

ONE-DIMENSIONAL Ti₂O₃-BASED NANOSTRUCTURES: SYNTHESIS AND APPLICATION

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Doctoral Dissertation
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Abstract

Three one-dimensional Ti,O-based nanomaterials, including the transformations among them, were studied in the following work: (i) protonated titanate, (ii) titanium dioxide (TiO_2), and (iii) titanium oxynitride (Ti(O,N)).

Protonated titanate nanotubes were successfully applied as a solid acid catalyst for the aldol condensation between benzaldehyde and cyclohexanone. They efficiently catalysed also other reaction systems with substituted benzaldehyde derivatives as well as the large scale (one gram) experiment. Recycling studies showed no significant decrease in the catalytic activity of protonated titanate nanotubes in five repetitive cycles. Obtained results show that protonated titanate nanotubes could therefore be used as a ‘greener’ alternative to the present performance of the aldol reaction at the industrial level.

In the next chapter, the transformation from protonated titanate nanoribbons (HTiNRs) to titanium dioxide (anatase) nanoribbons was studied. The reaction is a condensation that can be achieved with calcination or catalysis in aqueous medium. Calcination of HTiNRs in air initially led to TiO_2 -B phase, which was followed with anatase formation as the calcination temperature increased from 400 °C to 650 °C, whereas calcination in an ammonia flow resulted in N-doped TiO_2 NRs. Despite the stability of protonated titanate in the basic aqueous medium, it transformed to TiO_2 due to interaction with the basic cations. TiO_2 NRs that were prepared with a hydrothermal treatment had surface covered with small nanocrystals, leading to an increased specific surface area. In addition, the behaviour of protonated titanate in aqueous medium was rationalized for the whole pH range with the corresponding material’s zeta potential. Finally, photocatalytic activity of the key samples was estimated from the photooxidation of isopropanol to acetone. Photocatalytic activity of TiO_2 NRs prepared with calcination of HTiNRs in air increased with the employed calcination temperature. On the contrary, N-doped TiO_2 NRs had suppressed photocatalytic activity despite material’s absorption in the visible range of light as well. The best photocatalytic activity was of TiO_2 NRs that were initially prepared with a hydrothermal treatment in deionized water and were additionally calcined in air.

In the last chapter, Ti(O,N) nanoribbons, which are technologically a promising material, were synthesized with calcination of HTiNRs in an ammonia flow at 800 °C. A large scope of samples was synthesized with varying reaction parameters as an ammonia flow and a reaction time. A smooth surface of HTiNRs became porous and full of voids as Ti(O,N) was formed. The initial porosity emerged due to a lattice mismatch between the phases and was later additionally governed with the Kirkendall effect. During the transformation, two kinds of disorders are created in the material – ion vacancies, and a random O/N occupancy of anionic sites – that affect the material’s electronic properties. Measurements of magnetic properties revealed that all Ti(O,N) samples had metallic properties, whereas only those with the most suppressed disorder degrees also exhibited low-temperature superconductivity.

Povzetek

V sledečem delu bom predstavila rezultate sinteze in raziskav lastnosti treh eno-dimenzionalnih nanomaterialov na osnovi titana in kisika: protoniranega titanata, titanovega dioksida in titanovega oksinitrida.

Nanocevk protoniranega titanata so učinkovito katalizirale aldolno kondenzacijo med benzaldehidom in cikloheksanonom, za kar je zadoščala že katalitska količina materiala. Pred reakcijo nanocevk ni bilo potrebno aktivirati, po reakciji pa sem jih s centrifugiranjem reakcijske zmesi lahko regenerirala. Po petkratni uporabi nanocevk protoniranega titanata se je njihova aktivnost le rahlo znižala. Učinkovito so katalizirale tudi druge reakcijske sisteme s substituiranimi derivati benzaldehida ter poskus v večjem merilu (1 gram). Tako bi bile nanocevk protoniranega titanata primerna zamenjava, še posebej ob upoštevanju zahtev zelene kemije, trenutnim katalizatorjem aldolne kondenzacije v industriji.

V drugem poglavju sem raziskala pretvorbo nanopasov protoniranega titanata (NPT) v nanopasove titanovega dioksida in fotoaktivnost slednjega materiala. Protoniran titanat se med žganjem na zraku najprej pretvori v TiO_2 -B fazo (400 °C), ki ji sledi anataz (580 °C in 650 °C), medtem ko je žganje v atmosferi amonijaka vodilo do z dušikom dopiranega TiO_2 . Površina nanopasov anataza, ki so bili sintetizirani pod hidrotermalnimi pogoji, je bila prekrita z nanokristali, s čimer se je povečala specifična površina materiala. Navkljub stabilnosti NPT v bazičnem vodnem mediju so se le-ti pod hidrotermalnimi pogoji pretvorili v nanopasove anataza, ko so prisotni bazični kationi (NH_4^+) delovali tudi kot razplastitveni reagent. Končno sem obnašanje NPT v vodnem mediju razložila s pomočjo materialovega zeta potenciala za celotno pH območje. V drugem delu poglavja sem ovrednotila fotokatalitsko aktivnost najbolj značilnih vzorcev nanopasov TiO_2 iz fotooksidacije modelnega onesnaževalca, izopropanola, v aceton. Fotoaktivnost vzorcev, ki so bili sintetizirani z žganjem na zraku, se je večala z naraščajočo temperaturo žganja. Čeprav so z dušikom dopirani nanopasovi TiO_2 aktivni tudi v vidnem delu spektra, je bila njihova fotoaktivnost manjša v primerjavi z nedopiranimi vzorci. Najbolj fotoaktivni so bili nanopasovi anataza, ki sem jih sintetizirala pod hidrotermalnimi pogoji in jih dodatno žgala na zraku.

V zadnjem poglavju sem sintetizirala nanopasove titanovega oksinitrida, ki je tehnološko zelo obetaven material, iz nanopasov protoniranega titanata z žganjem v dinamični atmosferi amonijaka pri 800 °C. Raznolikost vzorcev sem dosegla s spreminjanjem pretoka amonijaka in reakcijskega časa. Sprva gladka površina nanopasov protoniranega titanata je postala porozna, 'čipkasta', ob pretvorbi v titanov oksinitrid. Začetna poroznost je nastala zaradi neujemanja osnovnih celic izhodnega in končnega materiala, medtem ko je bil njen kasnejši razvoj posledica Kirkendall-ovega efekta. Med pretvorbo sta se v materialu pojavili dve vrsti nereda – ionske vrzeli in naključna zasedenost anionskih mest z oksidnimi ali nitridnimi anioni – in obe sta vplivali na elektronske lastnosti materiala. Meritve magnetnih lastnosti so namreč razkrile, da so vsi vzorci nanopasov protoniranega titanata imeli kovinske lastnosti, medtem ko so samo najbolj urejeni vzorci (z najnižjo stopnjo nereda) bili tudi superprevodni.

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Abbreviations

NTs	... Nanotubes
NaTiNTs	... Sodium titanate nanotubes
HTiNTs	... Protonated titanate nanotubes
NRs	... Nanoribbons
NaTiNRs	... Sodium titanate nanoribbons
HTiNRs	... Protonated titanate nanoribbons
0D	... Zero-dimensional
1D	... One-dimensional
2D	... Two-dimensional
SEM	... Scanning electron microscopy
FE-SEM	... Field emission scanning electron microscopy
TEM	... Transmission electron microscopy
HRTEM	... High resolution transmission electron microscopy
EDXS	... Energy-dispersive X-ray spectroscopy
ED	... Electron diffraction
FFT	... Fast Fourier transform
EELS	... Electron energy loss spectroscopy
XRD	... X-ray diffraction
XPS	... X-ray photoelectron spectroscopy
FWHM	... Full width at half maximum
TGA	... Thermogravimetric analysis
MS	... Mass spectroscopy
DSC	... Differential scanning calorimetry
IR	... Infrared spectroscopy
FTIR	... Fourier transform infrared spectroscopy
DRIFT	... Diffuse reflectance infrared fourier transform
UV-Vis	... Ultraviolet-visible
MW	... Microwave
h ν	... Electromagnetic irradiation
SSA	... Specific surface area
BET	... Brunauer-Emmett-Teller
BJH	... Barret-Joyner-Halenda
TPD	... Temperature programmed desorption
SQUID	... Superconducting quantum interference device
EPR	... Electron paramagnetic resonance
NMR	... Nuclear magnetic resonance
TLC	... Thin liquid chromatography
s	... Singlet
d	... Doublet
dd	... Doublet of doublets
t	... Triplet

dt	... Doublet of triplets
tt	... Triplet of triplets
m	... Multiplet
iPrOH	... Isopropanol
TMS	... Tetramethylsilane
HFIP	... Hexafluoroisopropanol
EtOAc	... Ethyl acetate
MeCN	... Acetonitrile
DCM	... Dichloromethane
Hex	... Hexane
Hept	... Heptane
Me	... Methyl group
–OH	... Hydroxyl group
r.t.	... Room temperature

Symbols

t	... Reaction time
T	... Reaction temperature
2θ	... Scattering angle
S_{BET}	... Specific surface areas of the materials were determined with the Brunauer-Emmett-Teller (BET) method
ϕ	... Gas flow
x	... Length
y	... Width
z	... Height
r	... Radius
d	... Interplanar distance
a	... Lattice constant
J	... Indirect dipole-dipole coupling
δ	... Chemical shift
g	... Landé g -factor
E_{g}	... Band gap energy
Δ	... Deviation from Vegard's law
χ	... Magnetic susceptibility
H	... Magnetic field
M	... Magnetization
T_{c}	... Critical temperature
N_{F}	... Density of states on Fermi level
ξ	... Superconducting coherence length
R	... Resistance
φ	... Resistivity
φ_{e}	... Impurity scattering limited value of the resistivity
L_{φ}	... Temperature-dependent phase-breaking length
S	... Cross section
p	... Power-law exponent

Chapter 1

Introduction

Titanium is the ninth most abundant element on Earth that naturally occurs primarily in minerals like rutile, ilmenite, anatase, brookite, perovskite and sphene [1]. Its abundance makes TiO_2 a low-cost material which, in addition to its non-toxicity, results in its wide range of applications. TiO_2 is well known as a white pigment with a high refractory index being used in paints and cosmetics. Furthermore, it has been a subject of intense investigation since the 90s of the last century due to its photoactivity [1]. However, TiO_2 could also serve as a starting material to provide new Ti,O-based nanomaterials with novel properties.

1.1 Crystal Structures of Ti,O-Based Materials

In Table 1.1 crystal structures of all Ti,O-based compounds employed in this work and their typical characteristics are presented: sodium titanate ($\text{Na}_2\text{Ti}_3\text{O}_7$), protonated titanate ($\text{H}_2\text{Ti}_3\text{O}_7$), TiO_2 -B phase, anatase, rutile, and titanium oxynitride ($\text{Ti}(\text{O},\text{N})$).

Sodium and protonated titanate belong to the monoclinic crystal system and have a layered structure where the layers of the (100) plane consist of edge- and corner-sharing TiO_6 octahedra building up to zigzag structures [2], [3]. In between the negatively charged titanate layers there are cations stabilizing the structure. Titanates are named after cations embedded between the layers. Therefore, in sodium and protonated titanates, there are sodium ions and protons stabilizing the structure, respectively.

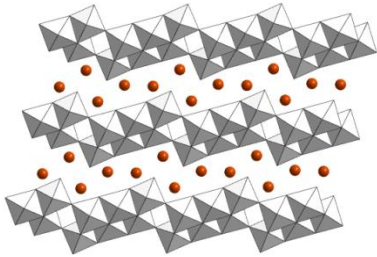
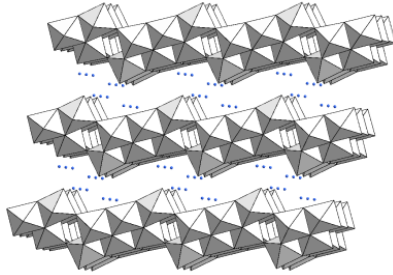
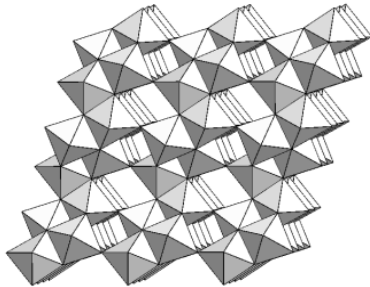
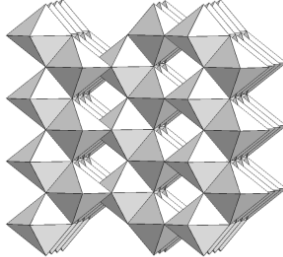
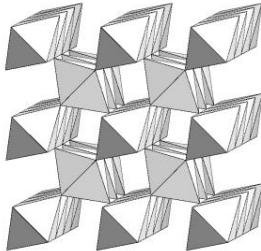
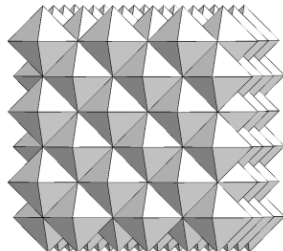
TiO_2 -B phase is also monoclinic with a basic structural unit of two 2-multiple octahedral ribbons sharing corners [4]. It has the least dense structure among TiO_2 natural polymorphs (anatase, rutile, brookite, TiO_2 -B) [5] and has the advantage of being a relatively open structure with large and continuous channels that are suitable for Li^+ intercalation [3], [6].

Finally, a ribbon structure is also present in anatase. It belongs to a tetragonal crystal system where each TiO_6 octahedron shares four edges with other octahedra to form a zigzag ribbon structure [7].

Rutile belongs to a tetragonal crystal system as anatase. However, TiO_6 octahedra are connected in a novel manner in the rutile structure as each octahedron shares two edges with the neighbouring ones to form a linear TiO_6 chain which then connects to four other chains with vertices obtaining a three-dimensional lattice [8].

Finally, cubic $\text{Ti}(\text{O},\text{N})$ is the most dense among the described Ti,O-based structures where each octahedron shares all the edges and corners with the neighbouring ones.

Table 1.1: Crystal structures of materials employed in the present work with the corresponding chemical formula, the crystal system and the space group.

Sodium titanate	Protonated titanate
 $\text{Na}_2\text{Ti}_3\text{O}_7$ Monoclinic P121/m1	 $\text{H}_2\text{Ti}_3\text{O}_7$ Monoclinic P121/m1
TiO_2 -B	Anatase
 TiO_2 Monoclinic C12/m1	 TiO_2 Tetragonal I41/amd
Rutile	Titanium oxynitride
 TiO_2 Tetragonal P42/mnm	 $\text{Ti}(\text{O},\text{N})$ Cubic Fm-3m

1.2 Morphology

When comparing different morphologies of nanostructures, 1D morphology has some advantages with respect to 0D and 2D nanostructures. 1D nanostructures have the smallest dimensionality that still allows both fast electron transport and effective charge transfer in the same material [10]. In addition, they also have a smaller interface area and a smaller amount of surface defects than 0D nanostructures [10]. In this work, we will be focused on two 1D morphologies, *i.e.* nanotubes (NTs) and nanoribbons (NRs) that can be named also nanobelts or nanofibers (Figure 1.1). On the right side of Figure 1.1 there is also a multi-layered nanosheet, which is an intermediate in titanate nanotube and nanoribbon synthesis.

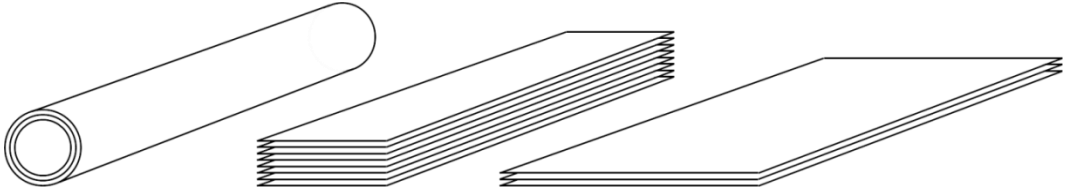


Figure 1.1: Two 1D nanostructures observed during alkaline hydrothermal reaction of TiO_2 : a nanotube (left), and a nanoribbon (middle). A multi-layered nanosheet (right) is the intermediate in nanotube and nanoribbon synthesis.

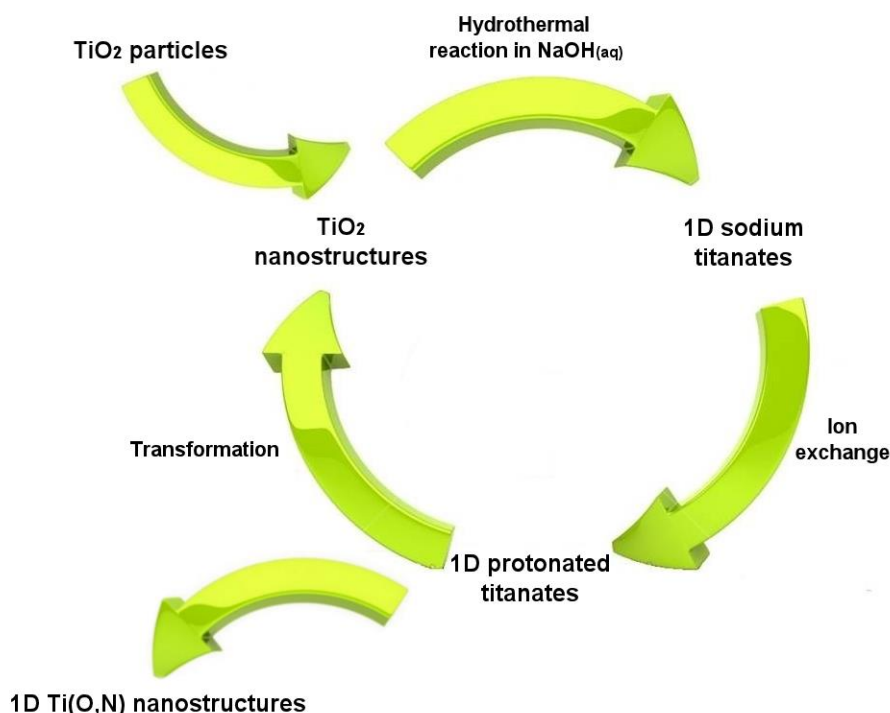
Nanotubes [1] represent long cylindrical structures with a hollow cavity in the centre running throughout the tube. Both ends of the tube are usually open. Typical outer diameters of hydrothermally prepared nanotubes are from 8 nm to 10 nm with aspect ratio (length *versus* diameter) between ten and thousand. Walls of titanate nanotubes are multi-layered, where the number of layers varies from 2 to 10. Even though the nanotubes are straight with relatively constant diameters, the opposite walls of the same nanotube can be composed of different numbers of layers. Therefore, several mechanisms of their formation have been proposed and will be described later.

Nanoribbons [1], [2] are one-dimensional parallelepiped structures that are much larger and with a better crystallinity than nanotubes. Nanoribbons are typically several micrometres or even several tens of micrometres long, the width range is from 10 nm to some hundreds of nanometres, and the thickness is usually between 10 nm and 100 nm. The aspect ratio can therefore be as large as several thousands.

1.3 Synthesis of 1D Ti₂O-Based Nanostructures

1D titanate nanostructures were first hydrothermally synthesized from TiO_2 by Kasuga in 1988 [3]. The advantages of this method are its simplicity, low-cost and the ability to synthesize a great variety of morphologically pure 1D nanomaterials in large (gram) quantities. Since then, additional transformations were explored and Scheme 1.1 presents a synthesis pathway that was employed in this work.

Scheme 1.1: The synthesis pathway of the transformations of Ti₂O-based nanomaterials used in this work.



In a typical experiment a suspension of TiO₂ particles in a highly concentrated NaOH(aq) is hydrothermally treated in a Teflon-lined autoclave for several hours. In the specific reaction temperature interval 1D sodium titanates are formed. Products are washed with a diluted acid and deionized water afterwards to exchange alkaline ions with protons. Protonated titanates still possess 1D structure and can be subsequently transformed into different Ti₂O-based materials with thermal or hydrothermal treatment. Properties of the final products are greatly affected by all the parameters from the first step of the synthesis till the last one and will be discussed below.

1.3.1 TiO₂ source

All TiO₂ polymorphs and also amorphous TiO₂ can serve as a starting material for the alkaline hydrothermal synthesis. Some other titanate sources like TiOSO₄·H₂O can be used as well [4]. Anatase is most commonly used for the synthesis of 1D titanates since it is considered to react more easily with concentrated base than rutile due to higher surface energy and lower stability of the former. This was confirmed also by Ou *et al.* [5] who performed a set of experiments under microwave irradiation with the starting material being a mixture of anatase and rutile (Degussa P-25). Alkaline hydrothermal reactions were terminated after different reaction times and the XRD analyses of the obtained products revealed that all anatase was consumed after the reaction time of 3 h when there was still some rutile left. Nevertheless, titanate nanotubes and nanoribbons can be successfully prepared from mixtures of anatase and rutile [5], [6] pure rutile powder [7], [8] or even brookite [9]. Finally, Wu *et al.* [10] managed to produce titanate nanotubes from amorphous TiO₂ as a starting material as well.

The influence of the average particle size of the starting material on the properties of the final product was also studied [11]. Two anatase powders with the average particle

diameters of 8 nm and 220 nm were used as a starting material. TiO₂ powder was suspended in 10 M NaOH(aq) and autoclaved at 120 °C between 15 h and 30 h. Product analysis revealed that the yield and the quality of sodium titanate nanotubes prepared in this way depended on the particle size of the starting material. Nanotubes prepared from larger anatase particles were morphologically well-defined with similar external (internal) diameters ranging from 6 nm to 11 nm (3 nm to 5 nm), walls of three to five layers and the lengths of several hundreds of nanometres. On the contrary, titanate nanotubes prepared from smaller TiO₂ particles revealed a lower yield of well-defined nanotubes. Dimensions of those nanotubes were significantly larger from the dimensions of nanotubes prepared from larger particles. External (internal) diameters of as-prepared nanotubes ranged from 10 nm to 30 nm (4 nm to 10 nm) and the walls were thicker. There were also many flat or slightly curved single and multi-layered nanosheets present in the product mixture. This could be explained with a dissolution-recrystallization mechanism during a nanosheet formation [11]. Firstly, irreversible dissolution of TiO₂ occurred and soluble titanate species were created. Since smaller crystals dissolved faster than the larger ones, there was a higher concentration of soluble titanate species present in the reaction mixture when smaller particles were used as a starting material. Subsequent proposed events were crystallization of nanosheets and their curving. Crystallization of nanosheets proceeded faster when there was a high concentration of soluble titanate species in the reaction mixture. Thick and rather rigid multi-layered nanosheets were formed, which were consequently difficult to curve into nanotubes. On the other hand, larger TiO₂ particles dissolved more slowly and smaller nanosheets were formed that curved into nanotubes more easily yielding in well-defined nanotubes with similar dimensions. This could also explain the difficulty of the synthesis of titanate nanotubes from freshly precipitated amorphous TiO₂ since the latter should dissolve extremely fast in alkali hydrothermal reactions [11].

1.3.2 Base

Since NaOH(aq) enables the synthesis of nanotubes and nanoribbons, it is the most commonly employed base in hydrothermal preparation of 1D titanates. When LiOH(aq) was used, only nanoparticles were formed [6], [12]. KOH(aq) provided nanorods [12], nanoplates [12] and nanowires [6], [13]. Optimal concentration range of NaOH(aq) varies between 5 M and a saturated solution. Sodium titanate nanotubes are formed in 5–10 M NaOH(aq) solution and no nanotubes were observed when NaOH(aq) with lower concentration than 5 M was employed [3]. Nanoribbons can be formed in the NaOH(aq) concentration range between 5 M and 15 M [6].

The ratio between TiO₂ and NaOH (g (TiO₂)/mL (10 M NaOH)) varies from 0.0025 to 0.125 [14]. Bavykin *et al.* [14] studied the influence of TiO₂/NaOH ratio on the nanotube formation. The results revealed that nanotubes with larger diameters were formed when there was more TiO₂ present in the reaction mixture [14]. This could be explained with the formation of larger nanosheets due to the abundance of dissolved Ti⁴⁺ species in the reaction mixture. Nanotubes with larger diameters were therefore formed with wrapping of wider multi-layered nanosheets.

1.3.3 Hydrothermal reaction performance

A suspension of TiO₂ and an aqueous basic solution is first stirred at room temperature until the mixture becomes homogenous. Hydrothermal reaction can be then executed with conventional convection heating in Teflon-lined autoclaves or under microwave irradiation in microwave reactors. Autoclaves are mainly used since they are easily

available. Different variations of them exist: from the most basic without stirring, where the pressure is regulated with the filling volume and reaction temperature, to those which enable stirring and pressure regulation. Since autoclaves are quite massive and Teflon liners have a low thermal conductivity, a large temperature gradient is present inside the reaction mixture, especially at the beginning of the reaction and in the absence of stirring. The result is a wider interval of the size distribution of the product. On the other hand, microwaves interact directly with the reaction mixture creating more homogenous heat distribution and consequently a narrow interval of the product size distribution [15].

1.3.4 Reaction time

Reaction times vary from several hours to a few days. Usually larger nanostructures with a higher level of crystallinity are obtained after the prolonged reaction time.

1.3.5 Reaction temperature

Reaction temperature is the main parameter to control the morphology of the product. Sodium titanate nanotubes are formed in the temperature range between 100 °C and 150 °C whereas sodium titanate nanoribbons are produced at higher temperatures, that is, between 170 °C and 250 °C [6], [16].

1.3.6 1D sodium titanate formation

It was first considered that $(\text{Na,H})_2\text{Ti}_3\text{O}_7$ or TiO_2 nanotubes are formed during the rolling of nanosheets that are peeled off from TiO_2 particles [16]. Since the final nanotubes were much longer than the initial TiO_2 particles, it became clear that some other intermediates were created [10]. During alkaline hydrothermal treatment, TiO_2 dissolves with breaking the Ti–O–Ti bonds and replacing them with the Ti–O[−] Na⁺ ones [17]. Dissolved Ti^{4+} species could be octahedra, surrounded with six O^{2-} ions [17] or ions like TiO_3^{2-} , $\text{TiO}_2(\text{OH})_2^{2-}$ or possibly polytitanates $\text{Ti}_n\text{O}_{2n+m}^{2m-}$ [10]. Explanations of $(\text{Na,H})_2\text{Ti}_3\text{O}_7$ crystallisation involve its creation inside the amorphous intermediate phase containing Ti, O and Na species [12] as well as nucleation and growth at the brims of undissolved TiO_2 particles [10]. Several mechanisms of the nanosheet formation have then been proposed. Nanosheets could be produced directly with crystallization inside the amorphous phase [12] or with splitting [10] or peeling off [12] from a larger titanate crystal.

1.3.6.1 Sodium titanate nanotubes

When Kasuga *et al.* [3] first reported the formation of nanotubes from titania, they considered washing the product of a hydrothermal reaction with diluted acid solution as the key factor in nanotube formation. However, it was later discovered that nanotubes are already formed during the hydrothermal treatment [10], [12], [18] and many formation mechanisms of sodium titanate nanotubes have been proposed since then. It is generally agreed that they are formed from nanosheets and the mechanisms involve rolling of single or double-layered nanosheets into nanotubes, wrapping of multi-layered nanosheets or overlapping of bent nanosheets into nanotubes.

1.3.6.1.1 Nanosheet rolling It was first believed that nanotubes are formed with rolling of single or double-layered nanosheets [6], [12], [14]. Zhang *et al.* [19] carried out *ab initio* calculations based on density function theory of the titanate nanotube formation from a H₂Ti₃O₇ crystal in a basic environment (NaOH(aq)) where sides of a surface layer of the crystal were exposed to different environments. The outer side is in contact with much more basic conditions than the inner one leading to its deprotonation and the increase in the surface tension. The latter increases with increasing hydrogen deficiency and may eventually overcome the coupling between the layers resulting in peeling off the surface layer from the crystal and its rolling into a tubular structure [19].

The optimal parameters of titanate nanotubes were established with the calculations of the total energy of the curved fragment of a titanate nanosheet as a function of the curvature radius [19]. Optimal titanate nanotubes would therefore have a diameter of 4 nm and walls composed of 4 layers. Wei *et al.* [20] reported the formation of nanotubes from Na₂Ti₃O₇ particles after a neutral aqueous suspension of Na₂Ti₃O₇ particles was hydrothermally treated in an autoclave at temperatures between 140 °C and 170 °C for several days. Water molecules would intercalate between the titanate layers under hydrothermal conditions leading to their exfoliation, curling and rolling into nanotubes [20].

1.3.6.1.2 Wrapping of multi-layered nanosheets If nanotubes were formed with rolling of single-layered nanosheets, then the wall thickness would vary by maximum of one layer when a single nanotube would be viewed axially [14]. Since the wall thickness of a single nanotube often varies by a higher number of layers, alternative mechanisms of nanotube formation have been proposed.

Bavykin *et al.* [14] suggested the formation of nanotubes by wrapping of multi-layered nanosheets due to the imbalance of layer widths. The interaction energy between the atoms of the neighbouring layers is smaller than the interaction energy between the atoms of the same layer in a multi-layered nanosheet and therefore the growth of nanosheets predominantly occurs at the edges of the layers. Outer layers of the multi-layered nanosheets are more easily accessible than the inner ones leading to the imbalance in the layer widths, which creates the tendency of the layers to move within the nanosheet to reduce the surface energy. The release of excess surface energy when a nanosheet wraps into a nanotube is large enough to overcome mechanical tensions arising in the material during curving [14]. The rate of nanosheet wrapping into a nanotube increases with the increasing difference of the layer widths of a single nanosheet resulting in a smaller nanotube diameter. This mechanism is widely accepted among researchers as well [10].

1.3.6.1.3 Tile overlapping model Wu *et al.* [16] proposed a tile overlapping model for nanotube formation where some of single-layered nanosheets or tiles would roll into tubules and other exfoliated tiles would overlap onto them creating a nanotube.

1.3.6.2 Sodium titanate nanoribbons

Nanoribbons are produced at reaction temperatures above 170 °C and two mechanisms of their formation are proposed. The first one considers rapid growth and layering of titanate nanosheets into more rigid thicker structures that suppress the structural forces responsible for any roll-up effect resulting in a nanoribbon formation [1], [21]. The second mechanism also proposes the formation of thicker titanate crystals due to the accelerated kinetic rates of TiO₂ dissolution and crystallization of titanates at higher temperatures.

Nanoribbons would then be formed with the splitting of crystals along specific crystallographic directions [10].

1.3.7 Crystal structure of sodium and protonated titanates

When Kasuga *et al.* [3] first prepared nanotubes with the alkaline hydrothermal treatment of titania, they denoted the crystal structure of nanotubes as anatase. It was only later that the product was determined to be sodium titanate even though the exact crystal structure was still under debate [13]. Difficulties in determining the crystal structure of titanates arise from a large variety of crystal modifications, small particle dimensions leading to the broadening of XRD peaks, and the structure sensitivity [1]. Titanates can be easily transformed under different conditions such as heating in air and acid treatment [1]. Protonated titanates can even dehydrate and shrink during the microscopy due to the high energy electronic probe [22]. Many possible structures of titanates have been proposed by different groups suggesting monoclinic trititanates $(\text{Na,H})_2\text{Ti}_3\text{O}_7$, orthorhombic titanates $(\text{Na,H})_2\text{Ti}_2\text{O}_4(\text{OH})_2$, tetratitanates $(\text{Na,H})_2\text{Ti}_4\text{O}_9$ and lepidocrocite-like titanates. All suggested structures are very similar and have the following properties in common:

- a well-defined layered structure with an interlayer distance between 0.7 nm and 0.8 nm,
- sodium ions are placed between the layers and can be exchanged with protons or some other monovalent transition ions or the transition ions with higher valence [23],
- the layers of the (100) plane consist of edge- and corner-sharing TiO_6 octahedra building up to zigzag structures [1], [13].

Now it is accepted that the chemical structure of sodium titanate is mainly determined with the titanium precursor. Application of TiO_2 leads to the formation of trititanates $(\text{Na,H})_2\text{Ti}_3\text{O}_7$ or tetratitanates $(\text{Na,H})_2\text{Ti}_4\text{O}_9$ whereas orthorhombic titanates $(\text{Na,H})_2\text{Ti}_2\text{O}_4(\text{OH})_2$ are mainly produced when $\text{Ti}(\text{OBu})_4$ and TiCl_4 are used as titanium sources [24].

1.3.8 Transformation from 1D sodium titanates to 1D protonated titanates

1D nanostructured sodium titanates are produced after a hydrothermal treatment of TiO_2 in a concentrated $\text{NaOH}(\text{aq})$ solution. Sodium cations need to be replaced with protons to produce protonated titanates that can be transformed into TiO_2 nanostructures afterwards. Zhang *et al.* [19] performed *ab initio* calculations which revealed that interlayer Na^+ ions and protons are differently positioned in titanates $((\text{Na,H})_2\text{Ti}_3\text{O}_7, \text{H}_2\text{Ti}_3\text{O}_7)$. H^+ ions are considered to be adsorbed on the surface of the titanate layers (bond length $\text{H}-\text{O}$ about 1 Å) while Na^+ ions are placed in the middle between the titanate layers (distance between Na and O above 2 Å), which makes the latter easily replaceable [19]. The ion exchange is performed with acid or water washing until the pH of the suspension decreases to the value of 7 or 6. Acids that are usually used in the washing procedure are HCl [3], [6], [8], CH_3COOH [13], H_2SO_4 [14] and HNO_3 [25] in the concentration range between 0.01 M and 0.1 M. Acids have to be diluted since they can affect the morphology of nanostructures [17]. As-prepared

protonated titanates preserve the morphology of the parent material. The interlayer distance is reduced due to the smaller diameters of intercalated ions from approximately 0.84 nm for $(\text{Na,H})_2\text{Ti}_3\text{O}_7$ to 0.78 nm when $\text{H}_2\text{Ti}_3\text{O}_7$ is formed [12].

1.3.9 Transformations of 1D protonated titanates

Protonated titanate is a rather temperature-sensitive compound, which makes it a convenient starting material. It can be transformed into different Ti,O-based compounds with calcination in different atmospheres and in an aqueous medium. However, energy demands for its transformation to different Ti,O-based compounds highly depend on the structural relation between protonated titanate and the product material.

Protonated titanate, $\text{TiO}_2\text{-B}$ phase, and anatase are structurally related as all the structures can be described with zigzag ribbon units. Therefore, the transformation from protonated titanate to $\text{TiO}_2\text{-B}$ phase and anatase proceeds rather easily.

On the other hand, rutile has a very distinct structure from protonated titanate, resulting in a larger energy demand for the transformation from protonated titanate to rutile. The structural difference is probably also the reason why the mentioned transformation almost never occurs with the morphology preservation [8].

Finally, the transformation from protonated titanate to Ti(O,N) does not contain only structural rearrangement of TiO_6 octahedral units (as in the cases for anatase and rutile formation) but also a certain degree of substitution of oxide anions with the nitride and a reduction of Ti^{4+} centres to lower oxidation states [26], [27]. As a result, a huge energy input is required to achieve such transformation.

1.4 Outline

All the materials – protonated titanates, TiO_2 and Ti(O,N) – are connected to each other through the synthesis. TiO_2 is a starting material for 1D titanate synthesis. Protonated titanate is then a convenient precursor for TiO_2 and Ti(O,N) . Finally, Ti(O,N) transforms back to TiO_2 under oxidative conditions. However, despite the synthesis relations between the materials, their chemical and physical properties are so distinct that they can be applied to completely different fields. Therefore, separated chapters will be dedicated to each individual material in this work.

Protonated titanates are rich in surface hydroxyl ($-\text{OH}$) groups, making them useful as solid acid catalysts. In Chapter 3 the results of the aldol condensation catalysed with 1D titanates will be presented.

The next chapter consists of two parts. In the first part, we will focus on the transformation pathway from protonated titanate nanoribbons to TiO_2 nanoribbons. Results were obtained from material's calcination in different atmospheres as well as transformation in liquid media under solvothermal and ambient conditions. In the second part, photocatalytic activity of the key TiO_2 samples, assessed from the photooxidation of isopropanol to acetone, will be discussed.

Finally, Ti(O,N) is a solid solution of cubic TiO and TiN . As such, its electronic properties can be tuned with the chemical composition. In Chapter 5, the processes during the transformation from protonated titanate nanoribbons to Ti(O,N) nanoribbons are described and the key parameters that control Ti(O,N) NRs synthesis as well as their electronic properties are determined.

Chapter 2

Experimental Techniques and Methods

2.1 Scanning Electron Microscopy

The morphology of the samples was investigated with a scanning electron microscope (FE-SEM, Jeol 7600F). For the SEM analysis the samples were dispersed in water and a drop of dispersion was deposited on a polished Al sample holder. Prior to the SEM investigation an about 3-nm-thick carbon or Au/Pd layer was deposited on the samples to reduce the charging effect.

2.2 Transmission Electron Microscopy

Morphology, crystallinity and size distribution of the samples was investigated with a transmission electron microscope (TEM Jeol 2100, 200 keV). Specimens for TEM analyses were dispersed ultrasonically in methanol and a drop of the dispersion was deposited onto a lacy carbon film supported by a copper grid.

2.3 Energy-Dispersive X-Ray Spectroscopy

A FE-SEM equipped with an EDXS elemental analysis system was used to perform elemental analyses of the samples. The samples were pressed into pellets and placed on a carbon tape on an Al sample holder. The holder with the samples was coated with a thin carbon layer prior to the EDXS analyses.

2.4 Electron Energy Loss Spectroscopy

EELS was employed to conduct the elemental mapping of a Ti(O,N) nanoribbon sample. The analysis was performed using a field emission transmission electron microscope JEOL 2200 FS operating at 200 kV with the spatial resolution of 0.19 nm. The microscope is equipped with an in-column filter (Omega Filter). The EELS maps were obtained with the three window method on the K edges at 401 eV and 530 eV for nitrogen and oxygen, respectively, and the L₂/L₃ edges at 460 eV/466 eV for titanium.

2.5 X-Ray Powder Diffraction

The phase composition of the samples was determined with XRD, using a D4 Endeavor, Bruker AXS diffractometer with Cu-K α radiation ($\lambda=1.5406$ Å) and a Sol-X energy-dispersive detector. Diffractograms were measured in the 2θ angular range with a step size of $0.02^\circ \text{ s}^{-1}$ and a collection time of 3 s.

2.6 X-Ray Photoelectron Spectroscopy

For the determination of the nitrogen content in N-doped TiO $_2$ and Ti(O,N) samples XPS measurements were performed with a VERSAPROBE PHI 5000 from Physical Electronics, equipped with a Monochromatic Al-K α X-Ray. The energy resolution was 0.6 eV. A dual beam charge neutralizer composed of an electron gun (~ 1 eV) and an Argon Ion gun (≤ 10 eV) was used in order to compensate the built up charge on the specimen's surface during the measurements. The specimens for the XPS measurements were prepared by pressing the specimen into a pellet. A conductive double-sided tape was used to attach the pellet to a sample holder.

2.7 Thermogravimetric Analysis and Differential Scanning Calorimetry

TGA were performed on a Mettler Toledo TGA/DSC1 Instrument from room temperature up to 800 °C with the heating rate of 10 K min $^{-1}$. Samples with an initial mass of around 10 mg were placed into 150 μL Pt crucibles. During the measurement, the furnace was purged with an air flow with the rate of 50 mL min $^{-1}$. The baseline was automatically subtracted from the measured TGA curve.

DSC measurements were performed separately on a Mettler Toledo DSC1 Instrument. Around 5 mg of samples were weighed into 70 μL min $^{-1}$ Pt crucibles; empty crucibles were used as a reference. The upper temperature of the measurements was 700 °C. Other parameters (heating rate, purge gas) were identical to those used for the TGA.

2.8 Thermogravimetric Analysis Coupled with Mass Spectrometry

TGA were performed on a Mettler Toledo TGA/DSC1 Instrument under a dynamic flow of air with the flow rate of 50 mL min $^{-1}$. For the analysis, approximately 5 mg of the sample was put into a 150 μL Pt crucible, and was heated from 25 °C to 600 °C with the heating rate of 10 °C min $^{-1}$. The baseline was automatically subtracted from the measured TGA curve. The evolved gases were detected with a Balzer ThermoStar mass spectrometer that was coupled to the TGA/DSC instrument with a 75 cm long heated capillary.

2.9 Raman Spectroscopy

Raman spectra were recorded at room temperature with a WITec Alpha 300 scanning confocal microscope using a 633 nm laser. The power of the laser beam was set to 4 mW in order to avoid any sample damage and the spectral resolution was 3–4 cm^{-1} . For the analysis, the samples were manually pressed onto an objective glass to obtain sufficiently flat surface, suitable for the analysis.

2.10 N_2 Adsorption Measurements

Nitrogen adsorption measurements were executed with a Micrometrics ASAP 2020 analyser. Specific surface areas of the samples were determined with BET method and BJH calculation was used to determine their pore size distribution. The samples were outgassed overnight at 100 $^{\circ}\text{C}$ prior the analyses which were then performed at -196°C .

2.11 NH_3 Thermal Programmed Desorption Measurements

NH_3 -TPD measurements were carried out using the AutoChem II 2920 station. The samples (30–50 mg), placed in a U-shaped quartz reactor with an inner diameter of 0.5 cm, were pre-treated under He (Purity 5.0, from Linde) at 100 $^{\circ}\text{C}$ for 1 h, and exposed to a flow of 10 % NH_3 in helium (from SIAD) for 1 h afterwards. The sample was then purged with a flow of He (50 mL min^{-1}) for 20 minutes at 25 $^{\circ}\text{C}$ in order to remove the weakly adsorbed species. TPD was executed with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ till 700 $^{\circ}\text{C}$. The desorbed products were analyzed with a thermal conductivity detector. The desorbed NH_3 , expressed as mmoles of NH_3 per grams of catalyst, was determined using a calibration curve.

2.12 *In-situ* Diffuse Reflectance Infrared Fourier Transform Analysis

In-situ DRIFT analysis was performed using a Thermo Electron Nicolet 4700 Fourier transform infrared spectrometer with a Smart Accessory for diffuse reflectance measurements and an *in-situ* cell. The DRIFT spectra were scanned in the region of 4000–400 cm^{-1} at the resolution of 4 cm^{-1} . The final spectra correspond to an accumulation of 200 scans. A gold mirror was used for reference measurements. The surface of the sample was cleaned by heating the cell at 100 $^{\circ}\text{C}$ and passing a flow of nitrogen as inert gas for 30 minutes. Then, the sample was cooled under the same flow at room temperature and the probe molecule was chemisorbed by passing a flow of 1 vol% NH_3 in He for 30 minutes. The non-bonded and physisorbed NH_3 was evacuated under the same flow of nitrogen for another 60 minutes afterwards. Desorption started with heating the cell at a rate of 10 $^{\circ}\text{C min}^{-1}$ under the same atmosphere and the spectra were collected every 50 $^{\circ}\text{C}$.

