

TITANIA NANOSTRUCTURES BASED PHOTOCATALYTIC AND PHOTOELECTROCATALYTIC REACTORS

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FOTOKATALITSKI IN FOTOELEKTROKATALITSKI
REAKTORJI NA OSNOVI NANOSTRUKTUR
TITANOVEGA DIOKSIDA
Doktorska disertacija

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Abstract

Water is one of the most important natural resources on Earth. Despite its abundant resources, the water pollution is present due to ever-growing human population and accompanying industrial development. Even though there are many ecological actions targeted to preserve this precious natural resource, it is quite impossible to eliminate or reduce water pollution completely. This is why there will always be a need for various technologies for water purification either following industrial processes (wastewaters) or even for conditioning of drinking water. This may be done by conventional available treatment technologies; however they may be ineffective for removal of hazardous organic compounds. This is why new advanced oxidation processes (AOP) are needed to eliminate pollutants from wastewaters as well as from drinking water in order to improve the quality of our life. In view of this, my R&D work within my thesis was focused on the use of photoelectrocatalytic technology for degradation of hazardous organic pollutants. Within my thesis, I have designed, assembled and characterized photoelectrocatalytic reactors with an immobilized photocatalyst. The goal of my studies was to develop novel designs of photoelectrocatalytic reactors and to investigate the influence of reactor design and operational parameters on the efficiency of such systems.

The first part of my thesis was dedicated to the synthesis and characterization of active photocatalyst in the form of ordered TiO₂ nanotubes arrays that were obtained by the anodic oxidation process of various metallic titanium forms (coils, foil, mesh). The influence of the anodization parameters and annealing conditions on the nanotubes' morphology and their photocatalytic activity was investigated. It was found out that the most photocatalytically active TiO₂ nanotube arrays films (tested on caffeine degradation) were obtained after anodization of metallic titanium forms at 60 V for 6 hours and after subsequent annealing at 450 °C for 1 hour. The resulting polycrystalline TiO₂ nanotubes had length of app. 40 µm, grain size of app. 5 to 10 nm and anatase crystal structure.

The second part of my thesis was focused on design and characterization of two types of photoelectrocatalytic reactors, namely coil-type microreactor and foil-type reactor. The photoelectrocatalytic activity of microreactors was investigated by measuring the degradation of caffeine and phenol at different flow rates, UV light intensities, applied external electrical potentials and supporting electrolyte conductivities. Four different configurations of the photoanode and cathode were used. When an applied anodic bias potential of 4 V was used in the most efficient microreactor configuration, 1 mL of the 40 mg L⁻¹ caffeine was fully decomposed in 55 min. It was found out that the most influential parameters contributing to the microreactor efficiency are the position and surface area of cathode coils placed inside the microreactor adjacent to photocatalytically active anode coils. Cathode coils enable the photoelectrocatalytic process, which is far more efficient compared to only photocatalytic oxidation. The scaled-up version of the coil-type microreactor was used for the photocatalytic, electrocatalytic and photoelectrocatalytic degradation of phenol. The highest initial phenol concentration of app. 45.7 mg L⁻¹ was completely degraded at an applied potential of 16 V, a UV-light intensity of app. 2.8 mW cm⁻², and a flow rate of 50 µL min⁻¹. In my study, the mechanisms of photocatalysis and photoelectrocatalysis were proposed and validated with a three-dimensional mathematical model describing the governing processes occurring during the microreactor's operation. Afterwards, a larger photoelectrocatalytic device, made of perforated anodized titanium foils, was assembled. This reactor enabled degradation of organic compounds with larger flow rates as compared to the coil-type microreactor.

Povzetek

Voda je eden najpomembnejših naravnih virov na Zemlji. Čeprav je prisotna na našem planetu v izobilju, postaja onesnaženost vodnih virov eden glavnih ekoloških problemov. To je razlog, da bomo vedno potrebovali ustrezne tehnologije za čiščenje industrijskih in komunalnih odpadnih vod kot tudi za pripravo pitne vode. Izkazalo se je, da obstoječe tehnologije velikokrat niso učinkovite pri odstranjevanju nevarnih organskih snovi, zaradi česar je potreben tudi razvoj novih, t. i. naprednih oksidacijskih postopkov (AOP), ki so sposobni v celoti odstraniti nevarne organske spojine. V iskanju novih in/ali izboljšanih postopkov odstranjevanja organskih spojin iz vod sem se v okviru svojega doktorskega dela osredotočil na preiskave procesa fotoelektrokatalize in njegovo uporabo za razgradnjo organskih onesnažil v vodnih medijih. V okviru svojega doktorskega dela sem tako načrtoval, sestavil in meril učinkovitost fotoelektrokatalitičnih reaktorjev s trdno vezanim fotokatalizatorjem na osnovi nanocevk TiO_2 . Cilj mojih raziskav sta bila razvoj novih fotoelektrokatalitičnih reaktorjev in študij vpliva različnih izvedb reaktorjev in pogojev obratovanja na učinkovitost takih čistilnih naprav.

V prvem delu doktorske naloge sem se osredotočil na sintezo in karakterizacijo aktivnega fotokatalizatorja v obliki nanocevk TiO_2 , ki sem jih pridobil z anodno oksidacijo različnih oblik kovinskega titana (navitje, folija, mreža). Preiskal sem vpliv parametrov anodne oksidacije in pogojev žganja na morfologijo nanocevk ter na njihovo fotokatalitično aktivnost. Ugotovil sem, da so imele najboljšo fotokatalitično aktivnost TiO_2 nanocevk, ki so bile sintetizirane z anodno oksidacijo 6 ur pri napetosti 60 V in ki so bile naknadno termično obdelane 1 uro pri 450 °C. Sintetizirane polikristalinične TiO_2 nanocevk so bile dolge približno 40 μm z velikostjo posameznih zrn v razponu od 5 do 10 nm. Rentgenska praškovna difrakcija je potrdila, da so imele nanocevk TiO_2 anatazno kristalno strukturo.

V drugem delu doktorskega dela sem se posvetil načrtovanju in karakterizaciji dveh izvedb fotoelektrokatalitičnih reaktorjev: mikroreaktorja z navitji ter reaktorja s titanovimi folijami. Fotoelektrokatalitično aktivnost mikroreaktorjev sem določeval z razgradnjo kofeina in fenola pri različnih pretokih in prevodnostih raztopine, intenziteti UV svetlobe ter priključeni električni napetosti. V mikroreaktorju z eno aktivno fotoanodo sem uporabil štiri različne postavitve anode in katode. V najbolj fotokatalitično učinkoviti izvedbi mikroreaktorja je bil 1 ml 40 mg L^{-1} kofeina po priključitvi pozitivne napetosti na anodo popolnoma razgrajen v 55 minutah. Ugotovil sem, da na fotokatalitično aktivnost mikroreaktorja najbolj odločujoče vplivata položaj in površina katodnih navitij. Večjo izvedbo mikroreaktorja z daljšimi aktivnimi navitji sem uporabil za fotokatalitično, elektrokatalitično in fotoelektrokatalitično razgradnjo fenola. Največja začetna koncentracija raztopine fenola (približno 45,7 mg L^{-1}) je bila v celoti razgrajena pri napetosti 16 V, intenziteti UV svetlobe 2,8 mW cm^{-2} in pri pretoku 50 $\mu\text{L min}^{-1}$. V raziskavi sem predlagal mehanizem fotokatalitične in fotoelektrokatalitične razgradnje fenola in ga preveril s tridimenzionalnim matematičnim modelom, ki opisuje procese, ki se odvijajo med delovanjem mikroreaktorja. Izdelal sem tudi večji fotoelektrokatalitični reaktor, ki je sestavljen iz luknjičastih titanovih folij. Ta reaktor omogoča razgradnjo organskih snovi pri večjih pretokih tekočega medija, kot so možni v mikroreaktorjih z navitji.

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Abbreviations

AOP	... advanced oxidation process
BDD	... boron-doped diamond
DSSC	... dye-sensitized solar cell
UV	... ultra-violet light
EG	... ethylene glycol
QY	... quantum yield (quantum efficiency)
RDPR	... rotating disk photocatalytic reactor
TFFBR	... thin film fixed bed reactor
DSSR	... double skin sheet reactor
PTR	... parabolic trough reactor
CVD	... chemical vapour deposition
COD	... chemical oxygen demand
VIS	... visible light
HPLC	... high-performance liquid chromatography
SEM	... scanning electron microscope
EDXS	... energy-dispersive X-ray spectroscopy
XRD	... X-ray diffraction
DC	... direct current
LED	... light-emitting diode
IR	... infrared light
Ph	... phenol
Bq	... benzoquinone

Symbols

h	... Planck's (or Planck) constant
ν	... frequency of incident light
e^-	... electron
h^+	... hole
R	... organic compound
d	... TiO ₂ nanotubes film thickness
f	... growth factor of TiO ₂ nanotubes
U	... anodization voltage
r	... reaction rate (molecules converted per second)
φ	... efficient photonic flux absorbed by the photocatalyst
σ	... electrolyte conductivity
c	... molar concentration
m	... mass
V	... volume
γ	... mass concentration
$R1$	... resistor 1
$R2$	... resistor 2
R_i	... initial reaction rates
ζ	... photonic efficiency
q_V	... volumetric flow rate
c_i	... species' concentrations
c_{Ph}	... phenol concentration
c_{Bq}	... benzoquinone concentration
c_{O_2}	... oxygen concentration
$c_{OH\cdot}$	... hydroxyl radical concentration
t	... time
v	... linear velocity
x	... axial dimension of a coil-type microreactor
r	... radial dimension of a coil-type microreactor
D_i	... diffusion coefficients
D_{Ph}	... diffusion coefficient of phenol
D_{Bq}	... diffusion coefficient of benzoquinone
D_{O_2}	... diffusion coefficient of oxygen
R_1	... inner channel wall of a coil-type microreactor
R_2	... non-catalytic outer wall of a coil-type microreactor
K_i	... absorption coefficients
K_{Ph}	... absorption coefficient of phenol
K_{Bq}	... absorption coefficient of benzoquinone
K_{O_2}	... absorption coefficient of oxygen
k_{i-i}	... kinetic constants

k_{Ph-Bq}	... kinetic constant for phenol conversion to benzoquinone
k_{Ph-deg}	... kinetic constant for phenol degradation
k_{Bq-deg}	... kinetic constant for benzoquinone degradation
$k_{elect.}$	... kinetic constant for electrocatalysis
$k_{red.}$	... kinetic constant for reduction of oxygen
r_{i-i}	... reaction rates
r_{Ph-Bq}	... reaction rate for phenol conversion to benzoquinone
r_{Ph-deg}	... reaction rate for phenol degradation
r_{Bq-deg}	... reaction rate for benzoquinone degradation
r_{O_2}	... reaction rate for oxygen
$r_{elect.}$	... reaction rate for electrocatalytic process
I_{UV}^{nl1}	... UV light intensity in photocatalysis
I_{UV}^{nl2}	... UV light intensity in photoelectrocatalysis
I_0	... constant for electrical current at zero UV light intensity
$I_{current}$	... electrical current
nl_1	... power law coefficient of light intensity for photocatalysis
nl_2	... power law coefficient of light intensity for photoelectrocatalysis
N_e	... power law constant
U	... electrical potential applied to the electrode in a coil-type microreactor

Chapter 1

Introduction

1.1 Photocatalytic Processes

1.1.1 Photocatalysis

Photocatalysis is an acceleration of a chemical reaction in the presence of a photocatalyst. It is an advanced oxidation process (AOP) in which organic compounds can be degraded during photocatalytic reaction down to their basic constituents, such as carbon dioxide and water (Figure 1). The mineralization products of complex molecules, such as dyes, are also innocuous inorganic ions (Cl^- , SO_4^{2-} , NO_3^-). Oxidation of organic contaminants occurs through reactions with highly reactive species (primarily hydroxyl radicals $\text{OH}^\bullet$), which are generated by illumination of a photocatalyst [1,2].

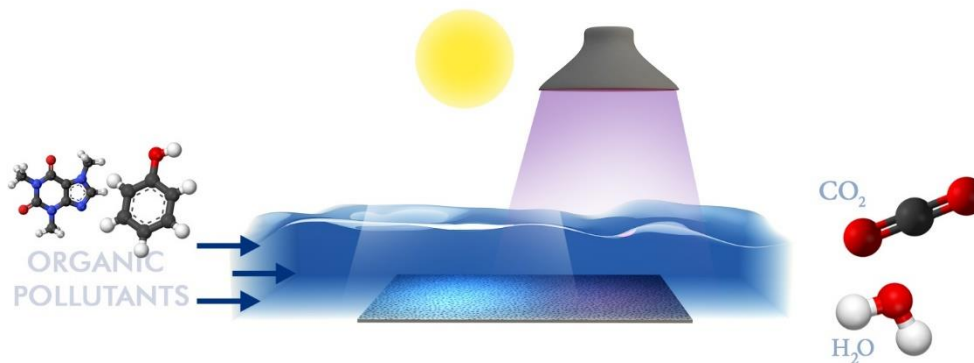


Figure 1: The photocatalytic reaction takes place at the surface of a photocatalyst where organic compounds are degraded to carbon dioxide and water.

