructures emerged as a promising method for designing advanced electrodes. They have wide opportunities in the energy storage field owing to their multifunctional properties, including high electrical, electrochemical, and surface redox properties.

Furthermore, as plasma discharge parameters can determine the structure and morphology of nanostructure during the growth process, it is important to optimise methods for tuning the interlayer distance between two graphene layers in graphitic carbon nanostructures. Since most of the emerging battery storage devices have similar intercalation reactions to LIBs, tuning the interlayer distance of carbon layers is a key method to improve the charge storage properties. Also, next-generation batteries, such as aluminium, zinc, sodium, and magnesium-based devices, require a larger interlayer distance for successful intercalation, considering their large atomic size. Therefore, it has to unravel the possibility of plasma to tune the interlayer distance between two graphene layers to extend the application of plasma-enabled techniques to design functional materials for next-generation energy storage devices. However, one of the main concerns that have to be resolved to use low-pressure PECVD systems as a commercial method is the production of the sufficient amount of carbon nanostructures in large-scale with higher mass-loading. Since the energy density and power density of an energy device are directly proportional to the mass of the active material used in the electrode, increasing the mass loading of electrode material is critical for commercial applications. The maximum mass loading of the active material achieved during this dissertation study has to be improved for practical applications. This can be achieved by prolonging the plasma deposition time, increasing precursor flow rate, and combining carbon nanostructures with different metal sulphide/ metal oxide composites. Further research into improving the chemical stability and mass loading of active material must be considered to extend the research into using our electrode materials for the full-cell batteries or hybrid supercapacitors. Designing a multifunctional hybrid electrode with minimum contact resistance and optimum mass loading could address the challenges in the energy density and power density of a device and extend the limits of currently available electrode materials. Therefore, plasma-enabled electrode designing approaches could be used as an alternative technique to design advanced functional electrode materials for next-generation energy storage devices.

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