2.13 ^1H Nuclear Magnetic Resonance Spectroscopy

The compositions of the product mixtures of the organic reactions were determined with ^1H NMR spectroscopy. The ^1H NMR spectra were recorded in CDCl_3 using a Varian Inova 300 spectrometer (300 MHz) with tetramethylsilane as an internal standard.

2.14 Electron Paramagnetic Resonance Spectroscopy

Continuous wave EPR measurements were performed in X-band (frequency about 9.5 GHz) with a custom-built spectrometer, which was equipped with a Varian E-101 microwave bridge. Approximately 5 mg of the samples were weighed in the EPR tubes in order to quantitatively compare the measured EPR intensities. The EPR tubes were then vacuumed and sealed. EPR spectra were first measured at room temperature and then the samples were quenched to 30 K where spectra were first measured in the dark and then after 5 min of UV-vis illumination. A mercury lamp was used for *in situ* UV-vis light illumination of the samples in an EPR cavity. An Oxford Cryogenics continuous-flow liquid He cryogenic system ensured temperature stability with a range of fluctuation below 0.1 K.

2.15 Band Gap Energy Determination

Diffuse reflectance spectra were acquired in the range between 200 nm and 800 nm with a 0.5-nm step using a UV-Vis-NIR spectrometer (Shimadzu UV-3600) equipped with an integrating sphere (ISR-3100, 60 mm) and BaSO₄ as a standard. The Kubelka-Munk function was applied to convert diffuse reflectance into absorbance. The optical band gap energy was determined from the wavelength at which the tangent of the absorbance line intersected the abscissa coordinate.

2.16 Photocatalytic Activity Evaluation

The photocatalytic performance of the prepared TiO₂ NRs was measured in a sealed gas-solid continuous flow reactor system. Concentration of iPrOH, as the model pollutant, and acetone, the first product of iPrOH oxidation, was continually monitored with FTIR spectroscopy. 50 mg of the sample was evenly spread on a petri dish, 60 mm in diameter, and put into the system. Then, 8 μ l of iPrOH, corresponding to $\sim$ 800 ppm, was injected into the system. After the adsorption-desorption equilibrium was reached, as indicated by the flat lines of the iPrOH and acetone concentration, the sample was illuminated. As the light was switched on, the iPrOH concentration began to decrease while the acetone concentration increased. The temperature of the system was kept at (25 ± 3) °C and a relative humidity of (22 ± 3) %. The light source was a 300 W Xe lamp (Newport Oriel Instrument, USA). The lamp imitates the solar spectrum and emits both UV and Vis light. The radiant flux density on the sample was 40 W m⁻². The iPrOH and acetone concentrations were calculated by observing characteristic peaks at 951 cm⁻¹ and 1207 cm⁻¹, respectively, using a FTIR spectrometer (Perkin Elmer BX II).

2.17 Magnetization Measurements

Magnetization was measured on powder samples between 1.9 K and 300 K in magnetic fields up to 50 kOe with Quantum Design MPMS-XL-5 SQUID magnetometer. The raw data were corrected for the sample holder contribution and for temperature independent Larmor diamagnetism, as calculated from Pascal's tables.

2.18 Resistivity Measurements

For resistivity measurements, $\text{Ti}(\text{O},\text{N})$ nanoribbons were dispersed in acetonitrile in an ultrasonic bath at 80 kHz for 5 minutes. The resulting dispersion was drop-cast on a silica substrate and examined under SEM. Focused Ion Beam (FIB) induced platinum deposition was achieved using beams with 30 kV acceleration voltage and a current of 80–430 pA with a FEI Helios NanoLab 600i. The thickness of the Pt deposition was roughly 1 μm and was chosen to make the contacts strong enough to withstand the mechanical strain caused by the differential contraction of the sample and the substrate during the cooling to low temperatures. The temperature and magnetic field dependent electrical measurements were performed on a Quantum Design Physical Properties Measuring System (PPMS) in the temperature range from 300 K to 2 K and in magnetic fields from 0 T to 9 T, respectively. The thickness and the length of the measured $\text{Ti}(\text{O},\text{N})$ nanoribbons was controlled by using a Veeco Dimension 3100 Atomic Force Microscope.

Chapter 3

Protonated Titanate Nanotubes as a Solid Acid Catalyst for the Aldol Condensation

3.1 Introduction

3.1.1 Heterogeneous catalysis

Green chemistry has emerged as a response to the growing demands for the environment protection in order to reduce the pollution caused by chemical industry. With its formulation in the early 1990s, green chemistry can be explained as following: *Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products* [28]. It was only later that now widely recognized 12 principles of green chemistry [28] were created and they comprise of:

1. waste prevention instead of remediation,
2. atom efficiency,
3. less hazardous/toxic chemicals,
4. safer products by design,
5. innocuous solvents and auxiliaries,
6. energy efficient by design,
7. preferably renewable raw materials,
8. shorter syntheses (avoid derivatization),
9. catalytic rather than stoichiometric reagents,
10. design products for degradation,
11. analytical methodologies for pollution prevention,
12. inherently safer processes.

Currently, the majority of waste produced in chemical industry are inorganic salts from the widespread use of inorganic reagents, where a major part originates from mineral acids [28]. Beside their common usage in stoichiometric amounts, mineral acids are also corrosive and difficult to handle. After reaction termination, a product mixture is isolated with extraction with organic solvents, whose later recovery demands energy. Finally, mineral acids cannot be directly recycled after once employed in a reaction and their later recovery is an energy-demanding process.

A good alternative to address the mentioned issues are solid acids [28], [29]. They are normally non corrosive, safer, and easier to handle than mineral acids. After reaction termination, a product is isolated with a simple filtration due to a solid-liquid heterogeneous system and a catalyst can be recycled. This leads to a significant reduction of waste produced. The substitution of mineral acids with solid ones is therefore beneficial in regard to the environment.

3.1.2 1D protonated titanates

1D protonated titanate nanostructures are convenient candidates for the application as solid acid catalysts due to:

- acidic properties,
- chemical non-toxicity,
- a low-cost production from 1D sodium titanates in large quantities,
- different morphologies like nanotubes and nanoribbons.

The acidic properties of protonated titanates originate from surface coordinatively unsaturated Ti^{4+} centres and surface $-\text{OH}$ groups (Figure 3.1) [30].

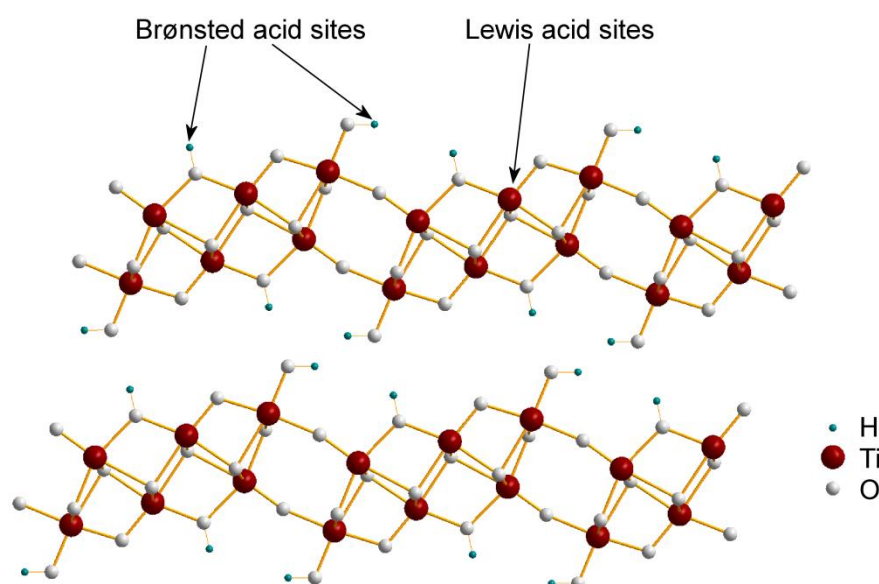


Figure 3.1: Structure of protonated titanate ($\text{H}_2\text{Ti}_3\text{O}_7$) with labelled Brønsted and Lewis acid sites.

Surface coordinatively unsaturated Ti^{4+} centres represent Lewis acid sites when surface $-\text{OH}$ groups are attributed to Brønsted acid sites that can be either in a terminal or

a bridging mode [30]. Brønsted acid strength of –OH groups depends on at least two criteria: (i) coordination of a –OH group and (ii) a nanoparticle’s morphology. It is a general rule that the Brønsted acidity of a –OH group increases with its coordination number [31]. That is also supported with the density functional theory (DFT) calculations showing that the bridging –OH groups have higher Brønsted acid strength than the terminal ones [30]. In regard to the morphology impact, protonated titanate nanotubes were reported to have a higher Brønsted acidity than nanosheets [30], [32], whereas protonated titanate nanoribbons were found to possess only Lewis acid sites and no effective Brønsted acid sites were detected [33]. Hydroxyl groups are also positioned in the interlayer space between the titanate layers but they do not participate in the catalytic reaction [33].

Acidic properties of protonated titanate nanotubes were first exploited by Kitano *et al.* to catalyse Friedel-Crafts alkylation of toluene [32]. The reaction was performed in toluene with benzyl chloride, and after the catalysis with HTiNTs at room temperature for 3 h, the product was obtained with the 90 % yield [32]. This result encouraged other research groups to explore the catalytic capabilities of protonated titanates. Dias *et al.* examined the catalysis of the dehydration of D-xylose into furfural with different protonated titanates [34]. The results showed that exfoliated protonate titanate nanosheets were a more efficient catalyst than the bulky protonated titanate. The former have a larger specific surface area and consequently more accessible active catalytic sites than the latter. The highest furfural yield of approximately 40 % was obtained after the reaction was carried out at 160 °C in a water-toluene solvent system in a microreactor [34]. Li *et al.* synthesized diesel precursors with catalysis of hydroxyalkylation/alkylation of 2-methylfuran and n-butanal from lignocellulose with protonated titanate nanotubes [35]. Under those conditions protonated titanate nanotubes were even a more efficient catalyst than conventional solid acid catalysts such as sulphated alumina, sulphated zirconia, and different zeolites (H-ZSM-5, H-MOR and H- β) [35].

3.1.3 Aldol condensation

When considering the most common reactions that are used in industrial processes and whose performance should be modernized in order to address green chemistry demands, we come to the aldol condensation [36]. It is one of the most commonly employed reactions as it provides a new C–C bond between two carbonyl compounds – ketones or aldehydes. When it proceeds between two identical molecules, it is known as self-condensation whereas a reaction between two different compounds leads to cross-condensation products. The mechanism of the reaction that needs to be catalysed either with acids or bases is presented in Scheme 3.1.

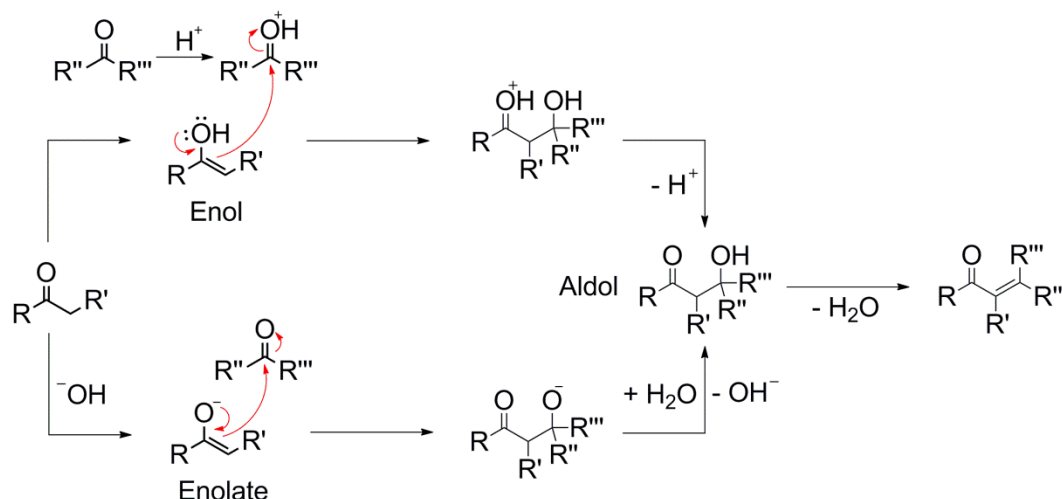
In principle, one carbonyl compound needs to be capable of enolization. After the first molecule is transformed to the enol (acid catalysed) or the enolate (basic catalysed), it reacts with the second carbonyl molecule to produce the β -hydroxy ketone or the β -hydroxy aldehyde – the aldol. This adduct can then easily dehydrate to the α,β -unsaturated carbonyl due to the stabilization of the product molecule with the conjugated π -system.

The practical value of the aldol condensation is the wide application of its products as intermediates or final fine chemicals in the fields ranging from pharmaceutical, food and perfume industry to biomass conversion and biofuel production [37]–[43]. However, against wide utility of the aldol condensation in industrial processes, its performance has several drawbacks in regard to the environment. Industrially, the aldol condensation is catalysed with stoichiometric amounts of aqueous base, meaning that (i) the process of

product isolation is extraction with organic solvents, (ii) after the reaction termination, the catalyst is neutralized, thus producing large quantities of waste salts that need to be disposed of, and (iii) the catalyst cannot be reused [44]. In addition, the selectivity of the aldol condensation is frequently poor.

Bearing this in mind the aldol condensation is a suitable reaction to study catalytic properties of protonated titanates as it can be catalysed with acids, is widely used, and a new ‘greener’ approach of its performance is needed.

Scheme 3.1: The mechanism of the aldol condensation catalysed with an acid (an upper path) and a base (a lower path).



3.2 Experimental Section

3.2.1 Material synthesis

All chemicals were obtained from commercial sources and were used as received.

1D sodium titanates were synthesized according to the modified method, first reported by Kasuga [3]. 3.5 g of TiO_2 (anatase, Aldrich, mesh 325) was suspended in 35 mL of 10.0 M NaOH(aq), stirred at r.t. for 1 h, and ultrasonicated for 30 minutes. 33 mL of the suspension was then transferred to a 42 mL Teflon-lined autoclave and heated at the selected temperature for three days. Sodium titanate nanotubes were produced at 135 °C whereas sodium titanate nanoribbons were formed at 175 °C. After three days of reacting, the autoclave was cooled down to room temperature, the product mixture was grounded in a mortar and washed twice with 300 mL of deionized water and once with 100 mL of EtOH. The product was dried in air at 100 °C for 12 h.

1D protonated titanates were prepared from the parent 1D sodium titanates with an ion exchange process. Approximately 4 g of sodium titanates (nanotubes or nanoribbons) were suspended in 500 mL of 0.1 M CH_3COOH (aq) and stirred for one hour. If the material did not sediment naturally afterwards, the suspension was centrifuged for 5 minutes at 1800 rpm. With the same procedure, the material was additionally washed for four times. Then, 1D protonated titanates were washed with water a few times until the pH of the supernatant was approximately 5.5. After the final rinsing with EtOH, the material was dried in air at 100 °C for 12 h.

3.2.2 Catalytic reactions

Catalytic reactions were performed in 125 mm long glass tubes with an inner diameter of 15 mm. In a typical experiment, 25 mg of a catalyst was weighted in a glass tube, 0.5 mL of a solvent was added, and the suspension was ultrasonicated for 30 seconds. The used solvents were hexafluoroisopropanol (HFIP), acetonitrile (MeCN), ethyl acetate (EtOAc), dichloromethane (DCM), hexane (Hex) and heptane (Hept). After homogenization of the suspension with ultrasonic treatment, equimolar amounts of aldehyde (1.0 mmol) and ketone (0.5 mmol or 1.0 mmol for acetophenone) were added to the stirring suspension. The reactions were executed at room or elevated (70 °C or reflux) temperatures. When the reaction mixture was heated, the glass tube was equipped with a condenser, and the reaction vessel was immersed into a preheated oil bath. A reaction progress was monitored with thin-layer chromatography where the mobile phase was composed of hexane and EtOAc in the ratio 7:1. After the reaction termination (2 h or 4 h), the catalyst was removed from the product mixture with centrifugation and was additionally washed with EtOAc twice to extract the remaining organic compounds. The organic phases were collected and finally concentrated under reduced pressure.

In the repetition reactions, the catalyst was washed with EtOAc three times during the product isolation and was dried overnight in air at room temperature. As such, without any activation, it was reused in the next reaction cycle.

A one-gram experiment was conducted in a 10 mL round bottom flask. 250 mg of HTiNTs were weighted into a flask, 3.5 mL of heptane was added and the suspension was ultrasonicated for 30 seconds. Then, 1.0 g (9.4 mmol) of benzaldehyde and a stoichiometric amount of cyclohexanone (4.7 mmol) were added dropwise to the stirring suspension. The reaction was performed under reflux for 4 h. The product mixture was isolated with centrifugation and rinsing of the catalyst with EtOAc for three times. The collected organic phases were finally concentrated under reduced pressure.

Compositions of product mixtures were analysed with ^1H NMR spectroscopy. Reaction conversions were calculated according to aldehyde. Experimental data for the catalytic reactions including the examples of conversion and selectivity calculation, and ^1H NMR data are given in Appendix A.

3.3 Results and Discussion

3.3.1 Material characterization

3.3.1.1 Structural determination

Crystal structure of 1D sodium and protonated titanates was analysed with XRD (Figure 3.2) The diffractograms correspond to trititanate structures, *i.e.* $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{H}_2\text{Ti}_3\text{O}_7$ for sodium and protonated titanate, respectively [34], [45], [46]. The diffraction peak at around 10° arises from the layered titanate structure [30], [47] where the corresponding interlayer distances calculated with Bragg equation for NaTiNRs, NaTiNTs, HTiNRs and HTiNTs are 8.60 Å, 8.98 Å, 7.78 Å and 8.96 Å, respectively. When comparing the interlayer distance of nanotubes and nanoribbons of either sodium or protonated titanate, nanotubes have a longer interlayer distance due to their distorted and less compact structure (Figure 3.2).

Sodium titanate generally has a larger interlayer distance than protonated titanate due to a larger size of sodium ions in comparison to protons embedded between titanate layers. This interlayer difference is present between sodium and protonated titanate

nanoribbons whereas the interlayer distances of NaTiNTs and HTiNTs are almost identical. It seems that the interlayer distance of titanate nanotubes is more affected with the bent nanotube structure than the cation's size present in the interlayer space (Figure 3.2).

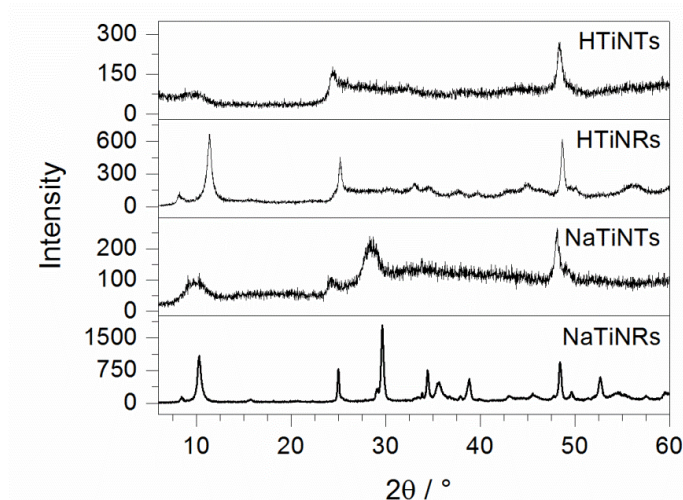


Figure 3.2: XRD patterns of sodium titanate nanoribbons, sodium titanate nanotubes, protonated titanate nanoribbons and protonated titanate nanotubes.

The efficiency of the transformation from sodium to protonated titanates can be evaluated from the XRD patterns as well. The peak positioned at around 30° in the XRD pattern of NaTiNRs is characteristic for sodium titanate [2]. The absence of this peak in the XRD patterns of 1D protonated titanates indicates that sodium ions were efficiently exchanged by protons in the titanate structure. Finally, the XRD patterns of nanoribbons have sharper peaks than patterns of nanotubes indicating better crystallinity of the former. This difference arises from (i) the reaction temperature at which the material is synthesised, and (ii) the number of stacked titanate layers building up the nanostructure. Nanoribbons are formed at a higher reaction temperature than nanotubes and are composed of a larger number of stacked titanate layers whereas nanotubes are scrolls of only few titanate layers.

3.3.1.2 Morphology characterization

The SEM investigation of 1D protonated titanates (Figure 3.3a and b) confirmed their one-dimensional morphology as well as the morphological homogeneity of materials from an individual batch. HTiNTs are fine elongated structures that tend to agglomerate (Figure 3.3a). HTiNRs, on the other hand, are much larger than HTiNTs, have a rectangular cross section and a smooth surface (Figure 3.3b).

Average dimensions of 1D protonated titanates as well as fine structural features like porosity of protonated titanate nanotubes were investigated with TEM and HRTEM (Figure 3.3c and d, Figure 3.4, and Figure 3.5). The investigation of protonated titanate nanotubes revealed their hollow tubular structure (Figure 3.3c). Quantitative analyses of HTiNTs revealed that their inner diameters range from 2 nm to 6 nm with the average value of 3.2 nm (Figure 3.4a), whereas the outer diameters vary between 6 nm and 13 nm with the average value of 8.3 nm (Figure 3.4b). The number of titanate layers in the nanotubes' walls is not constant and ranges from 1 to 8. The inset in Figure 3.3c shows the top view of two nanotubes with walls composed of five titanate layers.

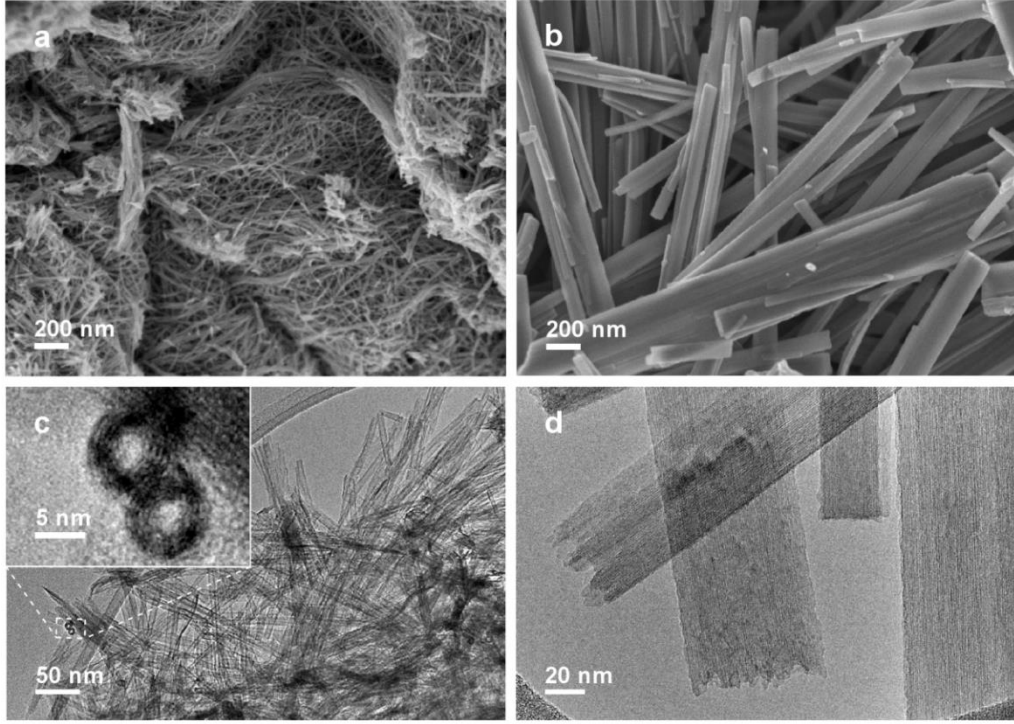


Figure 3.3: Images of protonated titanate nanotubes and nanoribbons, recorded with SEM (a, b) and TEM (c and d), respectively. The inset in the figure (c) shows a top view of two protonated titanate nanotubes with walls consisting of five titanate layers.

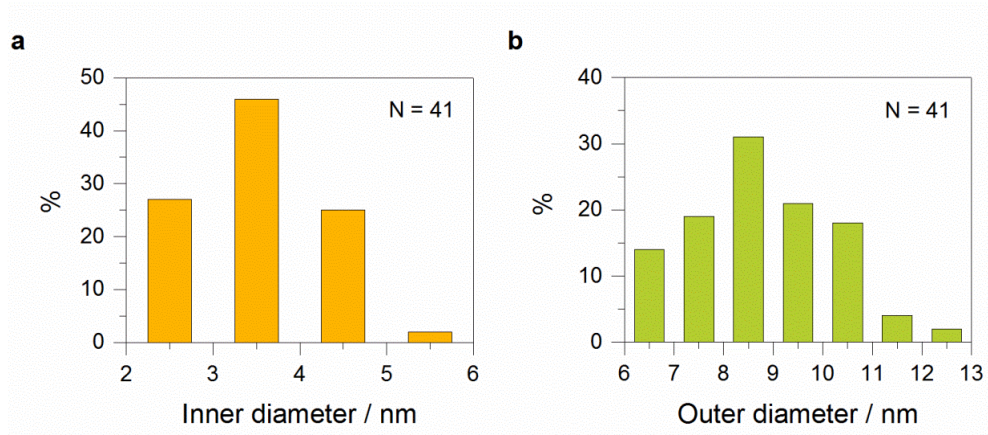


Figure 3.4: Size distributions of inner (a) and outer (b) diameters of protonated titanate nanotubes as determined with TEM.

Protonated titanate nanoribbons (Figure 3.3d) are parallelepiped structures that are elongated in the $[010]$ direction [2]. They have a broad width distribution from 10 nm to 300 nm with the approximate average value of 50 nm (Figure 3.5a). Nanoribbons' length distribution exponentially decreases from 1 μm to 6 μm , and the majority of protonated titanate nanoribbons are long up to 2 μm (Figure 3.5b). Nanoribbons' height is approximately 30 nm as determined with atomic force microscopy [48].

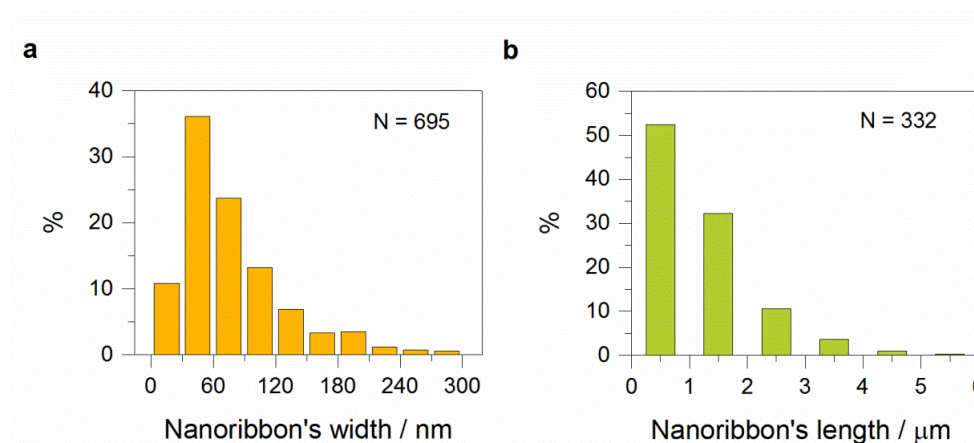


Figure 3.5: Size distributions of protonated titanate nanoribbons' widths (a) and lengths (b) as determined with TEM.

3.3.1.3 Chemical composition and textural properties

The efficiency of the ion exchange process, where 1D sodium titanates are transformed into 1D protonated titanates, was examined with EDXS analysis. The contents of sodium ions determined in the parent materials, NaTiNRs and NaTiNTs, were 11.2 wt% and 10.5 wt%, respectively. The sodium content in 1D protonated titanates dropped to less than 0.3 wt%. This confirms a successful transformation of sodium to protonated titanates (Table 3.1), as already indicated with XRD analysis (Figure 3.2).

Table 3.1: Textural and chemical properties of one-dimensional protonated titanates.

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume (mL g^{-1})	Average pore size (nm)	Na content (wt%)	Amount of acid sites (mmol g^{-1})	
					Medium	Strong
HTiNTs	324	1.13	3.2; 30	< 0.3	0.11	0.03
HTiNRs	41	0.12	-	< 0.3	0.18	-

Textural properties of one-dimensional protonated titanates were investigated with nitrogen adsorption-desorption analyses (Table 3.1, Figure 3.6). Specific surface areas of the materials were determined with the Brunauer-Emmett-Teller (BET) method. The N_2 adsorption isotherm for HTiNTs is presented in Figure 3.6a. Protonated titanate nanotubes have larger specific surface area ($324 \text{ m}^2 \text{g}^{-1}$) than nanoribbons ($41 \text{ m}^2 \text{g}^{-1}$) for almost one order of magnitude, which is a direct consequence of the morphological differences between the materials.

Figure 3.6b presents the BJH pore size distribution curves of 1D protonated titanates. Protonated titanate nanoribbons exhibit only a broad peak expanding over the region with the centre at approximately 60 nm. This mesoporosity arises from the interspace between the nanoribbons. Protonated titanate nanotubes, on the other hand, show two clear pore size maxima. The first peak with a narrow pore size distribution is located at 3.1 nm and corresponds to the inner diameter of the nanotubes. This is in a good concordance with the HRTEM analysis of protonated titanate nanotubes where the average inner diameter was determined to be 3.2 nm (Figure 3.4a). The second peak has a broader pore size distribution that is centred at 30 nm and arises from the material agglomeration (Figure 3.3a) [14].

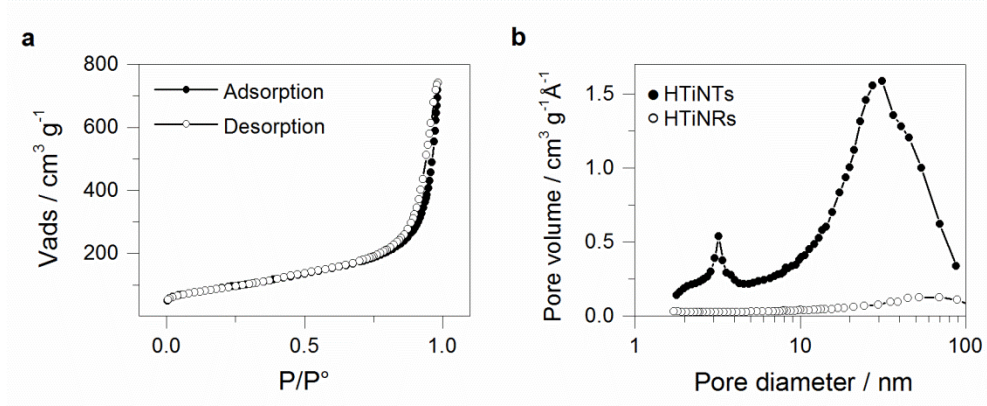


Figure 3.6: The N₂ adsorption isotherm at $-196\text{ }^{\circ}\text{C}$ for protonated titanate nanotubes (a), and the BJH pore size distribution curves for 1D protonated titanates (b).

3.3.1.4 Raman spectroscopy

Raman spectroscopy was employed to examine the influence of morphology on the bond strength in 1D protonated titanates (Figure 3.7).

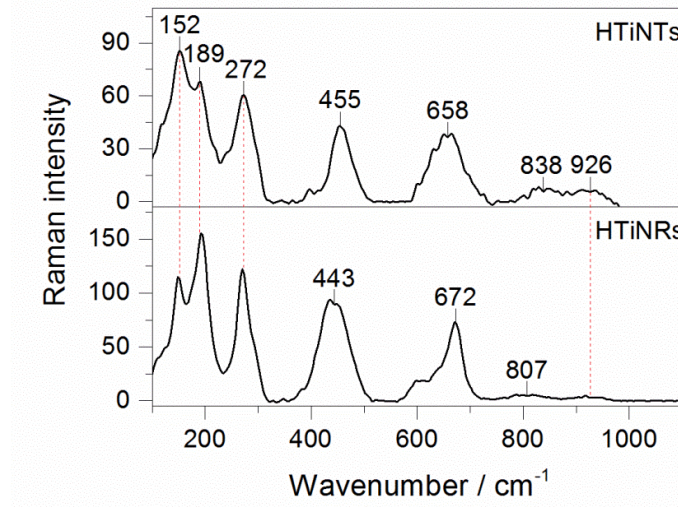


Figure 3.7: Raman spectra of protonated titanate nanotubes and nanoribbons.

Raman bands of analysed protonated titanate nanotubes and nanoribbons are attributed to trititanate $((\text{Na,H})_2\text{Ti}_3\text{O}_7)$ phase [49], [50]. Peaks positioned around 270 cm^{-1} , 455 cm^{-1} and 660 cm^{-1} are assigned to Ti–O–Ti stretching modes [30], [47]. As peaks of phonons involving displacements of light ions are generally located at higher wavenumbers, the peaks located at approximately 830 cm^{-1} and 930 cm^{-1} can be attributed to Ti–O–H oscillations with a very short Ti–O distance and four-coordinate Ti–O vibration in the titanate structure, respectively [30], [47], [51], [52]. In addition, the band at around 930 cm^{-1} is also reported to originate from a terminal Ti–O bond stretching directed either toward the interlayer space or to the outer surface of a nanostructure [45]. The main difference between the Raman spectra of protonated titanate nanotubes and nanoribbons is the red shift of the peak for a Ti–O–Ti stretching mode. It shifts from 672 cm^{-1} to 658 cm^{-1} as the morphology of protonated titanate changes from

the nanoribbon to the nanotube. This band shift can be attributed to the weakened Ti–O bond in nanotubes as TiO_6 octahedral are bent [30], [53].

3.3.1.5 Characterization of acid sites

3.3.1.5.1 NH_3 chemisorption and NH_3 -TPD Quantitative and qualitative analyses of the acidity of 1D protonated titanate nanostructures were performed with ammonia thermal programmed desorption and *in-situ* DRIFT spectroscopy of adsorbed ammonia, respectively. Figure 3.8 displays the NH_3 -TPD profiles for protonated titanate nanotubes and nanoribbons. NH_3 -TPD profile of HTiNTs can be fitted with two curves centred at 285 °C and 474 °C. The first peak corresponds to medium strong and the second to strong acid sites. In NH_3 -TDP curves of zeolites, the peaks positioned above 400 °C are attributed to the strong acid sites, which are of catalytic importance [54]. On the other hand, the NH_3 -TPD profile of HTiNRs consists of only a broad medium-temperature desorption peak with a maximum located at 290 °C, which corresponds to medium strong acid sites. The total amount of acid sites determined for HTiNRs is 0.18 mmol g^{-1} . For HTiNTs, the total acidity is smaller, 0.14 mmol g^{-1} , but 19 % of it correspond to strong acid sites.

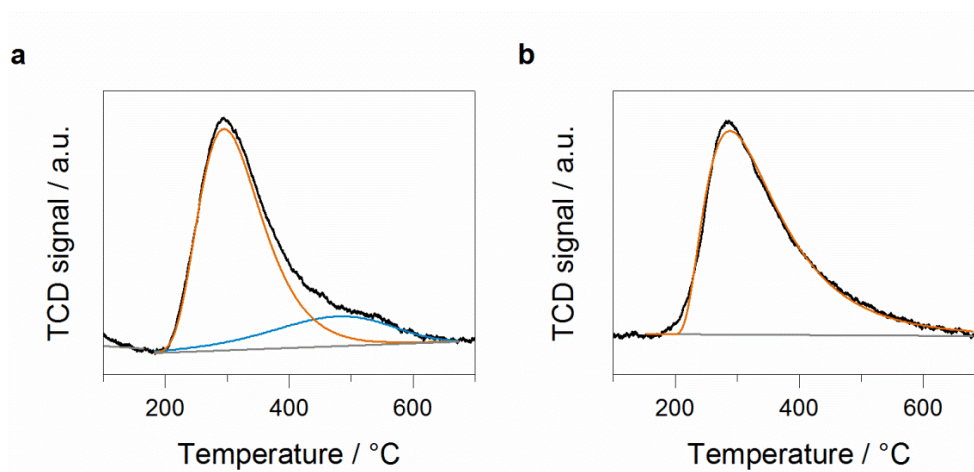
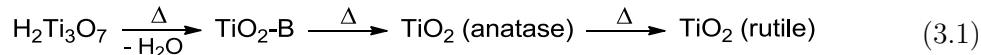


Figure 3.8: NH_3 -TPD profiles of protonated titanate nanotubes (a) and nanoribbons (b). The black line corresponds to the experimental measurement, whereas the orange and blue lines correspond to medium strong and strong acid sites, respectively.

The result that HTiNRs possess more acid sites than HTiNTs was not expected as HTiNTs have almost a 10 times larger specific surface area than HTiNRs. In order to elucidate this problem, numerous NH_3 -TPD measurements were carried out. The pre-treatment conditions of the measurements varied in temperature from 100 °C to 250 °C and time from 2 h to 10 h. The results showed that the amount of acid sites for HTiNTs was always comparable with the amount determined for HTiNRs. However, while TPD curve for HTiNRs always exhibited only one peak centred around 300 °C, the TPD line for HTiNTs had to be fitted with more curves where some of them corresponded also to strong acid sites.

For the critical evaluation of the NH_3 -TPD results, the understanding of the material is crucial. Protonated titanate is a very temperature-sensitive material that easily transforms to TiO_2 upon heating (Equation (3.1)) [21], [55]. This transformation can be considered as a condensation where the titanate layers connect to each other and water molecules leave the structure. During thermal treatment, three kinds of water leave

the material: physisorbed, chemisorbed, and water from the condensation among the titanate layers, which invokes crystal changes. Protonated titanate first transforms to a $\text{TiO}_2\text{-B}$ phase which is followed by the formation of anatase and finally a rutile phase as presented with Equation (3.1).



For NH_3 -TPD measurements only adsorbed water should be removed, but in reality the processes, when different ‘kinds’ of water leave the material, overlap. In addition, the temperature, at which all the processes take place, mainly depends on the morphology of nanoparticles [55]. Protonated titanate nanotubes are indeed much more temperature-sensitive than protonated titanate nanoribbons [21]. Therefore the determination of acid sites of the HTiNTs is very challenging as a longer thermal pre-treatment (or the one taking place at higher temperatures) has two opposite effects – adsorbed water is more efficiently removed, but the transformation to $\text{TiO}_2\text{-B}$ could start as well. Bearing all this in mind, the evidence that only HTiNTs possess strong acid sites is more important than the quantitative evaluation of acid sites in HTiNTs and HTiNRs.

3.3.1.5.2 *In-situ* DRIFT spectra with NH_3 adsorbed as a probe molecule on HTiNTs and HTiNRs The NH_3 -DRIFT spectrum of HTiNTs with pre-adsorbed NH_3 (Figure 3.9a) consists of two clear bands when recorded at room temperature. The first band is located at 1640 cm^{-1} and corresponds to Lewis acid sites to which ammonia is coordinatively bonded. The second peak is located at 1440 cm^{-1} and represents Brønsted acid sites (NH_4^+). With the increasing temperature, the intensity of both bands decreases. The band corresponding to Lewis acid sites disappears between 200°C and 250°C , while the one assigned to Brønsted acid sites is still visible at 350°C . Heating of the sample above 300°C led to the emergence of a new band. This is located at 1530 cm^{-1} and can be assigned to $-\text{NH}_2$ species [56]. It is reported that, under certain conditions, NH_3 can react with surface hydroxyl groups, which are preferably in a bridging mode, to form $-\text{NH}_2$ groups [56]. Therefore, this last band is attributed to very strong acid sites, which were also detected in the NH_3 -TPD profile of HTiNTs (Table 3.1, Figure 3.8a).

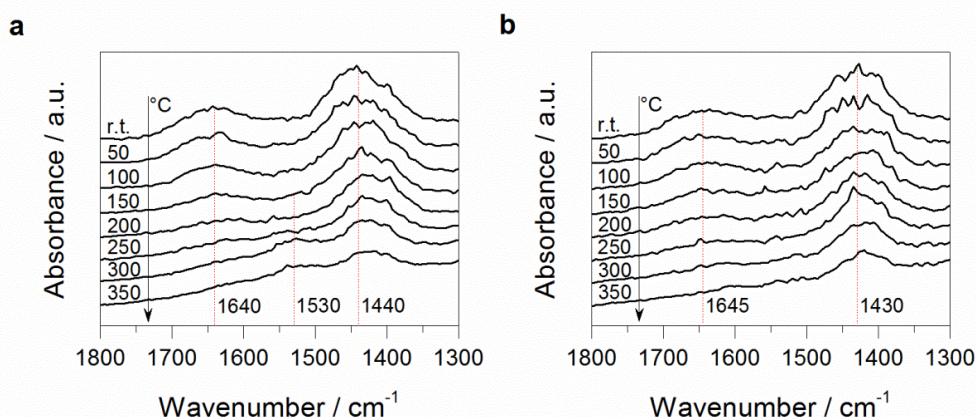


Figure 3.9: *In-situ* DRIFT spectra of HTiNTs (a) and HTiNRs (b) with adsorbed NH_3 .

Also the NH_3 -DRIFT spectra of HTiNRs with pre-adsorbed NH_3 (Figure 3.9b) show peaks corresponding to Lewis and Brønsted acid sites like in the case of HTiNTs, but at shifted wavenumbers, *i.e.* 1645 cm^{-1} and 1430 cm^{-1} , respectively. As for HTiNTs,

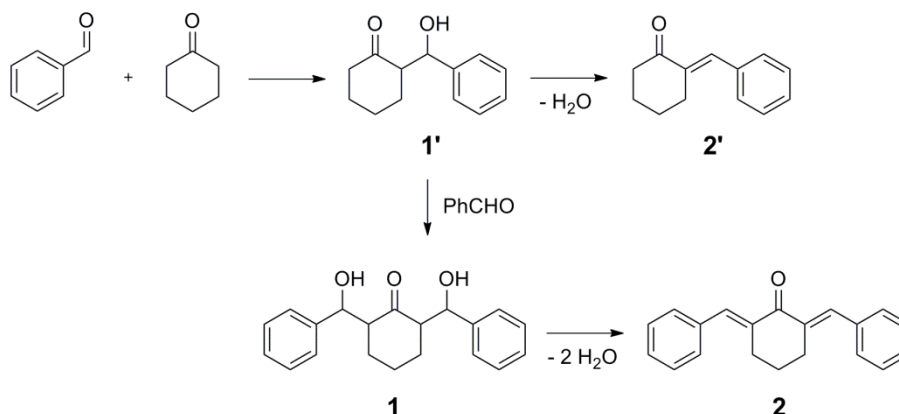
the band attributed to Lewis acid sites disappears between 200 °C and 250 °C, while the one assigned to Brønsted acid sites is still visible at 350 °C. The main difference between the spectra of HTiNTs and HTiNRs is that heating of HTiNRs with adsorbed ammonia molecules up to 350 °C did not lead to the formation of any additional band. This is again in very good concordance with the NH₃-TPD measurements, indicating only the existence of medium strong acid sites (Table 3.1, Figure 3.8b).