A photocatalyst is a semiconducting material which is activated by illumination with light of sufficient energy. The most studied photocatalyst is titanium dioxide (TiO_2) due to its high reactivity, inertness, biocompatibility, chemical stability, low cost, and extended use without substantial loss of photocatalytic activity [3]. Therefore, TiO_2 will be used to describe the mechanism of heterogeneous photocatalysis which is a five-step process [4]:

1. Mass transfer of reactants to the photocatalyst surface
2. Adsorption of reactants on the photocatalyst surface
3. Photocatalytic reaction in the adsorbed state
4. Product desorption
5. Mass transfer of the products to the bulk fluid

All the steps except step 3 are the same as in heterogeneous catalysis where the solid catalyst is thermally activated. In the photocatalytic reaction (step 3) solid photocatalyst is first activated by the absorption of photons of energy greater or equal to its band gap ($h\nu \geq E_g$). Anatase TiO_2 has to be illuminated with light of wavelength of app. 390 nm or lower which corresponds to its band gap energy of 3.2 eV. UV-light illumination excites the electrons in the TiO_2 semiconductor, moving them from the valence to the conduction band, which generates electron-hole pairs (Figure 2) [5,6].



The electrons and holes are highly charged, and if they do not recombine, they initiate reduction and oxidation reactions and degrade organic compounds.

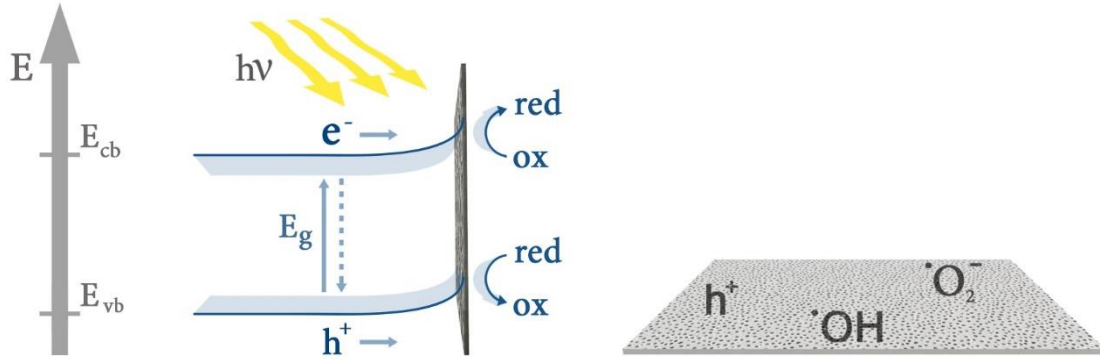
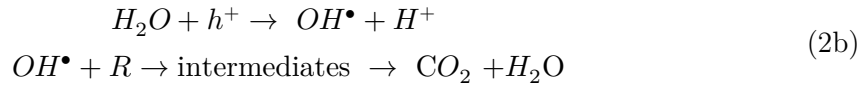
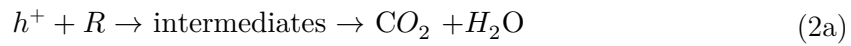
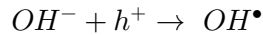
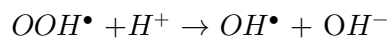
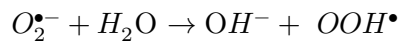


Figure 2: Schematic of semiconductor excitation by band gap illumination leading to the generation of electron-hole pairs which initiate reduction and oxidation reactions.

Holes can directly oxidize the organic compounds or react with water molecules to produce hydroxyl radicals according to the reactions 2a and 2b. Both reactions may proceed simultaneously: which mechanism dominates depends on the chemical and adsorption properties of the pollutant [7,8].



On the other hand the generated electrons react with dissolved oxygen and in the end facilitate the formation of hydroxyl radicals [7,8]. Dissolved oxygen, therefore, plays an important role in preventing electron-hole recombination, which reduces the catalytic capability of the catalyst [5].



One dissolved O_2 molecule reacts with one electron, which allows for the existence of one hole. In this way, one or two $\text{OH}^\bullet$ can be produced [5,8].

1.1.2 Photoelectrocatalysis and electrocatalysis

Electron-hole recombination is closely related to intrinsic (electronic) properties of a photocatalytic material. The most efficient approach for its reduction is to attach the photocatalyst to an electrically conductive support and connect it to external electric potential. In this case, the photocatalytic and electrocatalytic processes are combined into the photoelectrocatalytic process in which TiO_2 anode is paired with a cathodic material inside the photoelectrocatalytic system (Figure 3a) [5,9-11].

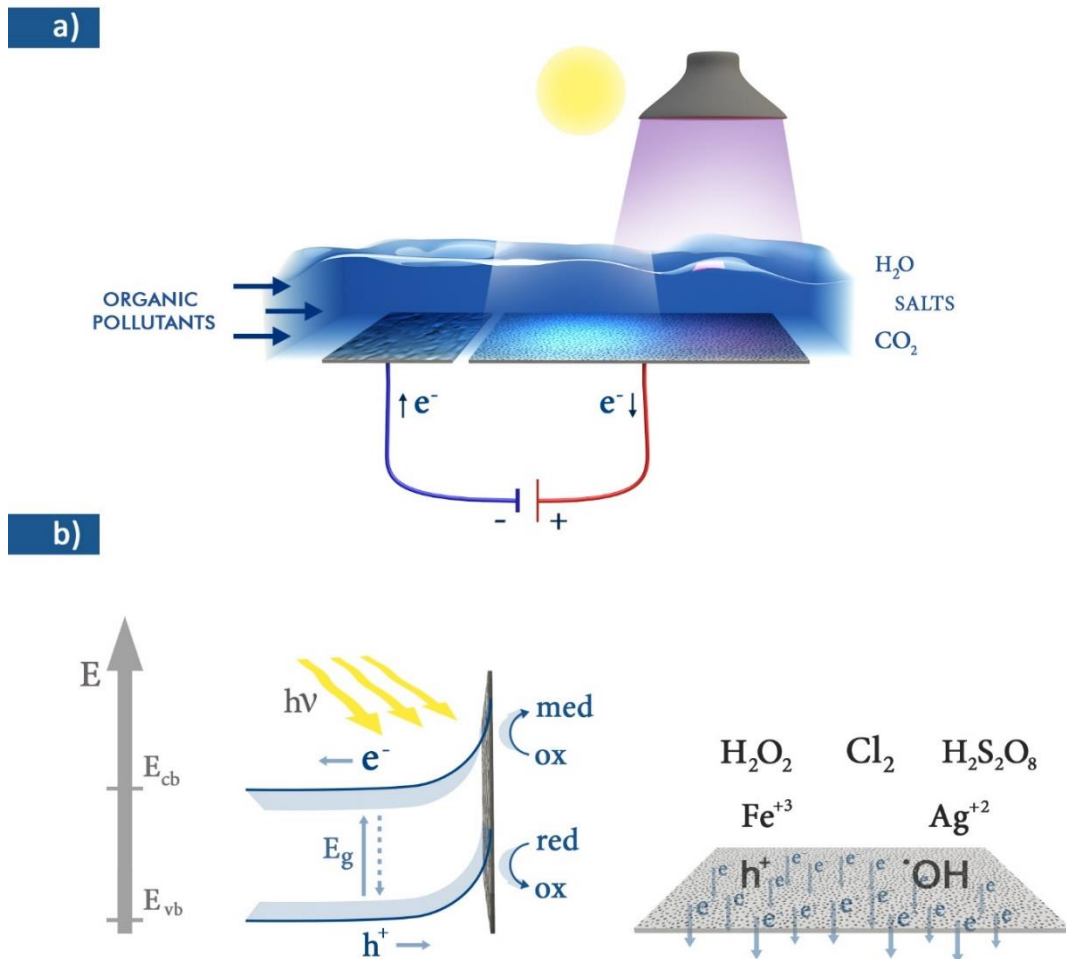
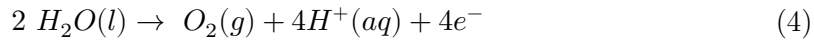


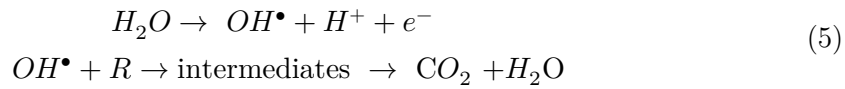
Figure 3: Schematic presentation of the principle of the photoelectrocatalytic degradation of organic pollutants. a) Photocatalytically active anode is connected to the positive electric potential while the cathodic material is connected to the negative one. b) Electron-hole pairs are formed at the anode from where electrons are forwarded to the cathode and holes degrade contaminants at the anode surface with the help of additional radicals generated by the electrochemical oxidation of different ions.

The electrocatalytic process reduces recombination of electron-hole pairs in two ways as we can separate the electrons and the holes by connecting the photocatalyst to the positive or negative side of the external bias potential. In the former case, the photogenerated electrons are forwarded to the cathode, and the holes degrade the contaminants at the contact of the electrolyte and the TiO_2 anode. When the photocatalyst is connected to a negative bias potential, the reduction by the electrons plays a crucial role at the semiconductor–electrolyte interface. In either case, with the application of an electrical potential, further considerations have to be taken into account (Figure 3b). The

photoelectrocatalytic process only works when the treated fluid is electrically conductive which results in the formation of additional radicals that are generated at the anode surface by the electrochemical oxidation of different ions. These oxidants can oxidize organic compounds in bulk, while direct oxidation only takes place at the anode surface after the adsorption of pollutants. This is also the case of $\text{OH}^\bullet$ generated in the photocatalytic process since $\text{OH}^\bullet$ diffusion distance is in the range of a few nanometers. The reason is in its short lifetime in the nanosecond range and its high reactivity. On the other hand, the radicals, including $\text{OH}^\bullet$, generated in the electrochemical process or even with photolysis of different anions also react in the bulk of a solution. Another phenomenon taking place in the electrocatalytic process is water splitting where water is split into O_2 and H_2 (reaction 4) if high enough electric potential is applied [5,9,10,12-17].



Beside the electrochemical oxidation of ions, electrocatalysis is also able to generate hydroxyl radicals via the oxidation of water on the anode surface (Figure 4) [18].



The four-electron oxidation to dioxygen mostly occurs well below the potential required for the one-electron oxidation of water to $\text{OH}^\bullet$ (+2.74 V at pH=0). Therefore, hydroxyl radicals are only formed when an electrode with high enough overpotential for oxygen evolution is selected. In other case, oxygen production pathway predominates which is the case of stoichiometric TiO_2 . At potentials where $\text{OH}^\bullet$ does not yet form, a direct electron transfer from the contaminant to the anode can take part. This mechanism of direct oxidation (reaction 6) is important in case of degradation of compounds that are unreactive towards $\text{OH}^\bullet$ such as fluorinated organics [18-21].

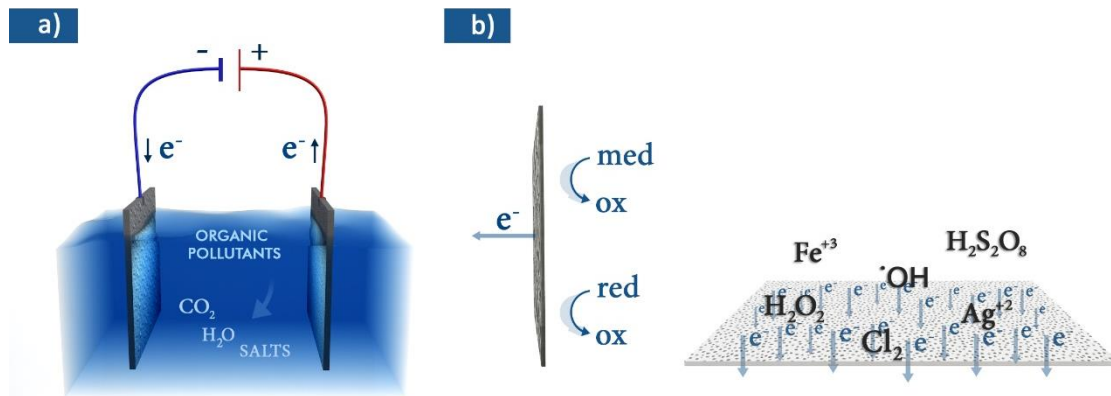


Figure 4: Schematic presentation of the principle of the electrocatalytic degradation of organic pollutants.

The most effective electrodes used in the electrochemical advanced oxidation process are doped SnO_2 [22], PbO_2 [23], boron-doped diamond (BDD) [24,25], and sub-stoichiometric and doped- TiO_2 [21]. The TiO_2 used as electrocatalyst differs from the one used in photocatalysis as the electrical conductivity is of greater importance in the former

case. Stoichiometric TiO_2 has a very low electrical conductivity that can be significantly changed by creating oxygen deficiency in the lattice structure. These are most commonly formed with annealing in reductive atmospheres or by doping with group five elements [18].

1.2 Titanium Dioxide: Structure and Properties

TiO_2 is an oxide semiconductor that is not only used for photocatalytic water and air treatment [26,27] but also in many other applications, ranging from dye-sensitized solar cells (DSSCs) [28], water splitting [29], sensors [30], supercapacitors [31] and lithium-ion batteries [32]. Since the photocatalytic reaction takes place on the surface, photocatalytic applications require a nanocrystalline photocatalyst. Nanostructured semiconductors have far larger surface areas than the same masses of larger-scale (bulk) materials. Thus, they have a far greater number of active surface sites that possess photocatalytic activity [33]. Depending on the desired properties, TiO_2 can be used in various morphological forms, such as nanoparticles [34], nanotubes [35,36], nanorods [37], nanowires [38,39], nanoleaves [40], mesosponge layers [41] or as various combinations of these [42,43]. There are several methods for producing nanostructured TiO_2 , among which anodic oxidation of titanium is the most suitable for growing a rigidly attached TiO_2 nanotube arrays. These have attracted a wide interest and can be used as an efficient photocatalyst inside a photo(electro)catalytic reactor with the immobilized photocatalyst.

Titanium dioxide is an active photocatalyst when used in one of its crystallized forms. The three major TiO_2 polymorphs are rutile, anatase and brookite (Figure 5). All three forms of titania have six titanium atoms in their unit cell. Rutile and anatase structures are tetragonal with the main difference in the elongated anatase unit cell. The atoms in the rutile form occupy the least space, which makes rutile the most stable at all temperatures [44]. In the case of nanosized titania, the rutile is thermodynamically the most stable crystallographic modification at temperatures higher than 600 °C [45].

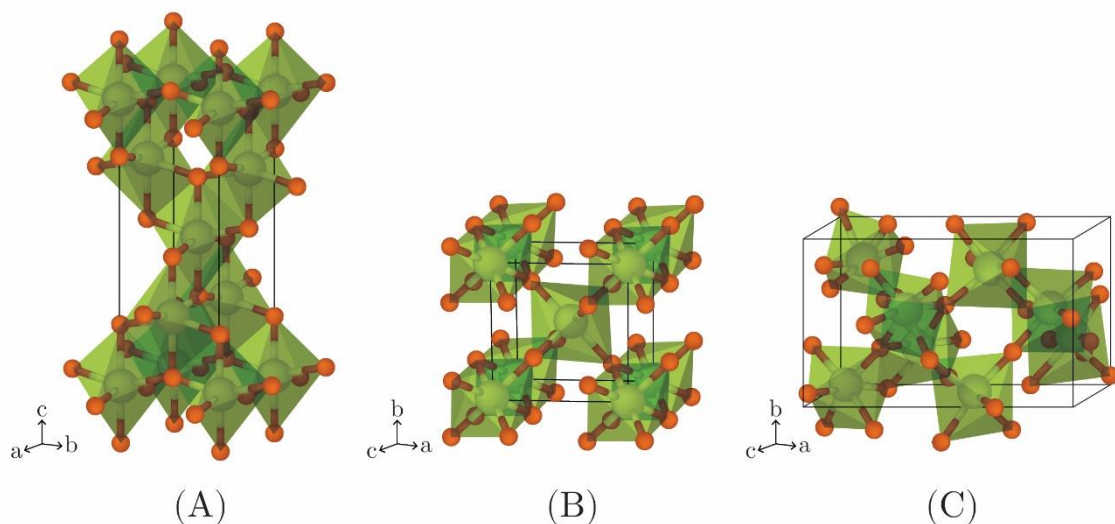


Figure 5: The structure of (A) anatase, (B) rutile and (C) brookite. White and red spheres represent titanium and oxygen, respectively [46].

Chemical composition and crystal structure are only two parameters influencing the photocatalytic activity of TiO_2 . The other important parameters characterizing TiO_2

nanostructures and influencing their photocatalytic activity are crystallinity, size, and the presence of dopants and impurities.

The exact crystallization temperature of TiO_2 nanotubes depends strongly on the process used to synthesize the nanotubes as it influences the concentration of the lattice and surface defects and the particle size. Crystallization of TiO_2 nanotubes grown by anodic oxidation process starts at around 300 °C where the amorphous phase is transformed into the anatase phase which has proven to be the most active photocatalyst [47]. However, it is possible to directly grow partially crystalized titania nanotubes but even in this case thermal annealing can significantly improve their crystallinity and therefore their photocatalytic activity [48].

As explained before, the particle size determines the transformation temperature from one TiO_2 crystal structure to another. When the particle size is sufficiently low, surface free energy and surface stress determine the particle's phase. It was determined that anatase is the most stable for particles below app. 11 nm, whereas rutile is most stable at sizes greater than app. 35 nm. Brookite is the most stable in the range between app. 11 and 35 nm [45,49-51]. Smaller particles exhibit better photoactivity since there are more available active sites on their surface. However, an optimal particle size exists for maximum photocatalytic activity as the smaller particle size also means more defects and lower utilization of photons. The most suitable particle size is related to the average distance between electron and hole in a material, which depends on its dielectric constant. In TiO_2 anatase, it is app. 3-4 nm, while TiO_2 particles between app. 5 and 10 nm in diameter exhibit the best photoactivity [50,52,53].

Electrical properties of TiO_2 depend strongly on its chemical composition. Amorphous TiO_2 has poor electrical properties as the amorphous phase comprises of impurities, dangling bonds and micro-voids which act as recombination centers [54]. Recombination of electrons and holes also greatly influences the photocatalytic activity of crystalline TiO_2 forms and has to be minimized in order to maximize the photoefficiency. It can be suppressed by trapping the photogenerated electrons or the photogenerated holes [55]. By trapping, the reductive power of electrons and oxidative power of holes are slightly lowered, whereas recombination can be delayed as much as it is needed to allow the charge transfer of electrons to molecular oxygen [56,57]. Trap states are energy states in the band gap of nanostructured semiconductors and can have undesired effect if they are so-called "deep trap states" [58]. The presence of such states far below the conduction band is detrimental since they slow the electron transport and act as recombination centers. On the other hand, shallow trap states 0.2-0.8 eV below the conduction or above the valence band enhance electrical properties of TiO_2 since trapped charge carriers can be easily released to the conduction or valence band by thermal excitation [59].

The band gap energy of undoped anatase is 3.2 eV, whereas rutile has a band gap of 3.0 eV. The band gap in TiO_2 is defined by Ti 3d states and O 2p energy levels. The former are the lowest empty energy levels and thus represent the conduction band edge, while the latter define the valence band. TiO_2 anatase has an indirect band gap, while TiO_2 rutile a direct band gap (Figure 6). Indirect band gap of anatase exhibits lower recombination rate of photogenerated electrons and holes since the direct transition of electrons from conduction to the valence band of anatase is impossible. This is one of the reasons for its higher photocatalytic activity compared to rutile. Besides, anatase has a larger band-gap which means slower recombination of photogenerated electrons and holes. It also possesses localized states within its band gap, where trapping of the electrons occurs leading to an increase of their lifetime. Last but not least, the surface of anatase is usually highly hydroxylated which means that oxygen and water molecules can adsorb on its surface and initiate the photocatalytic reaction [45,49-51,59-61].

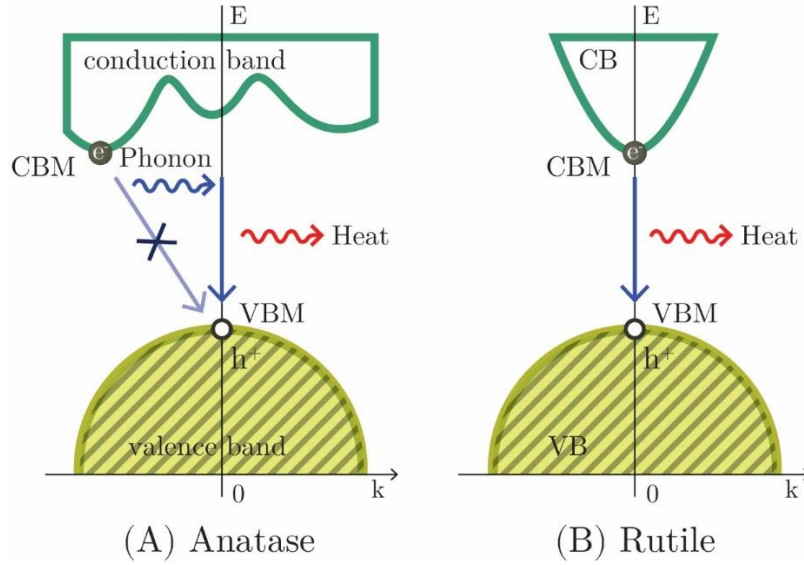


Figure 6: Comparison of the recombination of charge carriers in indirect band gap anatase (a) and direct band gap rutile (b) TiO_2 [60].

TiO_2 band gap values are important also due to the fact that they determine the light harvesting ability of the material. Therefore, anatase has to be illuminated with light of wavelength 387 nm or less for the excitation of its valence-band electrons meaning it is photocatalytically active when illuminated with UV-A light [62]. Since UV light represents only app. 5% of the entire solar spectrum, modifying the band structure of titania can be used to extend its wavelength range response to the visible region of electromagnetic spectrum [63]. Upon excitation, electron and hole migrate to the TiO_2 surface where they initiate reduction and oxidation reactions. TiO_2 donates electrons to reduce an electron acceptor (usually molecular oxygen), while a donor species combines with a surface hole and gets oxidized. The charge transfer to acceptor and donor species is possible if they adsorb on the TiO_2 surface. If the charge transfer to adsorbed species does not occur, the electron and hole recombine. Recombination of electrons and holes in nanosized TiO_2 usually occurs on its surface, although volume recombination is also possible. Decreasing the particle size reduces the volume recombination and increases surface recombination [50,52,53].

TiO_2 is an n-type semiconductor which means that its electron density is higher than the hole density. The reason for this is the tendency of TiO_2 for oxygen deficiency which in practice means the formation of donor-type defects such as oxygen vacancies or titanium interstitials [64]. Defects can be generated in the TiO_2 structure with annealing in the reductive atmosphere (Ar , H_2) due to a partial oxygen loss leading to a reduction of Ti^{4+} to Ti^{3+} and vacancy generation [65]. TiO_2 is also sensitive to self-doping during annealing in oxidizing conditions. The atmosphere during heat treatment is of great importance regarding the conductivity of the nanotubes as Ti^{3+} sites are responsible for their electronic conductivity [66]. The resistivity of undoped anatase is in the range of 10^4 - $10^7 \Omega \text{ cm}$. The resistivity of thermally reduced anatase is in the range of $10^{-1} \Omega \text{ cm}$ [59,67]. Electrical conductivity can be changed by introducing suitable intermediate states in the band gap of TiO_2 which narrow it and allow absorption of photons of lower energy.

Another aspect influencing the photocatalytic activity of the titanium dioxide phases is the type of crystalline planes exposed. The crystalline nanotubes produced by any synthetic procedure followed by possible post-reaction annealing are mostly composed of small polycrystalline crystal grains with exposed surface facets with different oxidative power [68]. In general, crystals are grown in the direction that minimizes overall surface free

energy. However, crystallites in the polycrystalline nanotube walls are mostly randomly oriented [69]. Among the planes of anatase, surface free energy of the anatase [70] lattice plane has been reported to be the smallest. Therefore, a truncated octahedral bipyramid (Figure 7b) exposing eight $\{101\}$ facets as well as two $\{001\}$ facets is the most thermodynamically stable shape of anatase crystallites [71,72]. Although oxidation of organic compounds by holes and reduction of molecular oxygen by electrons are easily promoted on $\{101\}$ surface of anatase, less abundant $\{100\}$ and $\{001\}$ facets exhibit considerably higher photocatalytic activity [73].