3.3.2 Catalytic reactions

3.3.2.1 Model reaction

Benzaldehyde and cyclohexanone were chosen as substrates for the model reaction of the aldol condensation. Since the aromatic aldehyde could act only as an electrophile, the self-condensation was prevented. The reaction pathway with the main intermediates and products is presented in Scheme 3.2.

Scheme 3.2: A reaction pathway of the aldol condensation between benzaldehyde and cyclohexanone.



Firstly, the aldol addition takes place where the aldols (**1**, **1'**) are formed. These then easily dehydrate to the final products, α,β -unsaturated cyclohexanone derivatives (**2**, **2'**), due to the stabilized conjugated π -system of the enone. The aldols were therefore never detected when the product mixture was analysed with ¹H NMR spectroscopy. The molar ratio between benzaldehyde and cyclohexanone was set to 2:1 in order to produce the target product **2**. However, the reaction selectivity most commonly decreased due to the condensation termination at the stage **2'**.

3.3.2.2 Optimization of the model reaction

A model reaction comprised of benzaldehyde and cyclohexanone, HTiNTs as a catalyst, and a solvent. The determination of the optimal reaction conditions for the model reaction started with the solvent scan. It included protic and aprotic solvents of different polarities (Figure 3.10a). The results show that the reaction conversions and selectivities increased with decreasing polarity of the solvent. The best results were therefore obtained in heptane as a greener alternative to hexane. The outcome of the solvent scan was surprising as the aldol condensation consists of two steps – the aldol addition, and the dehydration – that both have a polar transition state (Scheme 3.1). As such, polar solvents would be expected to better stabilize the transition states and enable faster product formation than the non-polar ones. To explain such behaviour, the catalyst's

surface needs to be included into consideration as well. Protonated titanate has a polar surface. Therefore, when employing a polar solvent, it competes with the substrate molecules for the active sites of the catalyst. On the contrary, non-polar solvents interfere less with the catalyst surface leading to better reaction progress. The results show that the reaction selectivity was more affected by the solvent polarity than the conversion. For the formation of the final product **2**, a molecule of **2'** has to adsorb on the catalyst surface. This requires more free space on the catalyst in comparison to the first condensation reaction when the product **2'** is formed.

Bearing this in mind, it is reasonable that the results of the model reaction improved from HFIP to heptane. The only result that outlays from the general trend is when the reaction was performed in DCM. There, the reaction conversion and selectivity are smaller than the expected ones. DCM molecules can have a pronounced interaction with the catalyst surface due to (i) non-bonding electron pairs located at the chlorine atoms, and (ii) a small size of DCM molecules in comparison to the reagents and substrates present in the reaction, which gives the solvent molecules high mobility. An increased interaction of the solvent with the catalyst active sites finally affected the reaction progress.

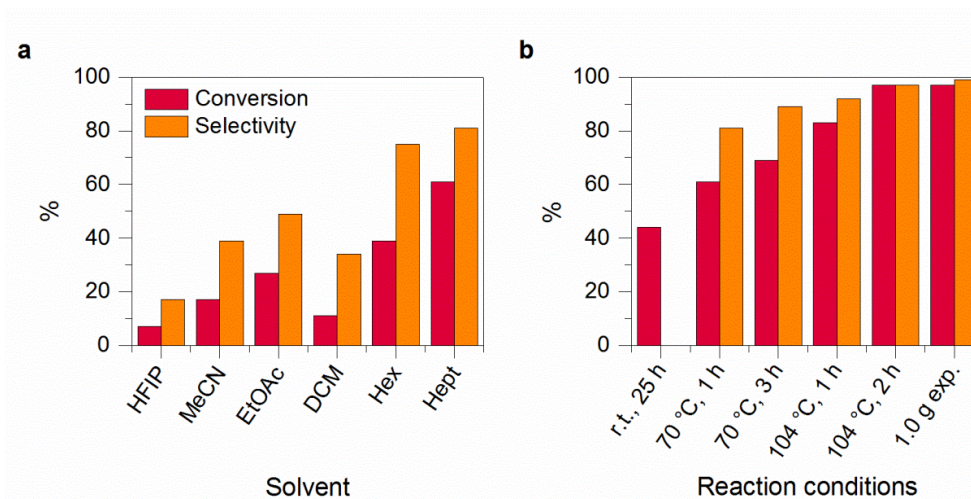


Figure 3.10: Results of the solvent scan (a) and optimisation (b) of model reaction. Reaction mixtures from (a) consisted of 1.0 mmol of benzaldehyde, 0.5 mmol of cyclohexanone, 25 mg of HTiNTs, and 0.5 mL of a solvent. The reactions were performed at 70 °C for 1 h. Reaction mixtures from (b) consisted of 1.0 mmol of benzaldehyde, 0.5 mmol of cyclohexanone, 25 mg of HTiNTs, and 0.5 mL of heptane. The reactions were performed as indicated in the diagram.

After the determination of the most suitable solvent for the model reaction, other reaction parameters were optimized (Figure 3.10b). When the reaction was performed at room temperature, 44 % of benzaldehyde oxidized to benzoic acid and no condensation product **2** was detected. The gas environment in the reaction vessels was air, therefore the oxidizing agent was oxygen. To initiate the condensation reaction, the system had to be heated. After the reaction was performed at 70 °C for 1 h, the reaction conversion already reached 60 % and the selectivity was higher than 80 % (Figure 3.10b, entry 2). The best results were obtained when the reaction was performed under reflux for 2 h (Figure 3.10b, entry 5). Under those conditions, 25 mg of the catalyst per 1.0 mmol of aldehyde sufficed for the almost quantitative conversion (97 %) with the same degree of the selectivity. This proves HTiNTs as a very efficient catalyst since the used amount of

HTiNTs corresponded to only 0.5 mol% of acid sites per 1.0 mmol of benzaldehyde. In homogeneous catalysis, typically 10 mol% of the catalyst is used.

Since the aldol condensation is commonly employed in industrial processes, a one gram experiment (according to benzaldehyde) was carried out too. The results of the reaction, performed under reflux for 4 h, were the 97 % conversion according to benzaldehyde and the 99 % selectivity (Figure 3.10b, entry 6). This reveals that HTiNTs are also potential candidates for the application in scaled-up processes.

3.3.2.3 Different catalysts

After the reaction conditions of the model reaction were optimized, catalytic efficiency of different catalysts was tested, including the blank experiment (Figure 3.11). When no catalyst was used, solely 28 % of benzaldehyde oxidised to benzoic acid. This reminds of the result obtained after the reaction was catalysed with HTiNTs but performed at room temperature (Figure 3.10b, entry 1). In both cases the activation energy was not overcome. Employment of concentrated HCl(aq) (37 %), as a homogeneous catalyst, did not result in any condensation product, and the results were comparable to those of the blank experiment.

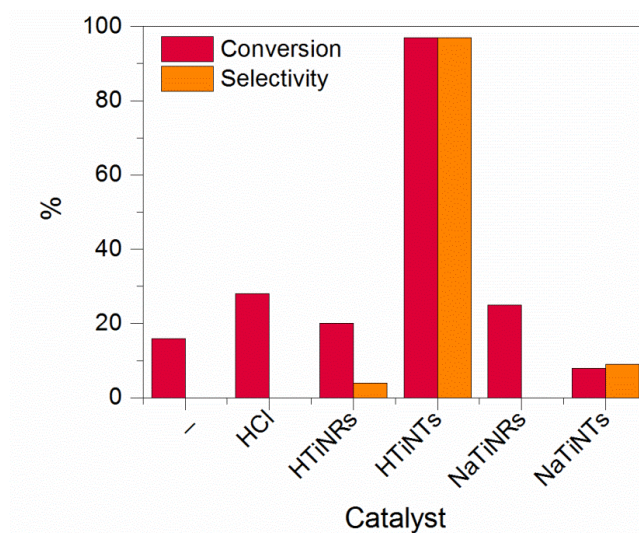


Figure 3.11: Results of the model reaction, catalysed with different catalysts. The reaction mixture consisted of 1.0 mmol of benzaldehyde, 0.5 mmol of cyclohexanone, catalyst (HCl – 10 mol%, nanomaterials – 25 mg), and 0.5 mL of heptane. The reactions were performed under reflux for 2 h.

In order to investigate the influence of morphology of 1D protonated titanates on the catalytic activity, protonated titanate nanoribbons were used as well (Figure 3.11, entry 3). However, HTiNTs have been proven as a more efficient acid catalyst than HTiNRs, which is also in good concordance with already published reports [33], [35]. Since HTiNTs and HTiNRs are chemically equal materials, the difference in the catalytic activity must arise from their distinct morphologies.

The characterization of acid sites of HTiNTs and HTiNRs revealed that only protonated titanate nanotubes possess strong acid sites. From the materials' NH_3 -DRIFT and Raman spectra, as well as other reports [30], [32], [56], it is suggested that those acid sites are surface –OH groups in a bridging mode, whose acidity increased during the nanotube formation.

When comparing protonated titanate nanotubes and nanoribbons, it is also evident that there are different fractions of a nanoparticle's surface which consist of protonated titanate layer's planes or edges (Figure 3.12).

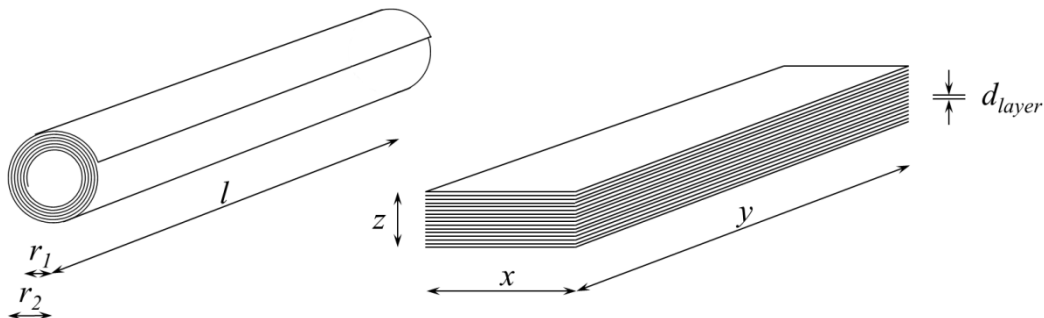


Figure 3.12: A schematic presentation of a protonated titanate nanotube (left) and a nanoribbon (right) with labelled measures.

The fraction (φ) of the nanostructure's surface consisting only of protonate titanate layer's edges can be geometrically evaluated with Equations (3.2) and (3.3).

$$\varphi_{nanotube} = \frac{2\pi(r_2^2 - r_1^2) + 2ld_{layer}}{2\pi l(r_1 + r_2) + 2\pi(r_2^2 - r_1^2) + 2ld_{layer}} \quad (3.2)$$

$$\varphi_{nanoribbon} = \frac{2(xz + yz)}{2(xy + xz + yz)} \quad (3.3)$$

r_1 and r_2 stand for the inner and the outer radii of the nanotube, l is the nanotube's length, d_{layer} is the thickness of one titanate layer, and x , y and z are the width, the length and the height of a nanoribbon, respectively. $\varphi_{nanotube}$ for a nanotube of average dimensions with $r_1 = 3.2$ nm, $r_2 = 8.3$ nm, $l = 1$ μ m and $d_{layer} = 0.7$ nm (estimated from Figure 3.3c), is approximately 2 %. On the other hand, $\varphi_{nanoribbon} = 39$ % for the average-sized protonated titanate nanoribbon with $x = 50$ nm, $y = 1$ μ m and $z = 30$ nm. Maybe this distinction in the surface composition of HTiNTs and HTiNRs also comprises a part to the final difference between the catalytic activities of the materials.

A reasonable question, in regard to HTiNTs, is also whether the reaction takes place exclusively on the outer surface of a nanotube or also in its channel. I believe that the reaction proceeds on the outer surface of the nanotube. Firstly, the inner diameter of nanotubes is around 3.2 nm. The larger diameter of the final product **2** is about 1.2 nm. Therefore, two product molecules could already block the nanotube's channel. In addition, the catalyst was not activated prior the reaction, therefore there was adsorbed water in the channel narrowing or even blocking it. Also in the case of carbon nanotubes, reactions, where the product molecule consists of more than one aromatic ring, proceed in nanotubes with significantly larger inner diameters (from 40 nm to 100 nm) [57].

Finally, the catalytic activity toward the aldol condensation of the parent materials of 1D protonated titanates, 1D sodium titanates, was tested (Figure 3.11). The aldol condensation can be catalysed either by acids or bases and sodium titanates were already reported to act as a solid basic catalyst [58], [59]. When sodium titanate nanotubes and nanoribbons were employed in the model reaction as solid catalysts, the results were rather poor (Figure 3.11, entries 5 and 6). In the case of NaTiNRs, no condensation product was detected as the oxidation of benzaldehyde prevailed over the condensation

reaction. NaTiNTs proved a better catalyst since also the condensation product **2** was formed. This can be most probably explained by the fact that not all sodium positions on the surface of NaTiNTs were occupied with Na^+ ions. Some of Na^+ ions were exchanged with H^+ that acted as acid sites afterwards. This corroborates well with the overall results of application of sodium titanates as solid catalysts. Sodium titanate can be theoretically considered as a material with only Lewis acid sites whereas protonated titanate possesses both – Brønsted and Lewis acid sites. Therefore the unique activity of HTiNTs and HTiNRs points to the vital importance of Brønsted acid sites possessed by protonated titanates.

3.3.2.4 Different substrates

The generality of HTiNTs as a catalyst for the aldol condensation was tested with switching either benzaldehyde or cyclohexanone for different electrophiles and enolisable compounds, respectively (Figure 3.13).

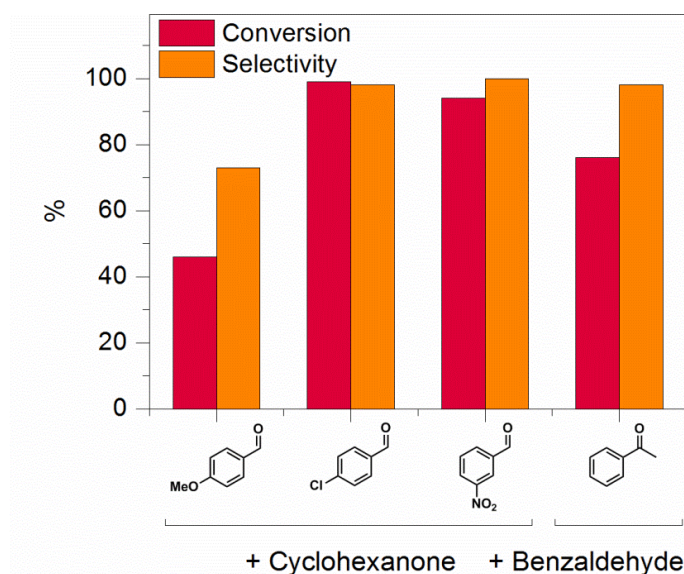


Figure 3.13: Results of catalysis of the aldol condensation between different substrates with protonated titanate nanotubes. Reaction mixture consisted of 1.0 mmol of substituted benzaldehyde, 0.5 mmol of cyclohexanone, 25 mg of HTiNTs, and 0.5 mL of heptane. Reactions were performed under reflux for 2 h (p-OMe) or 4 h (p-Cl, m-NO₂). In the entry 4, 1.0 mmol of acetophenone reacted with 1.0 mmol of benzaldehyde in 0.5 mL of heptane under reflux for 4 h.

When benzaldehyde was exchanged with aromatic aldehydes substituted with electron withdrawing groups (p-Cl, m-NO₂), the cross aldol condensation with cyclohexanone proceeded with high conversions and excellent selectivities (Figure 3.13, entries 2 and 3). Employment of an aromatic aldehyde substituted with an electron donating group (p-OMe) led to the decrease of the reaction conversion and the selectivity (Figure 3.13, entry 1). When an electron withdrawing group is located at the aromatic ring of an aldehyde, the electron density of the carbonyl group is also decreased, thus making it more electrophilic and prone to the nucleophilic enone addition. When cyclohexanone was replaced with acetophenone, the conversion decreased to 76 % (Figure 3.13, entry 4). Acetophenone is less reactive than cyclohexanone due to (i) the conjugation of the carbonyl bond with the aromatic system and (ii) electron donating characters of the aromatic ring and the methyl substituent, making the ketone less acidic. As such,

HTiNTs proves as a catalyst that can be used in different reaction systems for the aldol condensation. Since the reaction progress was affected with the reactivity of the substrates, reaction conditions should be readjusted for each individual reaction system.

3.3.2.5 Reuse of the catalyst

One of the important catalyst characteristics is also its reusability. Therefore, a set of experiments where HTiNTs were used for five repetition cycles was carried out (Figure 3.14). After the termination of one reaction, the catalyst was collected with centrifugation, rinsed with EtOAc for three times and dried overnight in air in a fume hood. The catalyst was not activated in any manner prior its application in the next reaction cycle. During the repetition cycles, the reaction conversion and selectivity decreased and remained constant at approximately 80 %. This is a good result, especially in comparison to the present practice in industry, where a homogeneous catalyst is used and cannot be recovered during the product isolation.

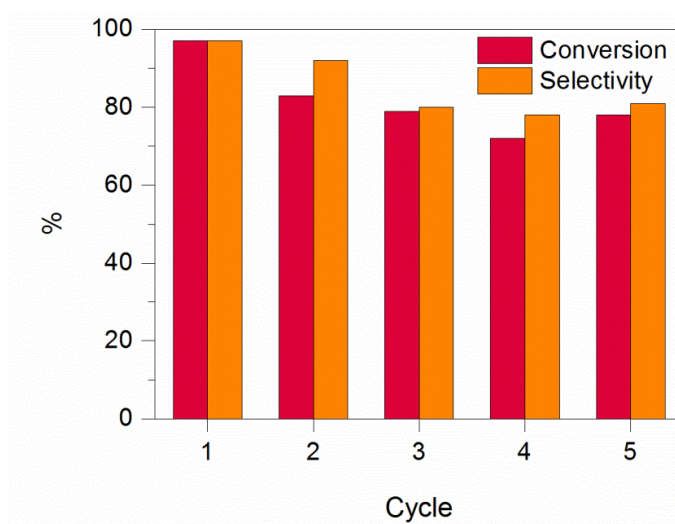


Figure 3.14: Results of the repetition of the model reaction catalysed with recovered protonated titanate nanotubes. Reaction mixture consisted of 1.0 mmol of benzaldehyde, 0.5 mmol of cyclohexanone, 25 mg of HTiNTs, and 0.5 mL of heptane. Reactions were performed under reflux for 2 h.

The diminishing of the catalytic activity of HTiNTs is attributed to the remaining organic compounds that are adsorbed on the catalyst's surface. In order to qualitatively and quantitatively investigate the catalyst poisoning, TGA-MS analyses of fresh and used protonated titanate nanotubes (after five repetition cycles) were carried out (Figure 3.15).

TGA of the fresh HTiNTs revealed that the material's mass loss occurs in two successive steps that overlap (Figure 3.15a). From room temperature to ~ 200 °C, water molecules ($m/z = 18$) are predominantly evolved, whereas the typical signal for the CO_2 evolution ($m/z = 44$) is observed from 200 °C to 450 °C. CO_2 formation is attributed to the thermal decomposition of EtOH that is used in the last step of the catalyst synthesis (3.2 Experimental section, p. 20). As EtOH molecules from the outer surface of a protonated titanate nanotube can more easily desorb than those from the nanotube's channel, I believe that the majority of adsorbed EtOH molecules originate from the nanotube's channel and do not interfere with the catalytic reaction.

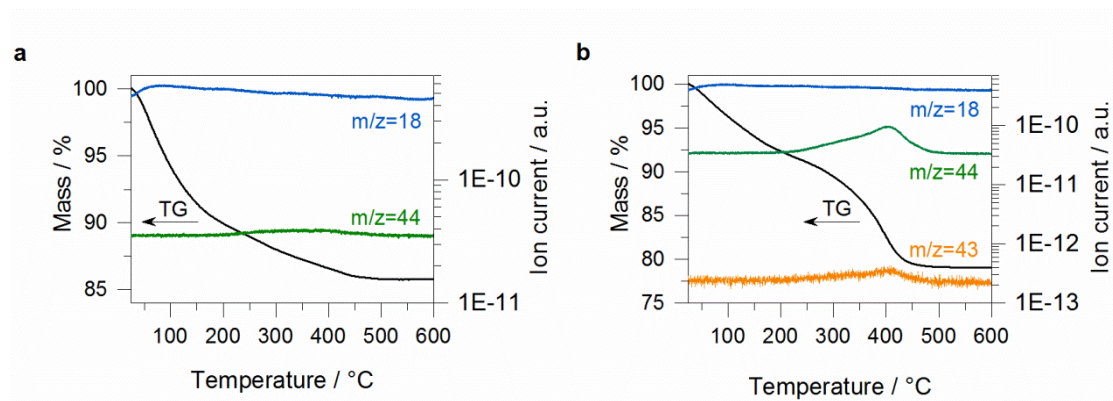


Figure 3.15: TGA-MS results of bare (a) and used (b) protonated titanate nanotubes.

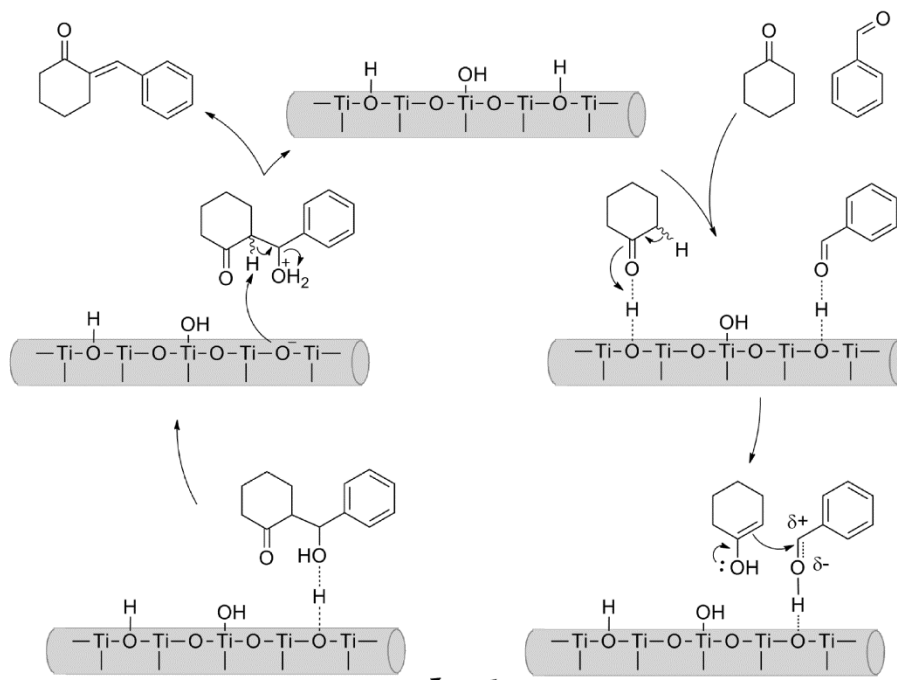
When considering the recovered catalyst, its appearance already indicates that some aromatic products **2'** and **2** are adsorbed on its surface. Fresh protonated titanate nanotubes have a white colour whereas the colour of the used catalyst is orange-red. TGA of the recovered catalyst reveals the mass loss of ~ 10 % in the temperature range from 300 °C to 450 °C, which is typical for thermal decomposition of organic compounds (Figure 3.15b). The signal for the CO₂ evolution is also more pronounced in comparison to the TGA-MS analysis of the fresh catalyst, which confirms adsorption of additional organics on the surface of the used catalyst. Furthermore, a new signal with $m/z = 43$ appears in the mass spectrum of the used catalyst. The signal corresponds to acetyl cations (CH₃CO⁺) from EtOAc that was used during the product isolation.

For the qualitative analysis of the organics, adsorbed on the surface of the recovered catalyst, TG curves of both catalysts in the temperature range from 200 °C to 450 °C were considered. The difference in the corresponding mass losses of the recovered and the fresh catalyst reveals that the adsorbed organics comprise approximately 5 wt% of the used catalyst.

3.3.2.6 Proposed mechanism

The proposed aldol condensation mechanism over a protonated titanate nanotube is presented in Scheme 3.3. For the sake of clarity, the reaction on only one side of a cyclohexanone molecule is presented. The mechanism is based on the material's possession of strong acid sites (bridging -OH groups), which was evidenced from the catalyst characterization, and is in good concordance with other reports [37]. The reaction starts with the activation of reagents and reactants through hydrogen transfer from the bridging -OH groups of HTiNTs. Then, ketone converts to enol *via* tautomerism and attacks the activated electrophile – benzaldehyde – to produce an aldol. The latter quickly dehydrates, producing the final enone product that desorbs from the protonated titanate surface afterwards.

Scheme 3.3: The proposed mechanism of the aldol condensation between benzaldehyde and cyclohexanone catalysed with protonated titanate nanotubes. The reaction is presented only on one side of a cyclohexanone molecule for the sake of clarity.



3.4 Conclusion

To conclude, protonated titanate nanotubes have proven as an efficient catalyst for the aldol condensation between benzaldehyde and cyclohexanone. Their unique catalytic activity originates from the possession of strong acid sites that are most probably bridging -OH groups located on the curved surface of the material. HTiNTs have been revealed as a material that fulfils the demands of today's chemistry, especially in regards to the green chemistry principles, due to the following features: (i) the catalyst did not require any activation prior the reaction, (ii) HTiNTs successfully catalysed the aldol condensation among different substrates, (iii) the catalyst could be recovered, and (iv) HTiNTs were efficient even in a one-gram experiment. All this makes HTiNTs a promising alternative to homogeneous catalysts for the aldol condensation which are currently applied in the industry.

Chapter 4

Transformation of Protonated Titanate Nanoribbons to Titanium Dioxide Nanoribbons and Their Photocatalytic Activity

4.1 Introduction

Protonated titanate is a temperature sensitive material that has a layered structure, composed of negatively charged titanate layers with protons that are embedded in between them [13], [60]. The crystal structure can also be described with TiO_6 octahedra building up zigzag ribbon units that the material is composed of [60]. Since the zigzag structure is also present in the TiO_2 -B phase as well as in anatase, the transformation from protonated titanate to TiO_2 -B and anatase proceeds quite easily [61], [62].

4.1.1 Transformation of protonated titanate to TiO_2

The transformation from protonated titanate to TiO_2 -B and anatase can be regarded as a condensation according to the equation $\text{H}_2\text{Ti}_3\text{O}_7 \rightarrow 3 \text{TiO}_2 + \text{H}_2\text{O}$. Theoretically, a condensation reaction can be achieved in two ways like all reactions: (i) with energy input large enough to overcome the activation energy of the reaction, or (ii) with lowering the activation energy, that is, with catalysing it, where catalysts for condensations are usually acids and bases [63]. In practice, the first way is performed with calcination of protonated titanate in air [18], [21], [64] or some other atmosphere [65]–[67] whereas the catalysis is performed in aqueous media under hydrothermal [4], [8], [22], [61] or even ambient conditions [47]. The transformation from protonated titanate to TiO_2 has already been a subject of many researches. However, some questions have still remained: How does protonated titanate behave under basic hydrothermal conditions and how do different bases influence the transformation? In addition, what is the exact role of water or other liquid reaction media? Now, the published results of the following transformation performances will be described:

- annealing in an oxidative atmosphere – air,
- annealing in a reductive atmosphere,
- treatment in aqueous media.

4.1.1.1 Annealing in an oxidative atmosphere – air

Annealing of 1D protonated titanates in air is the most common approach for their transformation to TiO_2 . During the heating of protonated titanates, the dehydration of intralayered $-\text{OH}$ groups first occurs and is followed by the dehydration of interlayered $-\text{OH}$ groups [64]. Qamar *et al.* [18] even proposed that the protons in the protonated titanates could serve as the acid catalyst of the condensation of $-\text{OH}$ groups during the heat treatment leading to an earlier anatase formation. Temperatures, at which all those changes take place, highly depend on the initial morphology of protonated titanates.

When heated in air, protonated titanate nanotubes started to transform to anatase at temperatures higher than 200 °C and it was the only phase obtained after 500 °C [21], [64]. The phase transition into anatase was also accompanied with the morphology collapse into nanoparticles [21]. With the increasing temperature the crystal size grew due to particle sintering [21].

Nanoribbons revealed to be more stable than nanotubes upon heating in terms of the morphology and the crystal structure preservation [21]. This can be attributed to the greater number of stacked nanosheets in nanoribbons that stabilize the crystal structure against rearrangement at higher temperatures [21]. As characterized, starting $\text{H}_2\text{Ti}_3\text{O}_7$ nanoribbons converted to monoclinic $\text{TiO}_2\text{-B}$ phase during calcination from 200 °C to 500 °C with no morphological changes. When protonated titanate nanotubes were annealed, no $\text{TiO}_2\text{-B}$ phase was detected. The authors [21] suggested that nanotubes could also transform to anatase through the $\text{TiO}_2\text{-B}$ phase. However, the latter is difficult to detect since $\text{TiO}_2\text{-B}$ presence might be short-lived due to the weaker nature of the nanotube configuration. Nanoribbon's transformation from $\text{TiO}_2\text{-B}$ phase to anatase started at temperatures above 500 °C, which also invoked some fragmentation and spherical nanoparticle formation. Anatase was the only phase obtained after annealing at 700 °C and no further change in morphology was observed when annealing the sample at 800 °C [21].

Morphological changes during the annealing of protonated titanate nanotubes and nanoribbons also affected a specific surface area of the materials. The specific surface area of initial nanotubes ($313 \text{ m}^2 \text{ g}^{-1}$) decreased to $106 \text{ m}^2 \text{ g}^{-1}$ after the calcination at 500 °C when the nanotube morphology was already destroyed. Increase in calcination temperature up to 800 °C invoked particle sintering and agglomeration that led to the final specific surface area of $5 \text{ m}^2 \text{ g}^{-1}$ [21]. Nanoribbons, in comparison with nanotubes, have a smaller specific surface area for one order of magnitude. Protonated titanate nanoribbons therefore had the specific surface area of $29 \text{ m}^2 \text{ g}^{-1}$ that reduced to $15 \text{ m}^2 \text{ g}^{-1}$ after the sample was annealed at 600 °C. The final specific surface area of nanoribbons calcined at 700 °C was $5 \text{ m}^2 \text{ g}^{-1}$ due to the structure collapse [21].

4.1.1.2 Annealing in a reductive atmosphere

Protonated titanate can convert to TiO_2 with annealing in a reductive atmosphere as well. Under such conditions, protonated titanate first transforms to TiO_2 and then doping and potential reduction of Ti^{4+} to lower oxidation states occur. Not many reports on the annealing of protonated titanate in a reductive atmosphere exist [65], [68], but there are quite a few about calcination of TiO_2 in different atmospheres. Most commonly used gasses are H_2 [66], H_2S [67], [69], and NH_3 [70]–[73]. They were mainly examined for tailoring the optical properties of TiO_2 . In this work I will limit to annealing in an ammonia atmosphere. When protonated titanate is annealed in a NH_3 atmosphere, it first transforms to anatase [68] and then N-doping begins. N-doped TiO_2 has attracted

a lot of attention in the past due to the material absorption also in the visible region of light [65], [74]–[76].

4.1.1.3 Conversion in aqueous media

The transformation from protonated titanate to TiO_2 in aqueous media proceeds with the two main mechanisms: (i) a topotactic reaction, and (ii) dissolution-recrystallization. A topotactic reaction occurs among protonated titanate and anatase due to their structural similarities (Figure 4.1). The reaction proceeds as condensations among $-\text{TiOH}$ entities and simultaneous *in situ* structural rearrangement of TiO_6 octahedra [4], [8], [22], [61]. This transformation usually happens under milder conditions when the morphology is preserved.

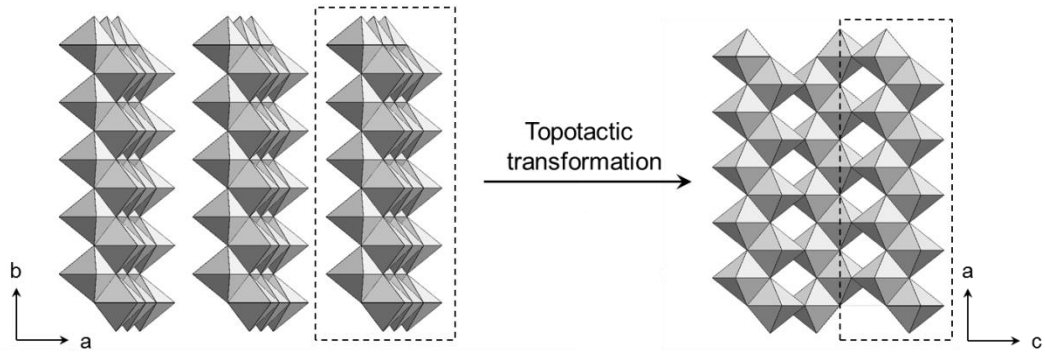


Figure 4.1: A schematic presentation of topotactic transformation from protonated titanate ($\text{H}_2\text{Ti}_3\text{O}_7$) to anatase.

Under stronger reaction conditions, *i.e.* in more acidic media and at higher reaction temperatures, protonated titanate dissolves and the material recrystallizes in a thermodynamically favoured rutile structure [4], [47]. In this case, the product TiO_2 nanoparticles have a new, non-related morphology when compared to the morphology of the starting material.

4.1.1.4 Conversion under neutral hydrothermal conditions

In 1999 the transformation of $\text{H}_2\text{Ti}_4\text{O}_9$ nanoribbons to anatase under hydrothermal conditions was first reported [77]. The starting protonated tetratitanate NRs were hydrothermally treated in water at only 250 °C for 1 h and the final anatase product retained one-dimensional morphology as nanocrystals formed nanofibrile aggregates. Mao *et al.* [22] treated HTiNRs hydrothermally in water at 170 °C from 12 h to 36 h and the resulting product were fibrile anatase aggregates. They observed that anatase nanocrystals grew from the HTiNRs surface which they attributed to epitaxial growth as there is a small lattice mismatch between the parent protonated titanate and the product anatase phase [22].

Furthermore, the influence of the morphology of protonated titanate on the morphology of TiO_2 NPs was investigated. HTiNTs are finer and more fragile structures when compared to HTiNRs. When HTiNTs were hydrothermally treated in water, anatase nanoparticles of bipyramidal [78] or cubic and rhombohedral [22] shape were obtained. The proposed mechanism included the growth of anatase crystals from the surface defects of HTiNTs [78]. As the anatase nanoparticles enlarged, the HTiNTs became thinner [22]. Similarly, when protonated titanate nanosheet arrays were

hydrothermally treated in water, anatase bipyramids were obtained that first grew from the nanosheet surface [79].

4.1.1.5 Conversion under acidic conditions

When the transformation of protonated titanate to TiO_2 is performed under acidic conditions, the acid can accelerate both mechanisms – a topotactic reaction [61], and material's dissolution [47]. The type of the process that the acid would promote is governed by other reaction conditions like the acid type, its concentration and a reaction temperature [4], [47].

Zhu *et al.* [61] reported on the transformation of protonated titanate nanofibers into long titanate nanofibers partially covered with anatase nanocrystals when the initial dispersion of nanofibers in 0.05 M $\text{HNO}_3(\text{aq})$ was heated at 100 °C for two days. When the reaction temperature was increased to 120 °C, the titanate phase completely converted into anatase where the nanocrystals aggregated into fibril nanostructures.

At higher acid concentrations the dissolution-recrystallization process is excelled over a topotactic reaction. Hydrothermal treatment of HTiNRs in 2.63 M $\text{HNO}_3(\text{aq})$ or in the reaction medium with the pH value of 0 resulted in rutile nanoparticles [4], [80]. Under such conditions, titanates are highly protonated and the structure is destabilized due to the repulsion between positively charged titanate layers [80]. When dissolved, TiO_6 octahedra are also protonated and they connect more easily with each other through corner instead of edge sharing due to charge repulsion. Corner sharing of TiO_6 octahedra leads to rutile formation whereas edge sharing would result in an anatase phase [80].

4.1.1.6 Room-temperature stability of protonated titanate

Transformation from protonated titanate to TiO_2 under hydrothermal conditions led to the investigation of the room-temperature stability of protonated titanate suspensions at different pH values [47], [81]. HTiNTs proved to be stable under basic and neutral conditions, as their aging in 0.1 M $\text{NaOH}(\text{aq})$ and deionized water for 5 months invoked minimal morphological changes in the material [47]. HTiNTs transformed to the mixture of anatase and rutile nanoparticles after being exposed to 0.1 M $\text{H}_2\text{SO}_4(\text{aq})$ for one month [81] whereas aging for two months resulted in a complete conversion to rutile nanoparticles [47]. The transformation of HTiNTs proceeded several times slower when 0.1 M $\text{HCl}(\text{aq})$ or $\text{HNO}_3(\text{aq})$ were used instead of sulfuric acid [47]. These results confirm that protonated titanate is not stable under acidic conditions and that the dissolution rate of protonated titanate depends on the acid nature ($\text{H}_2\text{SO}_4 > \text{HNO}_3 \approx \text{HCl}$).

4.1.1.7 Annealing *versus* hydrothermal treatment of protonated titanate

The conversion of protonated titanates to TiO_2 under hydrothermal conditions has some advantages in comparison with annealing in air. Hydrothermally converted anatase nanostructures could possess more –OH groups on the surface than the annealed ones [22]. The specific surface area of nanoribbons increased during the hydrothermal transformation into anatase from $18.3 \text{ m}^2 \text{ g}^{-1}$ (protonated titanate) to $61.6 \text{ m}^2 \text{ g}^{-1}$ (anatase phase), which was due to the formation of anatase nanocrystal aggregates [8]. On the contrary, the specific surface area of nanotubes or nanoribbons decreased during annealing in air [21]. Both properties yielding from the hydrothermal treatment improve the photocatalytic activity of the material. Furthermore, if protonated titanate contains a certain degree of sodium ions, and the ion exchange of the sodium titanate has not

been completed, they can be successfully exchanged with protons during the hydrothermal treatment [8].

4.1.2 Sodium titanate as a starting material

Sodium titanate can also serve as a TiO_2 precursor. Hydrothermal treatment of NaTiNTs in different reaction media mainly resulted in elongated anatase nanostructures. When NaTiNTs were hydrothermally treated in 0.1 M $\text{HNO}_3(\text{aq})$, anatase nanorods, elongated along the [001] direction, were formed [82]. Hydrothermal treatment of NaTiNTs in water led to anatase nanorods elongated along the [001] direction with the lateral {100} facets [83]. The proposed mechanism was a dissolution-recrystallization where OH^- ions acted as a capping agent that preferentially adsorbed on the {100} planes. When anatase spindle nanorods with the predominantly exposed {301} facets were obtained after hydrothermal treatment of sodium titanate that was initially synthesized at 150 °C, in water, Na^+ ions were also explained to have a shape-tailoring role [84]. The influence of the alkaline ions (Li^+ , Na^+ and K^+) on the shape of grown anatase nanoparticles was mainly attributed to the ion's size and charge density [84].

4.1.3 Photocatalytic activity

The term ‘photocatalysis’ was first used by Plotnikow [85] in 1910, whereas the milestone in the TiO_2 photoactivity represents photocatalytic water splitting by TiO_2 under UV irradiation, which was first achieved by Fujishima and co-workers in the 1970s [86]. Since then, TiO_2 has been a subject of intense research and its exploitation ranges nowadays from photovoltaics and photocatalysis to photoinduced superhydrophilicity [87]. Photocatalysis includes synthesis as well as degradation reactions. The latter are mainly used for degradation of organic pollutants from wastewater and exhaust air, as there are increasing demands for impeccable water and the restriction of atmosphere pollution.

TiO_2 is a wide band gap semiconductor of the n-type due to the defects in the structure (oxygen vacancies) [87]. The general mechanism of photocatalytic processes over illuminated TiO_2 is presented in Figure 4.2. For the success of photoinduced reactions, the potentials of a valence and a conduction band are important as well as the energy required to overcome this potential difference, namely band gap energy (E_g) [87]. When photons with energy exceeding E_g are absorbed by the material, electrons from the valence band are excited to the conduction one and positively charged holes are created in the valence band. The energy level at the bottom of the conduction band actually has the reduction potential of photoexcited electrons, whereas the top level of the valence band has an oxidation potential that photogenerated holes would inherit. Since the oxidation potential of photogenerated holes (2.7 V) is higher than the reduction potential of photogenerated electrons (0.5 V), the majority of photocatalytic reactions performed over TiO_2 are photooxidations [87].

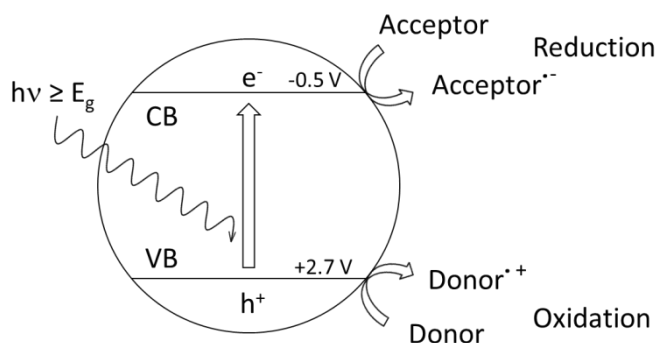


Figure 4.2: Photoinduced processes on a TiO_2 surface.

Let us summarize the mechanisms that are involved during the photocatalysis. After the generation of an exciton e^-h^+ , charges separate and diffuse to the surface (or bulk) where many processes can take place afterwards. It is still not undoubtedly clear whether charge carriers are always first trapped in the materials potential holes or if they directly interact with adsorbed species. Holes can be therefore trapped by surface $-\text{OH}$ groups or by adsorbed water. Both processes lead to the formation of $\text{OH}^\bullet$ radicals, which are highly oxidizing agents with only elemental fluorine exceeding their oxidation potential [87]. Photogenerated electrons can be trapped by Ti^{4+} centres creating Ti^{3+} or by adsorbed substrates. Among the latter, an electron is most commonly extracted by adsorbed O_2 leading to the formation of a superoxide radical ($\text{O}_2^{\bullet-}$), as other reducible substrates cannot kinetically compete with oxygen [87]. The reaction of superoxide radicals with water molecules also results in the formation of $\text{OH}^\bullet$ radicals afterwards [88]. All mentioned processes of charge carriers trapping and interfacial transfer simultaneously compete with the charge recombination which would lead to the lower photoactivity of the material. For enhanced photocatalysis, deep electron traps and highly hydroxylated surface are favoured to prolong the lifetime of electrons and holes and to ensure better adsorption of substrate molecules on the material's surface [87]. Substrate molecules are degraded mainly through oxidation processes governed by $\text{OH}^\bullet$ radicals or direct charge transfer from the material to the substrate. When the photodegradation of a compound is complete, the final products are CO_2 , H_2O and possible oxidized anions such as sulphates, nitrates, etc. if the substrate also contained the corresponding atoms [87].