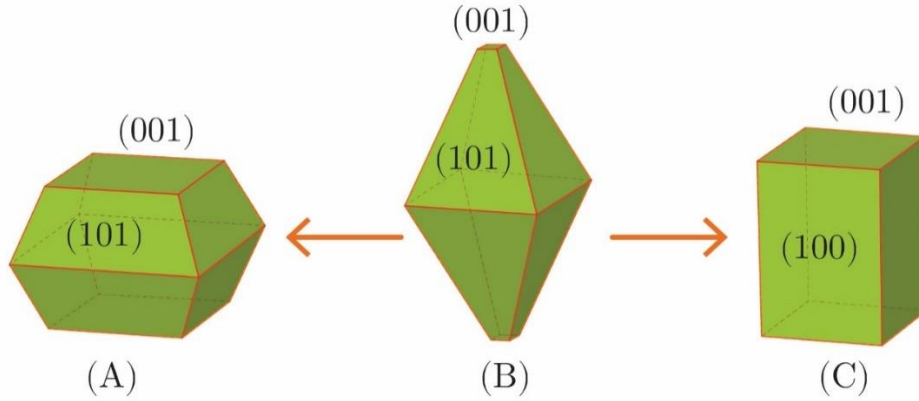


Figure 7: Scheme of anatase TiO_2 crystal facets: (A) a truncated octahedral shape, (B) the most common truncated octahedral bipyramid and (C) cuboid shape [73].

Like anatase, rutile also has its main crystal facets. The $\{110\}$ family has much lower surface energy than other facets and is, therefore, the most important for practical polycrystalline materials [74]. This is the crystal facet with most reduction sites on the rutile particles, whereas oxidation sites are mainly on the $\{011\}$ facets [75]. Rutile particles exhibit effective separation of oxidation and reduction sites due to the difference in the surface energy levels of the conduction and valence bands for $\{110\}$ facets and $\{011\}$ crystal facets. This separation of electrons and holes enables highly efficient photocatalytic reactions that require band bending in TiO_2 . Such reaction is water oxidation. The band bending in case of oxidation of reactive compounds like alcohols is not necessary [76].

1.3 Synthesis of TiO_2 by Anodic Oxidation

Electrochemical anodization of titanium enables synthesis of a well-ordered and vertically-aligned TiO_2 -nanotube arrays on the titanium substrate. It is a relatively simple and cheap process that provides a high degree of control over the surface morphology and other parameters of the tubular TiO_2 array. In the self-organized growth, each individual TiO_2 nanotube is perpendicular to the titanium surface, and the TiO_2 array is tightly bound to the titanium substrate. Due to this strong adhesion high photocatalytic activity of the TiO_2 is obtained due to improved electron transport and reduced charge recombination [77-81].

Despite the high photocatalytic activity of the TiO_2 nanotube arrays, there are different methods for their modification. These methods are primarily focused on increasing the TiO_2 surface area, reducing the rate of the recombination of electrons and holes or extending the wavelength range response of TiO_2 to the visible region. Two of the most investigated methods include modification with noble metals [82-84] and modification with transition metal [85,86] which both enable TiO_2 to be active in the energy range of visible light and

to lower the rate of recombination of electrons and holes [87]. One way to obtain doped TiO_2 nanotube arrays is to anodize noble metal-containing titanium alloys [88]. However, in some cases, the photocatalytic activity of TiO_2 modified with noble metals is reduced because the noble metals become recombination centers if the accumulated negative charges are not consumed or further transferred out of the metal particles [89]. To solve this problem, the external electric field has to be applied, which is beneficial also in the case of pure TiO_2 since the photoelectrochemical process is more efficient than the single application of electrochemical oxidation or photocatalytic degradation [90]. The fact that TiO_2 nanotubes are grown inside the electrically conductive metal titanium makes the anodic oxidation process even more preferable when growing TiO_2 nanotubes for photoelectrocatalytic applications. Titanium support is ideal for connecting the external electric potential to the TiO_2 anode.

1.3.1 Formation and growth of titanium dioxide during anodic oxidation

The TiO_2 array is grown when either a constant current or a constant potential is applied across two electrodes immersed in an electrolytic solution in an electrochemical cell (Figure 8). To form TiO_2 , the anode has to be any form of metal titanium (e.g. foil, wire, mesh, rod, etc.) as oxidation only occurs at the anode. The cathode is usually platinum but also other inert conductive materials such as stainless steel can also be used [91].

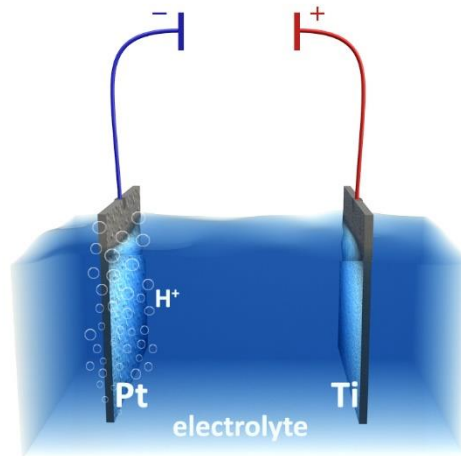


Figure 8: Schematic set-up for anodic oxidation.

TiO_2 nanotubes morphology depends strongly on the anodization conditions. The most important anodization parameters are applied potential, time of anodization and the composition and the temperature of the electrolyte. If there are no fluoride ions present in the electrolyte, the resulting solid oxide layer is compact instead of nanotubular (Figure 9) [91].

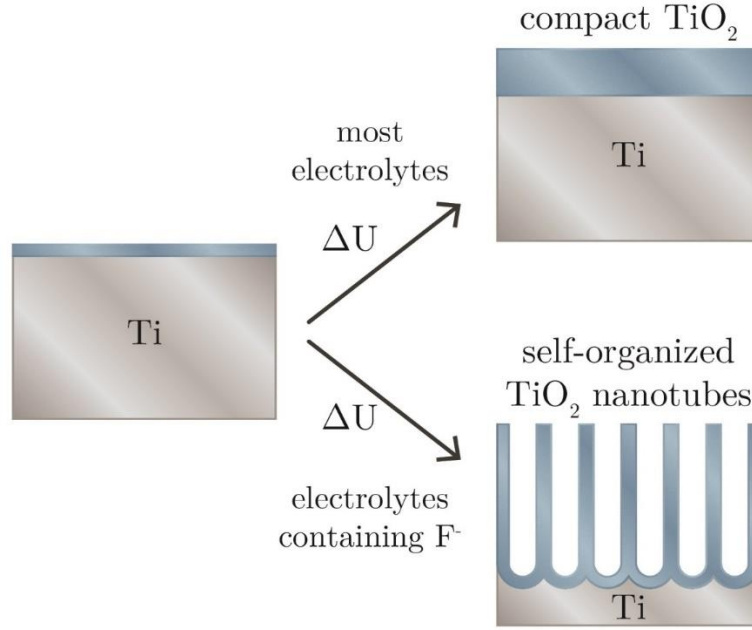


Figure 9: Depending on the anodization conditions (mainly electrolyte composition), the resulting oxide layer can be either compact or nanotubular [91].

Up to now, three generations of fluoride containing electrolytes have been employed for anodization of titanium to fabricate TiO_2 nanotube arrays. The first generation of the electrolyte is based on the dilute hydrofluoric acid (HF) aqueous solution. Because of the high rate of chemical dissolution of TiO_2 by fluorine ions, the thickness of TiO_2 nanotube arrays is limited to several hundred nanometers [92]. The second generation of electrolyte overcame this problem by controlling the pH gradient within the growing nanotube [93]. The third generation of electrolyte consists of fluoride and a viscous organic electrolyte such as ethylene glycol (EG) or glycerol. The most common are NH_4F -water-EG electrolytes that enable the production of ultrahigh aspect ratio TiO_2 nanotubes (Figure 10) [94].

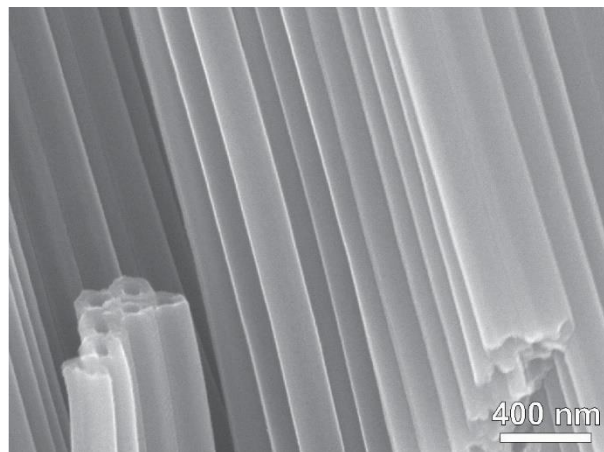


Figure 10: SEM image of ordered TiO_2 nanotubes grown by anodic oxidation showing large aspect ratio [95].

Anodization of titanium is usually carried out by applying a constant voltage. The growth of the TiO_2 compact or nanotubular layer is a result of three simultaneous processes schematically presented in Figure 11 [91].

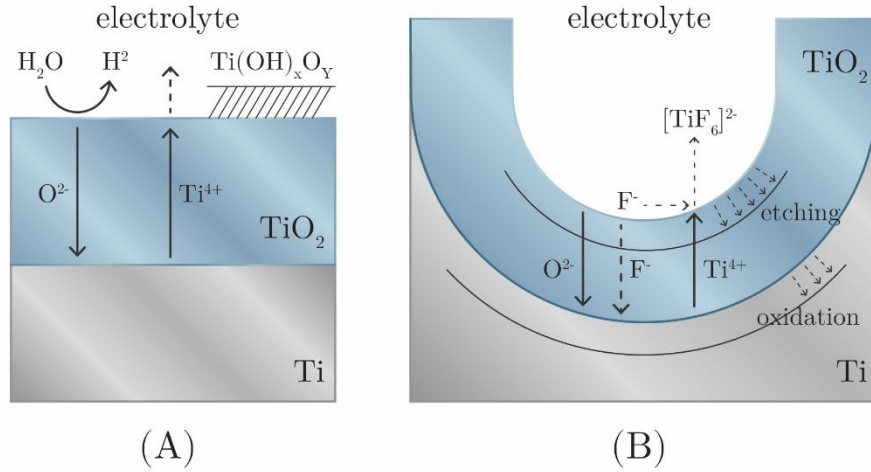
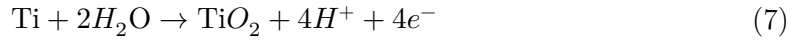


Figure 11: Schematic representation of titanium anodization in electrolyte without fluoride (A) and fluoride containing electrolyte (B) [91].

Oxidation of titanium to TiO_2



competes with chemical dissolution of the TiO_2 according to reaction (8)



Third reaction is complexation of titanium cations at the oxide/electrolyte interface



In reaction (7) titanium reacts with O^{2-} from H_2O to form an oxide layer. Oxide grows to a finite thickness due to applied voltage which aids the transport of O^{2-} and Ti^{4+} ions through the growing oxide. If titanium cations are not consumed in a complexation reaction (9), a hydroxide layer forms in most electrolytes (Figure 11a). On the other hand, the presence of fluoride ions changes the oxide formation process due to two effects of the fluoride ion. Firstly, it forms water-soluble $[\text{TiF}_6]^{2-}$ complexes according to reaction (8) and secondly it can be transported through the growing oxide by the applied electrical field. As shown in Figure 11a it competes with O^{2-} transport, etches formed TiO_2 and prevents hydroxide formation by solvating Ti^{4+} to $[\text{TiF}_6]^{2-}$ (9) before the cations react to precipitate hydroxide layer [91].

The growth of TiO_2 can be monitored by recording the current time characteristics, which is different in case of fluoride containing electrolytes and electrolytes without fluoride. In the latter case the anodic current drops exponentially with time as shown with continuous line in Figure 12 due to the lowering of the driving force with increasing film thickness. In case of electrolyte containing fluorides three phases in the current time behavior can be observed (dashed line in Figure 12). After an initial exponential decay (phase I), the current increases (phase II) and afterwards reaches a quasi-steady state (phase III) [91]. The final film thickness is given by

$$d = f \cdot U \quad (10)$$

where f is a growth factor of the oxide [59].

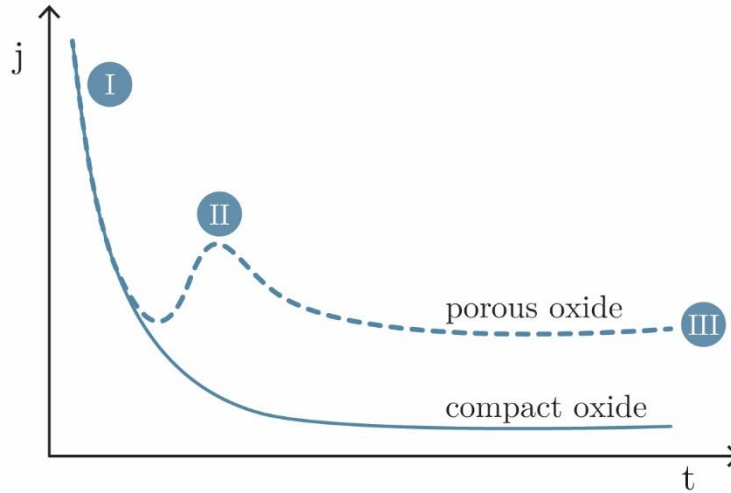


Figure 12: Current-time (j - t) characteristics for constant voltage anodic oxidation in the absence (—) and presence (---) of fluoride ions in the electrolyte [91].

As schematically shown in Figure 13 the three phases in the pore formation process correspond to barrier oxide formation (phase I), random growth of the pores (phase II) and establishment of self-ordering (phase III). In the latter phase pores equally share the available current [91].

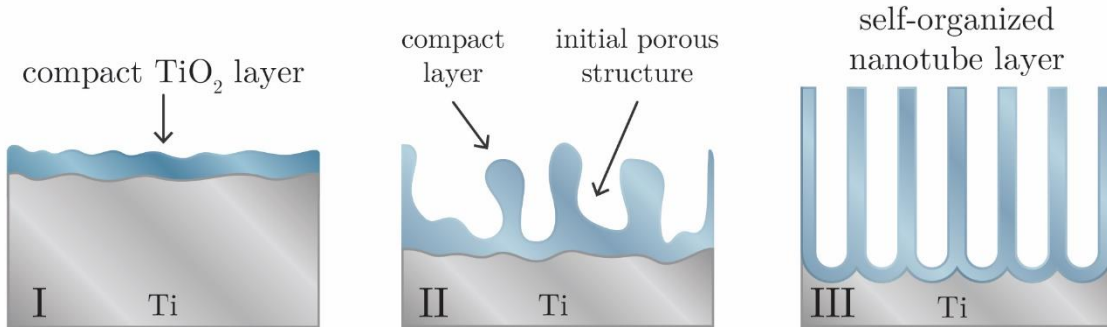


Figure 13: Evolution of TiO_2 nanotubes is a result of three different stages in the pore formation process [91].

The resulting TiO_2 arrays obtained by anodic oxidation are amorphous and have to be annealed to transform the amorphous phase into anatase TiO_2 . Although anatase shows better photocatalytic activity than rutile, it is very unlikely to obtain only anatase after annealing since even at relatively low annealing temperatures (app. 400 °C) the phase transformation from anatase to rutile occurs at the nanotube/titanium interface [80,96]. The phase composition of annealed titania nanotubes produced by anodic oxidation process supports the theory of anatase being more stable than rutile at small crystallite sizes. After heat-treatment at 450 °C, the nanotubes wall is composed of anatase, while the barrier layer is composed of rutile. The reason is that the nanotube wall thickness usually limits the initial anatase crystals size and suppresses their transformation to rutile. Since the barrier layer expands over the entire surface of the substrate, rutile transformation takes place already at 450 °C. The rutile phase formed has a preferred crystallographic

orientation that is influenced by titanium substrate. The thickness of the barrier layer increases with increasing annealing time [97].

1.3.2 Anodization parameters influencing the photocatalytic activity

There are many parameters that influence the photocatalytic activity of TiO_2 . However the most important for photocatalytic applications is the morphology of TiO_2 , i.e. the size of TiO_2 particles. Surface activity and reactivity are size-dependent properties because the specific surface area and surface-to-volume ratio increase as a size of material decreases.

The morphology of nanotubes grown by anodic oxidation process can be precisely controlled by changing the experimental conditions. Anodization voltage influences the nanotubes' growth rate, crystallinity, and length. The length increases with anodization time and also depends on the type of electrolyte we use. In order to grow the longer nanotubes, a nonaqueous electrolyte has to be chosen [48,94,98]. Longer tubes increase the photocatalytic degradation rate of organics up to a certain limit influenced by the penetration depth of light. An increase in anodizing voltage or an increase of water concentration increases the outer and inner nanotube pore diameter. However, the nanotube diameter and wall thickness are independent of anodization time, although with prolonged time the upper part of the nanotubes possesses thinner wall than their bottom part [63,91,99,100]. The surface roughness of the tube walls influences the electron diffusion length and therefore the photocatalytic activity. Rough tube walls formed in aqueous electrolytes lead to electron diffusion length of 1-2 μm , while electron diffusion length in tubes grown in organic electrolytes is in the range of 25 μm [59]. The latter number is much higher than for comparable nanoparticle layers because of lower surface recombination in the case of nanotubes. It has to be noted that the hole diffusion length in TiO_2 is much shorter (app. 10 nm) which means electron-hole pairs have to be generated very near the nanotube wall/electrolyte interface [63].

The morphology of the TiO_2 nanotube arrays is also influenced by the annealing process, in particular the heating rate. It was reported that a slow heating rate of app. 1 $^\circ\text{C/s}$ leads to tube separation into the inner and outer shell of the tube. In the case of the moderate heating rate the nanotube walls entirely consist of crystallites with diameters in the range of the tube wall thickness. There is no double wall. A more rapid heating rate of app. 50 $^\circ\text{C/s}$ or more results in slightly disordered morphology as some crystallites of the nanotube walls peel off and remain as flakes within the pores [69].

1.4 Photo(electro)catalytic Reactors

Photocatalytic and photoelectrocatalytic reactors are well-studied devices mostly used for removal of the organic compounds present in water and air. The difference between the two reactor types is in their components and operation. Photocatalytic reactors only require a UV light source and a nano-sized photocatalyst, whereas photoelectrocatalytic reactors comprise additional electrodes that serve as cathodes. Both reactor types can be operated in batch condition [101] or used as continuous flow reactors [102]. During operation, an external electric potential is applied to the electrodes inside the photoelectrocatalytic reactor.

Since it is much easier to design a photocatalytic reactor, many different photocatalytic reactor designs have been developed in comparison to the photoelectrocatalytic reactor. However, photoelectrocatalytic reactors are more effective and show more promise for large-scale industrial application.

The most important topics to consider in order to enhance the performance of the photo(electro)catalytic reactors are the nature of the photocatalyst and the design of the

photo(electro)catalytic device. The latter will be described in detail in the following section. Other factors affecting the degradation performance which are not directly related to photo(electro)catalytic reactor design are concentration and nature of pollutants, dissolved oxygen concentration, pH of the solution, inorganic ions present in the solution, reaction temperature and catalyst loading (concentration of TiO_2 particles). The understanding about their influence on the photo(electro)catalytic process is essential for designing an efficient reactor [7].

Concentration and nature of the pollutants influence the reaction rate in many different aspects. An optimum dosage exists of each organic compound being treated so that its degradation rate is maximized. The optimum concentration depends on many factors, among which photo(electro)catalytic reactor design is one of the most important. Too high concentration of pollutants saturates the TiO_2 surface and reduces its catalytic activity. Another issue to consider when oxidizing organic compounds inside a photo(electro)catalytic reactor is the chemical composition of intermediate products. Identification and monitoring of possible intermediate products are therefore crucial for the understanding of the mechanism of the photo(electro)catalytic oxidation of different pollutants [103,104].

Dissolved oxygen concentration plays a crucial role in photocatalytic reactions since it reacts with photogenerated electrons preventing their recombination with holes. Therefore, it is necessary for mineralization of organic compounds. On the contrary, in the photoelectrocatalytic process, electrons are forwarded to the cathode, which efficiently prevents recombination even if there is no dissolved oxygen [5].

The pH of the solution changes the surface charge state of a photocatalyst and affects its valence and conduction band edges. It was observed that valence and conduction band edges of TiO_2 shift by 0.059 eV per unit pH which affects the efficiency of electrons and holes. The lower pH value results in higher valence band energy and therefore higher oxidation power of TiO_2 . Nevertheless, the reaction rate can decrease due to excess H^+ concentration at low pH, which was observed in case of degradation of an azo dye. The surface charge of a photocatalyst also affects its efficiency as it significantly changes the adsorption-desorption properties of its surface. Titania surface charge is neutral when the solution pH is app. 6.3. It is positive when the pH is lower than the point of zero charge and negative when it is higher. The pH has to be tuned appropriately in order to maximize the degradation efficiency [105-108].

Inorganic ions that are usually present in wastewater affect the photocatalytic degradation rate as they adsorb on the TiO_2 surface. Most anions and cations inhibit the activity of the photocatalyst by fouling the TiO_2 surface and/or scavenging the hole and the hydroxyl radicals. However, the presence of inorganic ions is mandatory for efficient photoelectrocatalytic reaction [109,110].

Reaction temperature does not influence the reaction rate significantly in the range between 20 and 80 °C. The photocatalyst reactivity is reduced above 80 °C because of increased charge carrier recombination and decreased adsorption of reactants on the titania surface. Adsorption of the final products inhibits the reaction at temperatures below 20 °C, where activation energy is also increased [111].

Catalyst loading is directly related to its surface area and therefore has a very important effect on the degradation of the pollutants. Both degradation and mineralization rates increase with the increase in the photocatalyst surface area. This is particularly true in the case of the immobilized photocatalyst, whereas reduced light penetration in the case of suspended photocatalyst limits the reaction rates above certain catalyst concentrations [103].

All the above-mentioned parameters and other parameters influencing the photocatalytic activity can be represented by quantum yield (QY). It is defined as the

ratio of the reaction rate r (molecules converted per second) and efficient photonic flux absorbed by the photocatalyst φ (in photons per second):

$$(\text{QY}) = \frac{r}{\varphi} \quad (11)$$

Quantum yield is also called quantum efficiency and is often used to describe the efficiency of light utilization in photocatalytic systems. Its maximum value is obtained at a maximum coverage of reactants (high enough concentration of reactants) and is usually below 0.1 to 5 %. The quantum efficiency can be improved by the application of external bias potential which reduces recombination of electrons and holes and therefore increases the catalytic activity and quantum efficiency. During the photoelectrocatalytic process, additional energy needed to apply the external electrical potential is consumed. However, this energy consumption is negligible compared to the energy consumption needed to power the UV-lights [5,111-115].

1.4.1 Types of photo(electro)catalytic reactors

The aim of reactor design is to degrade as much pollutants as possible, while consuming the least amount of energy. During years of research, a number of different types of reactors have been developed and used in research and pilot plant studies. Examples of these photoreactors include rotating disk photocatalytic reactor (RDPR) [115], thin film fixed bed reactor (TFFBR) [116], double skin sheet reactor (DSSR) [117], swirl-flow reactor [118], compact reactor [119] and parabolic trough reactor (PTR) [117]. Most of them are large-scale reactors that can operate at relatively high flow rates. However, the listed reactor types do not just differ on the reactor design, but also on the deployed state of the photocatalyst that can be suspended or attached. This is a basic classification of photocatalytic reactors.

Slurry reactors have suspended photocatalytic nanoparticles, whereas photocatalytic reactors with immobilized photocatalysts have the catalyst attached to support via physical surface forces or chemical bonds [7]. Slurry reactors provide a high surface area of photocatalyst per unit volume and therefore exhibit larger photocatalytic activity compared to immobilized photocatalyst reactors. However, the most important advantage of the latter reactor types is that they do not require catalyst recovery. The photocatalyst can be used continuously. The use of the filtration systems increases the cost of the treatment process in slurry reactors, where the penetration depth of the UV light is decreasing due to its absorption by the suspended TiO_2 particles. The problem associated with immobilized photocatalytic reactors is that the diffusion of organic compounds to the photocatalyst surface is slow when the organic compounds concentration is low [120]. The exposed TiO_2 surface area in photocatalytic reactors with immobilized photocatalyst is limited and mostly leads to mass-transfer limitations. These can be solved by the use of a photocatalytic microreactor, which possesses a high photocatalytic surface-to-volume ratio. As reaction rates strongly depend on the illuminated surface area of the photocatalyst, the high surface-to-volume ratio is a very important property and may also compensate for the loss of surface area resulting from the use of an immobilized catalyst. Other advantages of microreactor technology include reduced cost, enhanced safety and the possibility for their optimization for a particular function in a research laboratory [80,121,122]. Most experimental work on aqueous systems has been performed using the suspended photocatalyst, whereas most work for treating gases has been done with immobilized catalysts. In a waste treatment application, it would be simpler if the photocatalyst was immobilized in the photo reactor so the photocatalytic material would not have to be

separated from the treated fluid in a subsequent process step. Another great advantage of catalyst immobilization is to increase catalyst durability. [123].