4.1.3.1 Influences on material's photoactivity

There are many factors that influence the overall efficiency of the photocatalytic process and will now be discussed.

4.1.3.1.1 Crystal phase All naturally occurring TiO_2 polymorphs are semiconductors with band gap energies ranging from 3.00 eV (rutile) to 3.20 eV (TiO_2 -B phase and anatase) and, finally, 3.30 eV (brookite) [88]. Among them, anatase is generally the most photoactive, being followed by rutile. Their adsorption thresholds correspond to 384 nm and 410 nm, respectively [87]. The superior photoactivity of anatase originates from higher electron mobility, higher degree of hydroxylation and lower recombination rate due to larger band gap energy when compared to rutile [87], [88]. It is well known that mixed phases can have enhanced photocatalytic performance when compared to single ones. A good example of this is a mixture of anatase (80 %) and rutile (20 %), which is commercially known as Degussa P25 and is commonly used as a photocatalytic standard.

The abundance of phase junctions and a small difference in the band gap positions of anatase and rutile enable efficient charge separation thereby reducing their recombination [60], [88].

4.1.3.1.2 Specific surface area and crystallinity Other important factors for efficient photocatalysis are the material's specific surface area (SSA) and crystallinity. Larger SSA provides more active sites on the material's surface where photocatalytic processes can take place. Also, better crystallinity enhances photocatalytic efficiency as there are fewer defects in the structure which act as recombination sites. However, nanostructures with high specific surface area are usually rich in crystalline defects whereas improvement of crystallinity, which is generally achieved with calcination, leads to material coarsening and decrease in SSA. Therefore these two parameters – SSA and crystallinity – must often be compromised in order to optimize the final material's photoactivity [87], [88].

4.1.3.1.3 Surface hydroxylation degree The degree of surface hydroxylation is important for photocatalytic performance of the material as hydroxyl groups have two functions: (i) they are a source of $\text{OH}^\bullet$ radicals which are the key reagents in the photooxidation reactions, and (ii) they act as adsorption sites for substrate molecules [87]. Their content can be increased with water impregnation, material synthesis at lower temperatures and also with tailoring nanostructure's shape with predominant exposure of specific crystal facets. The (001) surface facets are reported to trap holes more efficiently on O^- centres whereas the (101) facets promote electron trapping on Ti^{4+} centres producing Ti^{3+} . Therefore, the former facets can be considered to provide oxidation sites and the latter the reduction ones [88].

4.1.3.1.4 Material's morphology Finally, the nanoparticle's morphology also influences the material's photocatalytic performance. 1D morphology has some advantages over 0D: (i) 1D nanoparticles are normally better crystalline than 0D, leading to lower recombination rates of photoinduced electrons and holes of the former, and (ii) 1D morphology enables fast and efficient charge transfer [24], [60].

4.1.3.1.5 Doping TiO_2 is very close to being a perfect semiconductor photocatalyst as it is an abundant and a low-cost material which is chemically and biologically inert, and photocatalytically stable. Its main disadvantage is its wide band gap where only a small fraction of sun light (4–5 %, UV region) has enough energy to excite the material's valence electrons [87]. Therefore, attempts to modify TiO_2 to absorb also visible light were a reasonable step. Band gap modulations are most commonly achieved with introducing new elements and defects into the host lattice. TiO_2 can be doped either with cationic (metallic) or anionic (non-metallic) species and incorporation of nitrogen species has been the most studied among the latter [74].

4.1.3.2 Nitrogen doping of TiO_2

N-doped TiO_2 can be prepared with numerous synthesis methods ranging from sol-gel, dip-coating and a plasma treatment to the most traditional, annealing of TiO_2 in an NH_3 atmosphere at temperatures above 500 °C [74], [87]. Questions, originating from N-doping are: (i) what is the origin of the material light absorption in Vis region, and (ii) what is the state of the incorporated N species. Answering those questions was additionally more challenging as different doping methods could lead to distinct nature of introduced N species [74].

TiO₂ is an indirect wide band gap semiconductor where its valence band has mainly an O 2p character and the conduction band is mainly Ti 3d and 4s in character [74]. In general, N can be incorporated into the TiO₂ lattice in two different modes – substitutional and interstitial (Figure 4.3). In substitutional doping, lattice O²⁻ is replaced by N³⁻ which bonds to three Ti centres. During interstitial doping, N³⁻ binds to one lattice oxygen which it pushes from the Ti–O–Ti plane toward the interstitial cavity. A newly created NO fragment is connected to the lattice Ti centres through its π bonding system [74]. It was first considered that N-doping leads to the narrowing of a band gap due to the mixing of O 2p and N 2p states [75]. It was only later when Irie *et al.* conducted photocatalytic experiments on N-doped TiO₂ under the same flux of Vis and UV light and the obtained quantum efficiencies were different, indicating the formation of intra-band gap states [70].

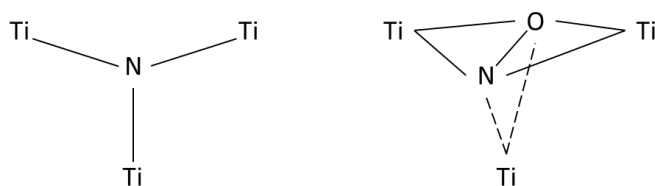


Figure 4.3: A schematic presentation of substitutional (left) and interstitial (right) N-doping of TiO₂. Adopted from the ref. [89].

Now it is agreed that soft N-doping does not affect the material's intrinsic band gap but creates new localized intra band gap states (Figure 4.4). Substitutional N-doping of TiO₂ leads to the creation of N 2p localized states 0.14 eV above the top of the valence band where the unpaired electron is almost entirely localized on the substitutional N-centre [89]. In interstitial N-doping, NO species create localized states with a π character. As the bonding π states are positioned beneath the top of the valence band, its antibonding π^* states are positioned 0.64–0.73 eV above the top of the valence band [74], [89]. Here, the unpaired electron is shared between N and O centres in the NO fragment [89].

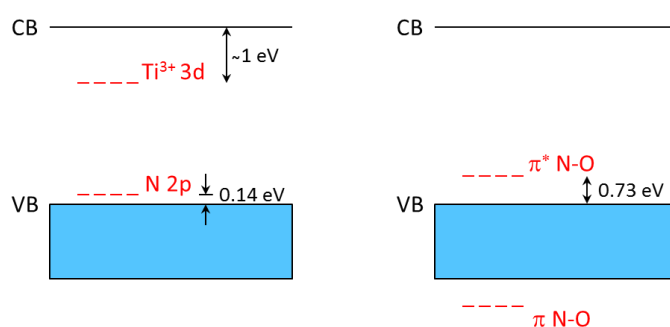


Figure 4.4: Electronic structure of TiO₂ doped with nitrogen in substitutional (left) and interstitial mode (right). Adopted from ref. [89].

DFT calculations revealed that during N-doping of TiO₂, the formation of oxygen vacancies (V_o) is favoured as well [76], [89], [90]. When an oxygen atom is removed from the lattice, two electrons localize on two Ti⁴⁺ centres reducing them to Ti³⁺. This induces the formation of localized intra band gap states that are positioned approximately 1 eV beneath the minimum of conduction band and have a Ti³⁺ 3d character (Figure 4.5) [74]. Intra band gap states, induced with N-doping are located beneath the Ti³⁺ 3d states. If

an electron transfers from Ti^{3+} centre to the N-defect (Ti^{3+} re-oxidizes to Ti^{4+}), the released energy almost compensates for the formation energy of V_o [89]. This is the driving force for the formation of oxygen vacancies during substitutional N-doping of TiO_2 . DFT calculations also confirmed that substitutional doping, accompanied with V_o formation, is energetically favoured under oxygen poor conditions, whereas the interstitial doping prevails under oxygen rich conditions [89].

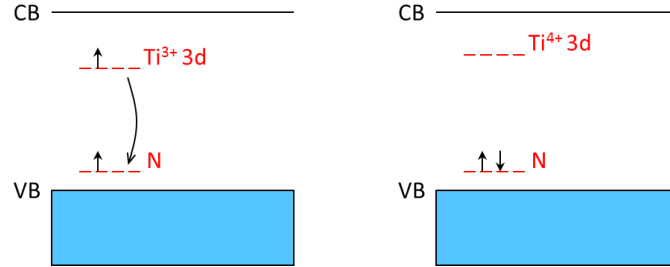


Figure 4.5: Electronic band modifications during the interaction of Ti^{3+} (oxygen vacancy) with N defects. Adopted from ref. [89].

A visible light absorption of N-doped TiO_2 is therefore a direct consequence of the presence of localized intra band gap states which are created either with substitutional or interstitial N-doping and oxygen vacancies [65], [74], [76], [89].

Even though N-doped TiO_2 absorbs visible light too, the results of photocatalytic experiments performed under UV-Vis light illumination are commonly contradictory. Some groups report on enhanced photoactivity of N-doped TiO_2 under UV-Vis illumination when compared to bare TiO_2 . Yet photocatalytic activity of N-doped TiO_2 is sometimes almost completely suppressed. N-doping is indeed responsible for Vis light absorption of the material but all the introduced defects – N centres and oxygen vacancies – can serve as recombination sites as well [70], [74], [89]. Holes, created during the excitation of electrons from the intra band gap states, are localized on defect sites that make them less mobile and more prone to the recombination [89]. In addition, such holes have lower oxidation potential than the ones from the valence band, leading to the smaller scope of adsorbates that holes from the localized states can still oxidize [89]. Bearing in mind the upper advantages and limitations, N-doping of TiO_2 is a promising way toward more efficient photocatalytic processes performed under Vis light where there is still some space for improvement to overcome higher recombination rates.

4.1.4 Outline

In this work I focused on the transformation of protonated titanate nanoribbons to TiO_2 under different reaction conditions. The work was motivated by two goals: (i) to understand the behaviour of HTiNRs under solvothermal conditions over the whole pH range, and (ii) to maximize the material's photocatalytic activity. Therefore, the transformation reactions of HTiNRs were conducted under various solvothermal conditions as well as with annealing in static air and a dynamic ammonia flow. Finally, photocatalytic activity of the most characteristic samples was assessed from the photooxidation rate of isopropanol to acetone.

4.2 Experimental Section

All the chemicals were purchased from commercial sources and used as received. The starting material, HTiNRs were synthesized as described in Chapter 3, Experimental Section 3.2.

4.2.1 Annealing in static air

In a typical experiment, 150 mg of HTiNRs were weighed in an alumina boat, placed into an oven, and heated at the ramp rate of $1\text{ }^{\circ}\text{C min}^{-1}$ to the target temperature ($400\text{ }^{\circ}\text{C}$, $580\text{ }^{\circ}\text{C}$ or $650\text{ }^{\circ}\text{C}$). Samples were maintained at the selected temperatures for 6 h and cooled down to room temperature afterwards. Samples' labels, reaction conditions and phase compositions are listed in Table 4.1.

4.2.2 Annealing in an $\text{NH}_3(\text{g})/\text{Ar}(\text{g})$ flow

HTiNRs (225 mg) were weighed in a quartz boat, placed into an oven, and heated at the ramp rate of $7.2\text{ }^{\circ}\text{C min}^{-1}$ to the target temperature ($400\text{ }^{\circ}\text{C}$, $580\text{ }^{\circ}\text{C}$ or $650\text{ }^{\circ}\text{C}$). Samples were maintained at the selected temperatures for 6 h and cooled down to room temperature afterwards. The flow ratio of $\text{NH}_3(\text{g})/\text{Ar}(\text{g})$ was $30\text{ mL min}^{-1}/10\text{ mL min}^{-1}$, respectively. Samples' labels, reaction conditions and phase compositions are listed in Table 4.2.

4.2.3 Solvothermal treatment in an autoclave

In a typical experiment, 150 mg of HTiNRs were suspended in 36 mL of a reaction medium. The reaction media were deionized water, aqueous solutions of different pH values, and organic liquids. A reaction was performed in a Teflon-lined autoclave (Berghof, BR25, the filling volume was 90 %). The suspension was stirred at 300 rpm and heated to the target temperature with the heating rate of $4\text{ }^{\circ}\text{C min}^{-1}$. After thermal treatment for the desired time, the suspension was left to cool down to room temperature. The product was isolated with repeated washing and centrifugation. When the reaction was performed in aqueous medium, the product mixture was washed with deionized water till the pH of the supernatant was 5–6 and finally rinsed with EtOH. Sometimes the material did not sediment during the centrifugation. That happened mainly when the reaction was performed under basic or acidic conditions. In such a case, the suspension was first neutralised with an aqueous solution of CH_3COOH or NH_3 which ensured product sedimentation and then washed with deionized water and EtOH. When the reaction was performed in an organic medium, the product mixture was washed with EtOH for several times. After the washing, the material was dried in an oven at $100\text{ }^{\circ}\text{C}$ for 12 h. Samples' labels, reaction conditions and phase compositions are listed in Table 4.3, Table 4.4, Table 4.5, Table 4.7, Table 4.8, and Table 4.9.

4.2.4 Hydrothermal treatment in a microwave reactor

In a typical experiment, 90 mg of HTiNRs were placed into a 30 mL glass vial and 20 mL of a reaction medium was added. The reaction media were either deionized water or an aqueous acidic solution. The reaction was performed with a microwave reactor (Anton Paar, Monowave 300). Firstly, the reaction mixture was heated to the target temperature (mode as fast as possible), where it remained heated for a desired time during which it was stirred at 300 rpm. After the thermal treatment, the product mixture was cooled down to $50\text{ }^{\circ}\text{C}$ with the aid of compressed air. The product was then

isolated with repeated washing with deionized water and centrifugation till the pH of the supernatant was 5–6, and finally rinsed with EtOH. Sometimes the material did not sediment during the centrifugation when the reaction was performed under acidic conditions. In such a case, the suspension was first neutralised with the aqueous solution of NH_3 , which ensured product sedimentation and then washed with deionized water and EtOH. After the final washing, the material was dried in an oven at 100 °C for 12 h. Samples' labels, reaction conditions and phase compositions are listed in Table 4.6 and Table 4.7.

4.2.5 Cross experiments

For the evaluation of the crucial parameters for the photocatalytic performance of TiO_2 NRs, some additional samples were prepared.

Firstly, 120 mg of TiO_2 NRs sample that was prepared with hydrothermal treatment in deionised water in a microwave reactor were weighed in an alumina boat, placed into an oven, and heated at the ramp rate of 1 °C min⁻¹ to 480 °C. The sample was maintained at the selected temperature for 6 h and cooled down to room temperature afterwards. The sample was labelled MW-W+TO.

The second sample was prepared from hydrothermally derived TiO_2 NRs in an autoclave. 225 mg of the sample were weighed in a quartz boat, placed into an oven, and heated at the ramp rate of 7.2 °C min⁻¹ to 400 °C. The sample was maintained at the selected temperature for 6 h and cooled down to room temperature afterwards. The flow ratio of $\text{NH}_3(\text{g})/\text{Ar}(\text{g})$ was 30 mL min⁻¹/10 mL min⁻¹, respectively. The sample was labelled CH-W+TN.

4.2.6 Photocatalytic assessment

Photocatalytic measurements were performed in a home-built continuous solid-gas reactor. The method is described in details in the reference [91]. Briefly, 50 mg of the TiO_2 sample were evenly spread on a petri dish that was placed into a reactor chamber afterwards. Then, 80 µL (corresponding to 800 ppm) of isopropanol, as a model pollutant, was injected into the system. The initial concentration of isopropanol slightly decreased even though the system had not yet been illuminated (Figure 4.6). That was due to the adsorption of isopropanol on the catalyst's surface. After the adsorption-desorption equilibrium had been established (the concentration of isopropanol remained constant), the light was switched on. Photocatalytic activity of the samples was determined from the rate constant of the photooxidation of isopropanol to acetone. As the oxidation is only the first conversion in the photodegradation process of isopropanol, the reaction rate was determined from the initial increase of acetone concentration when acetone did not convert to further products yet. Concentrations of isopropanol and acetone were constantly monitored with a FTIR spectrometer (Perkin Elmer BX II), at their characteristic peaks positioned at 951 cm⁻¹ and 1207 cm⁻¹, respectively. A 300 W Xe lamp was used as a light source as it imitates the sun spectrum and emits both UV and Vis light. The radiant flux density was 40 W m⁻². The system was kept at the constant temperature of (25 ± 3) °C and the humidity of (22 ± 3) %.

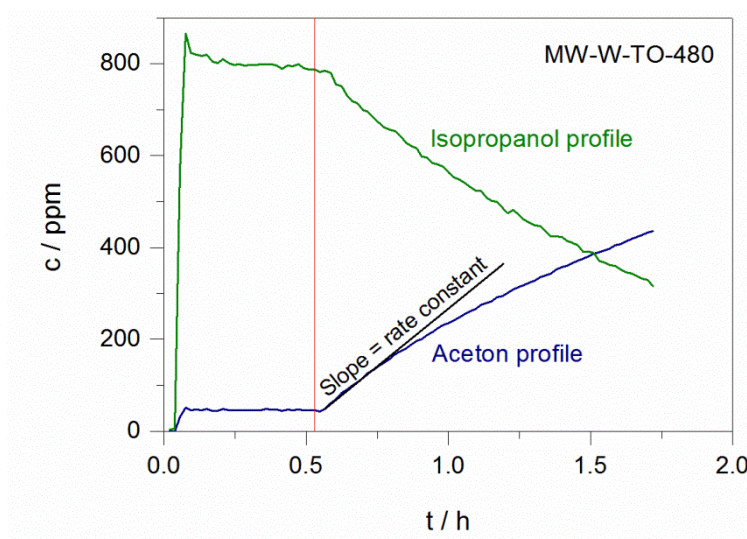


Figure 4.6: Typical isopropanol and acetone profiles during the photocatalytic test. The red vertical line indicates when the UV-vis light was switched on. The rate constant of the isopropanol photooxidation was evaluated from the initial acetone concentration profile.

4.3 Results and Discussion

4.3.1 Transformation of HTiNRs to TiO₂ NRs

4.3.1.1 Annealing of HTiNRs in static air

The exact experimental conditions, at which the samples were prepared, are listed in Table 4.1.

Table 4.1: Experimental conditions of TiO₂ NRs thermally derived from protonated titanate nanoribbons in static air and their phase composition.

Sample	Transformation environment	T (°C)	t (h)	$\Delta T/\Delta t$ (°C min ⁻¹)	Phase composition
TO-400	Static air	400	6	1	TiO ₂ -B
TO-580	Static air	580	6	1	TiO ₂ -B + anatase
TO-650	Static air	650	6	1	Anatase

Figure 4.7 presents XRD patterns of the starting material (HTiNRs) and samples, obtained by calcination of HTiNRs in static air. Calcination of HTiNRs at 400 °C for 6 h provided a complete transformation of protonated titanate to TiO₂-B phase (ICDD card no. 35-0088). With increasing temperature, new peaks corresponding to anatase (ICDD card no. 86-1157) arose (TO-580) and the latter was the only phase obtained after calcination of HTiNRs at 650 °C in static air for 6 h.

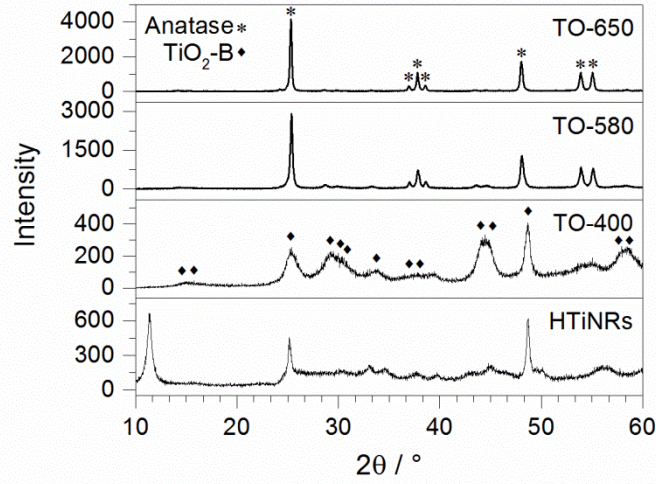


Figure 4.7: XRD patterns of the precursor, protonated titanate nanoribbons, and the product TiO_2 NRs prepared by calcination of HTiNRs at 400, 580, and 650 °C.

Annealing in air did not affect the nanoribbon morphology of the product TiO_2 NRs, as can be seen from the SEM images of the samples (Figure 4.8a, c, e). However, images taken with TEM reveal some morphological and surface changes (Figure 4.8b, d, f). Nanoribbons of the TO-400 sample became mesoporous as they contain pores with diameters ranging from 2 nm to 10 nm. The ‘mosaic’ porous appearance is a characteristic of TiO_2 -B phase, which seems to be related to the material’s low density [62]. The nanoribbons are elongated along the b-axis, as can be determined from the corresponding FFT pattern (Figure 4.8b with inserts). With increasing calcination temperature, the porosity of TiO_2 NRs is suppressed as fewer pores are observed in the TO-580 sample. This non-completed transformation of TiO_2 -B phase to anatase is evidenced also with FFT, as the majority of reflections correspond to anatase phase whereas reflections along [001] anatase direction still belong to the TiO_2 -B phase (Figure 4.8d). This indicates that the material condensation along the [100] direction of the TiO_2 -B phase has not finished yet. HRTEM and FFT analyses of the TO-650 sample confirm a complete transformation of TiO_2 -B phase to anatase. This is additionally supported with the fact that the mesoporosity has vanished. Nanoribbons have rounded edges due to partial sintering and are elongated along the a-axis (Figure 4.8f).

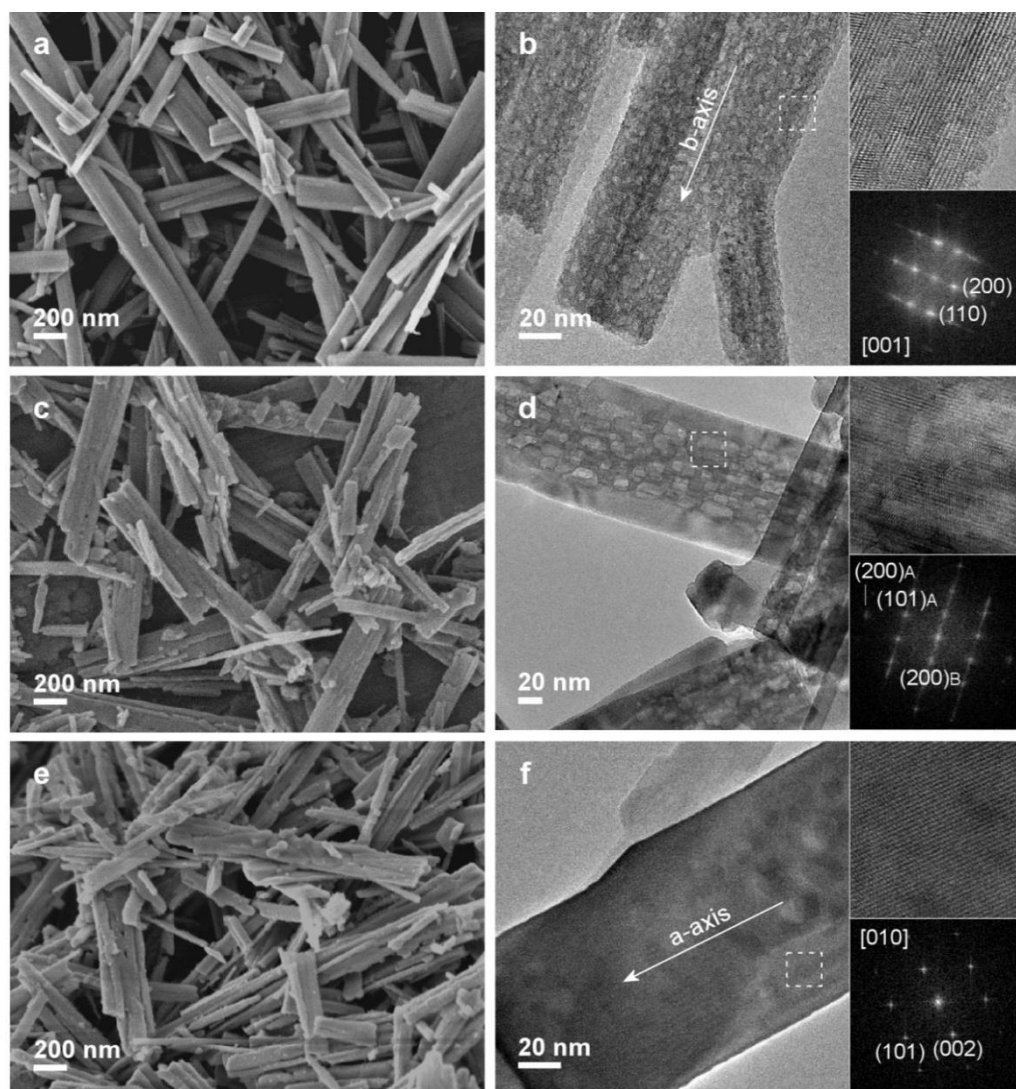


Figure 4.8: SEM and TEM images of the TO-400 (a, b), TO-580 (c, d), and TO-650 (e, f) samples. HRTEM insets with the corresponding FFT patterns reveal nanoribbon's phase and the direction of elongation. Labels A and B in the insert of the figure (d) refer to anatase and $\text{TiO}_2\text{-B}$ phase, respectively.

4.3.1.2 Annealing of HTiNRs in a dynamic ammonia atmosphere

In Table 4.2 there are experimental conditions for the synthesis of TiO_2 NRs with calcination of HTiNRs in a dynamic ammonia atmosphere.

The XRD patterns of TiO_2 NRs samples prepared by calcination of HTiNRs in a reductive NH_3 atmosphere reveal a similar development in the same temperature range as the transformations in static air (Figure 4.9). Firstly, protonated titanate is transformed to $\text{TiO}_2\text{-B}$ phase (TN-400), which later condensates to anatase (TN-580 and TN-650). However, transformation conditions at 580 °C and 650 °C did not suffice for a complete conversion to anatase as it always coexists with $\text{TiO}_2\text{-B}$ phase in the samples. This result could suggest that the reaction rate of the transformation from protonated titanate to anatase under reductive atmosphere is smaller than under oxidative conditions (static air). Nevertheless, the difference in the results could also emerge from different ramp rates of the reactions carried out in static air and an ammonia flow

(Table 4.1 and Table 4.2). In the XRD pattern of the TN-650 sample also a new peak appears which belongs to cubic titanium oxynitride (Ti(O,N)).

Table 4.2: Experimental conditions of TiO_2 NRs, prepared by calcination of HTiNRs in the flow of $\text{NH}_3(\text{g})/\text{Ar}(\text{g}) = 30 \text{ mL min}^{-1}/10 \text{ mL min}^{-1}$ and their phase composition.

Sample	Transformation environment	T (°C)	t (h)	$\Delta T/\Delta t$ (°C min ⁻¹)	Phase composition
TN-400	$\text{NH}_3(\text{g})/\text{Ar}(\text{g})$ flow	400	6	7.2	$\text{TiO}_2\text{-B}$
TN-580	$\text{NH}_3(\text{g})/\text{Ar}(\text{g})$ flow	580	6	7.2	$\text{TiO}_2\text{-B}$ + anatase
TN-650	$\text{NH}_3(\text{g})/\text{Ar}(\text{g})$ flow	650	6	7.2	$\text{TiO}_2\text{-B}$ + anatase + + Ti(O,N)

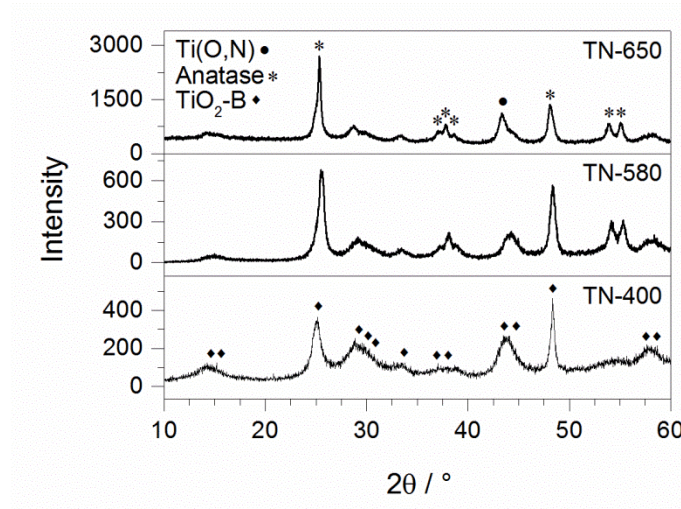


Figure 4.9: XRD patterns of the TN-400, TN-580, and TN-650 samples.

SEM and TEM images of TiO_2 NRs derived in the NH_3 atmosphere are similar to those, transformed in static air, and therefore only the images of the TN-650 sample are presented (Figure 4.10). The nanoribbon morphology is preserved during the thermal treatment of HTiNRs in the ammonia flow at temperatures up to 650 °C. The sample's mesoporosity indicates the presence of $\text{TiO}_2\text{-B}$ phase as well, even though the corresponding FFT pattern corresponds to the anatase phase.

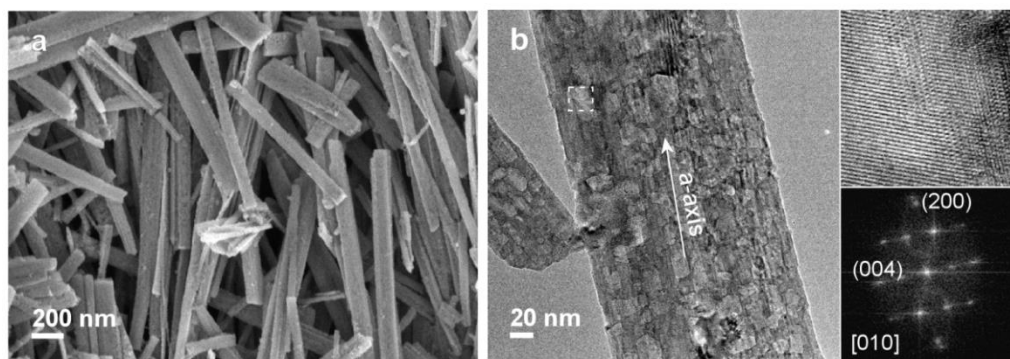


Figure 4.10: SEM (a) and TEM (b) images of the TN-650 sample. Even though the main phase is anatase, NRs are porous due to the presence of also $\text{TiO}_2\text{-B}$ phase and are elongated along the $\langle 100 \rangle$ direction as evidenced from the FFT pattern.

4.3.1.3 Transformation of HTiNRs under hydrothermal conditions

After the transformation of HTiNRs to TiO_2 NRs upon calcination had been examined, the same transformation was studied under hydrothermal and solvothermal conditions.

4.3.1.3.1 Basic conditions

4.3.1.3.1.1 NaOH HTiNRs were first hydrothermally treated in 0.5 M NaOH(aq) at 160 °C for 24 h (Table 4.3). XRD pattern of the CH-NaOH sample does not indicate the presence of any TiO_2 polymorph (Figure 4.11). On the contrary, the product XRD reveals a partial substitution of protons with sodium ions resulting in $(\text{Na,H})_2\text{Ti}_3\text{O}_7$. Sodium content increased from 0.1 wt% for HTiNRs to 0.7 wt% for the CH-NaOH sample, as determined with EDXS analyses. 1D sodium titanates are produced with hydrothermal treatment of TiO_2 in 10 M NaOH(aq) and titanate is a thermodynamically favoured phase under such conditions.

As expected, the product NRs seemed intact in comparison to the starting material when investigated with SEM and are therefore not shown.

Table 4.3: Experimental conditions for the preparation of the CH-NaOH sample and its phase composition.

Sample	Transformation environment	T (°C)	t (h)	$\Delta T/\Delta t$ (°C min ⁻¹)	Phase composition
CH-NaOH	0.5 M NaOH(aq)	160	24	4	$(\text{Na,H})_2\text{Ti}_3\text{O}_7$

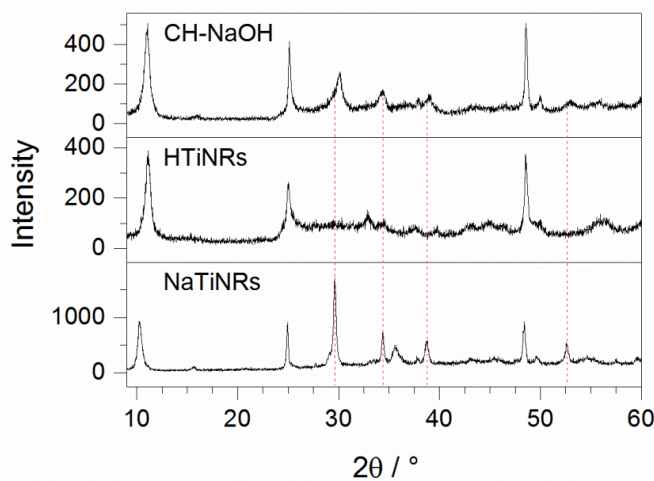


Figure 4.11: XRD patterns of sodium titanate nanoribbons, protonated titanate nanoribbons and the CH-NaOH sample. Vertical lines indicate the incorporation of sodium ions into the titanate structure during the hydrothermal treatment of HTiNRs in 0.5 M NaOH(aq).

4.3.1.3.1.2 NH_3 Table 4.4 summarizes the reaction conditions under which HTiNRs were hydrothermally treated in ammonia solution.

XRD analyses of the samples reveal that protonated titanate transforms to anatase as the ammonia concentration in the reaction medium decreases (Figure 4.12). After the hydrothermal treatment of HTiNRs in a 2.0 M $\text{NH}_3(\text{aq})$ solution, no TiO_2 phase is detected. However, with decreasing ammonia concentration to 1.0 M, anatase was the major phase and it was the only phase obtained in the product material when a 0.5 M $\text{NH}_3(\text{aq})$ solution was employed. HTiNRs are stable under highly basic conditions as they do not transform to TiO_2 . Hydrothermal treatment of HTiNRs in 0.5 M NaOH(aq) (CH-NaOH) did not result in any TiO_2 formation when that was the only phase obtained after 0.5 M $\text{NH}_3(\text{aq})$ was used as a reaction medium under otherwise identical reaction conditions. This points to the importance of the cations present in the reaction mixture. Ammonia and alkylamines can be used as exfoliating reagents [34], [92]–[94]. Therefore, penetration of NH_4^+ cations into the interlayer space could destabilise the titanate structure, leading to its conversion to anatase.

The nanoribbon morphology is preserved during the hydrothermal treatment of HTiNRs in $\text{NH}_3(\text{aq})$, as evidenced with SEM (Figure 4.13a). However, in contrast to the bare smooth HTiNRs, the product nanoribbons are covered with small crystals whose amount increases with the decreasing $\text{NH}_3(\text{aq})$ concentration. When NH_4^+ cations penetrate between the titanate layers in HTiNRs, a partial material's dissolution is invoked whereas the remaining protonated titanate transforms to anatase. Then, anatase nanocrystals recrystallize on the nanoribbon's surface. The more detailed structural information about those nanocrystals was revealed with TEM investigation (Figure 4.13b). There, the marked nanocrystal has well-defined facets and a shape of a highly truncated bipyramid. The corresponding fast Fourier transform pattern (FFT) confirms that the particle is a single crystal of anatase. The truncated facet is perpendicular to the $\langle 001 \rangle$ direction which makes it a member of the $\{001\}$ planes. The measured interfacial angle between two surrounding facets is 136.5° and corresponds to the angle between $(\bar{1}01)$ and $(\bar{1}0\bar{1})$ facets of anatase (136.6°). To summarize,

the truncated bipyramid of anatase grows in the $\langle 001 \rangle$ direction and is surrounded with the facets corresponding to $\{101\}$ planes whereas the truncated facet belongs to the $\{001\}$ planes of anatase.

Table 4.4: Experimental conditions of Ti₂O₃-based NRs prepared with the hydrothermal treatment of HTiNRs in NH₃(aq) solutions with the concentration ranging from 2.0 M to 0.5 M and their phase composition.

Sample	Transformation environment	T (°C)	t (h)	$\Delta T/\Delta t$ (°C min ⁻¹)	Phase composition
CH-N2	2.0 M NH ₃ (aq)	160	24	4	H ₂ Ti ₃ O ₇
CH-N1	1.0 M NH ₃ (aq)	160	24	4	H ₂ Ti ₃ O ₇ + anatase
CH-N0.5	0.5 M NH ₃ (aq)	160	24	4	anatase

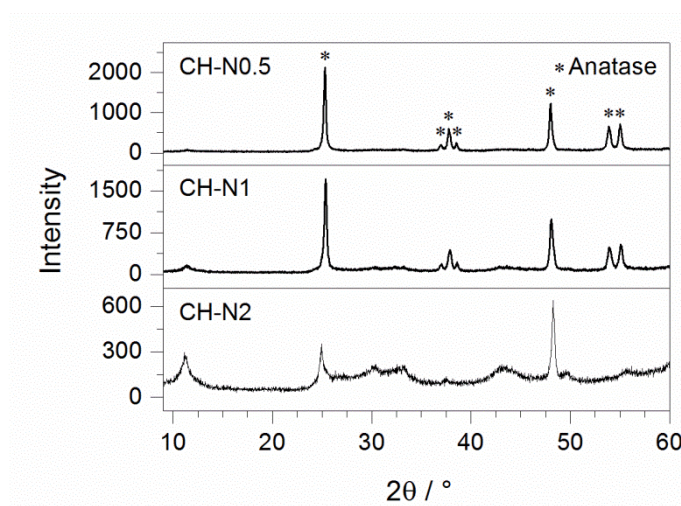


Figure 4.12: XRD patterns of TiO₂ NRs prepared with hydrothermal treatment of HTiNRs in NH₃(aq) solutions with 2.0, 1.0, and 0.5 molarities.

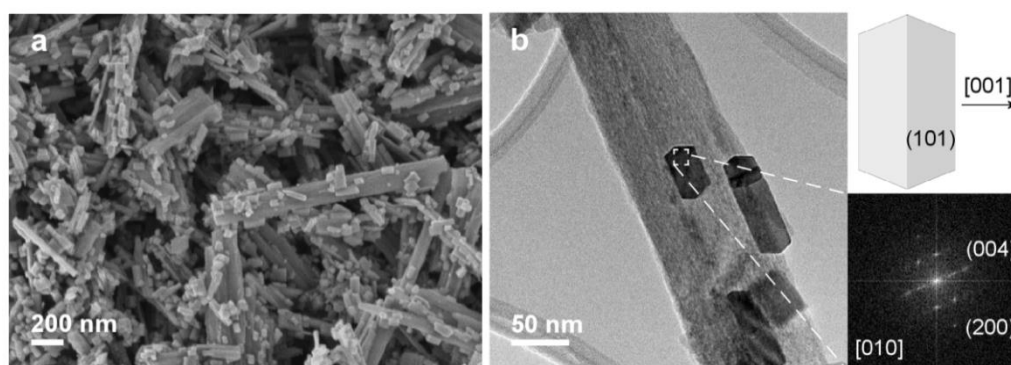


Figure 4.13: SEM (a) and TEM (b) images of the CH-N0.5 sample. The FFT analysis of the anatase nanocrystal, oriented along the $[010]$ zone axis, confirms its growth in the $[001]$ direction. The dihedral angle between the marked facets reveals that the lateral facets belong to the $\{101\}$ planes.

4.3.1.3.2 Neutral conditions

4.3.1.3.2.1 Convective heating in an autoclave Hydrothermal treatments of HTiNRs in deionized water were performed at different reaction temperatures and times to ensure the complete transformation of protonated titanate to anatase (Table 4.5 and Figure 4.14).

After hydrothermal treatment of HTiNRs at 120 °C for 10 h only protonated titanate is present in the product material. The peak positioned around 10° arises from the layered titanate structure (Figure 4.14). The decrease of this peak in the XRD pattern of the CH-W120 sample indicates a partial collapse of the layered structure. When the transformation was executed at 140 °C, the peaks attributed to anatase appeared and that was the only phase obtained after the reaction was performed at 160 °C for 10 h (Figure 4.14).

Table 4.5: Experimental conditions for samples, prepared with hydrothermal treatment of HTiNRs in deionized water in an autoclave and their phase composition.

Sample	Transformation environment	T (°C)	t (h)	$\Delta T/\Delta t$ (°C min ⁻¹)	Phase composition
CH-W120	deionized water	120	10	4	H ₂ Ti ₃ O ₇
CH-W140	deionized water	140	10	4	H ₂ Ti ₃ O ₇ + anatase
CH-W160-5	deionized water	160	5	4	H ₂ Ti ₃ O ₇ + anatase
CH-W160	deionized water	160	10	4	anatase

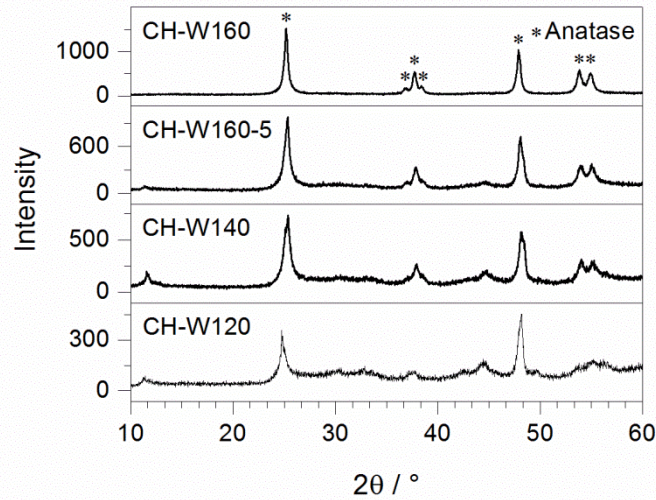


Figure 4.14: XRD patterns of Ti₂O₃-based NRs prepared in an autoclave with hydrothermal treatment of HTiNRs in deionized water at different reaction temperatures and for different reaction times.

4.3.1.3.2.2 Microwave-assisted heating Microwave-assisted reactions are well-known for higher effectiveness when compared to the analogue reaction systems performed with classical convective heating. This is due to the in-core volumetric heating of the reaction mixture when the reactants or reagents directly interact with microwave irradiation [15]. Transformation of HTiNRs to anatase was therefore investigated also

with the assistance of MW irradiation. In order to monitor the transformation progress, the reactions were terminated after different reaction times (Table 4.6, Figure 4.15).