Photo(electro)catalytic reactors with immobilized photocatalyst can differ from one another on the technique used to deposit TiO_2 photocatalyst on the substrate. The most commonly used techniques are anodic oxidation of metal titanium, sol-gel method, dip coating, spin coating, chemical vapour deposition (CVD), sputtering and electrophoretic deposition. Most of these techniques require sintering at temperatures above 400 °C to achieve the TiO_2 film adhesion. Thermal treatment by itself can also be used to form a TiO_2 film on the surface of metal titanium. The thickness of such film is small, which is not the case in anodic oxidation process where thickness can be controlled with anodization parameters. One of the most important properties of as-grown amorphous TiO_2 film grown by anodic oxidation process is its strong adhesion to titanium substrate which is further improved after the thermal treatment. Crystallization of TiO_2 nanotubes is needed for their photocatalytic applications. When TiO_2 nanotubes grown by anodic oxidation process are used for photoelectrocatalytic degradation, their good adhesion to the electrically conductive substrate is even more important. On the other hand, metal titanium is opaque which limits the options of UV light illumination to back-side illumination. When a photocatalyst is immobilized on a transparent substrate, such as glass, fused silica or glass fibers, it can be illuminated from both sides.

1.4.2 Illumination of a photocatalyst in a photo(electro)catalytic reactor

Illumination of the photocatalyst inside photo(electro)catalytic reactors can be achieved by artificial (lamps) or natural (Sun) sources of light. Lamps can be immersed into the fluid (internal illumination) or placed outside the reactor (external illumination). Solar radiated reactors that use natural illumination source can only be irradiated from outside. Their use is limited due to the large band gap energy of TiO_2 nanostructures [124,125]. However, unless using sunlight, the light source will tend to be the most costly component of any photocatalytic reactor [126]. This problem can be partly diminished by modification of the band gap of nanocrystalline titanium dioxide [127] or by the use of reflectors to concentrate sunlight so that it can enhance photoreaction [128].

Efficient exposure of the photocatalyst to irradiation is one of the most important parameters when designing a photocatalytic reactor. Ideally, light directly illuminates the photocatalyst surface, as a tilted light source creates a shadow which reduces the light intensity and efficiency of the reactor. Other parameters that need to be optimized in a large-scale reactor are to ensure the contact between illuminated catalyst and water and to overcome the mixing and mass transfer limitations of a reactor. When designing a photoelectrocatalytic reactor, the position and surface area of cathodes placed inside the reactor beside photocatalytically active anodes also has to be considered and studied in order to design a photoelectrocatalytic reactor with optimal efficiency [9,129,130].

1.5 Degradation of Organic Pollutants by Photo(electro)catalysis

The heterogeneous photocatalysis has been implemented in various applications: from water and air treatment [131,132] to the synthesis of different organic molecules [133] and determination of chemical oxygen demand (COD) [132]. During water and air treatment, many different pollutants have to be removed including organic and inorganic compounds

[134,135], bacteria and viruses [136], and trace metals (mercury, chromium, lead) [137] which are all at least partially susceptible to photocatalytic degradation or elimination. However, photo(electro)catalysis is mostly used for the degradation of organic pollutants [1,138].

The degradation of organic pollutants present in industrial wastewaters is of critical importance and cannot always be achieved only with a biological treatment. Photo(electro)catalytic degradation is especially suitable for the degradation of the potentially harmful organic compounds in low quantities that are the most difficult to degrade with a biological treatment. These are emerging contaminants which can be naturally produced compounds like cyanotoxins and taste and odor compounds, or man-made compounds such as antibiotics, insecticides, and organochlorinated compounds. Organic contaminants of emerging concern are usually present in waters long after the biological treatment as such treatment plants are usually insufficiently equipped for their treatment [139].

Before a photo(electro)catalytic reactor can be used for industrial water purification, it has to be first extensively studied for the degradation of model organic compounds. The most widely used include phenol and chlorophenols [140], azo dyes [81], and pharmaceuticals [141].

Phenol is one of the important organic pollutants that can accumulate in the environment and which poses health problems to living organisms [142,143]. Phenols are found in the effluents of oil refineries, production of pesticides and herbicides, dyes and textiles, pharmaceuticals, pulp and paper, plastics, and detergents [18]. The main sources of azo dyes are textile dyeing and paper printing. They are the largest class of synthetic dyes and are non-biodegradable, but are toxic and potentially carcinogenic [108,144]. Pharmaceuticals are released into the environment through different sources such as individuals, pets, disposal of outdated medications, industrial waste streams and more. Their presence is still unregulated, or they are undergoing a regularization process. Since they are persistent against biological degradation, alternative water treatment technologies will have to be applied. They can be successfully degraded with photo(electro)catalytic process [145-148].

Oxidation of organics follows different reaction pathways that depend on the active oxidative species and the treatment process. Since oxidative reactions on TiO_2 surface mainly occur via $\text{OH}^\bullet$, its reaction pathways with organic compounds are the most important. In general, $\text{OH}^\bullet$ mostly react via electrophilic addition and hydrogen atom abstraction. The fastest reaction pathway is hydroxyl radical addition [139].

If simplified, organic compounds of a general chemical structure $\text{C}_x\text{H}_y\text{O}_z$ are mineralized in a photocatalytic reaction in accordance with reaction 12. The number of electrons (and holes) in each mineralization process is equal to $4x + y - 2z$ [149,150].



Chapter 2

Aims and Hypothesis

The aim of my doctoral thesis was to develop and characterize novel continuous flow photo(electro)catalytic reactors with the immobilized photocatalyst. Since most of the reactors described in literature utilize only photocatalytic technology, my main focus was to develop new reactors that can operate in a photocatalytic and/or photoelectrocatalytic mode. My main work hypothesis was that photoelectrocatalysis is more efficient compared to photocatalysis in degradation of organic pollutants/compounds due to the imposed external electric field that determines/influences the recombination rate of electrons at the active surface of the photocatalyst. Additionally, I expected that optimization of the catalytic properties of the anode, changing the cathode materials, and varying the position and surface ratios between both electrodes will provide new results which will be important for the entire photo(electro)catalysis field. I tackled the main problems of photoelectrocatalytic reactors in a new way and therefore I expected to get original results. This is why the emphasis of my R&D work was targeted on the systematic investigation of both active components of the photoelectrocatalytic reactor as both, the anode and the cathode, are crucial for its high efficiency. In order to achieve a high degradation rate of the organic pollutants in water, it is also mandatory to select a photocatalyst with good/improved photocatalytic properties which is rigidly attached to support. Due to this reason, the preferred choice of the photocatalyst synthesis in my work was anodic oxidation of metal titanium. This process can be used to grow a highly photocatalytically active polycrystalline titania nanotubes rigidly attached to different titanium forms (foil, mesh, wire, etc.). Since anodic oxidation of each titanium form requires unique design of the anodization cell, my aim was to design such anodization cells that would fulfill two important goals. The first goal is to ensure optimum anodization process in order to grow the most photocatalytically active titania nanotubes, which were characterized regarding their photocatalytic activity, structure, chemical composition and morphology. The second goal is to enable subsequent growth of the high photocatalytic film on different titanium shapes that are incorporated into a photo(electro)catalytic reactor after annealing at the most appropriate temperature. As the photoelectrocatalytic reactor is made of photocatalytically active anode and many possible cathode materials, my goal was also to determine the most suitable cathode material and the ratio and relative position of the cathode and anode.

Furthermore, I aimed to test the efficiency of the developed photo(electro)catalytic reactors with high photocatalytic surface-to-volume ratios for photocatalytic, electrocatalytic and photoelectrocatalytic oxidation of selected model organic compounds. I planned to determine the most appropriate operational parameters to achieve the highest degradation rates. The main challenge was to understand the processes that govern efficient catalytic degradation of organic compounds at the surface of the active photocatalytic material. For this reason, part of my PhD work also included identification of intermediate

products and determination of their degradation kinetics. I aimed to propose and validate the mechanisms of photocatalysis compared to photoelectrocatalysis in order to understand critical parameters that influence the efficiency of photocatalytic and photoelectrocatalytic degradation of organic compounds. Only then, an efficient photo(electro)catalytic reactor can be readily designed and tested.

Chapter 3

Experimental Procedures

Experimental procedures include anodic oxidation of metal titanium in different forms, chemical and morphological characterization of the photocatalyst, measurements of its photocatalytic properties, design and assembly of the photo(electro)catalytic reactors, measurements of the model organic compounds degradation with various analytic techniques and determination of the degradation mechanisms.

The most suitable anodization potential and time to grow the most photocatalytically active TiO₂ nanotube arrays on titanium foils were first determined. Before measuring their photocatalytic activity, the TiO₂ films were annealed at different temperatures for a different time. I measured the photocatalytic activity of the annealed TiO₂ nanotubes with degradation of caffeine in a batch type measuring system.

Photocatalytic properties of rigidly attached TiO₂ nanotubes were monitored by decomposition of different model substances. Caffeine was used in preliminary experiments to determine the most appropriate anodization and annealing conditions. After a coil-type continuous flow photo(electro)catalytic microreactor was assembled its efficiency for the degradation of caffeine and phenol was studied. The concentration of caffeine was determined by the UV/VIS spectrophotometry, whereas a high-performance liquid chromatography apparatus (HPLC) was used to determine the concentration of phenol and its intermediate products that formed during phenol oxidation. The photocatalytic, electrocatalytic and photoelectrocatalytic activities of the assembled microreactor were measured systematically while changing the main parameters that affect the device's efficiency.

The mechanisms of photocatalytic and photoelectrocatalytic degradation of phenol were proposed and validated with a mathematical model, which describes the governing processes occurring during the microreactor's operation.

Morphological changes during individual experiments were monitored by scanning electron microscope (SEM) with accompanying spectroscopic technique EDXS. X-ray diffraction (XRD) was used to determine the crystal structure of TiO₂ samples.

3.1 Anodic Oxidation of Titanium

Anodic oxidation of titanium foil, titanium coil and perforated titanium foil was used to grow highly ordered TiO₂ nanotube arrays. Each titanium form was anodized in a different anodization set-up that enabled anodization of a well-defined surface area of the titanium form. In the case of titanium foil, the anodized surface area was determined by the use of rubber o-ring, whereas titanium coil and perforated titanium foil required some non-anodized part for the electrical contact in case of photoelectrocatalytic and electrocatalytic experiments.

Before the anodization of any titanium metal form, its surface was ultrasonically cleaned in acetone and ethanol. Every anodization was carried out at room temperature which was maintained by cooling of the anodization electrolyte when larger surface areas were anodized.

Titanium foil was used to determine the most appropriate anodization potential and time and annealing temperature and time for the growth of the most photocatalytically active TiO_2 nanotube arrays. Titanium coils of different lengths were made of titanium wire and afterwards anodized and annealed. They were placed inside a coil-type photo(electro)catalytic microreactor of different sizes that were used to degrade model degradation compounds. Perforated titanium foil was used in a larger-scale photo(electro)catalytic reactor.

3.1.1 Anodization setup and electrolyte composition

All the titanium metal forms were subjected to potentiostatic anodization in a two-electrode electrochemical cell using a platinum or stainless steel counter electrode. The anodization voltage was kept constant using a DC power supply (Toellner). The anodization setup for anodizing titanium foils is schematically presented in Figure 14a, while the schematic of anodization setup for anodization of titanium coils is shown in Figure 14b.

Anodization electrolyte composition was the same for all the titanium forms. The viscous organic electrolyte was prepared by dissolving 0.3 wt.% of ammonium fluoride (NH_4F , Kemika d.d., Zagreb, Croatia or 99.99%, Sigma-Aldrich) in ethylene glycol (99.5%, Carlo Erba Reagents, Val de Reuil, France) with the addition of 2 vol.% of distilled water.