The phase evolution of samples is similar to the one of the samples obtained under hydrothermal conditions with convective heating (Figure 4.15). However, a systematic monitoring of the transformation performed in a microwave reactor provided a deeper insight to the transformation progress. Under neutral hydrothermal conditions, the collapse of the layered structure of protonated titanate (0–60 min) is followed with the direct formation of anatase without the presence of an intermediate $\text{TiO}_2\text{-B}$ phase. This is in contrast to the results obtained with calcination of HTiNRs in either an oxidative (air) or a reductive ($\text{NH}_3(\text{g})$) atmosphere. Under hydrothermal conditions, the transformation from protonated titanate to anatase proceeds faster than with calcination.

As products derived from HTiNRs with the hydrothermal treatment in deionized water with either convective heating (autoclave) or with the assistance of microwave irradiation seemed morphologically and structurally identical, only SEM and TEM images of the MW-W120 sample are shown and will be discussed. Nanoribbon morphology is preserved during the hydrothermal treatment, as evidenced from the SEM analysis (Figure 4.16a). Nanoribbons' surface is fissured and covered with small crystals. From the TEM investigation it seems that the marked nanoparticle grows from the top of the nanoribbon rather than being deposited on it (Figure 4.16b). The particle has a trapezoidal shape that can also be described as a truncated pyramid. The corresponding FFT pattern reveals that the basal line of the nanoparticle is perpendicular to the $\langle 001 \rangle$ direction for anatase. The measured dihedral angle between lateral and truncated facet is 69.0° and corresponds to the interfacial angle between the $(\bar{1}01)$ and the (001) planes of anatase. To sum up, the nanoparticle is a truncated pyramid of anatase that grows in the $\langle 001 \rangle$ direction, its lateral facets belong to the $\{101\}$ planes whereas the truncated facet is attributed to the $\{001\}$ planes.

Table 4.6: Experimental conditions for samples, prepared with microwave-assisted hydrothermal treatment of HTiNRs in deionized water and their phase composition.

Sample	Transformation environment	T (°C)	t (min)	$\Delta T/\Delta t$ (°C min ⁻¹)	Phase composition
MW-W5	deionized water	200	5	as fast as possible	$\text{H}_2\text{Ti}_3\text{O}_7$
MW-W10	deionized water	200	10	as fast as possible	$\text{H}_2\text{Ti}_3\text{O}_7$
MW-W20	deionized water	200	20	as fast as possible	$\text{H}_2\text{Ti}_3\text{O}_7$
MW-W30	deionized water	200	30	as fast as possible	$\text{H}_2\text{Ti}_3\text{O}_7$ + + anatase
MW-W60	deionized water	200	60	as fast as possible	$\text{H}_2\text{Ti}_3\text{O}_7$ + + anatase
MW-W90	deionized water	200	90	as fast as possible	$\text{H}_2\text{Ti}_3\text{O}_7$ + + anatase
MW-W120	deionized water	200	120	as fast as possible	anatase

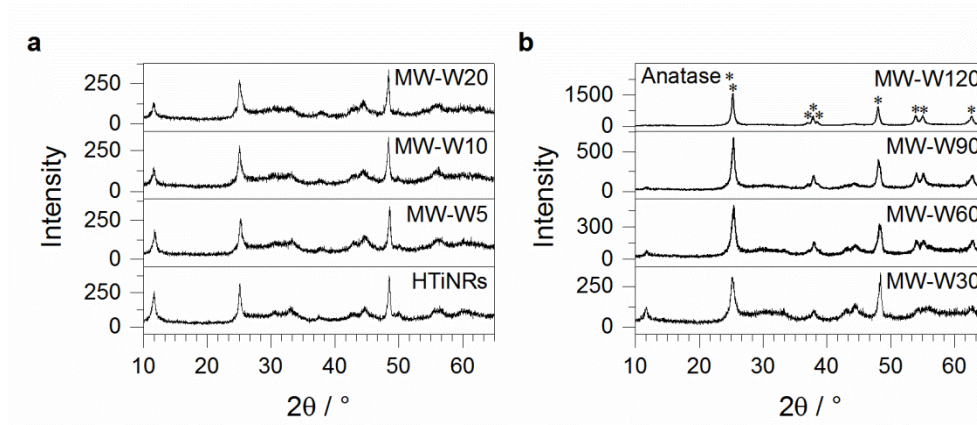


Figure 4.15: XRD patterns of Ti_2O_3 -based NRs prepared with the microwave-assisted hydrothermal treatment of HTiNRs in deionized water at 200 °C for different reaction times.

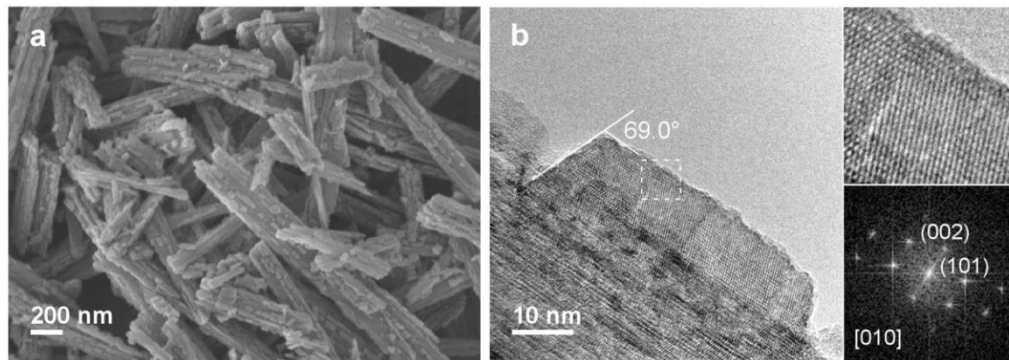


Figure 4.16: SEM (a) and TEM (b) images of the MW-W120 sample. The trapezoidal nanocrystal grows in the $\langle 001 \rangle$ direction and has lateral facets belonging to the $\{101\}$ planes and a truncated facet belonging to the $\{001\}$ planes, as evidenced from the corresponding FFT analysis and the dihedral angle.

4.3.1.3.3 Acidic conditions Finally, the transformation of HTiNRs was conducted also under hydrothermal acidic conditions. For this, different acids and heating techniques (an autoclave and a MW reactor) were used (Table 4.7).

XRD analyses of the samples confirmed that they all transformed to anatase phase under the selected reaction conditions. When the reaction was performed in an autoclave (CH-Cl), the reaction time of 5 h already sufficed for a complete conversion of protonated titanate to anatase. That is two times faster in comparison to the transformation, conducted in pure water (CH-W160). Conversion of protonated titanate to anatase is a condensation reaction that acids catalyse [80].

SEM analyses of the samples revealed that they all consist of nanoribbons that are covered with nanocrystals, whose shape depends on the acid type used in the reaction (Figure 4.17). When the reaction was performed in HCl(aq) , the nanoribbon morphology was the most affected. This can be due to longer reaction time (5 h) when compared to reaction times of other reaction systems (2 h). Products obtained after hydrothermal treatment in $\text{H}_2\text{SO}_4\text{(aq)}$ and the aqueous solution of acetic acid are rather similar (Figure 4.17b and c) whereas the major discrepancy from the shape of nanocrystals

covering the nanoribbons' surface is obtained after employing the aqueous solution of citric acid as a reaction medium (Figure 4.17d).

Table 4.7: Experimental conditions for TiO₂ NRs synthesis with the hydrothermal treatment of HTiNRs in different acid solutions and their phase composition.

Sample	Transformation environment	T (°C)	t (h)	$\Delta T/\Delta t$ (°C min ⁻¹)	Phase composition
CH-HCl	0.05 M HCl(aq)	160	5	4	anatase
MW-H ₂ SO ₄	0.05 M H ₂ SO ₄ (aq)	200	2	as fast as possible	anatase
MW-acetic	0.1 M acetic acid(aq)	200	2	as fast as possible	anatase
MW-citric	0.1 M citric acid(aq)	200	2	as fast as possible	anatase

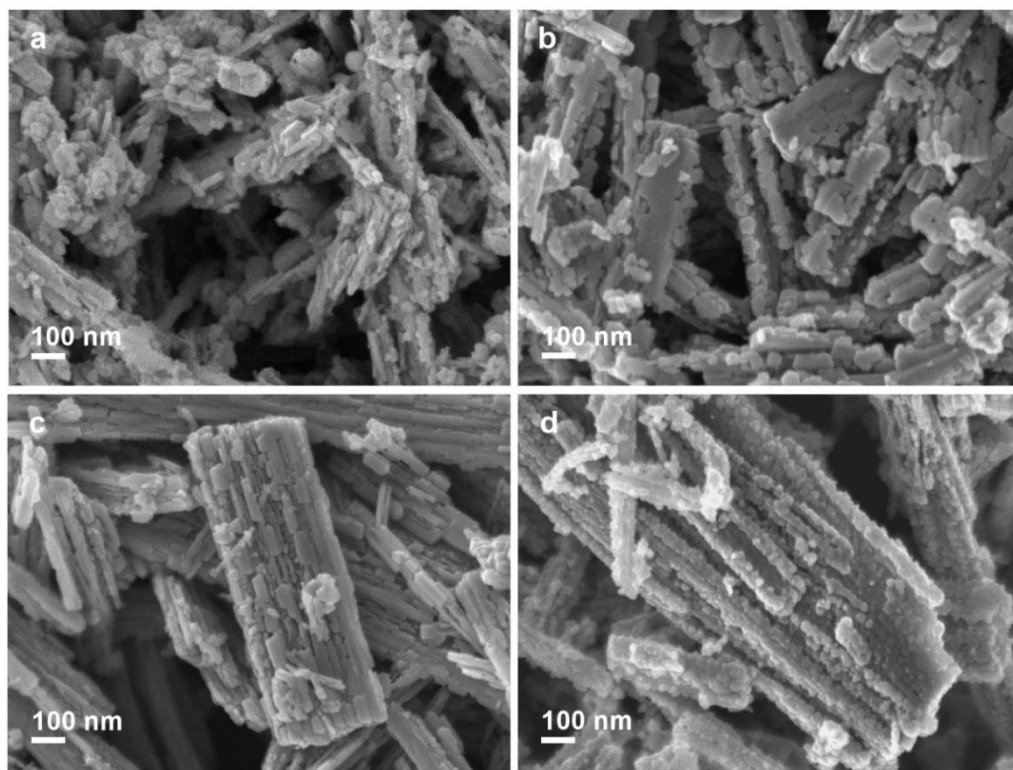


Figure 4.17: SEM images of anatase NRs hydrothermally prepared from protonated titanate nanoribbons in 0.05 M HCl(aq) (a), 0.05 M H₂SO₄(aq) (b), 0.1 M acetic acid(aq) (c), and 0.1 M citric acid(aq) (d). All nanoribbons are covered with smaller nanocrystals whose shape depends on the acid type used during the synthesis.

TEM analyses of MW-acetic and MW-citric samples provided a deeper insight into the role of counter ions during the transformation from protonated titanate to anatase. The transformation in aqueous 0.1 M acetic acid solution resulted in the growth of truncated pyramidal crystals on the top of nanoribbons (Figure 4.18a). From the corresponding FFT pattern 1 it is clear that the truncated pyramid grows in the $\langle 001 \rangle$ direction whereas the dihedral angle between the lateral and truncated facets corresponds to the angle between the $(\bar{1}01)$ and the (001) planes of anatase. A nanocrystal is surrounded with the $\{101\}$ planes and truncated with a facet belonging to the $\{001\}$ planes. The identity between FFT patterns taken from the nanocrystal (1)

and the nanoribbon (2) regions suggests that the nanocrystal epitaxially grew from the nanoribbons' surface which functioned as a substrate.

Crystals covering the NRs surface of the MW-citric sample are pyramidal (Figure 4.18b). Due to a large number of nanoparticles on individual nanoribbons, the HRTEM analysis was difficult. The measured interplanar distance between the planes that are parallel to the pyramid's lateral facet belongs to the $\{101\}$ anatase planes (insert of Figure 4.18b). The measured angles between the opposite circumferential planes of the pyramidal particles vary from approximately 40° to 55° . The theoretical angle between the opposite circumferential $\{101\}$ planes of the anatase pyramid is 43.4° . Even though the measured dihedral angle of some particles was around 44° , the variation in angle value appears most probably due to non-fully-developed particle's facets.

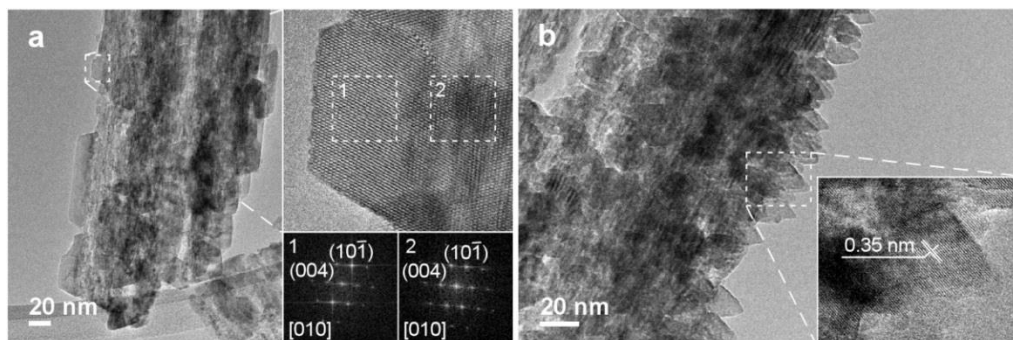


Figure 4.18: TEM and HRTEM analyses of the MW-acetic (a) and MW-citric (b) samples. The identity of the FFT patterns from the nanocrystal and the nanoribbon of the MW-acetic sample suggests that the nanocrystal epitaxially grows from the nanoribbon (insets in a). The distance between the lattice fringes in the particles from the MW-citric sample corresponds to the interplanar distance of the anatase $\{101\}$ planes indicating that the circumferential facets of pyramidal nanoparticles also belong to the $\{101\}$ planes (b).

The appearance of the MW-citric nanoribbons differs the most from the products obtained with other acids. Nanoribbons of the MW-citric sample are covered with more numerous and smaller nanoparticles that often do not have well-developed facets when compared to the nanocrystals of other samples. Yet the MW-citric sample is the only one where the particles have a pyramidal shape. Cl^- , CH_3COO^- and SO_4^{2-} anions are smaller than citrate anion which is also the only tridentate adsorbate. Cl^- and SO_4^{2-} anions are reported to preferentially adsorb on $\{101\}$ anatase planes [95], [96]. The lowering of the energy of the $\{101\}$ planes would additionally promote the growth of the truncated $\{001\}$ facet leading to the pyramidal shape of the particles. Since the pyramidal shape of the particles was obtained only after the employment of citric acid, the plausible explanation could be that citrate anions even better stabilize the $\{101\}$ anatase planes than other anions. Since the citrate anion is a tridentate adsorbent, one anion could adsorb also on the neighbouring facets limiting the particle growth and affecting its size. This could explain the smaller size of nanoparticles covering the nanoribbons' surface when compared to samples produced in other acidic reaction media as well.

4.3.1.4 Transformation of HTiNRs under solvothermal conditions

4.3.1.4.1 Convective heating in an autoclave In order to determine the role of water in the transformation of protonated titanate to TiO_2 under hydrothermal conditions, experiments in organic liquids were conducted as well. Table 4.8 summarized the reaction conditions.

When the reaction was performed in a polar aprotic solvent (MeCN), no protonated titanate transformed to TiO_2 as evidenced with the XRD analysis (Figure 4.19a). The employment of a protic solvent (BuOH) did not improve the transformation progress and in the same way an increase in polarity of the solvent (EtOH) did not result in any TiO_2 formation either. Finally, the addition of water to EtOH as a solvent (25 vol%) led to the complete transformation of protonated titanate to anatase (Figure 4.19b). The condensation of protonated titanate to anatase can be catalysed with acids as well [80], but when pure acetic acid was used as a reaction medium, no transformation occurred.

SEM analyses of the products revealed that when protonated titanate did not transform to TiO_2 , no morphological or surface changes of NRs were created (Figure 4.20a). Those NRs appeared identical as the starting material. When water was added to the reaction medium, the product anatase NRs had a typical appearance of the hydrothermally transformed anatase NRs – the nanoribbon’s surface was covered with small nanocrystals (Figure 4.20b).

The reduction of the reaction temperature from 580 °C for annealing in air to 160 °C for the hydrothermal treatment is attributed to the catalytic role of water and species derived from it (H^+). The results suggest that when the reaction is performed in an organic solvent, the latter cannot donate protons to catalyse the condensation reaction. Therefore, the solvent acts only as a thermal medium where heating at 160 °C does not suffice for the transformation of protonated titanate to anatase.

Table 4.8: Experimental conditions of HTiNRs solvothermally treated in different solvents and the products’ phase compositions.

Sample	Transformation environment	T (°C)	t (h)	$\Delta T/\Delta t$ (°C min ⁻¹)	Phase composition
CH-MeCN	MeCN	160	24	4	$\text{H}_2\text{Ti}_3\text{O}_7$
CH-BuOH	BuOH	160	24	4	$\text{H}_2\text{Ti}_3\text{O}_7$
CH-EtOH	EtOH	160	24	4	$\text{H}_2\text{Ti}_3\text{O}_7$
CH-EtOH/ H_2O	EtOH/ H_2O ^a	160	24	4	anatase
CH-AcOH	AcOH	160	10	4	$\text{H}_2\text{Ti}_3\text{O}_7$

^a $V(\text{EtOH}) : V(\text{H}_2\text{O}) = 3 : 1$

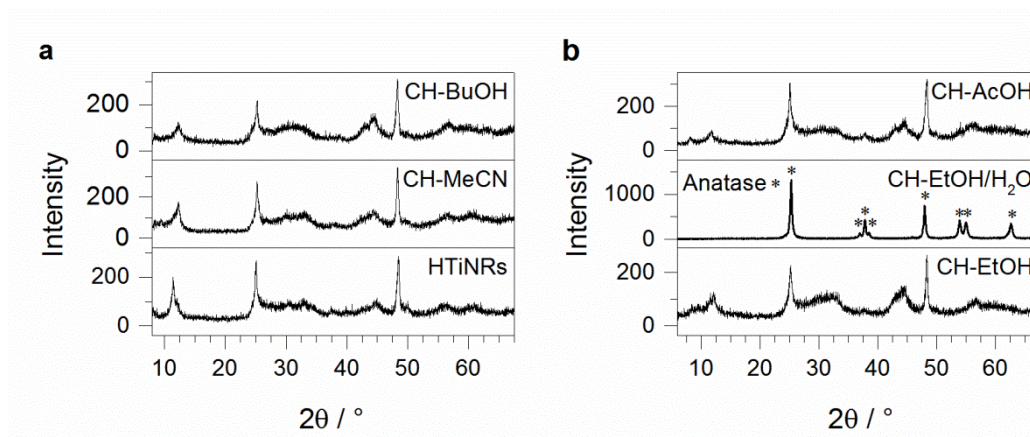


Figure 4.19: XRD patterns of samples, prepared with solvothermal treatment of protonated titanate nanoribbons in different solvents. Under the selected reaction conditions, HTiNRs transformed to anatase only when water was also present in the reaction mixture.

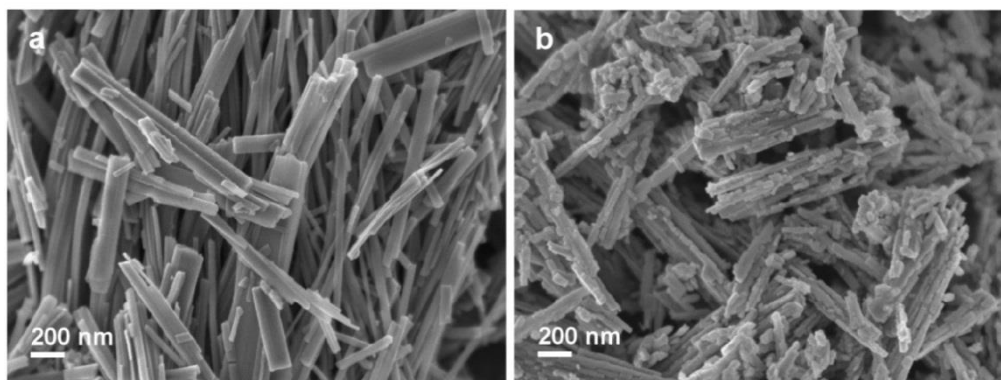


Figure 4.20: SEM images of the CH-EtOH (a) and the CH-EtOH/H₂O (b) samples. When water was absent in the reaction mixture, HTiNRs did not transform to TiO₂ and the nanoribbons' surface was not affected.

4.3.2 Transformation of NaTiNRs to TiO₂ NRs

In order to increase the process effectiveness of the transformation from titanate to anatase, also sodium titanate nanoribbons were used as a starting material for a one-pot transformation to TiO₂ (Table 4.9).

Even though anatase was the major phase, obtained after 10 h of the hydrothermal treatment in deionized water at 160 °C, the reaction time of 24 h was required to completely transform sodium titanate to anatase as evident from the corresponding XRD patterns (Figure 4.21).

The sample obtained after the reaction time of 10 h was composed of nanoribbons that were covered with (truncated) pyramidal crystals growing from the nanoribbon's surface (Figure 4.22a). It resembles of rose stem with horns. With prolonged reaction time, the amount of nanocrystals increased at the expense of nanoribbons (Figure 4.22b). There, more individual bipyramidal particles are present. Individual particles are elongated and not all have equally developed facets. Figure 4.22c and d represent TEM and HRTEM images of an anatase bipyramid from the CH-NaTiNRs-10 sample.

The particle grows in the $\langle 001 \rangle$ direction and is enclosed with $\{201\}$ facets as deduced from the corresponding FFT pattern and interfacial angles.

Hydroxyl anions are assumed to preferentially adsorb onto $\{100\}$ facets lowering their growth rate [97]. In addition, also cations can tailor the nanoparticle's shape through preferential adsorption, where the cation's size and charge density play an important role [84]. On anatase facets, O^{2-} are present on the surface of $\{100\}$ planes, but slightly beneath the layers of $\{001\}$ planes. Li^+ ions were reported to be able to successfully adsorb on $\{100\}$ and $\{001\}$ planes, whereas larger K^+ with smaller charge density could adsorb only on $\{100\}$ planes [84]. Na^+ ions that lie between Li^+ and K^+ , when considering their ionic size and charge density, could probably adsorb on O^{2-} sites of both planes, however the adsorption on $\{100\}$ planes would be easier. Therefore, the combination of retaining the crystal growth in $\langle 101 \rangle$ (Na^+) and $\langle 100 \rangle$ (OH^-) directions would result in particles with predominating $\{201\}$ facets as evidenced in the CH-NaTiNRs10 sample.

Table 4.9: Experimental conditions for the transformation of NaTiNRs to TiO_2 under hydrothermal conditions and products' phase compositions.

Sample	Transformation environment	T (°C)	t (h)	$\Delta T/\Delta t$ (°C min ⁻¹)	Phase composition
CH-NaTiNRs10	deionized water	160	10	4	$H_2Ti_3O_7$ + anatase
CH-NaTiNRs17	deionized water	160	17	4	$H_2Ti_3O_7$ + anatase
CH-NaTiNRs24	deionized water	160	24	4	anatase

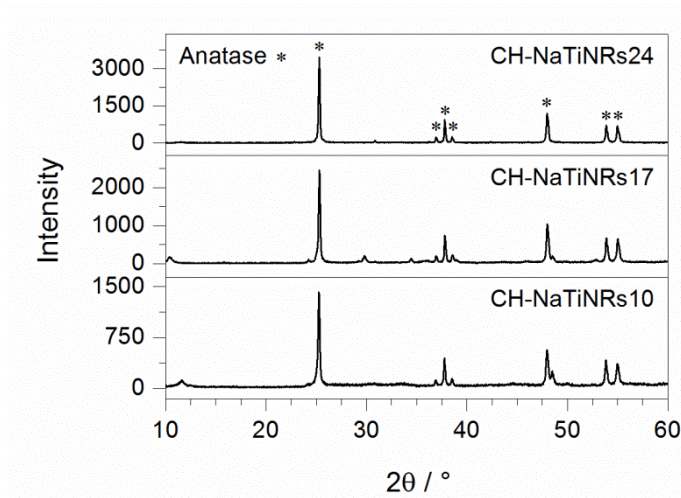


Figure 4.21: XRD patterns of sodium titanate nanoribbons hydrothermally treated in water at 160 °C for different reaction times. After the reaction time of 24 h, the pure anatase material was obtained.

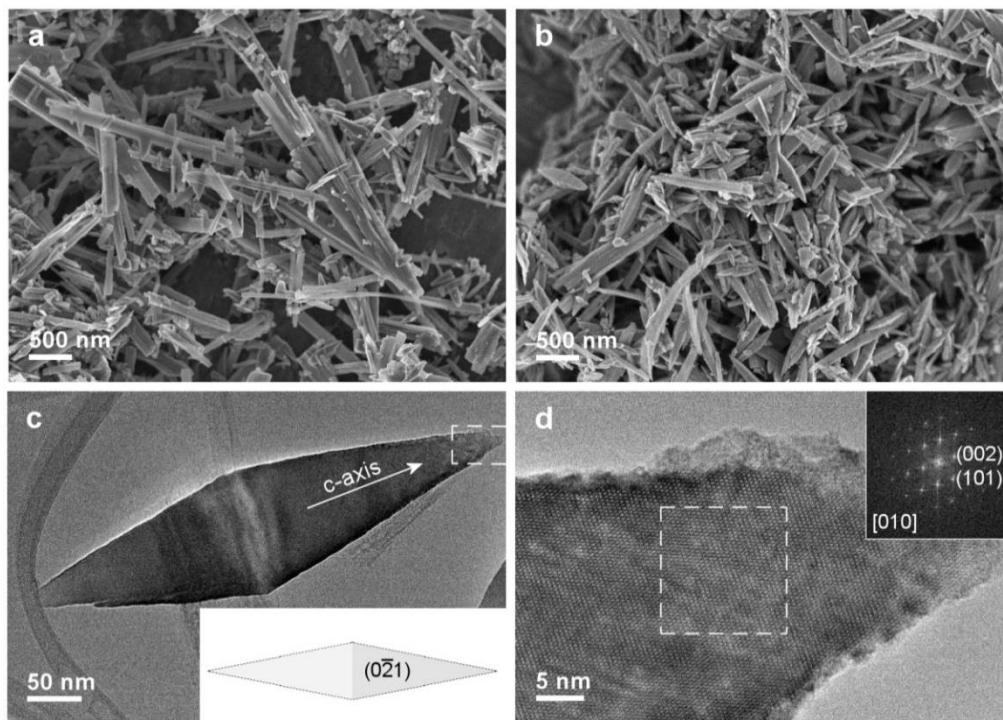


Figure 4.22: SEM images of the CH-NaTiNRs10 (a) and CH-NaTiNRs24 (b) samples, and the more detailed analysis of the CH-NaTiNRs10 sample with TEM (c), and HRTEM (d). With a prolonged reaction time, more (bi)pyramidal particles are formed at the expense of nanoribbons (a and b). The bipyramidal anatase particle grows in the $\langle 001 \rangle$ direction and is enclosed with facets belonging to the $\{201\}$ planes (c and d).

4.3.3 HTiNRs zeta potential and behaviour in aqueous media

Let us try to rationalize the results of the hydrothermal treatment of HTiNRs under different hydrothermal conditions. The *in situ* transformation from protonated titanate to anatase is a condensation [80], which can be theoretically catalysed either with bases or acids [63]. The experimental results revealed that the transformation proceeds under a wide pH range of the reaction medium (1 (0.1 M HCl(aq))–13.7 (0.5 M NH₃(aq))). When trying to rationalize the behaviour of HTiNRs in different reaction media, their zeta (ζ) potential can be of a considerable help. Figure 4.23 shows the HTiNRs ζ potential dependence on the suspension's pH.

Titanates are formed in highly concentrated alkaline medium (10 M NaOH(aq)) and are therefore stable under highly basic conditions. Under those conditions, the HTiNRs surface is negatively charged and OH[−] anions from the solution, which might theoretically catalyse the reaction, are repelled from the HTiNRs surface (Region III in Figure 4.23). With lowering the base concentration in the reaction medium, the cation's role of the base becomes significant. While HTiNRs did not transform to anatase when exposed to 0.5 M NaOH(aq) (CH-NaOH), HTiNRs completely transformed to anatase NRs when hydrothermally treated in ammonia solution under otherwise identical reaction conditions (CH-N0.5). Ammonium cations most probably intercalated between the titanate layers [92], destabilizing the structure and promoting the material's transformation to anatase.

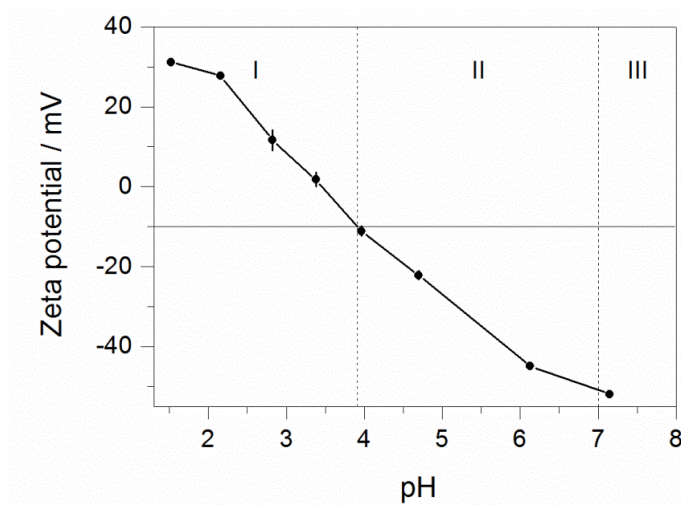


Figure 4.23: The dependence of the zeta potential of HTiNRs on the suspension's pH.

Under neutral and slightly acidic conditions ($3.9 \leq \text{pH} \leq 7$, Region II in Figure 4.23) HTiNRs have a negative ζ potential due to their weak acidic nature. pH of deionized water, used in the reactions, was 5.5 due to dissolved CO_2 from air. Therefore, when the transformation of HTiNRs was hydrothermally performed in water, the material's surface was negatively charged and attracted H_3O^+ from the reaction medium. Therefore protons could dissociate from H_3O^+ and penetrate between the titanate layers to catalyse the condensation from protonated titanate to anatase.

With the decreasing pH of the reaction medium ($\text{pH} < 3.9$, Region I in Figure 4.23), the HTiNRs surface becomes positively charged. Nevertheless, when aqueous 0.1 M acidic solutions were used as reaction media, the transformation to anatase NRs proceeded faster than in deionized water. From SEM analyses of the samples it is obvious that material's dissolution was also promoted. Protons from the reaction medium have therefore two functions: (i) they catalyse the condensation reaction, and (ii) destabilise the titanate structure leading to its dissolution. When aqueous 0.1 M acidic solutions were used as reaction media, it seems that protons did not have a sufficiently high chemical potential to completely dissolve the material before it would transform to anatase. Maybe under those reaction conditions the acid anions (like Cl^- , CH_3COO^-) also succeeded to efficiently stabilise the titanate surface against dissolution.

With increasing the acid concentration in the reaction medium (*e.g.* for HNO_3 , $c \geq 2.65$ M, [4]) the dissolution of the material excels over a topotactic reaction. The protonated titanate surface is highly protonated, which destabilises the crystal structure leading to leaching of the surface TiO_6 octahedra and material dissolution [47]. Finally, material recrystallises in a thermodynamically favoured rutile phase with normally a new, to precursor non-related, morphology [4], [80].

Let us now consider the morphology of anatase samples synthesized under various hydrothermal conditions. All the anatase samples are composed of nanoribbons that are covered with nanocrystals. The amount of nanocrystals covering NRs strongly depends on the reaction medium as the solubility of protonated titanate increases with the decreasing pH of an aqueous suspension and also varies with the acid type [47].

Furthermore, the shape of nanocrystals covering the nanoribbons depends on the reaction medium as well. Nanocrystals, produced under 0.5 M $\text{NH}_3(\text{aq})$ appear more rectangular, whereas those obtained under neutral conditions are more trapezoidal. Finally, under acidic conditions pyramidal particles were obtained too (MW-citric).

However, a more detailed HRTEM investigation revealed that those particles are closely related as: (i) they all have a differently truncated (bi)pyramidal shape, (ii) they grow in the $\langle 001 \rangle$ direction, and (iii) their lateral facets belong to the $\{101\}$ planes and the truncated one to the $\{001\}$ planes. This rather small morphology variety of nanocrystals, when considering the numerous different reaction conditions employed, can be due to the templated growth of nanoparticles. Heterogeneous nucleation requires less energy than the homogeneous and protonated titanate or anatase nanoribbons served excellently as a substrate on which nanocrystals grew. Epitaxial growth was supported also with some HRTEM investigations (Figure 4.18a). Counter ions influenced mainly the solubility of protonated titanate and consequently the number and size of the grown crystals. However, in the case of the MW-citric sample citrate anions had the biggest influence on the nanocrystals appearance – they were smaller in comparison to other obtained samples and with finished pyramidal shape which is most probably due to the tridentate ability of citrate anions.

When NaTiNRs are used as a precursor for a TiO_2 synthesis, they cannot directly transform to anatase due to the presence of Na^+ ions. Therefore, either first the ion exchange process takes place and then topotactic transformation from protonated titanate to anatase occurs, or sodium titanate is dissolved and anatase nanocrystals recrystallize from the solution. From the SEM investigation it seems that both processes took place. But since the *in situ* transformation from NaTiNRs to TiO_2 NRs is slower than the transformation from HTiNRs to TiO_2 due to the additional ion exchange step, more material dissolves. Then, counter ions influence the crystal growth through preferential adsorption on specific anatase planes.

Finally, transformation progress from HTiNRs to TiO_2 NRs under solvothermal conditions appears more similar to the processes induced by calcination than hydrothermal treatment. Organic solvents do not ensure species that could catalyse the condensation in protonated titanate and seem to serve only as a thermal medium.

4.3.4 Assessment of photocatalytic activity of TiO_2 NRs

The most distinguished TiO_2 samples prepared by different techniques (calcination and hydrothermal treatment) and with different doping degrees (N-doping) were characterized for their photoactivity. In Table 4.10 the parameters that influence the materials photoactivity the most are listed. The last two samples are cross experiments that combine synthesis with hydrothermal treatment and additional annealing in air (MW-W+TO) and an NH_3 flow (CH-W+TN).

4.3.4.1 Crystal phase and crystallinity

Samples that were prepared by calcination of HTiNRs at 400 °C in air (TO-400) and an NH_3 flow (TN-400) are both of TiO_2 -B phase (Table 4.10). With increasing calcination temperature, anatase formation starts and it is the only phase in the TO-650 sample. However, when calcined in an NH_3 flow, anatase is never obtained as the only phase as there is still some monoclinic TiO_2 -B phase present. In the TN-650 sample, the formation of $\text{Ti}(\text{O},\text{N})$ has even already started. On the contrary, TiO_2 NRs samples obtained by hydrothermal treatment of HTiNRs are all of anatase phase.

When comparing the XRD spectra of TiO_2 samples, the samples prepared with calcination have sharper peaks with smaller full width at half maximum (FWHM) indicating better crystallinity than samples prepared under hydrothermal conditions (Figure 4.24). Also subsequent thermal treatment of initially hydrothermally synthesized TiO_2 samples (MW-W+TO and CH-W+TN) improved their crystallinity (not shown).

Table 4.10: Titanium dioxide parameters with the largest impact on the material's photoactivity.

Sample	Crystal phase	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	N (wt%) ^a	Band gap (eV)	Colour
TO-400	TiO ₂ -B	31	-	3.50	white
TO-580	TiO ₂ -B + anatase	23	-	3.50	white
TO-650	anatase	21	-	3.30	white
TN-400	TiO ₂ -B	31	0.8	3.44	pale yellow
TN-580	TiO ₂ -B + anatase	32	1.3	3.15	yellowish green
TN-650	TiO ₂ -B + anatase + Ti(O,N)	32	2.5	3.10	grey
CH-W160	anatase	64	-	3.49	white
CH-N0.5	anatase	45	0.6	3.51	white
MW-W120	anatase	61	-	3.52	white
MW-W+TO	anatase	57	-	3.50	white
CH-W+TN	anatase	53	0.3	3.52	white

^a N content was determined with XPS

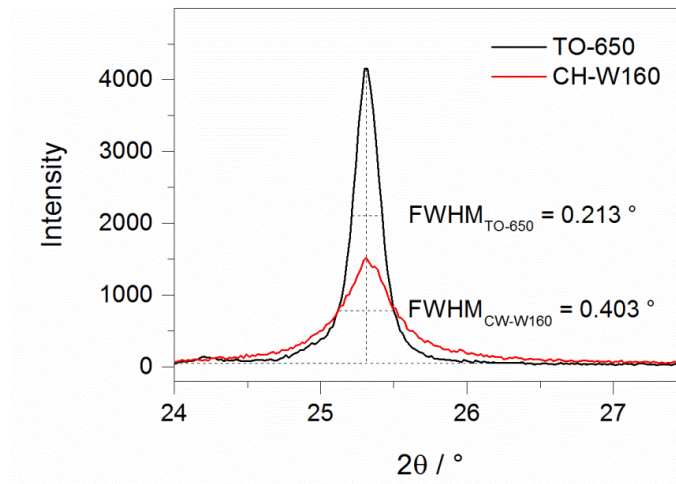


Figure 4.24: Full width at half maximum values determined from the (011) diffraction peak of the anatase phase for the samples TO-650 and CH-W160.

4.3.4.2 Specific surface area

When calcination of HTiNRs in different atmospheres did not significantly affect the material's SSA, it increased for a factor of 3 when TiO₂ samples were synthesised under hydrothermal conditions (Table 4.10). This is mainly due to the partial dissolution-recrystallization processes during the hydrothermal treatment of HTiNRs where smaller nanocrystals grew on the nanoribbons' surface.

4.3.4.3 Nitrogen doping

Transformations of HTiNRs performed in NH_3 media with calcination or hydrothermal treatment resulted in N-doping (Table 4.10). With increasing calcination temperature, the amount of incorporated N increases and N-doping was more sufficient when the starting material was protonated titanate than anatase (TN-400 *versus* CH-W+TN).

4.3.4.4 Nature of nitrogen doping

The nature of N incorporated into the TiO_2 matrix was examined with XPS (Figure 4.25). The N 1s signal of the TN-400 sample is deconvoluted into four main peaks positioned at 395.7 eV, 397.3 eV, 399.2 eV, and 400.4 eV. The first peak located at 395.7 eV is assigned as substitutional doping where N^{3-} anion replaces the oxide one in the TiO_2 lattice producing a N–Ti–O linkage [68], [70], [72], [89], [98], [99]. The second peak, centred at 397.3 eV is described as the N–Ti linkage in TiN in the literature [26], [100]. Ti(O,N) phase was indeed detected in the TN-650 sample with XRD analysis. Maybe there was also some Ti(O,N) phase present in the TN-400 sample but its quantity was under the detection limit of XRD analysis and was consequently not observed. The peak positioned at 397.3 eV can therefore originate from the Ti(O,N) phase or at least a locally highly nitrated region in the material. The peak at 399.2 eV corresponds to surface adsorbed NH_3 [72]. The last peak, centred at 400.4 eV, is attributed to oxidized nitrogen species that can be positioned at interstitial sites in the form of N–O–Ti [65], [68], [89], [98].

When considering the N 1s spectrum of the TN-650 sample, the ratio between different peaks in the region from 396 eV to 400 eV is changed when compared to the N 1s spectrum of the TN-400 sample. The intensity of the peaks arising from substitutional doping (385.8 eV and 387.3 eV) increase at the expense of the peak originating from interstitial doping (400.4 eV) and adsorbed NH_3 (398.6 eV). Also one new peak, positioned at 403.8 eV, is present and can be assigned to chemisorbed N_2 molecules [101]. Elemental nitrogen can originate from thermal decomposition of NH_3 at temperatures higher than 550 °C [70].

In contrast to thermally derived N-doped TiO_2 NRs (TN-400 and TN-650), the N 1s XPS spectrum of the CN-N0.5 sample has a broad asymmetric peak centred around 400 eV. Its deconvolution reveals that the majority of incorporated N is present in the interstitial mode (400.3 eV) whereas also N species in the form of adsorbed NH_3 (398.7 eV) and NH_4^+ (402.2 eV) [102] are present.

To summarize, during the thermal treatment of HTiNRs in a reductive NH_3 atmosphere, N^{3-} can be incorporated into the TiO_2 matrix in two different ways. At lower temperatures, interstitial doping is predominant whereas with increasing temperature, more O^{2-} anions from the lattice are substituted with N^{3-} anions. At temperatures above 550 °C also NH_3 thermally decomposes leading to the presence of trapped or adsorbed N_2 molecules onto the TiO_2 surface. In contrast to calcination in an NH_3 flow, hydrothermal treatment of HTiNRs in 0.5 M $\text{NH}_3(\text{aq})$ leads only to interstitial N-doping of TiO_2 .

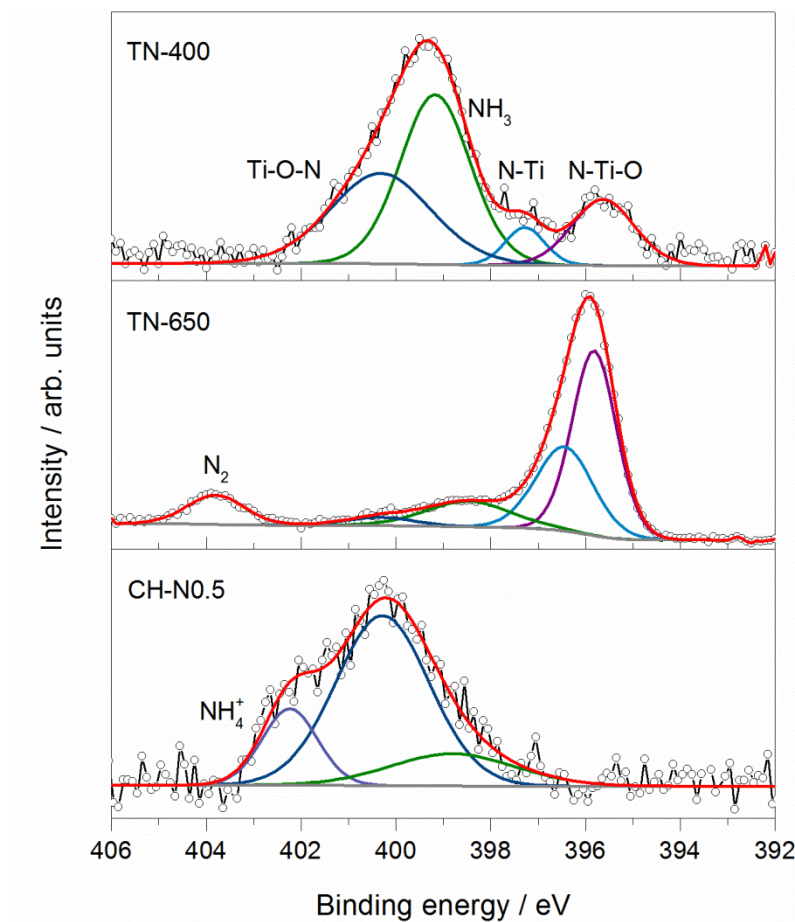


Figure 4.25: N 1s XPS analyses of the TN-400, TN-650 and CH-N0.5 samples. Calcination in an NH_3 atmosphere invokes interstitial and substitutional doping, whereas hydrothermal treatment of HTiNRs in 0.5 M $\text{NH}_3(\text{aq})$ leads only to interstitial incorporation of N^{3-} anions into the TiO_2 matrix.

4.3.4.5 Band gap energy and sample's colour

Both last two columns in Table 4.10 reflect the band gap energies of the prepared TiO_2 samples. The band gap energies were determined from the absorption (Kubelka-Munk units) *versus* wavelength graphs. The band gap energy decreases during the transformation from HTiNRs to TiO_2 NRs, as measured HTiNRs band gap values are 3.65 eV. During thermal treatment in air, the E_g lowers with increasing calcination temperature. This can be attributed to the anatase formation in the TO-580 sample and its exclusive presence in the TO-650 sample.

The band gap values of samples that were calcined in an ammonia atmosphere were smaller in comparison to samples calcined in air. That is normal as N-doping induces localised intra-band gap states [70]. Higher degree of N-doping is obtained with increasing calcination temperature which is reflected in smaller band gap values and the yellow-greenish coloration of the samples as the absorption of visible light starts. However, grey colour of the TN-650 sample most probably originates from the presence of titanium oxynitride ($\text{Ti}(\text{O},\text{N})$) phase, which is conductive.

The band gap values of hydrothermally prepared anatase NRs are larger than the band gap value of the TO-650 sample where anatase was the only phase. The band

gap widening could be a consequence of the presence of smaller anatase nanocrystals on the surface of hydrothermally prepared anatase nanoribbons and lower crystallinity. Finally, the additional thermal treatment of hydrothermally prepared TiO₂ NRs did not significantly affect their band gap values or the materials' colour.

Band gap energies of well-crystalline bulk anatase and TiO₂-B phase are equal, namely 3.2 eV [88] and much smaller than the measured band gap values of our TiO₂ samples. During the size reduction from micro to nano-sized particles, the band gap value of semiconductors usually increases. The measured band gap value of Degussa P25, composed of crystallites with average size between 25 nm and 35 nm [103], [104], is 3.46 eV. The smallest dimension of our nanoribbons is comparable in size with Degussa P25 as it ranges from 20 nm to 30 nm [48].

4.3.4.6 Hydroxylation degree

Surface hydroxylation is important for the material's photocatalytic performance as –OH groups are a source for hydroxyl radicals, and adsorption sites for the substrates. It is reported that the transformation of HTiNRs to TiO₂ NRs under hydrothermal conditions could increase the degree of surface hydroxylation [22]. Table 4.11 summarized the results of TGA and XPS analyses of differently prepared TiO₂ samples in regard to the –OH content.

Table 4.11: Analyses of the –OH content of differently prepared titanium dioxide nanoribbons with TGA and XPS.

Sample	Relative –OH content (wt% / g m ⁻²) ^a	O fraction (wt%) ^b	
		–OH	Bulk
TO-580	0.03	15.4	84.6
CH-W160	0.05	19.6	80.4
MW-W120	0.06	19.4	80.6

^a determined as the ratio between the weight loss of the sample in the temperature range from 140 °C to 600 °C (TGA) and its specific surface area

^b determined with XPS analyses

When determining the –OH content of the samples with TGA, the corresponding graph can be divided into three regions of weight losses: (i) the first one, from room temperature to ~ 120 °C, is attributed to the removal of physically adsorbed water, (ii) the weight reduction in the region from 120 °C to 300 °C comes from the dehydroxylation of weakly bonded –OH groups, whereas (iii) weight loss between 300 °C and 600 °C is due to the dehydroxylation of strongly bonded –OH groups [104]. For the evaluation of the surface hydroxylation of TiO₂ NRs, the region from 140 °C to 600 °C, which was determined with the DSC analysis (not shown), was taken into account (Figure 4.26a). The relative –OH content of the samples was then determined as the ratio between the –OH content of the sample and its SSA. As a result, the relative –OH contents of the CH-W160 and MW-W120 samples were approximately two times larger than of the TO-580 sample (Table 4.11).

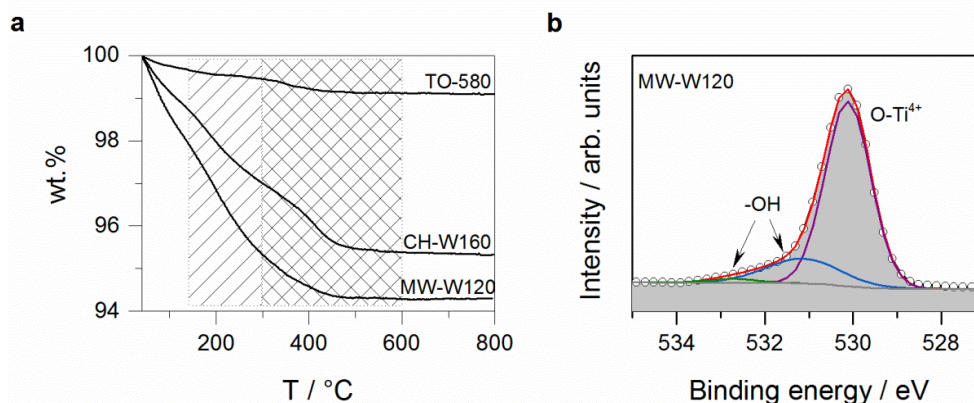


Figure 4.26: TGA curves of the TO-580, CH-W160, and MW-W120 samples (a), and the O 1s XPS spectrum of the MW-W120 sample. The marked regions in (a) correspond to weakly (left) and strongly (right) bound -OH groups that were included in the evaluation of the -OH content. The O 1s XPS spectrum of the MW-W120 sample is deconvoluted into three signals – two corresponding to -OH groups and one originating from the lattice oxygen bonded to Ti^{4+} (b).

The amount of -OH groups was also estimated from the XPS spectra of TiO_2 samples (Figure 4.26b). The O 1s peak of the MW-W120 sample is deconvoluted into three peaks located around 529.8 eV, 531.0 eV, and 531.9 eV. Peak positioned at 529.8 eV is attributed to the lattice oxygen in O-Ti^{4+} , whereas the other two, positioned at 531.0 eV, and 531.9 eV, can be assigned to surface -OH groups or also some defects like oxygen vacancies [105]–[107]. The -OH content was evaluated from the ratio between oxygen centres from -OH groups and the bulk. With such an evaluation, the samples have comparable -OH contents as their values vary like 0.18 for the TO-580 sample, and 0.24 for the CH-W160 and MW-W120 samples.

TGA results indicate that samples prepared by hydrothermal treatment of HTiNRs have a two times higher degree of hydroxylation than the TO-580 sample. On the other side, according to XPS analyses, there is a comparable degree of hydroxylation among all the analysed samples. TGA is not a species-sensitive technique and therefore some weight loss could come from other physisorbed and chemisorbed species which were difficult to remove at lower temperatures due to tight inter-particle space between nanocrystals covering the nanoribbons' surface. To sum up, it is more likely that the absolute amount of surface hydroxyl groups is larger in hydrothermally prepared samples than in samples prepared with calcination of HTiNRs due to the larger SSA and not the higher degree of hydroxylation.

4.3.4.7 Detection of reactive species

It is well-known that thermal treatment of TiO_2 in an NH_3 atmosphere can invoke the reduction of Ti^{4+} to lower oxidation states. This can be a consequence of different mechanisms: (i) a direct reduction of TiO_2 with NH_3 or H_2 obtained after thermal decomposition of ammonia ($2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$), and (ii) after oxygen vacancy formation the electrons can be trapped on Ti^{4+} producing Ti^{3+} [72]. Additional Ti^{3+} centres can be created during photoactivation of the material as light-promoted electrons can be trapped on Ti^{4+} centres. Since no Ti^{3+} was detected with the XPS analysis of the samples, EPR spectroscopy, which is a much more sensitive and a local probe technique than XPS, was employed.

Figure 4.27 presents room temperature EPR spectra of TiO₂ NRs derived by thermal treatment of HTiNRs in air (TO-580) and an ammonia atmosphere (TN-400, TN-580 and TN-650). The TO-580 sample does not show the presence of any paramagnetic centre. On the contrary, all N-doped samples exhibit two paramagnetic signals located at g values of 2.005 and 1.988. The first peak is commonly related to single electron trapped oxygen vacancies in N-doped TiO₂ [71], [72] or superoxide radicals, O₂^{•-} [71], [73], [89]. Since the spectra were collected without sample illumination and superoxide radicals are formed when surface adsorbed O₂ molecules trap photoinduced electrons, the peak positioned at $g = 2.005$ most probably originates from oxygen vacancies formed during N-doping of TiO₂. The second EPR signal, located at $g = 1.988$ corresponds to bulk Ti³⁺ centres [71] proving that thermal treatment of HTiNRs in NH₃(g) indeed invoked a partial reduction of Ti⁴⁺ centres. The intensity of both resonance lines increases with nitrogen content from the TN-400 to TN-580 sample. However, the most nitrated sample, TN-650, exhibits smaller EPR response than the TN-580 one. This can be due to the presence of a metallic Ti(O,N) phase in the TN-650 sample.

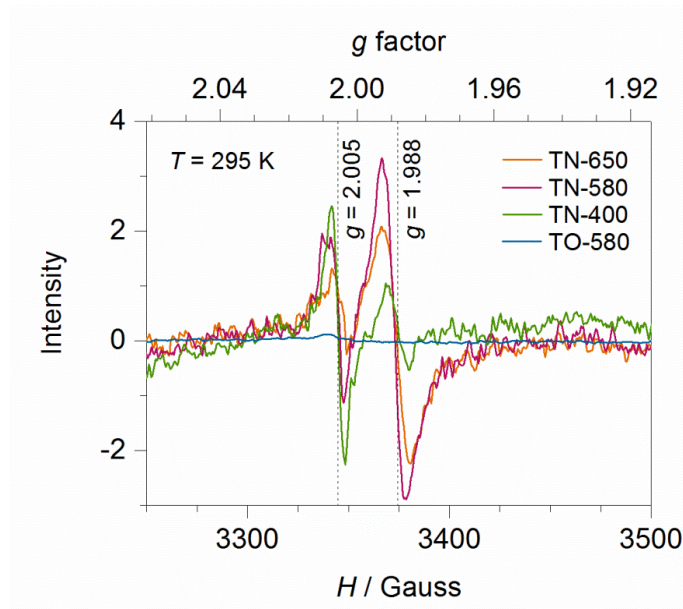


Figure 4.27: EPR responses of the TO-580, TN-400, TN-580, and TN-650 samples measured at room temperature without sample illumination. Pure TiO₂ (TO-580) has no paramagnetic response whereas N-doped TiO₂ samples have intrinsic paramagnetic centres.

To elucidate the processes during photoactivation of the material, the dependence of the EPR response on UV-Vis illumination was also investigated (Figure 4.28). The samples were quenched from r.t. to 30 K in order to ensure sufficient life span of the excited paramagnetic species and EPR spectra were collected in darkness and after 5 minutes of sample illumination with UV-Vis light. Prolonged sample illumination did not result in further changes of the EPR response.

The TO-580 sample did not show any EPR signal when analysed in darkness. After illumination, three resonance lines positioned at $g = 2.037$, 2.007 and 1.993 appeared. The first two can be attributed to oxygen-related paramagnetic species: (i) oxygen radicals formed with either surface-adsorbed O₂ trapping the electrons (O₂^{•-}) or lattice O²⁻ or -OH groups trapping photogenerated holes (O^{•-}, [•]OH), and (ii) oxygen vacancies [108], [109]. The resonance line at $g = 1.993$ arises from Ti³⁺ centres in the bulk [72]

which were created after the acceptance of photoinduced electrons. This is a normal behaviour of anatase under UV-Vis illumination.

All N-doped samples contain intrinsic paramagnetic species as detected with EPR analyses performed in darkness. As signals arising from Ti^{3+} centres can be undoubtedly assigned, more plausible interpretation of resonance lines with g values higher than 2.000 exist. EPR signals of Ti^{3+} in the bulk and surface of the material have g values of 1.985 and 1.932, respectively [71]. In TN-400 and TN-580 samples a triplet centred at approximately g value of 2.007 is present. In the literature, this triplet is attributed to paramagnetic nitrogen species where N atom could be bonded to lattice oxygen O^{2-} , indicating interstitially N-doped species [65]. The last resonance line, positioned at $g = 2.006$ can be again attributed to oxygen vacancies or oxygen-related radicals.

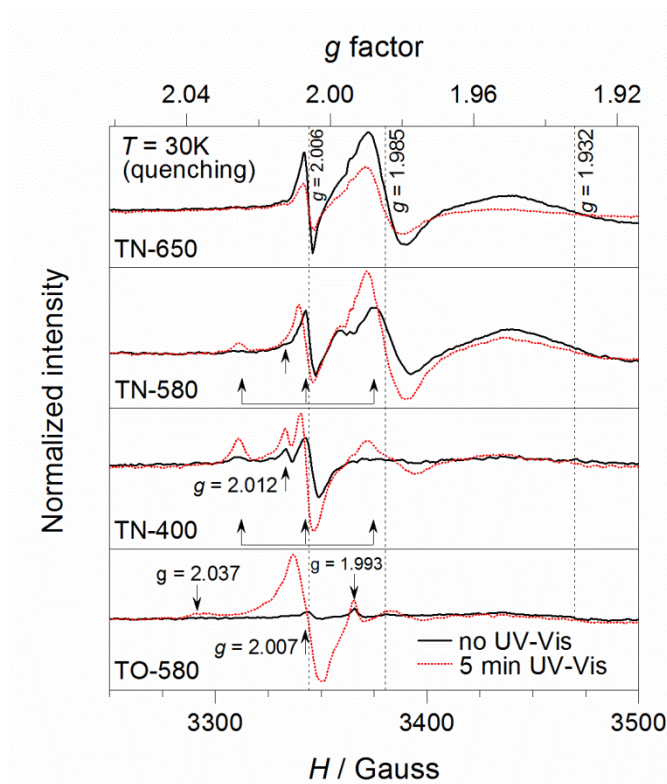
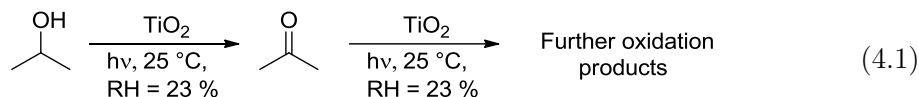


Figure 4.28: EPR response of TiO_2 samples, quenched from r.t. to 30 K, measured in darkness and under UV-Vis illumination. After illumination, all samples have Ti^{3+} and oxygen-related paramagnetic centres when also the intensity of N-related paramagnetic species in N-doped TiO_2 samples changes.

The intensity of EPR signals (N and Ti centres) of the TN-400 and TN-580 samples increased after UV-Vis illumination. This result indicates that some diamagnetic N centres transformed to paramagnetic under UV-Vis illumination. Photoinduced electrons got trapped on Ti^{4+} centres afterwards creating paramagnetic Ti^{3+} . This behaviour is in good agreement with the results reported by other research groups [72], [89]. The EPR response of the TN-650 sample decreased after sample illumination. Again, this is attributed to enhanced charge mobility in the sample due to the presence of the metallic $\text{Ti}(\text{O},\text{N})$ phase.

4.3.4.8 Photocatalytic test

In the end, photocatalytic activity of the samples was evaluated from the photooxidation of a model pollutant isopropanol to acetone (Equation (4.1)).



The results are gathered in Figure 4.29. Among the samples prepared with calcination in air the photocatalytic activity increases with the calcination temperature, which is due to the increasing fraction of anatase phase present in the samples. Surprisingly, N-doped TiO₂ samples' (TN-400, TN-580 and TN-650) photoactivity is almost suppressed. Even though none of these samples are of a pure anatase phase, the decrease in photocatalytic activity is mainly attributed to N-doping. N centres incorporated in the TiO₂ matrix are indeed responsible for Vis light absorption of the material, but also represent defect sites at which recombination of photogenerated electron-hole pairs takes place [70], [74], [89]. In addition, also oxygen vacancies, which are created during N-doping, can act as recombination sites [74], [89]. M. Miyauchi *et al.* [101] showed that N-doped TiO₂ is suitable for the degradation of cations in aqueous solution, as its zeta potential becomes negative with N-doping resulting in better adsorption of pollutants on negatively charged surface of the material. Therefore maybe also N-doped TiO₂ NRs that are presented here, would be more efficient in a different reaction system.

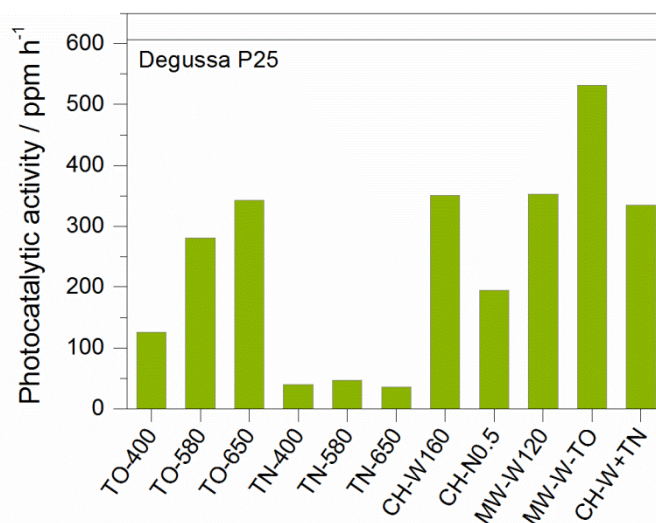


Figure 4.29: Photocatalytic activity of titanium dioxide nanoribbons toward photooxidation of isopropanol to acetone. A horizontal line indicates the photocatalytic activity of a commercial Degussa P25.

TiO₂ NRs that were hydrothermally derived in deionized water with convective or microwave-assisted heating have a comparable photocatalytic activity as the TO-650 sample. The former samples possess 3 times larger SSA than the TO-650 sample but have poorer crystallinity. On the other hand, thermally derived TO-650 sample is highly crystalline with suppressed amount of defects that could act as recombination sites.

When TiO₂ NRs were hydrothermally prepared in a NH₃(aq) solution, the product's photoactivity was smaller than of analogue samples, prepared in deionised water. The decrease in photocatalytic activity is again attributed to N-doping.

As both SSA and crystallinity have a positive impact on the material's photoactivity, hydrothermally derived TiO_2 NRs in water were additionally heated in air (MW-W+TO) or an NH_3 atmosphere (CH-W+TN). Calcination of the MW-W sample with increased SSA in air improved the sample's crystallinity, resulting in enhanced photoactivity. This sample is therefore the most photoactive among the synthesized TiO_2 NRs and is close to the photoactivity of Degussa P25, which is commonly used as a reference in photocatalytic tests. Finally, calcination of the CH-W sample in an NH_3 atmosphere led to better crystallinity of the material and N-doping. It seems that those two parameters nullified each other's contributions to the photoactivity of the material as the CH-W+TN sample exhibits similar efficiency toward isopropanol photooxidation as its precursor, the CH-W160 sample.

4.4 Conclusion

This work is composed of two parts. In the first one, protonated titanate nanoribbons were treated under numerous reaction conditions in order to understand their transformation to TiO_2 . In the second part, photocatalytic activity of the most distinguished samples was evaluated.

The transformation from protonated titanate to anatase is a condensation. However, when performed under hydrothermal conditions, the condensation (topotactic reaction) competes with a dissolution-recrystallisation process. Which process would prevail depends on the medium's pH and counter ions present in the reaction mixture. In this part, three main contributions were achieved. Firstly, the HTiNRs behaviour under different pH values of reaction medium was explained with the aid of the material's zeta potential. Secondly, HTiNRs were successfully transformed to anatase NRs also under basic hydrothermal conditions. There, ammonium cations intercalated between the titanate layers, destabilising the structure and promoting its transformation to anatase. Finally, when the transformation was performed in organic liquids up to the reaction temperature of 160 °C, no TiO_2 phase was detected. Organic solvents therefore serve only as a thermal medium as they cannot donate species (like protons) that could catalyse the transformation.

In the second part of this chapter, photocatalytic activity of the most characteristic samples was evaluated from the photooxidation rate of isopropanol to acetone. Anatase phase, good crystallinity and a high SSA confirmed a positive impact on material's photoactivity. Calcination of HTiNRs in air ensured good crystallinity of TiO_2 NRs when the hydrothermal treatment of HTiNRs provided TiO_2 NRs with an increased SSA. Since the main drawback of TiO_2 as a photocatalytic material is its absorption in only UV region, TiO_2 NRs were also doped with nitrogen, leading to the material absorption also in Vis region. Different doping techniques led to different modes of N incorporation into the TiO_2 matrix. During N incorporation, Ti^{4+} centres are partially reduced to Ti^{3+} and oxygen vacancies are formed, as confirmed with EPR measurements. Even though N centres are responsible for visible light absorption, N-doped TiO_2 NRs exhibited lower photocatalytic activity toward isopropanol photooxidation than non-doped analogues. This is attributed to N centres and oxygen vacancies that act as recombination sites leading to suppressed material's photoactivity. Finally, anatase NRs that were initially prepared from HTiNRs with the hydrothermal treatment in water and were additionally calcined in air expressed the best photoactivity due to the increased SSA and improved crystallinity.

Chapter 5

Controlling Disorder in Titanium Oxynitride Nanoribbons

5.1 Introduction

5.1.1 Titanium oxynitride as a solid solution of cubic TiO and TiN

Titanium oxynitride, $\text{Ti}(\text{O},\text{N})$, belongs to the class of solid solutions. Those exist among isostructural phases where the final properties of the material depend on the content of each individual phase. $\text{Ti}(\text{O},\text{N})$ is therefore a solid solution of cubic TiO and TiN.

TiO has a wide range of non-stoichiometry where its composition varies from $\text{TiO}_{0.7}$ to $\text{TiO}_{1.25}$, depending on temperature [110]. It also has two polymorphs – a high-temperature cubic form where ion vacancies are randomly arranged, and a low-temperature monoclinic with ordered ion vacancies [110]. TiO has metallic properties and also a superconductive transition at temperatures lower than 1 K [111].

TiN also has a cubic structure like TiO but due to its remarkable properties it is far more used in industry than TiO. TiN has extreme hardness of 2160 kG mm^{-2} , which is near the hardness of diamond [112]. It has high temperature (melting point at 2927°C) and corrosion resistance, high thermal and electrical resistivity, a low friction coefficient, and a golden colour [27], [100], [112]. Those properties make TiN widely used in the fields ranging from electronics (integrated circuits and diffusion barriers) to coatings (resistant coatings on cutting tools and for decorative purposes) [27], [100], [112]. In addition, its applications as sensors and a catalyst have also been reported [27], [113]. When magnetic properties were measured on a high-quality bulk TiN sample, it also exhibited low-temperature superconductivity with the critical temperature of 5.6 K [114]. $\text{Ti}(\text{O},\text{N})$ has therefore a huge potential as it combines properties of TiO and TiN and its applications as a catalyst [115]–[117] and an electrode material for energy storage [118], [119] have already been reported.

5.1.2 Anion exchange

Next to chemical composition it is also a nanomaterial's morphology that is important when desiring to employ a nanomaterial in an application. In regard to this, conversion chemistry has emerged as a promising area where morphological changes of nanoparticles are governed with the chemical reaction itself and no additional templates are needed [120], [121]. Conversion chemistry can be divided into four subsections: alloy formation, galvanic replacement, cation exchange and anion exchange [120], [121]. Those processes can be additionally accompanied with Kirkendall effect, leading into even more

pronounced morphological changes as void formation [122]. Anion exchange and Kirkendall effect will be described now as they are the most relevant to the present work.

Anion exchange refers to reactions where compound's anions are exchanged like presented with $M_aX_b \rightarrow M_cY_d$. During the reaction, the oxidation state of the cation can also change [120]. The anion exchange process is usually limited with slow anion diffusion, which leads to two consequences: (i) high reaction temperatures and long reaction times are required for the conversion progress, and (ii) the transformation is also accompanied with cation diffusion since cations are more mobile than anions [120]. Bearing in mind that diffusion coefficients of entering and exiting anions are normally different and that cations also diffuse during the transformation, anion exchange usually triggers morphological changes in the material. For example, initially spherical particles often become hollow after an anion exchange process [120]–[122]. However, it is not always easy to predict the product morphology, especially if the morphology of a starting material is extremely anisotropic.

5.1.3 Kirkendall effect

The Kirkendall effect was discovered in 1947 by Ernest Kirkendall when studying interdiffusion between copper and zinc in brass and observing the interface movement [123]. He discovered that atomic diffusion occurs *via* vacancy exchange. If we consider a diffusion couple of two metals with different diffusion coefficients, there will be a larger mass flux of the element with a higher diffusion coefficient into the region of the element with a smaller diffusion coefficient than *vice versa* during interdiffusion. This has two consequences: (i) the interface shifts toward the region of the element with the smaller diffusion coefficient, and (ii) voids are formed in the region of the element with the higher diffusion coefficient. Those voids are formed after supersaturation of lattice vacancies and are nowadays known as 'Kirkendall voids' [123], [124]. This effect was first observed in metallurgy where it is undesirable since it deteriorates the interface properties. Later it was recognized as beneficial in nanomaterial synthesis, especially for the formation of hollow nanostructures [124]–[129].

5.1.4 Ti(O,N) synthesis

The most common methods for Ti(O,N) synthesis, with special attention paid to the morphology that an individual method provides, will now be described.

Ti(O,N) is most classically produced with a solid state reaction. There TiO and TiN are used in a desired ratio, grounded, pressed into a briquette, and sintered in vacuum at 1450 °C [130]. The reaction temperature is high enough to pronounce particle sintering during the reaction which results in particles with a size exceeding the nanometre range.

Nanoparticles of Ti(O,N) were successfully prepared with a plasmochemical method. They were prepared with reduction of $TiCl_4$ with H_2 in a stream of N_2 plasma also containing small amounts of O_2 and $H_2O(g)$. The size of thus prepared Ti(O,N) nanoparticles ranged from 20 nm to 60 nm [130].

The last and now most commonly applied method for the synthesis of Ti(O,N) nanoparticles is calcination of titania or titanate nanomaterials in ammonia flow at temperatures higher than 600 °C [27], [100], [112], [115]–[118], [130]. The main advantage of this method is a great morphology variety of formed Ti(O,N) nanomaterials that originates from numerous particle shapes of the precursor (titania or titanate) as well as from the diffusion-governed processes during the transformation.

0D Ti(O,N) nano- or micro-particles were prepared with pyrolysis of spherical TiO_2 particles, produced with solvothermal method from different titanium precursors [117],

[131], or TiO_2 aerosols [26], [112] in an ammonia atmosphere. Also, dendritic TiO_2 nanostructures were synthesized with a solvothermal method and, after the thermal treatment in ammonia gas, Ti(O,N) nanostructures of the same morphology were obtained [116].

2D structures – thin films of Ti(O,N) – were obtained when the starting material, TiO_2 thin films, were synthesized with the sol-gel technique in combination with flash crystallization [115]. Finally, also aerogels of TiO_2 served as a precursor for the Ti(O,N) synthesis [130].

When electrical conductivity of Ti(O,N) would be exploited in an application, one-dimensional morphology is beneficial in comparison to other morphologies. The first publication on the synthesis of 1D Ti(O,N) fibres was reported by Zukalova *et al.* in 2010 [27]. The starting material were nanocrystalline anatase fibres that were synthesized with electrostatic spinning from the precursor Ti(IV) butoxide, and subsequently calcined at 500 °C in air. Ti(O,N) fibers were then obtained with calcination of anatase fibers in a dynamic ammonia atmosphere at 600 °C. The researchers additionally confirmed that the transformation between TiO_2 and Ti(O,N) is reversible as Ti(O,N) fibers oxidized to TiO_2 nanofibers upon annealing in air at 500 °C. Thus recovered TiO_2 fibers could be then again transformed to Ti(O,N) fibers [27].

Han and Bang reported the synthesis of hollow Ti(O,N) nanorod array that could serve as an electrode substrate for supercapacitor applications [119]. The array was obtained with calcination of a solid nanorod array of TiO_2 in an ammonia atmosphere at 800 °C. Major attention was attributed to a reaction pathway. Electron microscopy revealed that the transformation from TiO_2 to Ti(O,N) proceeds from the nanorod surface toward its centre. Authors suggested that TiO_2 is initially reduced to TiO by ammonia. Oxygen vacancies that are present in TiO then serve as incorporation sites for nitride anions. Morphological change from solid TiO_2 nanorod array to hollow Ti(O,N) nanorod array was then explained with the Kirkendall effect [119].

Also 1D titanate nanostructures that were prepared with different methods were recognized as a suitable starting material for the Ti(O,N) synthesis [100], [118], [132]. Wei *et al.* reported the conversion of potassium titanate ($\text{K}_3\text{Ti}_8\text{O}_{17}$) nanowires, that were initially prepared with a solid reaction of Ti and KF , to Ti(O,N) nanotubes and nanorods upon calcination in a dynamic ammonia atmosphere at 800 °C for 10 h [100]. The morphology change from nanowires (the starting material) to nanotubes and nanorods (the product) was explained with Ostwald ripening. At the beginning of the reaction, product Ti(O,N) crystals started growing on the surface of potassium titanate nanowires that served as a reactant as well as a template. In the next step, smaller Ti(O,N) crystals would recrystallize into larger Ti(O,N) particles *via* Ostwald ripening to form thick nanotube walls [100]. Even though the morphology evolution was attributed to Ostwald ripening by the authors, this reaction could be an example of conversion chemistry as well. The morphological change from a nanowire to a nanotube seems to occur during the chemical reaction when titanium and oxide ions diffuse in outward direction from the centre of the nanowire to form a nanotube wall of Ti(O,N) . Therefore, the reaction could be an example of anion exchange, accompanied with cation diffusion and potentially even with Kirkendall effect.

Another well-known method to prepare 1D titanate nanostructures is the alkaline hydrothermal synthesis. Kiyono *et al.* [132] used protonated titanate nanowires, derived from potassium titanate nanowires, of two thicknesses – 3 nm and approximately 50 nm. When both materials were calcined in ammonia atmosphere at temperatures between 600 °C and 1000 °C, the thinner nanowires transformed to Ti(O,N) nanoparticles. After the thermal treatment of thicker protonated titanate nanowires, the one-dimensional morphology was preserved, but previously smooth surface of protonated titanate

nanowires became granular. This surface change was explained with two subsequent transformations (i) the chemical reaction – from protonated titanate to anatase, and finally to Ti(O,N) , and (ii) additional particle sintering [132].

Chen *et al.* synthesized a flexible membrane composed of interlaced Ti(O,N) nanofibres and tested it as an electrochemical electrode for energy storage [118]. The starting material was a membrane of interlaced protonated titanate nanoribbons which was prepared with filtration of the corresponding suspension. After the thermal treatment in an ammonia atmosphere at reaction temperatures between 600 °C and 800 °C for 4 h, flexible Ti(O,N) sheets were obtained. Investigation with electron microscopy revealed that the initially smooth surface of protonated titanate nanofibers became porous, full of voids, when the material transformed to Ti(O,N) . The change in the nanofibers' appearance was explained with first formation of defects during the nitridation, and subsequent breaking and coarsening of the material as Ti(O,N) phase crystallised [118].

5.1.5 Outline

From the literature overview it is obvious that the Ti(O,N) synthesis has attracted a broad attention from the research society. Numerous methods for the Ti(O,N) synthesis have been developed when in parallel potential material's applications are being tested as well. However, a controllable material synthesis and its understanding are vital for a successful exploitation of remarkable properties that Ti(O,N) can possess. In the present work, Ti(O,N) nanoribbons were synthesized from protonated titanate nanoribbons with calcination in an ammonia atmosphere at 800 °C. The diversity of Ti(O,N) NR products was achieved with controlling synthesis parameters like a reaction time and an ammonia flow. Different characterization techniques enabled explaining the morphological change from solid protonated titanate nanoribbons to porous Ti(O,N) NRs. Since Ti(O,N) is mainly being tested for electronic applications, electronic properties of Ti(O,N) NRs were also investigated. Finally, the key parameters for driving morphological as well as electronic changes were determined.

5.2 Experimental Section

In a typical experiment, 225 mg of a starting material (protonated titanate or anatase nanoribbons) were weighed in a quartz boat, placed into an oven, and heated to the target temperature of 800 °C. The samples were kept at 800 °C for the selected time and cooled down to room temperature afterwards. The experiments varied in a heating rate, a reaction time and an ammonia flow. All reactions with experimental details are listed in Table 5.1. The samples were labelled as TiON-a/b where 'a' stands for the ammonia flow and 'b' for the reaction time.

Table 5.1: Samples' labels with their reaction conditions: a starting material, a heating rate, a reaction atmosphere, and a reaction time. All samples were synthesized at 800 °C.

Sample	Starting material	$\Delta T/\Delta t$ (°C min ⁻¹)	$\phi(\text{NH}_3)/\phi(\text{Ar})$ (mL min ⁻¹ / mL min ⁻¹)	t (h)
TiON-30/0	H ₂ Ti ₃ O ₇	7	30/10	0
TiON-25/4	H ₂ Ti ₃ O ₇	7	25/15	4
TiON-25/6	H ₂ Ti ₃ O ₇	7	25/15	6
TiON-25/7	H ₂ Ti ₃ O ₇	7	25/15	7
TiON-25/10	H ₂ Ti ₃ O ₇	7	25/15	10
TiON-25/13	H ₂ Ti ₃ O ₇	7	25/15	13
TiON-25/15	H ₂ Ti ₃ O ₇	7	25/15	15
TiON-25/27	H ₂ Ti ₃ O ₇	7	25/15	27
TiON-25/30	H ₂ Ti ₃ O ₇	7	25/15	30
TiON-30/3	H ₂ Ti ₃ O ₇	7	30/10	3
TiON-30/4	H ₂ Ti ₃ O ₇	7	30/10	4
TiON-30/8	H ₂ Ti ₃ O ₇	7	30/10	8
TiON-30/30	H ₂ Ti ₃ O ₇	7	30/10	30
TiON-100/4	H ₂ Ti ₃ O ₇	14	100/10	4
TiON-150/0.67	H ₂ Ti ₃ O ₇	21	150/10	0.67
TiON-30/6a	anatase	7	30/10	6
TiON-30/15a	anatase	7	30/10	15

5.3 Results and Discussion

5.3.1 Structural determination of Ti(O,N) nanoribbons

5.3.1.1 Ammonia flow of 30 mL min⁻¹

Crystal structure of the materials was analysed with X-ray diffraction. The XRD patterns of samples obtained after calcination of HTiNRs at 800 °C in the ammonia flow of 30 mL min⁻¹ for reaction times, ranging from 0 h to 30 h, are presented in Figure 5.1.

Firstly, the XRD pattern of the TiON-30/0 sample was investigated. From there it is evident that HTiNRs first completely transform to anatase NRs during the heating to 800 °C, and also some titanium oxynitride phase is already present. As expected, anatase is therefore a direct starting material for the formation of Ti(O,N) NRs and not protonated titanate. For the complete transformation to titanium oxynitride, three hours of calcination under such reaction conditions were required (TiON-30/3). With prolonging the calcination time up to 30 h, the XRD peaks of the Ti(O,N) phase move to lower angles, as also indicated with the red dotted lines. This peak shift reveals the growth of the titanium oxynitride lattice constant with a reaction time.

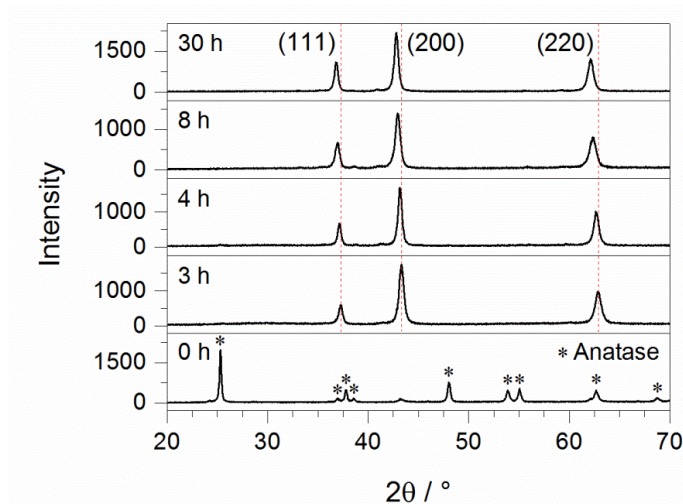


Figure 5.1: XRD patterns of Ti(O,N) nanoribbons prepared from protonated titanate nanoribbons by calcination at 800 °C in the ammonia flow of 30 mL min⁻¹ for reaction times ranging from 0 h to 30 h. Vertical dotted red lines are positioned at the scattering angles of the TiON-30/3 sample's peaks for an easier observation of the shift of the diffraction peaks to lower scattering angles with the increasing reaction time. The X-ray diffraction profile at $t = 0$ h belongs to the anatase phase and its diffraction peaks are labelled with *.

5.3.1.2 Ammonia flow of 25 mL min⁻¹

The phase evolution of Ti(O,N) nanoribbons that were prepared in a lower ammonia flow, that is 25 mL min⁻¹, is similar to already described samples obtained after the reaction in the ammonia flow of 30 mL min⁻¹ (Figure 5.1). The current results are presented as a contour diagram with enlarged regions of the three main diffraction peaks of the Ti(O,N) phase where the peak shift to lower angles with increasing reaction time is clearly seen (Figure 5.2). The main distinction from the results obtained under the ammonia flow of 30 mL min⁻¹ is a longer reaction time required for a complete transformation to the titanium oxynitride phase. When the flow of ammonia was set to 25 mL min⁻¹, pure titanium oxynitride was obtained after 4 h of reacting.

5.3.1.3 Control experiments

Two control experiments were conducted in higher ammonia flows (100 mL min⁻¹ and 150 mL min⁻¹) in order to obtain the samples with the maximal nitridation levels (Figure 5.3). As expected, HTiNRs completely transformed to Ti(O,N) NRs after heating in the ammonia flow of 100 mL min⁻¹ for 4 h (TiON-100/4). When the ammonia flow was increased to 150 mL min⁻¹, 40 min of reacting already sufficed for obtaining a pure Ti(O,N) phase (TiON-150/0.67).

In the last two control experiments anatase NRs were used instead of HTiNRs as a starting material. Anatase NRs were prepared from HTiNRs with heating in air at 580 °C for 15 h. The XRD analyses of the TiON-30/6a and TiON-30/15a samples reveal that both materials comprise of the solely Ti(O,N) phase (Figure 5.3).

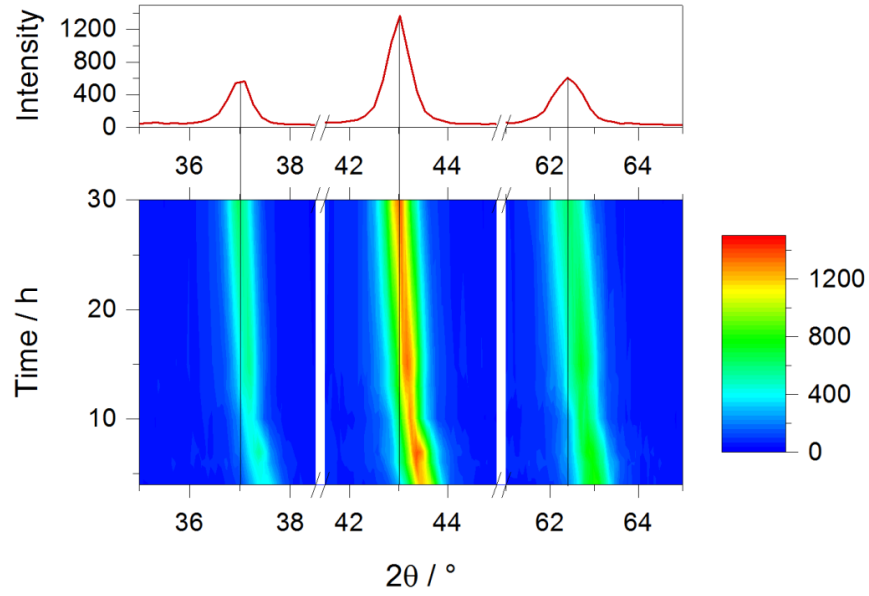


Figure 5.2: The evolution of the titanium oxynitride structure with the reaction time. The room temperature powder X-ray diffraction profile of the TiON-25/30 sample (upper panel) and the time evolution of (111), (200) and (220) powder X-ray diffraction peaks of Ti(O,N) nanoribbons, synthesized in the 25 mL min^{-1} flow of $\text{NH}_3(\text{g})$ at 800°C for reaction times ranging from 4 h to 30 h (lower panel). The 2θ scale is expanded around the centres of the three main peaks, corresponding to reflections of the $\text{Fm}\bar{3}\text{m}$ structure due to clarity reasons.

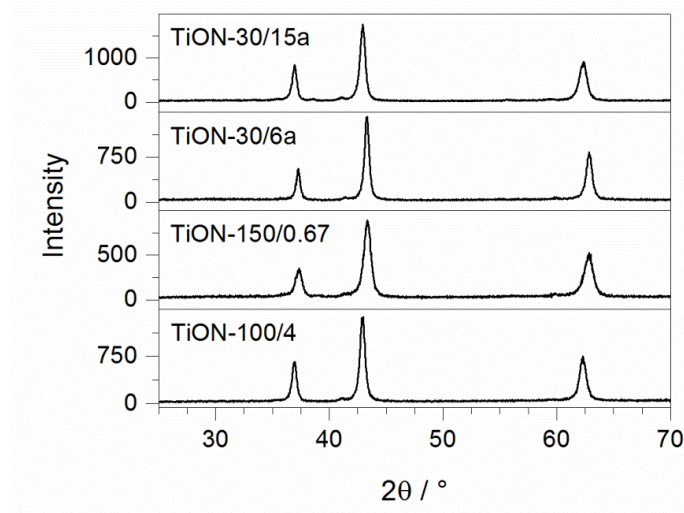


Figure 5.3: XRD patterns of Ti(O,N) nanoribbons from the control experiments. In the first two experiments, Ti(O,N) nanoribbons were prepared from protonated titanate nanoribbons in higher ammonia flows that are 100 mL min^{-1} and 150 mL min^{-1} . Ti(O,N) nanoribbons from the last two control experiments (TiON-30/6a and TiON-30/15a) were prepared from anatase nanoribbons as a starting material.