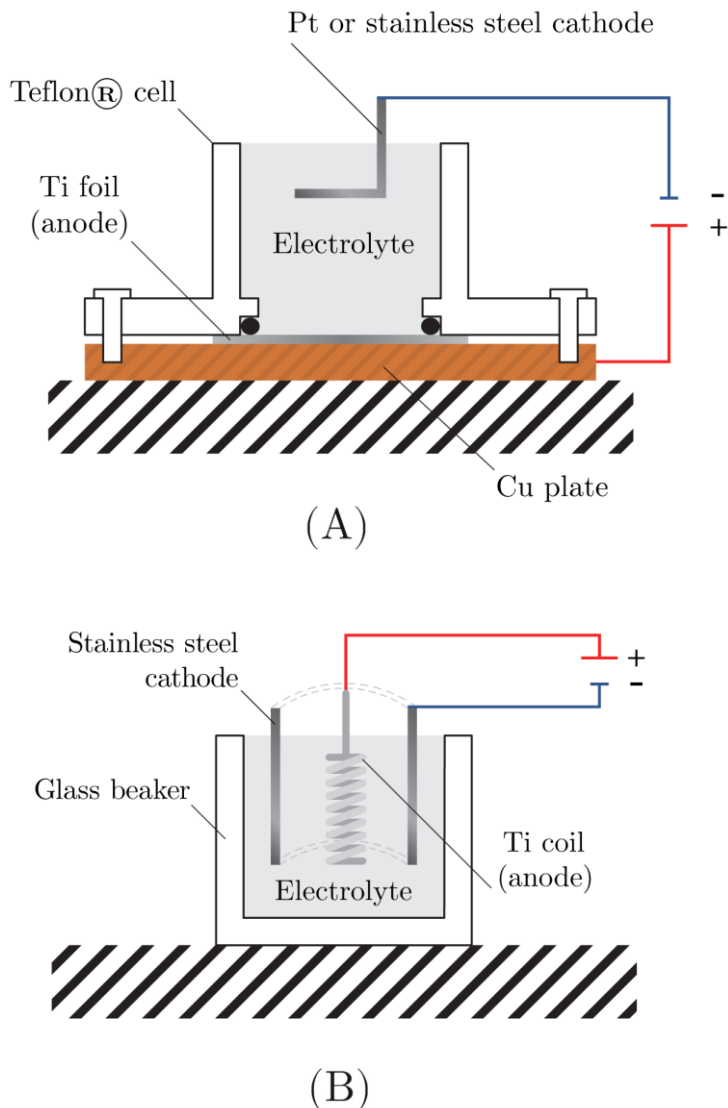


Figure 14: Schematic presentation of anodization setup for anodic oxidation of titanium foils (A) and titanium coils (B).

3.1.2 Anodization of titanium foil

Titanium foils (125 μm thick, 99.6+%, Advent Research Materials Ltd.) were anodized at 60 V or 120 V for a different anodization time (from 1 minute to 3 hours) to study the influence of the two most important anodization parameters. After the anodization, the foils were annealed in air for different times (from 30 minutes to 3 hours) at different temperatures (from 400 $^{\circ}\text{C}$ to 650 $^{\circ}\text{C}$) with heating and cooling rates of 5 $^{\circ}\text{C min}^{-1}$. The anodized area of titanium foils was $0.8 \pm 0.03 \text{ cm}^2$; the cathode material was platinum.

3.1.3 Anodization of titanium coil

An anodized coil made of titanium wire (250 μm diameter, 99.8%, Advent Research Materials Ltd.) was used to study the photo(electro)catalytic degradation of caffeine and phenol in two coil-type microreactors with a different size and also in the scaled-up coil-type microreactor.

The length of the coil that was used for the degradation of caffeine was 10 mm, whereas the length of the one used for phenol degradation was 64 mm. The former was anodized at 100 V for 30 minutes in an anodization cell with a stainless-steel cathode. The latter was anodized at 60 V for 3 hours in the same anodization cell. The app. 32-mm-long anode coils for the scaled-up reactor were anodized at 60 V for 5 hours. All the anodized titanium coils were annealed in air for 3 h at 450 °C with heating and cooling rates of 5 °C min⁻¹.

3.1.4 Anodization of perforated titanium foil

Perforated titanium foil (200 µm thick, 99.8+%, Baoji Lyne Metals Co., Ltd.) was anodized at 60 V for 6 h as this anodization time was determined to result in the most photocatalytically active TiO₂ nanotube arrays. The anodized area was 210 cm². The perforated foils were annealed at 450 °C for 1 hour.

3.2 Fabrication and Assembly of Photo(electro)catalytic Reactors

3.2.1 A coil-type microreactor

A coil-type photoelectrocatalytic microreactor was made from a UV-transparent Plexiglas (Acrytech d.o.o.) housing with a mechanically engraved cylindrical channel, in which a photocatalytically active unit was placed. In the case of studies on phenol degradation, one active unit was placed into 92-mm-long channel (Figure 15a), whereas in the case of the scaled-up coil-type microreactor, eight active units were placed into 55-mm-long channels (Figure 15b).

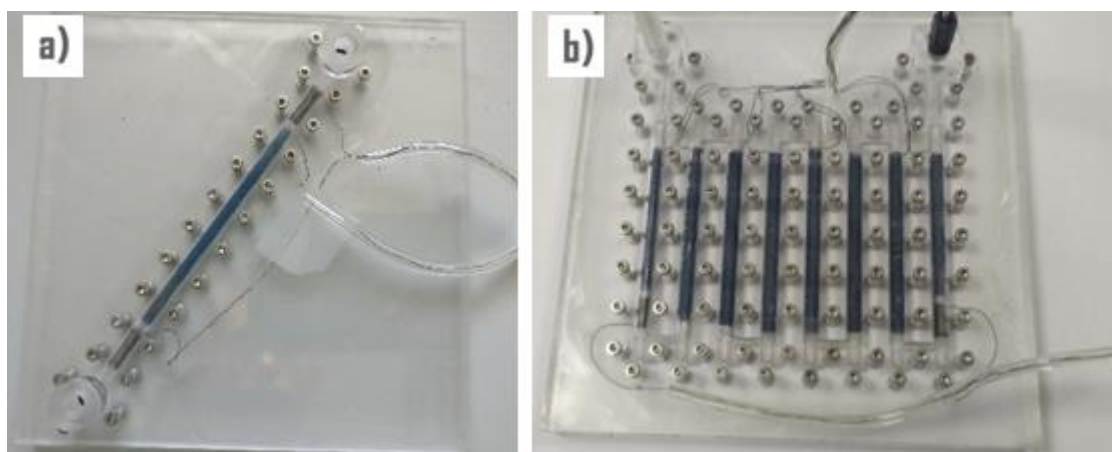


Figure 15: Coil-type photo(electro)catalytic reactor with one active unit used in phenol degradation studies (a) and a scaled-up coil-type photo(electro)catalytic microreactor with 8 active units (b).

The active unit of the photo(electro)catalytic microreactor was made of an anodized titanium anode coil which was placed in the middle of a 3-mm-diameter silica glass rod or tube depending on the microreactor configuration. Figure 16 displays how the silica rod or tube was mounted within the channel of the Plexiglas housing. It shows the longitudinal section and the cross-section of the reactor; Figure 16b shows the cross-section of the reactor along the line A–A of Figure 16a. It can be seen that the chamber provides retaining

sections which are adapted to hold the ends of the silica rod/tube. This assures a strong mounting of the silica rod/tube, which, as shown in Figure 16a, has some extension beyond the area, occupied by the anode coils and the optional cathode coils.

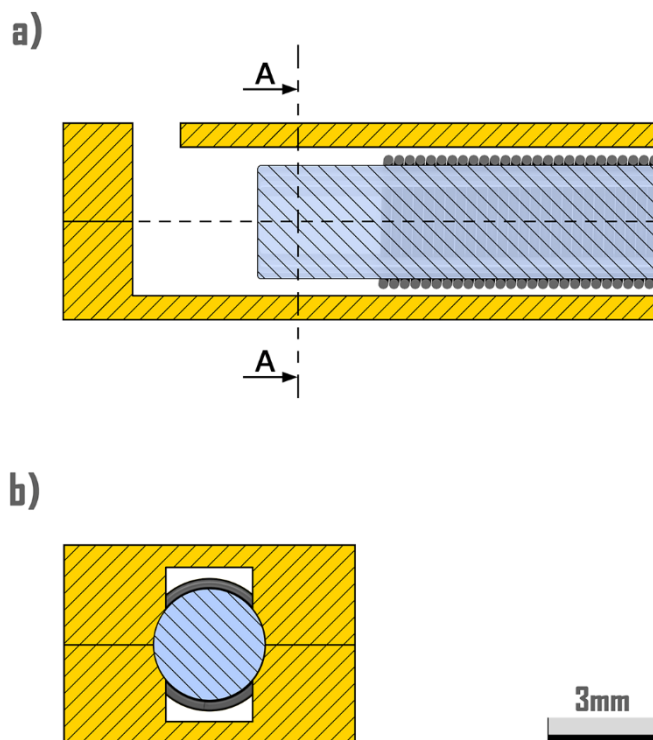


Figure 16: The longitudinal section (a) of the reactor and the cross-section (b) along the line A–A of (a), where the silica rod is mounted to the Plexiglas housing.

The position of the anode and cathode inside the microreactor (configuration) that resulted in the best photo(electro)catalytic activity of the microreactor was determined in the study of caffeine degradation. In future experiments done on phenol degradation, a larger unit with the similar surface ratio between the cathode and the photoanode was used (Figure 17). The length of the anodized titanium-anode coil in this configuration was app. 64 mm. Two titanium-cathode coils with lengths of app. 12 mm were placed on each side of the anode coil, separated by 2-mm plastic spacers to prevent a short-circuit. The length of the entire active unit of the photoelectrocatalytic microreactor was app. 92 mm. All the coils were made of 250- μ m titanium wire (99.8%, Advent Research Materials Ltd), which was wound into tightly packed coils.



Figure 17: The active unit of the photo(electro)catalytic reactor used in the study of phenol degradation.

In case of the caffeine degradation a smaller active unit was used, although in the end also a scaled-up microreactor with eight 55-mm-long active units was assembled and tested. The purpose of this study was to explore different positions of the cathode in relation to the photoanode as well as different surface ratios between the cathode and the photoanode.

Therefore, four different configurations of the photoanode and the cathode were used (Figure 18) beside the one used in the scaled-up version which was similar to configuration d. The cathode was either a straight 250- μm -diameter titanium or copper wire that was put through the app. 20 mm-long silica-glass tube (Figure 18b,c) or a titanium coil with four windings placed next to one side of the photoanode, or placed on both sides (Figure 18c,d). The surface ratio between the photoanode and the titanium cathode in the latter case was app. 5:1. The length of the anodized titanium-anode coil in all configurations was app. 10 mm, whereas the length in the case of scaled-up version was app. 35 mm. In configuration, two different anodized titanium coil densities were tested: the one with closely packed turns and the one with a reduced number of turns. The scaled-up version had active units with a slightly reduced number of windings.

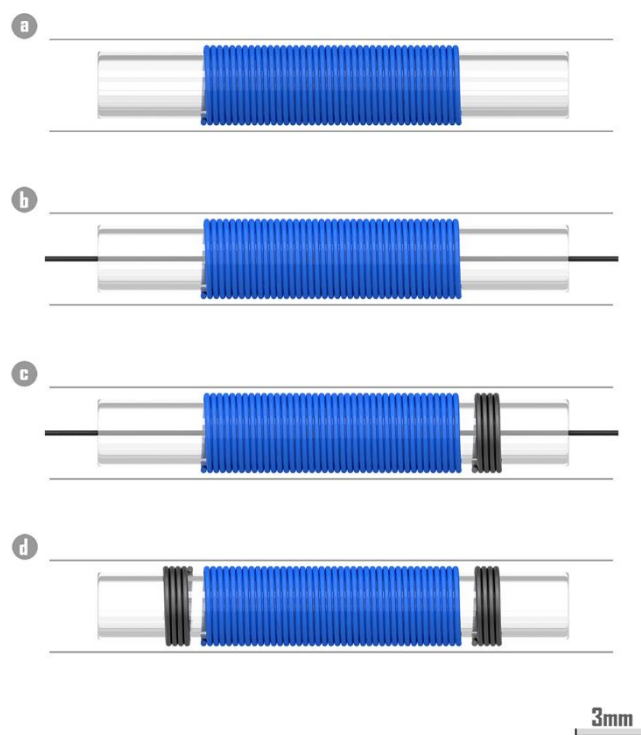


Figure 18: Different configurations of the cathode and photoanode within the photocatalytically active unit used for the photocatalytic (a) and photoelectrocatalytic (b–d) measurements. The glass rod in configurations (a) and (d) was replaced by a glass tube in configurations (b) and (c) so that a cathode in the form of a metal wire was placed inside the glass tube. In configuration (d) a cathode coil with four turns was placed on each side of the anode coil.