5.3.1.4 Lattice constant evolution

Finally, lattice constants of the Ti(O,N) NRs samples were extracted from the (200) XRD peak with Bragg equation and their plot as a function of a reaction time is presented in Figure 5.4. Samples are depicted as coloured dots where the colour refers to the ammonia flow used in the reaction and, where possible, solid lines as a guide to the eye are added. Horizontal dotted lines refer to the values of lattice constants of pure TiO (lower line) and TiN (upper line) phase with the values of 4.177 Å (ICDD card no. 08-117) and 4.2374 Å (Aldrich), respectively.

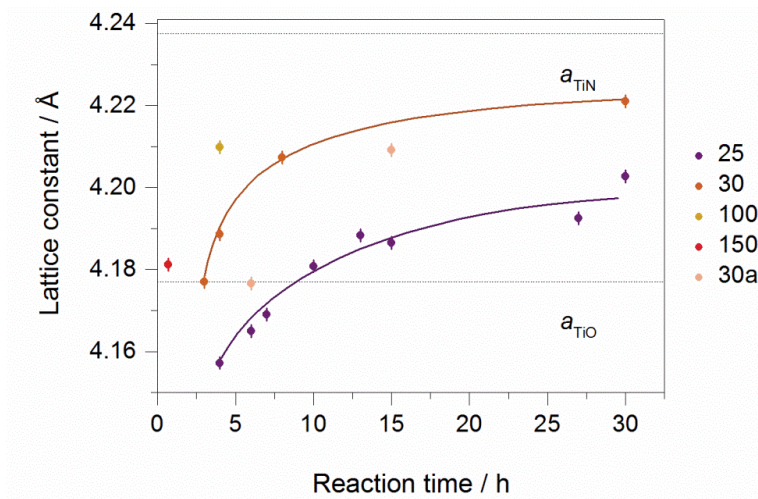


Figure 5.4: The time evolution of lattice constants of Ti(O,N) nanoribbons, synthesized from protonated titanate nanoribbons in 25 mL min⁻¹ (●), 30 mL min⁻¹ (●), 100 mL min⁻¹ (●) and 150 mL min⁻¹ (●) flow of NH₃(g). Ti(O,N) nanoribbons labelled with (●) were prepared in the 30 mL min⁻¹ flow of NH₃(g) from anatase nanoribbons. Solid lines are guides to the eye whereas dashed horizontal lines mark the lattice constants of TiO and TiN structures, respectively.

From such presentation of the results it is clearly seen that the lattice parameter of the Ti(O,N) samples increases with a reaction time. Also, employment of higher ammonia flows led to Ti(O,N) samples with a larger lattice constant. Ti(O,N) is a solid solution of TiO and TiN. Therefore it is logical that products exposed to a larger amount of ammonia (a higher ammonia flow or a longer reaction time) would more resemble TiN and would have a larger unit cell.

When the starting material were anatase NRs instead of HTiNRs, longer reaction time was required to obtain Ti(O,N) NRs with a comparable unit cell under otherwise identical reaction conditions (see TiON-30/3 and TiON-30/6a, and TiON-30/8 and TiON-30/15a). Anatase NRs that were used as a starting material were prepared by calcination of HTiNRs in air at 580 °C for 15 h (for the XRD pattern see Chapter 4, Figure 4.7). As such, they had better crystallinity than anatase nanoribbons, formed during heating of HTiNRs to 800 °C, and it took a longer time for the reaction, which is diffusion controlled, to proceed.

The most unexpected results were the lattice values of Ti(O,N) NRs that were prepared in the ammonia flow of 25 mL min⁻¹ for the shortest reaction times (TiON-25/4, TiON-25/6, TiON-25/7), as they had a smaller unit cell than pure TiO. To explain this, the first type of disorder that is present in Ti(O,N) NRs needs to be defined. The transformation from anatase to Ti(O,N) is an anion exchange reaction that is diffusion controlled. Since oxide anions are smaller than the nitride, the former have

a larger diffusion coefficient. The non-equivalence of diffusion rates results in ion vacancy creation during the formation of $\text{Ti}(\text{O},\text{N})$. Those ion vacancies therefore cause internal chemical pressure in the material and the shrinkage of the unit cell.

5.3.2 Electron microscopy characterization of $\text{Ti}(\text{O},\text{N})$ nanoribbons

5.3.2.1 Morphology characterization – SEM

In the next stage, the samples' morphology was investigated. SEM analyses of the starting material, HTiNRs and the product $\text{Ti}(\text{O},\text{N})$ confirmed that one-dimensional nanoribbon morphology was preserved during the reaction as shown in Figure 5.5.

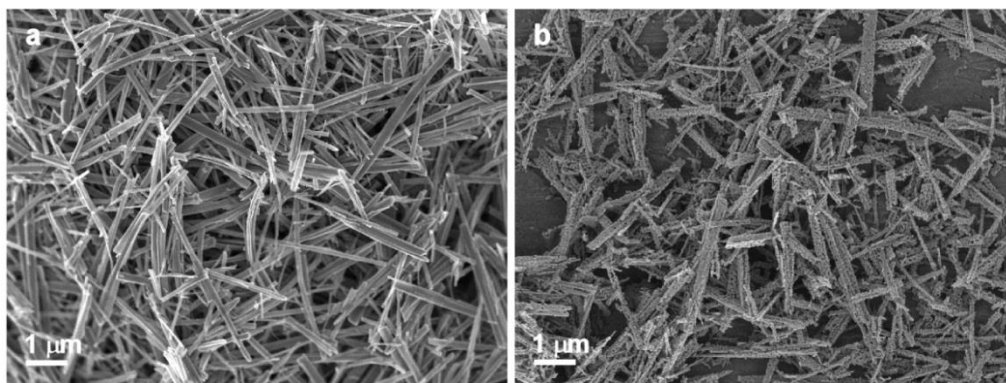


Figure 5.5: SEM images of protonated titanate nanoribbons (a) and titanium oxynitride nanoribbons, TiON-30/30 (b) confirming the preservation of one-dimensional morphology during the transformation.

Fine surface features were then analysed from the SEM images, recorded at the $160.000\times$ magnification (Figure 5.6). HTiNRs have a smooth surface (Figure 5.6a) that is preserved after the material transformation to anatase NRs, which occurs during the heating to the target temperature (Figure 5.6b). However, $\text{Ti}(\text{O},\text{N})$ nanoribbons are porous and full of channels as can be seen from Figure 5.6c–f. The pores of the TiON-30/3 sample are classified as meso and macro pores as their size ranges from a few nm up to ≈ 100 nm. In addition, from the observation of SEM images of the TiON-30/4 , TiON-30/8 and TiON-30/30 samples (Figure 5.6d–f), it seems that channels grow with a prolonged reaction time and even new pores are created in the meantime.

In order to explain the porosity emergence, processes, present during the anion exchange reaction from TiO_2 to $\text{Ti}(\text{O},\text{N})$, need to be considered. Just before TiO_2 converts to the cubic $\text{Ti}(\text{O},\text{N})$ phase, there are many ion vacancies present in the material as: (i) the transformation is diffusion controlled where oxide and nitride anions have different diffusion coefficients, and (ii) the number of anionic sites reduces for a factor of two during the transformation. In addition, there is also a lattice mismatch between tetragonal anatase and cubic $\text{Ti}(\text{O},\text{N})$ phases. Therefore, the material breaks during the rearrangement from the tetragonal anatase to the cubic $\text{Ti}(\text{O},\text{N})$ phase to release the stress. The breaking of the material can also be potentially accompanied with the simultaneous coalescence of ion vacancies into pores. Finally, cation diffusion could also contribute to the final nanoribbons' appearance as cations are generally more mobile than anions. Later, when the $\text{Ti}(\text{O},\text{N})$ phase is already formed and the nitridation process is still in progress, the pores continue to grow. This is a direct consequence of different diffusion rates of oxide and nitride anions, as also described by Kirkendall effect.

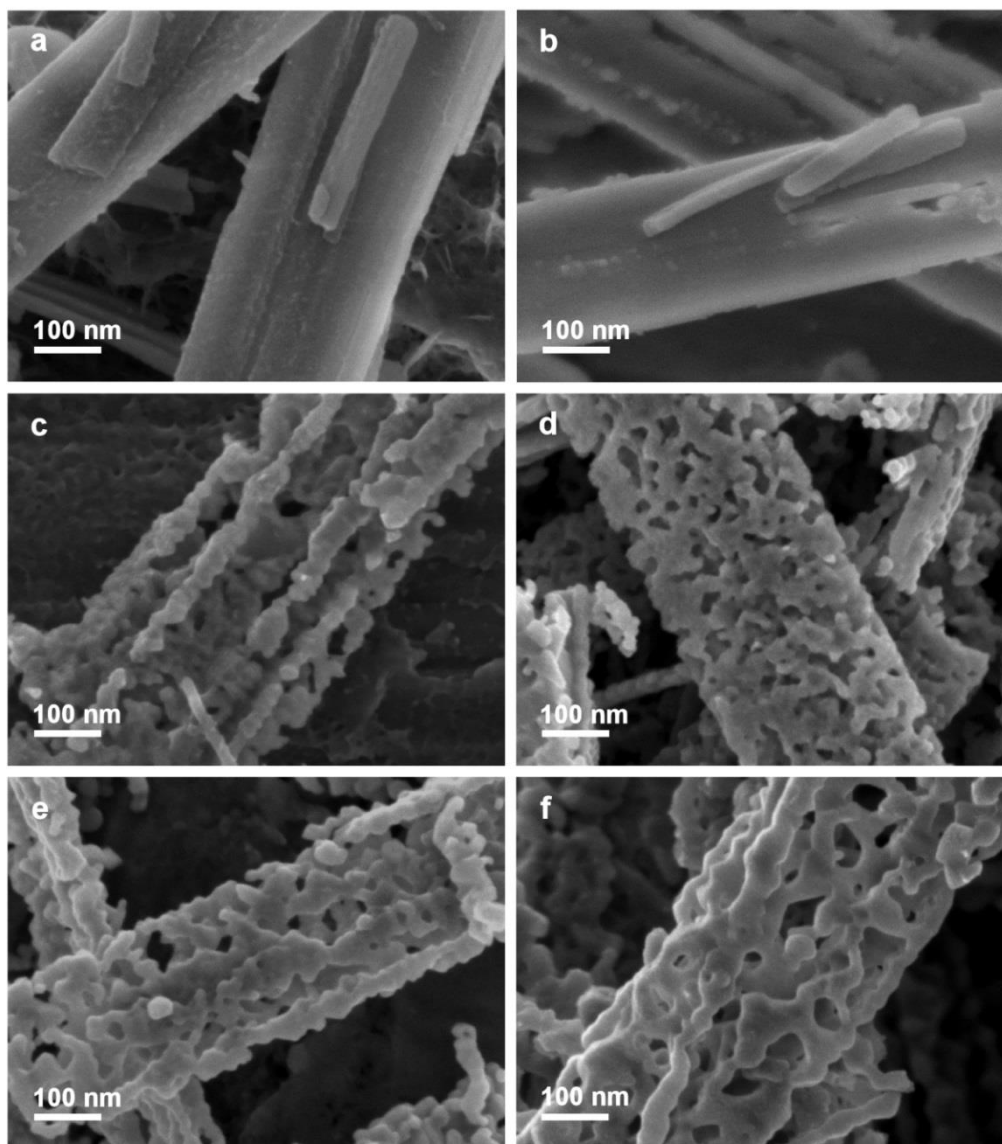


Figure 5.6: SEM images of the starting material, protonated titanate nanoribbons (a), and samples that were obtained after calcination of protonated titanate nanoribbons at 800 °C in the ammonia flow of 30 mL min⁻¹ for 0 h (b), 3 h (c), 4 h (d), 8 h (e), and 30 h (f).

In the end, Ti(O,N) NRs prepared from anatase NRs were investigated (Figure 5.7). SEM analyses of the Ti(O,N)-30/6a and Ti(O,N)-30/15a samples indicate that their porosity is less developed than the porosity of Ti(O,N) NRs prepared from HTiNRs under the same reaction conditions. When anatase NRs with good crystallinity were used as a starting material, all the processes during the transformation to Ti(O,N) required longer reaction times when compared to the transformations with HTiNRs as the starting material.

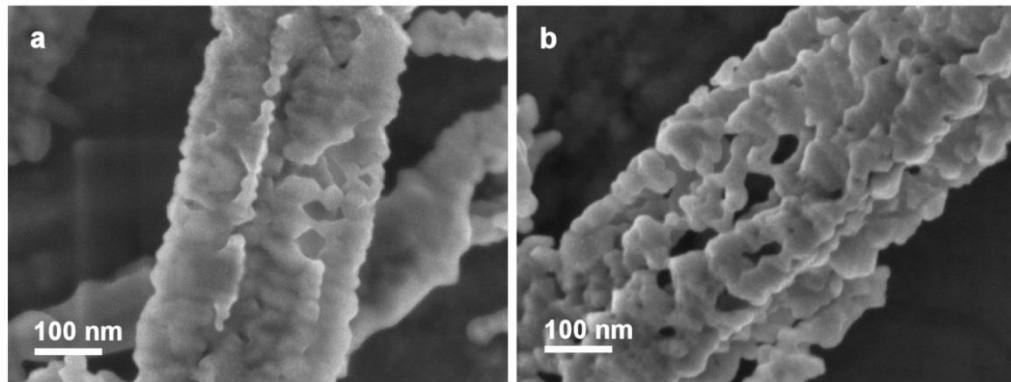


Figure 5.7: SEM micrographs of titanium oxynitride nanoribbons obtained after calcination of anatase nanoribbons in the ammonia flow of 30 mL min^{-1} at 800°C for 6 h (a) and 15 h (b).

5.3.2.2 Ti(O,N) nanoribbons' width evolution – TEM

Kirkendall effect is nowadays most commonly employed for the fabrication of hollow nanostructures [120], [124], [125], [127]–[129]. Since produced Ti(O,N) NRs are penetrated with channels and do not have a perfect hollow structure, a question arises whether the Kirkendall effect is present during the transformation at all. It is accepted that the formation of hollow objects during the Kirkendall effect is sometimes prevented with the nanomaterial's specific morphology [124]. Indeed, the nanoribbon morphology is highly anisotropic. One of the side effects of the Kirkendall effect is also particles' enlargement. Therefore, a statistical analysis of nanoribbons' widths of the TiON-30/0, TiON-30/4, and TiON-30/30 samples was carried out (Figure 5.8).

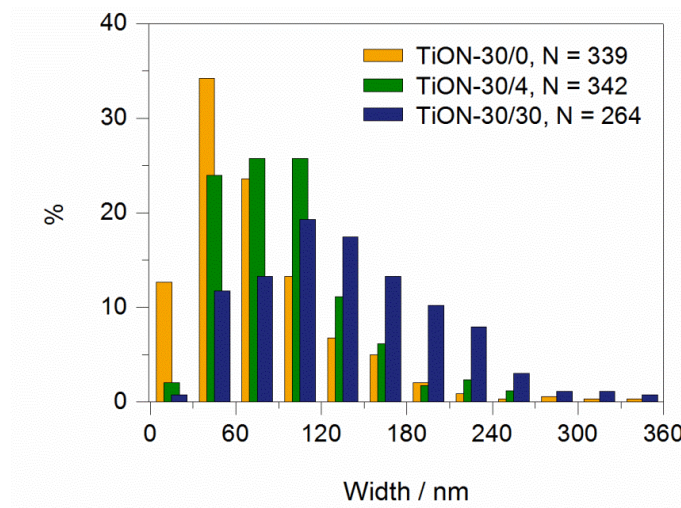


Figure 5.8: Width distribution of nanoribbons derived from protonated titanate nanoribbons with calcination at 800°C in the ammonia flow of 30 mL min^{-1} for 0 h, 4 h, and 30 h.

The nanoribbons' widths were extracted from TEM images that were all recorded at the magnification of $25,000\times$. The results show that the average diameter of the TiON-30/0, TiON-30/4 and TiON-30/30 samples increases as $(78 \pm 51) \text{ nm}$,

(95 ± 46) nm, and (137 ± 66) nm, respectively. Those results therefore report in favour of the presence of Kirkendall effect during the porosity development of Ti(O,N) NRs.

5.3.2.3 Crystallinity of individual Ti(O,N) nanoribbons – (HR)TEM

Ti(O,N) NRs could be a suitable candidate for the application in electronic devices due to the one-dimensional morphology and electrical conductivity. Since crystal defects could affect a material's performance, crystallinity of individual Ti(O,N) NRs was investigated. Nanoribbons of the starting material, protonated titanate, have a smooth surface and are single crystals. But what is in the case of Ti(O,N) NRs that have very distinct crystal structure from the starting material and are additionally penetrated with channels? To answer this question, numerous Ti(O,N) NRs were analysed with (HR)TEM in combination with electron diffraction. Since the results from different individual Ti(O,N) NRs were similar, only one example of a nanoribbon from the Ti(O,N)-30/30 batch is presented (Figure 5.9).

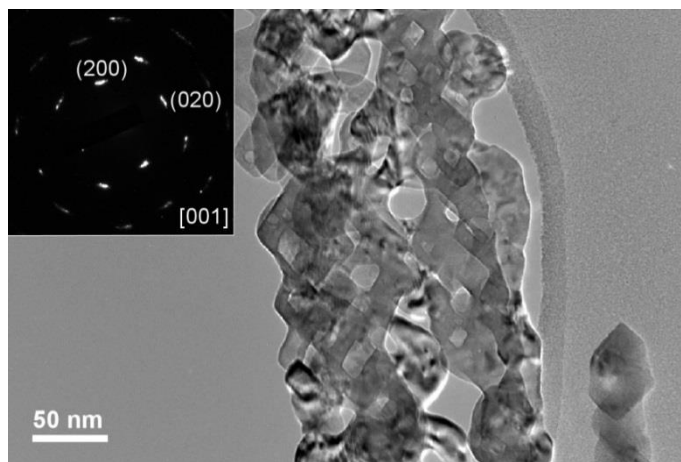


Figure 5.9: The TEM image of a titanium oxynitride nanoribbon from the Ti(O,N)-30/30 batch with the corresponding selected area electron diffraction pattern as the insert.

The electron diffraction pattern reflects cubic structure of Ti(O,N). However, individual reflections seem more like elongated ellipsoids than perfect dots. If the Ti(O,N) nanoribbon was a single crystal, the corresponding ED pattern would be composed of single circular reflection dots. The obtained results therefore indicate that an individual Ti(O,N) NR is most probably polycrystalline with highly, or even almost perfectly, aligned crystallites.

This was additionally supported with a live FFT analysis of a region of the nanoribbon from the Ti(O,N)-30/30 batch (Figure 5.10). There, the FFT pattern slightly rotates, when moving over the region of the nanoribbon indicating a slight variation in the crystallite orientation. Also, $d_{(200)}$ values were extracted from the FFT patterns of the marked regions (Figure 5.10c–f). Their values vary as 2.216 Å, 2.190 Å, 2.187 Å, and 2.913 Å, for the regions 1–4 (Figure 5.10b), respectively. The variation of $d_{(200)}$ values points to changes in the local chemical composition of the Ti(O,N) NR.

5.3.2.4 Element mapping – EELS

A local chemical composition and especially oxygen and nitrogen distribution over a part of an individual nanoribbon from the Ti(O,N)-30/30 batch was more precisely analysed with EELS (Figure 5.11). Here the pink map corresponds to Ti L_2/L_3 , the blue map to N K, and the green map to O K edges (Figure 5.11b–d). The element maps are

overlapped in Figure 5.11e where it is clearly seen that nitride anions prevail over the oxide in the central region of the nanoribbon. On the contrary, edges of the nanoribbon are rich in oxide anions due to passivation of the material after its exposure to the ambient atmosphere.

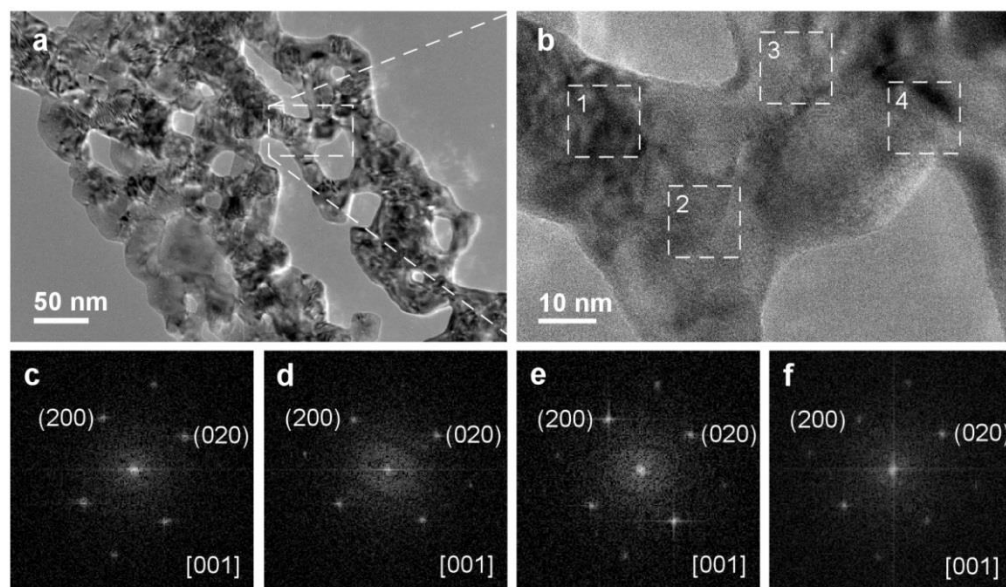


Figure 5.10: The TEM study on an isolated titanium oxynitride nanoribbon from the TiON-30/30 batch. The low-magnification image (a), and the enlarged image of the selected region from the nanoribbon in (b). The corresponding fast Fourier transform patterns of the marked regions 1–4 in image (b) are presented in images (c)–(f), respectively.

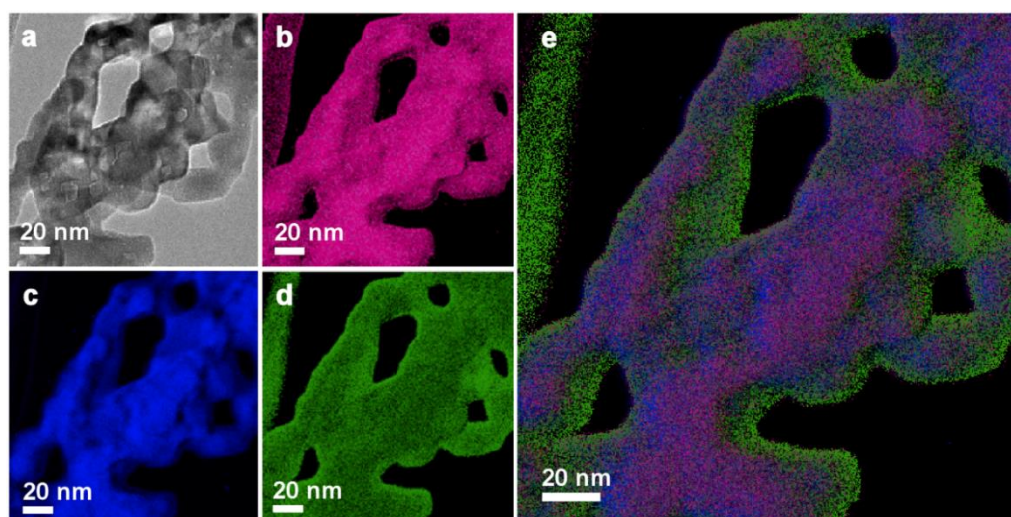


Figure 5.11: The EELS study of the selected region of the Ti(O,N) nanoribbon from the TiON-30/30 batch. The TEM image is presented in (a), whereas element maps of Ti L_2/L_3 , N K, and O K edges are presented in (b)–(d) images, respectively. Individual element maps are overlapped in the image (e), elucidating element distribution over the selected region of the nanoribbon.

5.3.3 X-ray photoelectron spectroscopy of Ti(O,N) nanoribbons

XPS is a powerful tool to analyse a chemical composition and a chemical state of atomic species with the corresponding environment in a material. Since anion exchange between TiO_2 and Ti(O,N) involves substitution of oxide with nitride anions and reduction of Ti^{4+} to lower oxidation states, XPS spectra of Ti 2p and N 1s centres of different Ti(O,N) samples were analysed.

The Ti 2p XPS spectrum of the $\text{Ti(O,N)}\text{-30/30}$ sample is presented in Figure 5.12. It is fitted with four doublets (originating from Ti $2p_{1/2}$ and Ti $2p_{3/2}$) corresponding to four chemical states of Ti centres in the material. The doublet with the peaks located at 464.1 eV and 458.3 eV corresponds to Ti^{4+} in TiO_2 [27], [100], [112], [117]. Doublets located at lower binding energies arise from Ti centres with lower oxidation states [100]. Therefore, Ti^{3+} from a N–Ti–O linkage has the XPS peaks located at 457.0 eV and 463.1 eV [112], [117], where the peaks, originating from Ti^{2+} are located at even lower binding energies that are at 456.0 eV and 461.4 eV [117], [119]. The last doublet, located at 455.0 eV and 460.6 eV, is difficult to identify due to the overlap of TiO and TiN signals [100]. However, considering the slip of the Ti 2p level, the Ti $2p_{1/2}$ component appears at a much lower binding energy indicating that this peak is mainly related to the presence of TiN.

Atomic fractions of individual Ti centres were determined from the quantitative analysis of the Ti 2p XPS spectrum. The resulting fractions of Ti centres, ordered with decreasing binding energy, are 41 % (Ti^{4+}), 12 % (Ti^{3+}), 23 % (Ti^{2+}) and 24 % (TiN). One could be surprised that the major fraction of Ti centres has a 4+ oxidation state. Here we should note that XPS is a surface sensitive technique and Ti(O,N) passivates when exposed to air. Therefore the proof that Ti^{4+} centres are reduced to lower oxidation states during the transformation from TiO_2 to Ti(O,N) is the main contribution of just described XPS analysis.

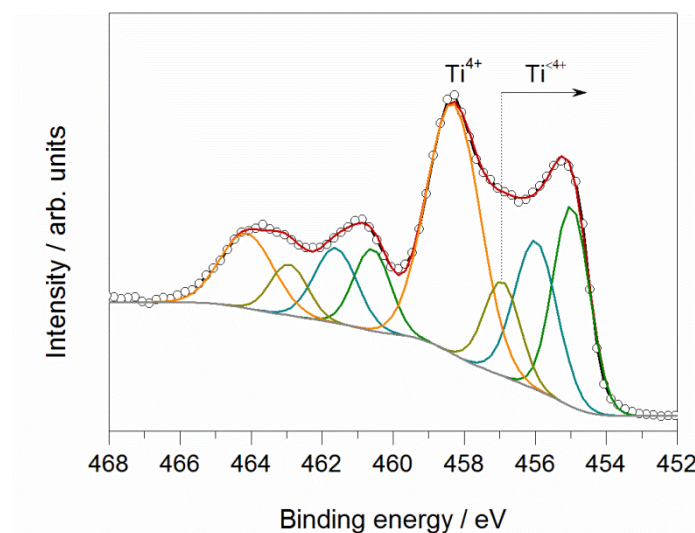


Figure 5.12: The Ti 2p XPS spectrum of the $\text{Ti(O,N)}\text{-30/30}$ sample. The white circles are the experimental measurement, whereas the coloured lines belong to the fits of individual Ti species. Orange line corresponds to Ti^{4+} centres whereas brown, blue and green lines are attributed to Ti^{3+} , Ti^{2+} and Ti in TiN, respectively. The sum of the fits is presented with the red line.

Nitridation process during the transformation from TiO_2 to $\text{Ti}(\text{O},\text{N})$ was investigated with the analyses of N 1s XPS spectra of the TiON-30/3, TiON-30/8, and TiON-30/30 samples (Figure 5.13).

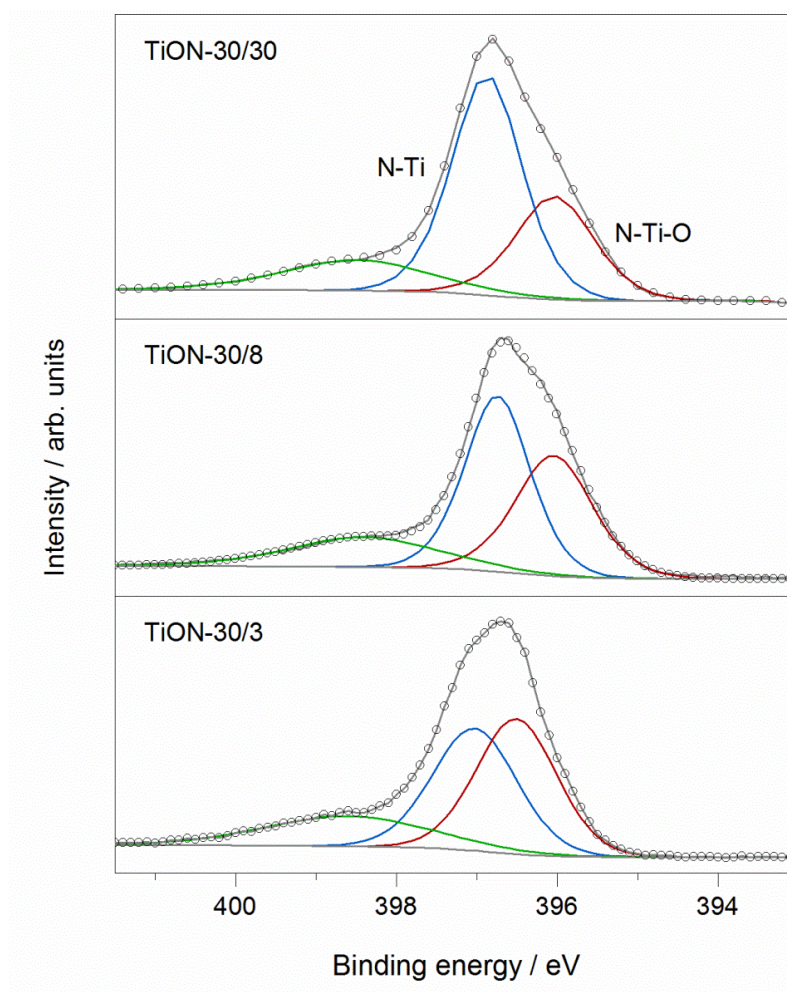


Figure 5.13: Nitrogen 1s X-ray photoelectron spectroscopy spectra of titanium oxynitride nanoribbons that were synthesized in the $\text{NH}_3(\text{g})$ flow of 30 mL min^{-1} at 800°C for 3 h, 8 h, and 30 h. The circles represent the experimental measurement whereas the coloured lines are the corresponding fits. Green, blue, and red lines are attributed to adsorbed ammonia, a fully nitrated TiN phase, and a N–Ti–O linkage, respectively. The sum of the fits is presented with the grey line.

Each individual N 1s XPS spectrum is fitted with three lines with maxima at 398.6 eV, 397.0 eV, and 396.0 eV. The first low-intensity peak centred at 398.6 eV has the binding energy very close to that of NH_3 (398.7 eV), meaning the peak probably originates from adsorbed ammonia [72]. Since this is extrinsic to $\text{Ti}(\text{O},\text{N})$ phase, it will be eliminated from further discussion. The remaining two peaks give the insight into the nitridation process. The peak centred at 397.0 eV is assigned to fully nitrated TiN phase [100]. The last peak positioned at 396.0 eV originates from a N–Ti–O linkage, therefore interstitial substitution of an oxide with a nitride anion [112]. The peaks for Ti–N and N–Ti–O linkages are of comparable intensity in the XPS spectrum of the TiON-30/3 sample. With prolonging the reaction time to 8 h (TiON-30/8) and finally to 30 h (TiON-30/30), the intensity of the peak characteristic for interstitial doping decreases at the expense of the peak attributed to the fully nitrated TiN phase. Such development is

reasonable since anion exchange between oxide and nitride anions is more efficient with a prolonged reaction time.

5.3.4 Disorder quantification in Ti(O,N) nanoribbons

5.3.4.1 Nitridation level

At this point, we will define the second type of disorder present in Ti(O,N) NRs, which is N/O occupancy or a nitridation degree. This kind of disorder controls whether the material would more resemble TiO or TiN. Nitridation level of Ti(O,N) NRs was determined from the XPS analyses as the ratio between nitrogen and titanium species, expressed in at%. Oxygen species were excluded from the calculation of nitridation level due to the material's passivation after exposure to air. Resulting nitridation levels of all Ti(O,N) samples are listed in Table 5.2 whereas their evolution with the reaction time is depicted in Figure 5.14a.

As expected, the nitridation level of the Ti(O,N) NRs samples, formed in the identical reaction medium, increases with a reaction time. When a higher ammonia flow was used, a shorter reaction time already sufficed for a comparable nitridation degree. As a result, the TiON-30/30 and TiON-150/0.67 samples have a comparable degree of nitridation. From the comparison of the time evolution of the nitridation level (Figure 5.14a) and the time evolution of the lattice constant (Figure 5.4) we see that they are quite similar. That is reasonable since the lattice constant value is proportional with the nitridation degree.

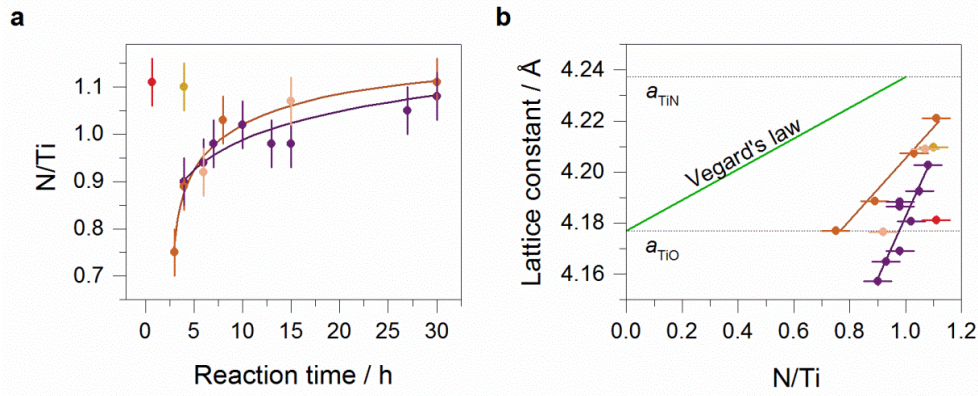


Figure 5.14: Time evolution of nitridation levels in Ti(O,N) nanoribbons (a) and the quantification of ion vacancies that are present in Ti(O,N) nanoribbons as the deviation from the corresponding Vegard's law (b). The Ti(O,N) NRs samples are presented with colored dots where the color indicates the ammonia flow, employed for the Ti(O,N) NRs synthesis: 25 mL min⁻¹ (●), 30 mL min⁻¹ (●), 100 mL min⁻¹ (●), and 150 mL min⁻¹ (●). Ti(O,N) nanoribbons labelled with (●) were prepared in the 30 mL min⁻¹ flow of NH₃(g) from anatase nanoribbons. The solid lines are guides to the eye.

5.3.4.2 Ion vacancy content

During characterization of Ti(O,N) NRs with different analytical techniques, two types of disorder have been defined in the material: (i) ion vacancies, as evidenced with XRD, and (ii) random N/O occupancy of anionic positions in the material, as shown with XPS. As

nitridation levels of Ti(O,N) NRs were determined with XPS, the quantification of ion vacancies was a bit more tricky – how to determine something that is missing? The solution was obtained with the Vegard’s law. It stands for solid solutions stating that the lattice parameter of a solid solution of two components approximately equals to the role of mixtures of the two individual component’s lattice parameters (Equation (5.1)).

$$a_{AxB(1-x)} = xa_A + (1-x)a_B \quad (5.1)$$

Here a is a lattice parameter, A and B are labels for individual components that the solid solution is composed of, and x and $(1-x)$ are their molar fractions, respectively.

Vegard’s law for solid solutions of TiO and TiN is plotted in Figure 5.14b with a green line whereas the experimental results are presented with coloured dots. The discrepancy between the supposed ‘Vegard’ value and the experimental one (Δ) is therefore a direct measure for the amount of ion vacancies present in Ti(O,N) samples (Table 5.2). All Ti(O,N) NRs have much smaller lattice parameters from the predicted ones by Vegard’s law meaning that all the samples still contain a considerable amount of ion vacancies (Figure 5.14b).

However, there is a trend that the amount of ion vacancies in Ti(O,N) NRs, obtained under the same flow of ammonia, decreases with a prolonged reaction time (Figure 5.14b). From the comparison of results obtained from Ti(O,N) NRs produced in the ammonia flow of 30 mL min^{-1} and 25 mL min^{-1} , it is suggested that Ti(O,N) NRs with fewer ion vacancies (therefore more ordered NRs) were produced under the higher flow of ammonia. It is reasonable that the nitridation process is faster when a larger amount of the nitridation reagent is present in the reaction atmosphere.

From the results it is evident that a reaction time also affects the final amount of ion vacancies in Ti(O,N) NRs. A convenient example of this is the TiON-150/0.67 sample (red dot in Figure 5.14b). It has the highest nitridation level ($N/Ti = 1.11$), but since the reaction time was only 40 minutes, the Δ value is also large, that is $0.063 \text{ \AA}$. For comparison, Ti(O,N) NRs with a comparable nitridation level, which were synthesized in the lower ammonia flow but for 30 h, have much smaller Δ ranging from $0.040 \text{ \AA}$ (TiON-25/30) to $0.023 \text{ \AA}$ (TiON-30/30). Ion vacancies created during the transformation from TiO_2 to Ti(O,N) can be divided into two parts: the first part gets occupied with entering nitride anions when the second part remains unoccupied. The trapped ion vacancies can get occupied later or are eliminated from the material with diffusion to the material’s surface or coalescence into pores if the reaction time is long enough. Therefore, the amount of ion vacancies in the material depends on both parameters – on the amount of nitridation reagent as well as the reaction time.

When anatase NRs were employed as the starting material, Ti(O,N) NRs with a slightly larger amount of ion vacancies were produced in comparison to Ti(O,N) NRs prepared from HTiNRs (Figure 5.14b). When denser and better crystalline anatase NRs were used (in comparison to HTiNRs), all the processes rates were lower. And this includes nitridation of Ti(O,N) as well as diffusion and elimination of ion vacancies from the material.

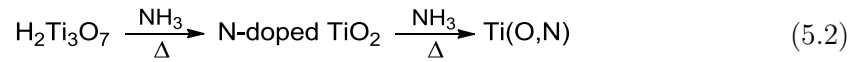
Table 5.2: Lattice constants of the Ti(O,N) samples, their deviation from Vegard's law (Δ), N/Ti ratio, and critical temperature of superconducting samples determined with magnetization measurements.

Sample	Lattice const. (Å)	Δ (Å)	N/Ti ratio	T_c (K)
TiON-25/4	4.157	0.074	0.90	-
TiON-25/6	4.165	0.068	0.94	-
TiON-25/7	4.169	0.067	0.98	-
TiON-25/10	4.181	0.058	1.02	-
TiON-25/13	4.188	0.048	0.98	-
TiON-25/15	4.187	0.050	0.98	-
TiON-25/27	4.193	0.048	1.05	2.4
TiON-25/30	4.203	0.040	1.08	2.4
TiON-30/3	4.177	0.045	0.75	-
TiON-30/4	4.189	0.042	0.89	-
TiON-30/8	4.207	0.032	1.03	2.5
TiON-30/30	4.221	0.023	1.11	3.5
TiON-100/4	4.210	0.034	1.10	2.3
TiON-150/0.67	4.181	0.063	1.11	-
TiON-30/6-a	4.177	0.055	0.92	-
TiON-30/15-a	4.209	0.033	1.07	2.3
TiN standard	4.237	0	1	3.7

5.3.5 Transformation pathway from protonated titanate nanoribbons to Ti(O,N) nanoribbons

From the results obtained from the characterization of Ti(O,N) NRs with all the described analytical techniques, the transformation pathway from HTiNRs to Ti(O,N) NRs can be proposed.

The most concise reaction pathway is expressed with Equation (5.2). HTiNRs first convert to anatase NRs during heating to the target temperature of 800 °C. This transformation is accompanied with N-doping, which after the prolonged reaction time leads to conversion to Ti(O,N).



The first interaction of ammonia molecules and TiO_2 is considered to happen on the surface under-coordinated (5-fold) Ti^{4+} centres, which act as Lewis acid sites, where ammonia molecules are anchored [27], [118]. Then, two processes govern the transformation of TiO_2 to Ti(O,N): (i) reduction of Ti^{4+} to lower oxidation states, and (ii) substitution of oxide with nitride anions.

We already have some knowledge about the initial reduction of Ti^{4+} centres from the EPR analyses of N-doped TiO_2 nanoribbons from Chapter 4, page 70. From there it is evident that N-doping of titania is accompanied with reduction of Ti^{4+} to Ti^{3+} (Figure 4.27 and Figure 4.28). When considering the reducing agent, we should note that ammonia appreciably dissociates ($2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$) at temperatures higher than 500 °C [133]. Luckily, its extent can be controlled with the flow rate due to the slow

kinetics of dissociation. For example, at 700 °C and the ammonia flow of 150 mL min⁻¹, 10 % of ammonia dissociates. When the flow is decreased to 50 mL min⁻¹, the ammonia decomposition increases to 45 % [133]. Ti⁴⁺ centres can be therefore reduced *via* different mechanisms: (i) a direct reduction with NH₃ from the reaction medium, (ii) reduction with H₂ [134]–[137] after ammonia dissociation, and (iii) reduction of Ti⁴⁺ centres after trapping electrons from oxygen vacancies, formed during N-doping of the material [72]. Also DFT calculations report that the formation of oxygen vacancies is favoured during N-doping of TiO₂ [76], [89], [90]. This seems reasonable, since fewer N³⁻ are needed to counterbalance Ti⁴⁺ centres than O²⁻.

Let us now consider nitridation – anion exchange of oxide with nitride anions in the material. Firstly, ammonia molecules, which are anchored on the surface under-coordinated Ti⁴⁺ centres, decompose into active nitrogen species that would replace oxide anions in the material [118]. Then the material simultaneously undergoes nitridation, reduction of Ti⁴⁺ centres, and oxygen vacancy formation. At the point when N-doped TiO₂ has too many defects, the material transforms into the cubic Ti(O,N) phase. After Ti(O,N) is formed, nitridation process is still in progress. Substitution of oxide anions with the nitride ones is a diffusion-controlled process where diffusion of nitride anions is a rate-determining step due to their larger size and consequently a smaller diffusion rate when compared to oxide anions. This non-equivalence of diffusion rates of oxide and nitride anions results in the formation of ion vacancies. With prolonged reaction time, they either get occupied with nitride anions or are eliminated from the material through its surface or with coalescing into pores.

In the end, defects and disorders that are present in the material are also manifested on its surface. The porosity of Ti(O,N) NRs develops in two stages: (i) during the transformation of TiO₂ to Ti(O,N), and (ii) during further nitridation of Ti(O,N) NRs. The initial porosity most probably occurs after stress release during the transformation from the tetragonal anatase structure to the cubic Ti(O,N) phase. The latter porosity is then driven by the Kirkendall effect, which also results in nanoribbons' widening.

5.3.6 Characterization of electrical properties of Ti(O,N) nanoribbons

5.3.6.1 Magnetic properties – SQUID

The advantage of solid solutions is gathering properties of two isostructural materials in a single component. Up to now, we have analysed chemical and morphological properties of Ti(O,N) samples. The next step is to perform physical characterization, in particular, determining material's magnetic and transport properties.

Magnetic properties of Ti(O,N) NRs were measured with the SQUID magnetometer. The obtained results can be categorized into two different groups as shown by their typical representatives in Figure 5.15a.

A typical example of the first category is the TiON-30/4 sample (Figure 5.15a, green dots). This sample shows the highest magnetic susceptibility at room temperature of 9.5×10^{-5} emu mol⁻¹. With decreasing temperature, χ slightly increases and saturates, forming a plateau at approximately 2×10^{-4} emu mol⁻¹ between 180 K and 30 K. Upon further cooling, χ increase can be described as a low-temperature Curie-like enhancement due to the presence of localized paramagnetic defects. Their amount was estimated from fitting the $\chi(T)$ curve at low temperatures to Curie law with the assumption of having $S = 1/2$, and corresponded to approximately 450 ppm. Such localized paramagnetic defects were detected in all analysed samples.

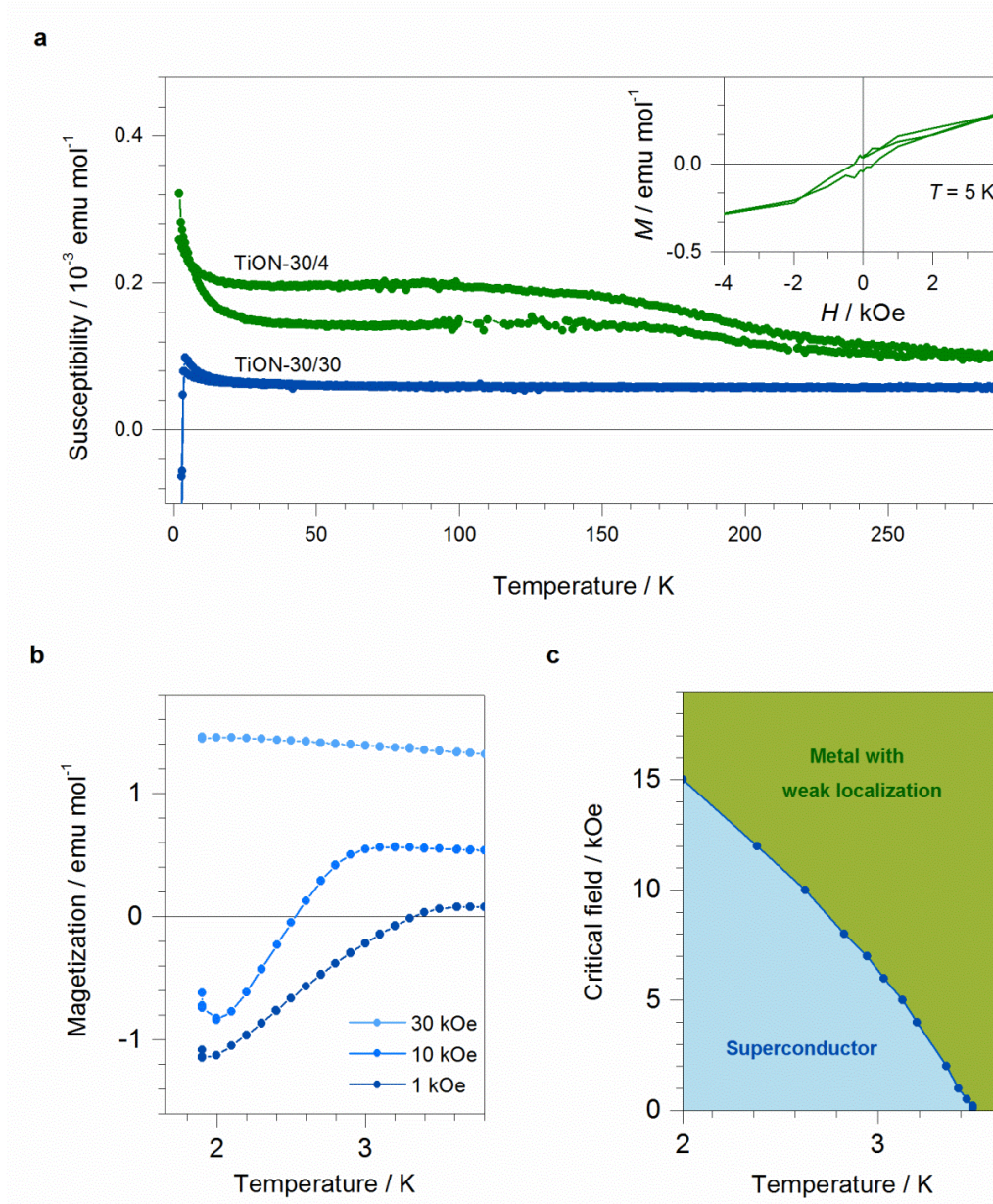


Figure 5.15: Magnetic measurements of titanium oxynitride samples. Temperature dependences of magnetic susceptibility, $\chi(T)$, measured for the TiON-30/4 (●) and TiON-30/30 (●) samples (a) When measuring the susceptibility under the field-cooled protocol, the magnetic field of 1 kOe was applied. The data is corrected for the diamagnetic core contributions of Ti, O and N. The magnetic hysteresis loop measured at 5 K for the TiON-30/4 sample is shown in the inset of (a). The low-temperature dependence of the superconducting TiON-30/30 magnetization on several magnetic fields is presented in (b). (c) shows the temperature dependence of the critical field of the TiON-30/30 sample.

The splitting of $\chi(T)$ when measuring under zero-field and field-cooled conditions together with the hysteresis loop measured at 5 K (inset Figure 5.15a) are indicative of a weak ferromagnetic component. Such behaviour was detected in the most disordered samples that were prepared during short reaction times and had a large deviation from the expected lattice constant according to the Vegard's law (Figure 5.14b and Table 5.2).

Ferromagnetic response is exclusively related to the Ti(O,N) phase since the parent material, protonated titanate, exhibits diamagnetic properties [138]. However, additional analyses are required to undoubtedly determine whether described ferromagnetic response is intrinsic to the disordered Ti(O,N) material. Alternatively, a similar behaviour could originate from surface magnetization, possibly connected to the oxygen rich amorphous layer of the material.

The second category comprises of Ti(O,N) NRs that were highly nitridated ($N/Ti \geq 1.03$) and had the lowest degree of ion vacancies as determined with the deviation from the Vegard's law ($\Delta \leq 0.048 \text{ \AA}$), and therefore resulted in a completely different $\chi(T)$ response. Among these samples, $\chi(T)$ of the TiON-30/30 sample was selected as a typical representative and is shown in Figure 5.15a with blue dots. For this sample $\chi(T)$ is temperature independent from room temperature down to 30 K, which is a hallmark of a metallic state and is described by Pauli spin susceptibility. From its value of $\chi = 5.7 \times 10^{-5} \text{ emu mol}^{-1}$, density of states on Fermi level was determined and corresponded to $N_F \approx 1.7 \text{ states eV}^{-1}$ per formula unit. Upon further cooling, $\chi(T)$ slightly increases and reaches the value $\chi = 9.9 \times 10^{-5} \text{ emu mol}^{-1}$ and then sharply drops at the critical temperature of 3.5 K. The sharp transition and the diamagnetic response below T_c indicate that the material exhibits a transition into the superconducting phase. Magnetic measurements of all Ti(O,N) samples show that highly nitrated Ti(O,N) NRs ($N/Ti \geq 1.03$) with the suppressed value of ion vacancies ($\Delta \leq 0.048 \text{ \AA}$) are superconducting with critical temperatures ranging from 2.3 K to 3.5 K (Table 5.2). The measured critical temperatures are lower than those of bulk TiN ($T_c \approx 5.6 \text{ K}$) [114], [139] or even of stoichiometric TiN thin films ($T_c \approx 4.5 \text{ K}$) [140]–[142]. This could be attributed to the defects and the disorder present in Ti(O,N) nanoribbons, as for instance, ion vacancies and off-stoichiometry. Measurements of critical magnetic field for the TiON-30/30 sample, where magnetization was measured as a function of external magnetic field, revealed the presence of only one critical field and no intermediate transition corresponding to the second critical field could be observed (Figure 5.15b and c). In this measurement the critical temperature decreases to 2.1 K when the magnetic field of 15 kOe is applied, resulting in the superconducting coherence length $\xi(2.1 \text{ K}) \approx 15 \text{ nm}$, which is of the order of a nanoribbon's height. When the magnetic field of 30 kOe (or more) is applied, critical behaviour is completely suppressed. A single critical field and a hardly observable difference between zero-field cooled and field-cooled measurements below the critical temperature confirm that TiON-30/30 is a type I superconductor. This is also in agreement with the already reported data on bulk analogues [114].

5.3.6.2 Transport properties

The low density of states on the Fermi level and the presence of localized moments, determined with susceptibility measurements, led to the investigation of transport properties of individual Ti(O,N) nanoribbons (Figure 5.16). The analyses were conducted with the two most characteristic samples that are labelled as TiON-30/4 and TiON-30/30 (Figure 5.17).

Measuring transport properties of an individual nanoribbon, which is a few micrometres long and has a width and a height of the order of a few tens of nanometres, is rather challenging. Therefore, the largest Ti(O,N) nanoribbons from the individual batches were selected. Figure 5.16 shows a SEM image of a Ti(O,N) nanoribbon from the TiON-30/30 batch.

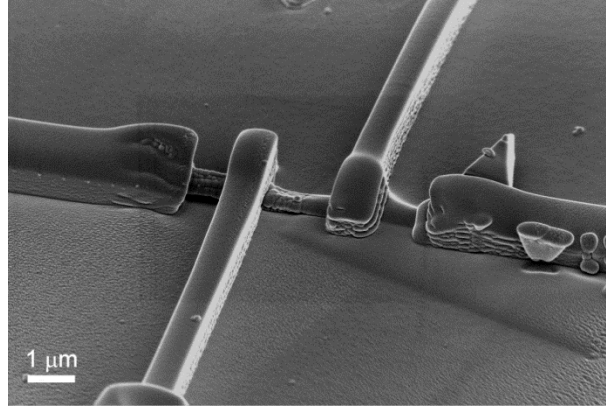


Figure 5.16: The SEM image of the Ti(O,N) nanoribbons from the TiON-30/30 batch with four platinum contacts made with a focused ion beam technique.

The nanoribbon has the cross-section of $144 \text{ nm} \times 680 \text{ nm}$ and the length exceeding 3 μm . Four Pt contacts were made with focused ion beam platinum deposition in order to avoid contact resistivity and the distance between the two central Pt electrodes is 1.34 μm . Thus, the measured room-temperature resistance is $R(300 \text{ K}) = 241 \text{ Ω}$, which corresponds to the resistivity of $\rho = 1760 \text{ μΩ} \cdot \text{cm}$ (Figure 5.17a, green dots). That is more than the resistivity of TiN thin films ($\rho \sim 100 \text{ μΩ} \cdot \text{cm}$) [143]. With decreasing temperature, resistivity increases, which is just the opposite behaviour from simple metals. When fitting the resistance measurement of the TiON-30/30 sample, a successful fit of the measurement section between 300 K and 50 K is obtained with $R(T)$ considering weak localization corrections of R_0 (Figure 5.17a, light blue line). The fit is described with $R(T) = R_0(1 + (\rho_e e^2 / 2\pi\hbar S) L_\varphi)$ where ρ_e is the impurity scattering limited value of the resistivity, S is the nanoribbons' cross-section, and L_φ is the temperature-dependent phase-breaking length [144], [145]. The fit results in $R_0 = 24(1) \text{ Ω}$ and $L_\varphi \propto T^{-p}$, where the power-law exponent of $p = 0.35(1)$ matches well the expected $p = 1/3$ for dephasing through weakly inelastic electron-electron collisions in one-dimension [146], [147]. One can notice that L_φ saturates at low temperatures, which is a common feature in one-dimensional nanostructures [145], [148]. Therefore, both – the magnitude of room temperature resistivity and $R(T)$ behaviour – point to the pronounced effects of disorder causing weak localization effects in all Ti(O,N) NRs samples.

The distinction between the TiON-30/4 and TiON-30/30 samples becomes apparent after cooling them beneath 10 K (Figure 5.17a). As the resistivity of the TiON-30/4 sample constantly increases with a decreasing temperature down to 1.5 K, the resistivity of the TiON-30/30 sample exhibits a sharp drop at $T_c = 2.7 \text{ K}$ confirming the materials' transition into a superconducting phase. Measurements of the critical temperature for the TiON-30/30 sample give similar results to the ones obtained with SQUID measurements (Figure 5.15b), confirming the type I superconductor. The critical temperature of the TiON-30/30 sample rapidly decreases with an increasing external magnetic field and the superconducting transition of the TiON-30/30 sample is completely suppressed when exposed to the magnetic field of 3.0 T (Figure 5.17b).

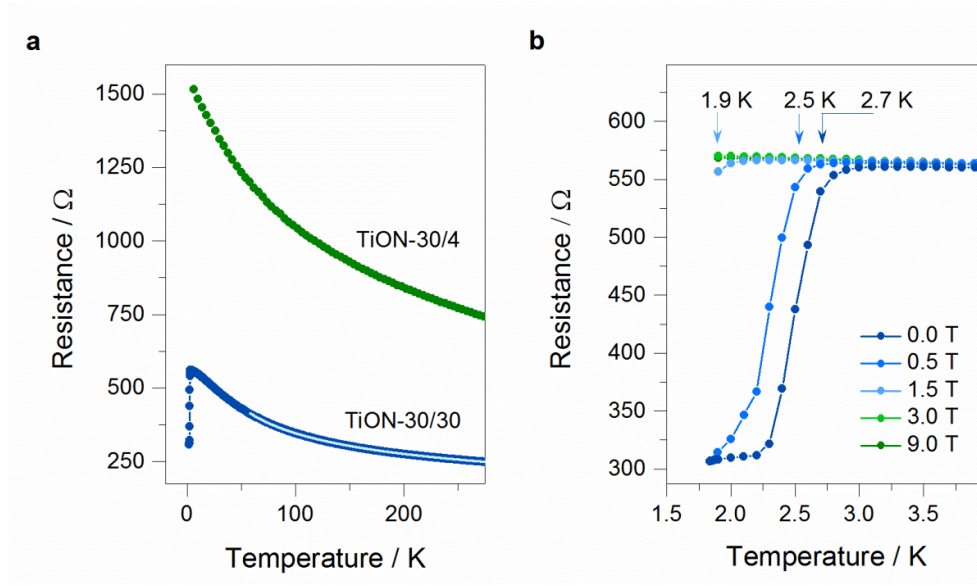


Figure 5.17: Transport properties of individual titanium oxynitride nanoribbons. Temperature dependences of resistance $R(T)$, measured on single Ti(O,N) nanoribbons from the TiON-30/30 (•) and TiON-4/30 (•) batches (a). The thick white line is the fit of the TiON-30/30 data (a). Low-temperature resistance measured for the Ti(O,N) nanoribbon from the TiON-30/30 batch in magnetic fields ranging from 0 T to 9 T (b).

One can also notice that the T_c value of the TiON-30/30 sample depends on an analytical technique – it was 3.5 K when determined with the SQUID magnetometer and decreased to 2.7 K when resistivity measurements were applied. SQUID measurements were conducted on powder samples whereas individual nanoribbons were analysed in resistivity measurements. Ti(O,N) nanoribbons from the same batch slightly vary in the nitridation level as well as amount of defects affecting T_c and, consequently, widening the superconducting transition of the material as observed with the bulk magnetization measurements (Figure 5.15).

However, one obvious question arises – why does the resistivity of the TiON-30/30 sample not drop to zero when the material is in the superconducting phase? More plausible explanations exist. A non-vanishing low-temperature resistivity in very thin nanoribbons [149] or in certain granular metal thin films [150] was rationalized with thermal and quantum fluctuations of the order parameter. Alternatively, a low-temperature resistivity could be due to the Andreev reflection when a normal current in a metallic lead is converted into a supercurrent in the superconductor [151]–[154]. For a comprehensive explanation of the phenomenon further investigations are required.

5.3.7 Phase diagram

In the end, all the obtained information about disorder and superconductivity of Ti(O,N) NRs is gathered in one diagram that is composed of three panels (Figure 5.18). The upper panel describes the first kind of disorder in the material – N/O occupancy where dependence of the nitridation degree of Ti(O,N) NRs on the lattice parameter is depicted. As expected, the nitridation level of Ti(O,N) NRs produced under the same ammonia flow increases with the increasing lattice parameter. However, if we compare samples produced under different ammonia flows, we see that they can have

similar nitridation degrees but very distinct lattice constants. For example, both the TiON-150/0.67 and TiON-30/30 sample have the nitridation degree of 1.11, whereas their lattice parameter values are 4.181 Å and 4.221 Å, respectively. The difference in the lattice parameters is caused by the second kind of disorder present in Ti(O,N) NRs, which are ion vacancies.

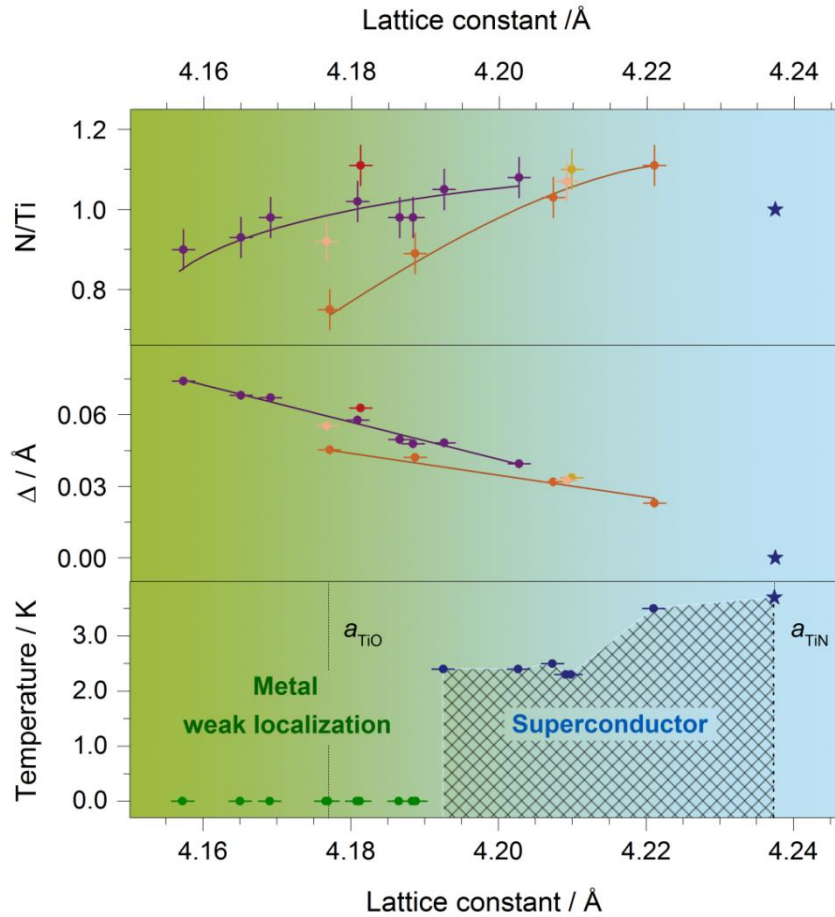


Figure 5.18: The phase diagram of titanium oxynitride nanoribbons. It presents: (i) dependence of the nitridation level on the lattice constant (the upper panel), (ii) dependence of the ion vacancy content on the lattice constant (the middle panel), and (iii) the evolution of superconducting critical temperatures, T_c , (•) as a function of the lattice parameter (the bottom panel). The samples are presented in the top two panels with coloured dots where the colour indicates the ammonia flow, employed for the Ti(O,N) NRs synthesis: 25 mL min⁻¹ (•), 30 mL min⁻¹ (•), 100 mL min⁻¹ (•), and 150 mL min⁻¹ (•). Ti(O,N) nanoribbons labelled with (•) were prepared in the 30 mL min⁻¹ flow of NH₃(g) from anatase nanoribbons. The solid lines are guides to the eye.

The dependence of the ion vacancy content on the lattice constant is depicted in the middle panel. The general trend is that the ion vacancy content (expressed as the deviation from Vegard's law, Δ) decreases with the increasing lattice constant of Ti(O,N) NRs regardless of the ammonia flow employed in the synthesis. This is reasonable since the lattice parameter expands when the ion vacancy content in the material is suppressed either with elimination of ion vacancies through diffusion or their occupation with nitride anions.

Finally, the lowest panel summarized the results obtained from the magnetic measurements of Ti(O,N) NRs. Here, the critical temperatures of the phase transition from a normal metallic to a superconducting phase are plotted as the function of the lattice parameter. The lattice parameters of pure TiO and TiN phases are also marked. The prediction whether Ti(O,N) NRs would be superconducting becomes very straightforward from such a result presentation. Simply – samples with $a \geq 4.1925 \text{ \AA}$ exhibit the superconducting phase when cooled under the critical temperature that ranges from 2.3 K to 3.5 K for the synthesized samples (Table 5.2, Figure 5.15). We have already discussed that the presence of the superconducting phase in Ti(O,N) NRs is conditioned with the degrees of disorders, which are the nitridation degree and the ion vacancy content. Now, the last question remains: does any disorder type influence magnetic properties of Ti(O,N) NRs more than the other one? To answer this question, we need to compare the limit sample, which are the most disordered Ti(O,N) NRs among the superconducting ones, with other Ti(O,N) NRs that have comparable degrees of disorders. The limit sample is TiON-25/27 that has the smallest lattice parameter among the superconducting ones. We will first consider the nitridation degree where the N/Ti value for the TiON-25/27 sample is 1.05. The general trend is that samples that are the most nitridated are also superconducting. However, after observation of the upper panel, we find the superconducting TiON-30/15 sample that has lower N/Ti = 1.03 than the TiON-25/27 sample. What is more, the TiON-150/0.67 sample exists which has a higher nitridation degree of 1.11, but does not exhibit superconductivity. Therefore, the nitridation degree itself does not suffice for forecasting whether Ti(O,N) NRs would be superconducting.

Let us now consider the second disorder type, ion vacancies (middle panel). The TiON-25/27 sample has $\Delta = 0.048 \text{ \AA}$, which is the highest value among those of the superconducting samples. However, a look on the left side of the panel from the TiON-25/27 sample reveals that there are the TiON-30/3 and TiON-30/4 samples with even smaller Δ values of $0.045 \text{ \AA}$ and $0.042 \text{ \AA}$, respectively, but are not superconducting. This also means that the ion vacancy content solely cannot be a direct measure for the prediction of the superconductivity in Ti(O,N) NRs. They are both disorder types – the nitridation degree as well as the amount of ion vacancies – that are crucial for the emergence of superconductivity in Ti(O,N) NRs and the individual type of disorder cannot be evaluated separately. The nitridation degree and the ion vacancy content go hand in hand and it is their combination that is reflected in the material's lattice constant and can be a direct measure for prediction whether Ti(O,N) NRs would be superconducting.

5.4 Conclusion

Titanium oxynitride nanoribbons were successfully synthesized with calcination of protonated titanate nanoribbons in the ammonia atmosphere at $800 \text{ }^\circ\text{C}$. Samples with a broad spectrum of properties were synthesized with the fine control over the reaction atmosphere and time. XRD analyses of the samples revealed that protonated titanate first dehydrates into anatase that later acts as a starting material for transformation to Ti(O,N). During the formation of Ti(O,N) phase, two kinds of disorder are created – random N/O occupancy that is also regarded as a nitridation degree, and ion vacancies. The presence of both disorder types has many consequences on Ti(O,N) NRs – surface, textural and electronic. Firstly, monocrystalline protonated titanate nanoribbons with smooth surface are transformed to Ti(O,N) NRs, which are porous and appear to be polycrystalline. The initial porosity emerges during the anion exchange process from

anatase to Ti(O,N) due to lattice mismatch between the two phases whereas the additional pore evolution is driven by Kirkendall effect. The second material's properties that are affected by the presence of disorders are electronic properties. All Ti(O,N) NRs samples are metallic when only Ti(O,N) NRs with $a \geq 4.1925 \text{ \AA}$ exhibit also low-temperature superconductivity. The emergence of superconductivity is conditioned with both disorders – N/O occupancy as well as ion vacancies and is expressed only when both disorders are sufficiently suppressed. The present study is more fundamental aiming to master the tuning of Ti(O,N) NRs properties through synthesis parameters and to understand the processes that the material undergoes. With achieving those goals, the future work would be focused on exploitation of Ti(O,N) NRs properties especially in the field of catalysis as Ti(O,N) is already reported to be a suitable electrode material [118] and could also be used as a heterogeneous catalyst [115]–[117].

Chapter 6

Conclusions

Clean air, water, and environment are demands for a good quality life and nanotechnology can substantially contribute to them when it is coupled with green chemistry. In this work, we focused on three one-dimensional Ti,O-based nanomaterials – protonated titanate, TiO_2 , and titanium oxynitride – that considerably address the green chemistry demands as follows: (i) they are chemically non-toxic, (i) their initial precursor is TiO_2 , which is an abundant and economically accessible material, (iii) they can be transformed to each other, which enables materials' modification as well as regeneration, and (iv) they can be produced in relatively large amounts, which would lower their production costs. Despite the ease of transforming the materials among each other, they are also different enough to have distinct chemical properties and fields of application.

Protonated titanate nanotubes successfully catalysed the aldol condensation. In the model reaction between benzaldehyde and cyclohexanone, a catalytic amount of the material that did not require any activation prior the reaction, already sufficed. The catalytic power of protonated titanate nanotubes originates from their strong acid sites. Those seem to be surface $-\text{OH}$ groups that are in a bridging configuration whose acidity is increased due to the nanotube's bent structure. At the end of the reaction, the product mixture was isolated with centrifugation, which enabled catalyst recovery as well as the decrease of organic solvent consumption. Protonated titanate nanotubes were then used for five repetition cycles with only a slight decrease in the material's activity. Finally, protonated titanate nanotubes successfully catalysed also the condensation among different substrates and a scaled-up (1-gram) reaction. Bearing all this in mind, employment of protonated titanate nanotubes as a solid acid catalyst for the aldol condensation has many benefits when compared to the reaction's current performance in the industry, fulfils green chemistry demands, and will hopefully be further examined for the industrial application.

In the next part of the work, I focused on TiO_2 nanoribbons. Thanks to the material's photoactivity, TiO_2 is a subject of intense research aiming to apply it in air and water purification technologies. In the present work, the transformation of protonated titanate nanoribbons to TiO_2 nanoribbons was first studied and the photocatalytic activity of the key samples was later evaluated.

The transformation of protonated titanate to anatase is a condensation where $\text{Ti}-\text{OH}$ entities of a single or neighbouring titanate layers connect. The transformation can occur rather easily due to structural similarities between the materials. HTiNRs were transformed to TiO_2 NRs with calcination in air and an ammonia flow at 400 °C and higher temperatures. The reaction temperature drastically reduced to 160 °C when the transformation was performed under hydrothermal conditions. For the understanding of HTiNRs behaviour in aqueous media, material's zeta potential was taken into

consideration. Even though HTiNRs are nominally stable under basic conditions, they can be transformed to anatase NRs if the right base is chosen. HTiNRs were successfully transformed in 0.5 M $\text{NH}_3(\text{aq})$ under hydrothermal conditions where NH_4^+ cations could intercalate in between the titanate layers, destabilise the structure, and promote its transformation to anatase. With increasing acidity of the reaction medium (pH value down to 1), the transformation proceeds faster due to the proton catalysis. Finally, solvothermal treatment of HTiNRs in organic liquids did not result in any TiO_2 phase formation. When the reaction medium cannot donate species to catalyse the transformation, it acts only as a thermal medium and the reaction temperature of 160 °C does not suffice for the material's transformation.

In the next step, photocatalytic activity of the most characteristic TiO_2 samples was evaluated from the photooxidation of isopropanol as a model pollutant to acetone. The tests were performed in a solid-gas reactor mimicking air purification technologies. The results confirmed the positive impact of the anatase phase, crystallinity, and a specific surface area on material's photoactivity. TiO_2 samples prepared with calcination had better crystallinity than the samples prepared with the hydrothermal treatment. On the contrary, the latter samples possessed a larger specific surface area than the former. Nitrogen doping, achieved with calcination in an ammonia flow or the hydrothermal treatment of HTiNRs in an $\text{NH}_3(\text{aq})$ solution, caused the decrease of the samples' band gap energy. Despite the expectations, N-doped TiO_2 NRs expressed lower photoactivity from the non-doped ones. Nitrogen doping is accompanied with partial reduction of Ti^{4+} centres and oxygen vacancy formation. As a result, the introduced nitrogen atoms as well as oxygen vacancies can act as recombination sites suppressing the material's photoactivity. The best results were obtained with the anatase sample that had an increased specific surface area, obtained during the hydrothermal treatment of HTiNRs in water, and good crystallinity as the material was subsequently calcined in air.

The last part of the research was focused on $\text{Ti}(\text{O},\text{N})$. The material has a huge application potential since it is a solid solution of TiO and TiN where the latter compound is already widely used in the fields ranging from protective coatings to electronic devices. The added values of $\text{Ti}(\text{O},\text{N})$ is that, as a solid solution, its final properties can be tuned. Our study was more of a fundamental nature providing the insight into the processes that the material undergoes during the synthesis and their effect on the material's electronic properties. $\text{Ti}(\text{O},\text{N})$ NRs were prepared with calcination of HTiNRs in an ammonia flow at 800 °C where the property tuning was achieved with the delicate control over reaction parameters like an ammonia flow and a reaction time. XRD analyses of the samples revealed that protonated titanate nanoribbons first transform to anatase NRs that finally serve as a $\text{Ti}(\text{O},\text{N})$ precursor. Electron microscopy analyses of the samples revealed that initially smooth and solid nanoribbons of protonated titanate become porous and full of voids with the $\text{Ti}(\text{O},\text{N})$ formation. The initial porosity emergence is attributed to the lattice mismatch between the materials whereas the porosity, developed after $\text{Ti}(\text{O},\text{N})$ phase formation, is driven with the so-called Kirkendall effect. During the anion exchange process from anatase to $\text{Ti}(\text{O},\text{N})$ two kinds of disorder are created – ion vacancies, and a random N/O occupancy of anionic positions – that affect material's electronic properties. Magnetic measurements performed on powder samples and transport analyses of individual $\text{Ti}(\text{O},\text{N})$ nanoribbons revealed that all the samples have metallic properties whereas only those with the lattice parameter $a \geq 4.1925 \text{ \AA}$ also exhibit low-temperature superconductivity. The results confirmed that superconductivity development is conditioned with both disorder kinds and emerges only when both of them are sufficiently suppressed.

To conclude, three one-dimensional Ti,O-based nanomaterials were studied. The aim of this work was to understand the materials' reactivity, the transformations among them and, finally, to exploit their properties in applications addressing contemporary issues. I believe that one of the main opportunities that nanomaterials offer is their use as heterogeneous solid catalysts. With such an application, the benefits originating from their nano-size can be exploited, yet the nanomaterials' use is laboratory controlled, which is especially important in regard to potential health issues. As protonated titanate nanotubes and TiO_2 nanoribbons were tested as solid catalysts in this work, the future prospective would therefore be to examine the catalytic properties of $\text{Ti}(\text{O},\text{N})$ nanoribbons, starting in the area of coupling reactions.

Appendix A

Protonated Titanate Nanotubes as a Solid Acid Catalyst for the Aldol Condensation

A.1 Experimental Conditions and Results of Organic Reactions

Experimental conditions and results of organic reactions are presented in the following tables. Each individual table corresponds to the figure from the main text as noted where the experiments are listed in the same order as in the figure. In the column ‘Amount’ are the amounts of first aldehyde and then ketone used in the reaction in mmoles. Conv. and Select. stand for conversion and selectivity, respectively.

Table A.1: Experimental conditions and results from the solvent scan (p. 29, Figure 3.10a).

Aldehyde	Ketone	Amount (mmol:mmol)	Catalyst (mg)	Solvent (mL)	T (°C)	t (h)	Conv. (%)	Select. (%)
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	HFIP, 0.5	70	1	7	17
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	MeCN, 0.5	70	1	17	39
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	EtOAc, 0.5	70	1	27	49
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	DCM, 0.5	70	1	11	34
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hex, 0.5	70	1	39	75
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	70	1	61	81

Table A.2: Experimental conditions and results of optimization of the model reaction (p. 29, Figure 3.10b).

Aldehyde	Ketone	Amount (mmol:mmol)	Catalyst (mg)	Solvent (mL)	T (°C)	t (h)	Conv. (%)	Select. (%)
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	r.t.	25	44	0
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	70	1	61	81
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	70	3	69	89
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	1	83	92
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	2	97	97
Benzaldehyde	Cyclohexanone	9.4:4.7	HTiNTs, 250	Hept, 10	Reflux	4	97	99

Table A.3: Experimental conditions and results of the aldol condensation between benzaldehyde and cyclohexanone, catalyzed with different catalysts (p. 30, Figure 3.11).

Aldehyde	Ketone	Amount (mmol:mmol)	Catalyst (mg)	Solvent (mL)	T (°C)	t (h)	Conv. (%)	Select. (%)
Benzaldehyde	Cyclohexanone	1:0.5	-	Hept, 0.5	Reflux	2	16	0
Benzaldehyde	Cyclohexanone	1:0.5	HCl, 10 mol%	Hept, 0.5	Reflux	2	28	0
Benzaldehyde	Cyclohexanone	1:0.5	HTiNRs, 25	Hept, 0.5	Reflux	2	20	4
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	2	97	97
Benzaldehyde	Cyclohexanone	1:0.5	NaTiNRs, 25	Hept, 0.5	Reflux	2	25	0
Benzaldehyde	Cyclohexanone	1:0.5	NaTiNTs, 25	Hept, 0.5	Reflux	2	8	9

Table A.4: Experimental conditions and results of the aldol condensation between different substrates (p. 32, Figure 3.13).

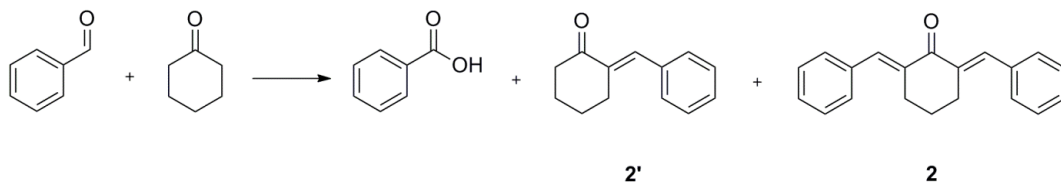
Aldehyde	Ketone	Amount (mmol:mmol)	Catalyst (mg)	Solvent (mL)	T (°C)	t (h)	Conv. (%)	Select. (%)
4-MeO- benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	2	46	73
4-Cl- benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	4	99	98
3-NO ₂ - benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	4	94	100
Benzaldehyde	Acetophenone	1:1	HTiNTs, 25	Hept, 0.5	Reflux	4	76	98

Table A.5: Experimental conditions and results of the repetition cycles (p. 33, Figure 3.14).

Aldehyde	Ketone	Amount (mmol:mmol)	Catalyst (mg)	Solvent (mL)	T (°C)	t (h)	Conv. (%)	Select. (%)
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	2	97	97
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	2	83	92
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	2	79	80
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	2	72	78
Benzaldehyde	Cyclohexanone	1:0.5	HTiNTs, 25	Hept, 0.5	Reflux	2	78	81

A.2 Conversion and Selectivity Calculation

Examples of conversion and selectivity determination for the model reaction between benzaldehyde and cyclohexanone are provided with equations (A.1) and (A.2).



$$Conversion = \frac{n(\text{benzoic acid}) + n(\text{product } \mathbf{2}') + 2 * n(\text{product } \mathbf{2})}{n(\text{benzaldehyde}) + n(\text{benzoic acid}) + n(\text{product } \mathbf{2}') + 2 * n(\text{product } \mathbf{2})} \quad (\text{A.1})$$

$$Selectivity = \frac{n(\text{product } \mathbf{2})}{n(\text{benzoic acid}) + n(\text{product } \mathbf{2}') + n(\text{product } \mathbf{2})} \quad (\text{A.2})$$

A.3 ^1H NMR Data

Benzaldehyde [155]:

^1H NMR (300 MHz, CDCl_3): δ 7.52 (dd, $J_1 = 7.7$ Hz, $J_2 = 8.2$ Hz, 2H), 7.63 (tt, $J_1 = 7.3$ Hz, $J_3 = 1.4$ Hz, 1H), 7.88 (dd, $J_3 = 1.4$ Hz, $J_2 = 8.2$ Hz, 2H), 10.02 (s, 1H).

Cyclohexanone [156]:

^1H NMR (300 MHz, CDCl_3): δ 1.68 – 1.75 (m, 2H), 1.82 – 1.90 (m, 4H), 2.31 – 2.36 (m, 4H).

Benzoic acid [157]:

^1H NMR (300 MHz, CDCl_3): δ 7.48 (dd, $J_1 = 7.48$ Hz, $J_2 = 8.55$ Hz, 2H), 7.62 (tt, $J_3 = 1.37$ Hz, $J_1 = 7.48$ Hz, 1H), 8.12 (dd, $J_3 = 1.37$ Hz, $J_2 = 8.39$ Hz, 2H).

(E)-2-benzylidenecyclohexanone [158]:

^1H NMR (300 MHz, CDCl_3): δ 1.73 – 1.81 (m, 2H), 1.89 – 1.98 (m, 2H), 2.54 (t, $J_1 = 6.7$ Hz, 2H), 2.84 (dt, $J_2 = 2.1$ Hz, $J_3 = 6.4$ Hz, 2H), 7.30 – 7.41 (m, 5 H), 7.50 (t, $J_2 = 2.1$ Hz, 1H).

(2E,6E)-2,6-dibenzylidenecyclohexanone [159]:

^1H NMR (300 MHz, CDCl_3): δ 1.74 – 1.83 (m, 2H), 2.93 (dt, $J_1 = 1.9$ Hz, $J_2 = 6.4$ Hz, 4H), 7.31 – 7.48 (m, 10H), 7.80 (s, 2H).

4-methoxybenzaldehyde [156]:

^1H NMR (300 MHz, CDCl_3): δ 3.88 (s, 3H), 6.95 (d, $J = 8.84$ Hz, 2H), 7.82 (d, $J = 9.0$ Hz, 2H), 9.88 (s, 1H).

(E)-2-(4-methoxybenzylidene)cyclohexanone [158]:

^1H NMR (300 MHz, CDCl_3): δ 1.71 – 1.95 (m, 4H), 2.52 (t, $J_1 = 6.6$ Hz, 2H), 2.84 (dt, $J_2 = 6.6$ Hz, $J_3 = 2.1$ Hz, 2H), 3.83 (s, 3H), 6.90 – 7.46 (m, 4H), 7.50 (t, $J_3 = 2.3$ Hz, 1H).

(2E,6E)-2,6-bis(4-methoxybenzylidene)cyclohexanone [160]:

^1H NMR (300 MHz, CDCl_3): δ 1.71 – 1.93 (m, 2H), 2.91 (dt, $J_1 = 1.96$ Hz, $J_2 = 5.89$ Hz, 4H), 3.81 (s, 6H), 6.90 – 7.50 (m, 8H), 7.76 (s, 2H).

4-chlorobenzaldehyde [156]:

^1H NMR (300 MHz, CDCl_3): δ 7.52 (d, $J = 8.7$ Hz, 2H), 7.83 (d, $J = 8.7$ Hz, 2H), 9.99 (s, 1H).

(2E,6E)-2,6-bis(4-chlorobenzylidene)cyclohexanone [160]:

^1H NMR (300 MHz, CDCl_3): δ 1.75 – 1.83 (m, 2H), 2.88 (dt, $J_1 = 1.96$ Hz, $J_2 = 6.39$ Hz, 4H), 7.34 – 7.41 (m, 8H), 7.72 (t, $J_1 = 1.96$ Hz, 2H).

3-nitrobenzaldehyde [161]:

^1H NMR (300 MHz, CDCl_3): δ 7.80 (m, 1H), 8.23 – 8.26 (m, 1H), 8.48 – 8.52 (m, 1H), 8.73 (t, $J = 1.8$ Hz, 1H), 10.13 (s, 1H).

(2E,6E)-2,6-bis(3-nitrobenzylidene)cyclohexanone [159]:

^1H NMR (300 MHz, CDCl_3): δ 1.83 – 1.91 (m, 2H), 2.98 (t, $J_1 = 6.5$ Hz, 4H), 7.61, (dd, $J_2 = 7.9$ Hz, $J_3 = 8.0$ Hz, 2H), 7.76, (d, $J_2 = 7.7$ Hz, 2H), 7.81 (s, 2H), 8.22 (d, $J_3 = 8.19$ Hz, 2H), 8.32, (s, 2H).

Acetophenone [156]:

^1H NMR (300 MHz, CDCl_3): δ 2.58 (s, 3H), 7.44 (dd, $J_1 = 7.63$ Hz, $J_2 = 8.24$ Hz, 2H), 7.51 (t, $J_1 = 7.63$ Hz, 1H), 7.93 (dd, $J_2 = 8.39$ Hz, $J_3 = 1.37$ Hz, 2H).

(E)-chalcone [162]:

^1H NMR (300 MHz, CDCl_3): δ 7.39 – 7.42 (m, 3H), 7.44 – 7.55 (m, 2 H), 7.53 (d, $J = 15.7$ Hz, 1H), 7.57 – 7.65 (m, 3H), 7.81 (d, $J = 15.7$ Hz, 1H), 8.00 – 8.03 (m, 2H).

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Publications Related to the Thesis

Journal Articles

- M. Rutar, N. Rozman, M. Pregelj, C. Bittencourt, R. Cerc Korošec, A. Sever Škapin, A. Mrzel, S. D. Škapin, P. Umek, 'Transformation of hydrogen titanate nanoribbons to TiO_2 nanoribbons and the influence of the transformation strategies on the photocatalytic performance', *Beilstein J. Nanotechnol.*, vol. 6, pp. 831–844, 2015.
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Biography

Melita Sluban was born on June 19, 1988 in Šempeter pri Gorici, Slovenia. She attended primary and secondary school in Tolmin. In 2007, she started her studies at the Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia. She finished her studies and defended her MSc thesis in August 2012 under the supervision of Assoc. Prof. Dr. Jernej Iskra and Prof. Dr. Marjan Jereb.

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