Coil density influences the photocatalytic surface-to-volume ratio which is one of the most important parameters influencing the photocatalytic activity of a photo(electro)catalytic reactor. It is the ratio between the surface of the photocatalyst and the volume of the liquid. When using the 250- μm -diameter titanium wire, the maximum possible number of turns on a 1-cm-long glass support was 40 closely packed turns. The calculated illuminated surface of the anodized titanium coil, in this case, was $1.50 \pm 0.08 \text{ cm}^2$. If, however, the number of turns was reduced by 25%, with the same coil length of 1 cm, the calculated surface area of the titanium coil was $2.20 \pm 0.11 \text{ cm}^2$. The illuminated surface area of the anodized titanium coils in a scaled-up coil-type microreactor was app. $62 \pm 3 \text{ cm}^2$. The calculated surface area of the tightly packed coils in the case of the larger photocatalytically active unit used for phenol degradation was $9.5 \pm 0.4 \text{ cm}^2$. The available

volume of the microreactor in the part of the photoactive TiO_2 depends on the distance between the outer diameter of the anodized titanium coil and the inner diameter of the channel. The distance was app. 200 μm in every configuration of a coil-type microreactor. This gave us the calculated available volume of the microreactor of $27 \pm 3 \mu\text{L}$ in the case of tightly packed turns and a coil length of 10 mm and $170 \pm 8 \mu\text{L}$ in the case of 64 mm-long coil. In the case of the reduced number of turns, the volume of the reactor in the part of the photoactive TiO_2 was determined to be $35 \pm 3 \mu\text{L}$. The volume of the scaled-up microreactor was $975 \pm 25 \mu\text{L}$. Consequently, this leads to a surface-to-volume ratio of 5550 $\text{m}^2 \text{m}^{-3}$ in the case of closely packed turns and 6300 $\text{m}^2 \text{m}^{-3}$ in the case of a reduced number of turns. It is assumed that the entire TiO_2 coil surface receives UV illumination when the coil with a reduced number of turns is used. The most important geometrical characteristics of the four different configurations of the microreactor used for caffeine degradation and of the one configuration used for phenol degradation are summarized in Table 1.

Table 1: Characteristics of the different configurations of the photo(electro)catalytic coil-type microreactor.

Configuration	Photocatalytic surface area (cm ²)	Cathode surface area (cm ²)	Reactor volume (μL) ^a	Photocatalytic surface-to-volume ratio (m ² m ⁻³)	UV-light intensity (mW cm ⁻²) ^b
a	1.50±0.08 or 2.20±0.11	0	27±3 or 35±3	5550 or 6300	1.2
b	1.50±0.08	0.20±0.01	27±3	5550	
c		0.50±0.03			
d		0.60±0.03			
longer active unit	9.5±0.4	7±0.3	170±8	5550	0.1 to 2.8
scaled-up microreactor	62±3	37.5±0.5	975±25	6300	2

^aThe volume measured between the illuminated photocatalytically active coil and the channel's inner surface.

^bThe total integrated incident intensity between 290 and 390 nm measured with the PCE-UV34 UVA/UVB radiation meter.

3.2.2 A foil-type large-scale photoelectrocatalytic reactor

A larger photo(electro)catalytic device (Figure 19) was developed based on knowledge gained through research done on photocatalyst synthesis and design of coil-type reactors. The main purpose was to develop a larger reactor that could be used in the studies of real wastewater purification and where a larger sample volume is needed to analyze the very low quantities of contaminants (e.g. pharmaceuticals). The designed reactor enables degradation of organic compounds at larger flow rates than coil-type microreactor. Additionally, the larger photo(electro)catalytic reactor enables quick and easy changes in its design. It can be assembled into a photocatalytic device or many possible variations of a photoelectrocatalytic device. Therefore, the developed reactor is ideal for studying the

influence of many operational and design-related parameters on the efficiency of a photo(electro)catalytic reactor.

The photocatalytically active unit of the reactor is made of 20 anodized perforated titanium foils. The surface of the foils is illuminated with at least three UV lights (Philips) with the emission maximum at 365 nm. Different size and shape of cathodes can be placed inside the reactor or removed from it when it is only used for the photocatalytic experiments. The active surface area of the anodized foils is 0.42 m^2 , while the effective reactor volume depends on the size and shape of the cathodes. In case when the outside metal tube is the only cathode of the reactor, the volume is app. 1.5 L. Since the photocatalytic surface-to-volume ratio is in the range of $300 \text{ m}^2 \text{ m}^{-3}$ which is a lot lower than in the case of a microreactor system, one of the important operational tasks is to assure the mixing of the treated fluid. It can be achieved by the rotation of the device.



Figure 19: A large-scale photo(electro)catalytic reactor with a volume of app. 1.5 L.

3.2.3 Illumination of photo(electro)catalytic reactors

In all different coil-type microreactor configurations, the anode coil was illuminated by two UV light sources, with one placed on the top and the other on the bottom of the microreactor housing. However, the UV-light source used for the illumination of smaller coil-type microreactor (configuration a-d) had an incident light intensity of 1.2 mW cm^{-2} , whereas the light intensity of the UV lights used to illuminate the longer active unit was set from 0.1 to 2.8 mW cm^{-2} by changing the operating potential of the lights. The non-adjustable UV-light source was placed at a distance of 3 mm from the photoanode coil and was made of four 0.8-mW UV-LED diodes (Roithner Lasertechnik GmbH). The adjustable UV LED light source (Shenzhen Justar Electronic Technology Co., Ltd., Guangdong, China) was placed at a distance of app. 40 mm and was also used for the illumination of the scaled-up microreactor. The light intensity in the latter case was set to app. 2 mW cm^{-2} . The emission spectra of both UV LED light sources are shown in Figure 20.

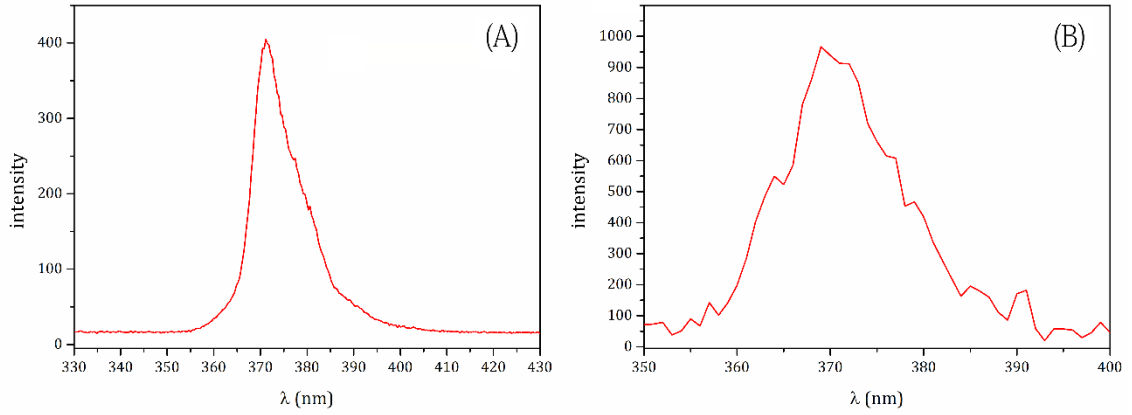


Figure 20: Emission spectra of UV LED light source with adjustable (A) and non-adjustable (B) light intensity.

3.3 Characterization Methods

3.3.1 Scanning electron microscopy (SEM)

The morphological characterization of the anodized titanium coil was made in a field-emission scanning electron microscope (FSEM) (Jeol JSM-7600F) with energy-dispersive X-ray spectrometer (EDXS).

3.3.2 X-ray powder diffraction (XRD)

XRD diffractometer (XRD; D4 Endeavor, Bruker AXS) with a Bragg-Bretano geometry, a Cu-K α radiation source ($\lambda = 0.154$ nm), and a Sol-X energy-dispersive detector was used to analyze the chemical composition of as-grown and annealed TiO₂ nanotubes. The XRD data were analyzed by the X'Pert PRO software from PANalytical.

3.3.3 Electrical conductivity measurements

The electrolyte conductivity was measured with a ProLine Plus M330 conductivity meter. For the electrocatalytic and photoelectrocatalytic experiments, the electrolyte conductivity was varied with sodium chloride (99.99%, Acros Organics) or sodium nitrate (99+%, Merck) in deionized water. The calibration curves for both salts are shown in Figure 21, whereas the conductivity measurements are provided in Table 2 and 3. The equations of the calibration curves are

$$\sigma = 1.8214c_{NaCl} \quad (13)$$

$$\sigma = 1.0691c_{NaNO_3} \quad (14)$$

The calculated coefficient of determination, R^2 , is 0.9978 in the case of NaCl and 0.9977 in the case of NaNO₃.

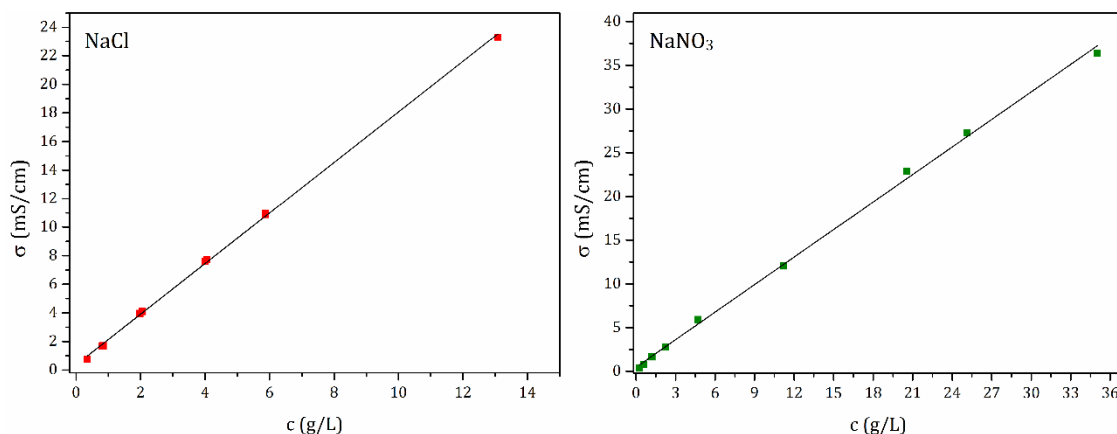


Figure 21: The calibration curves for the electrolyte conductivities of NaCl or NaNO₃ addition to deionized water.

Table 2: The NaCl conductivity measurements.

m (g)	V (L)	γ (g L ⁻¹)	c (mol L ⁻¹)	σ (mS cm ⁻¹)
0.0172	0.05	0.344	0.0059	0.734
0.0402	0.05	0.804	0.0138	1.686
0.1028	0.05	2.056	0.0352	4.09
0.2005	0.05	4.01	0.0686	7.6
0.2936	0.05	5.872	0.1005	10.96
0.6539	0.05	13.078	0.2238	23.3

Table 3: The NaNO₃ conductivity measurements.

m (g)	V (L)	γ (g L ⁻¹)	c (mol L ⁻¹)	σ (mS cm ⁻¹)
0.013	0.05	0.26	0.0031	0.393
0.029	0.05	0.58	0.0068	0.814
0.061	0.05	1.22	0.0144	1.656
0.113	0.05	2.26	0.0266	2.77
0.235	0.05	4.7	0.0553	5.93
0.56	0.05	11.2	0.1318	12.04
1.028	0.05	20.56	0.2419	22.9
1.256	0.05	25.12	0.2955	27.3
1.751	0.05	35.02	0.4120	36.4

3.3.4 UV light intensity and spectra measurements

The total integrated incident UV light intensity between 290 nm and 390 nm was measured with the PCE-UV34 UVA/UVB radiation meter. The emission spectrum of the UV light sources was measured using a spectroradiometer (Ocean Optics USB2000 Spectrometer).

3.3.5 Photo(electro)catalytic activity measurements

UV-Vis-IR spectrophotometer and HPLC were used to study the photo(electro)catalytic activity of anodized titanium foils and the efficiency of different photo(electro)catalytic devices.

3.3.5.1 UV-Vis-IR measurements

Caffeine degradation was monitored by UV-Vis-IR spectrophotometer. Foils with an anodized area of app. $0.8 \pm 0.03 \text{ cm}^2$ were placed into a small beaker with 5 mL of the initial caffeine solution of 10 mg/L and then illuminated in a sterilizer (Kambič I-265 CK UV). The solution was first stirred for 30 min in the dark to achieve the adsorption-desorption equilibrium of caffeine on the surface of TiO_2 nanotube arrays. Afterwards, the samples were exposed to the illumination source. A sample volume of 200 μL was collected after 30 min in the dark and then four times throughout the entire illumination period of 3 h. All the samples were analyzed in a high-precision UV-Vis-IR spectrophotometer.

A different measuring principle was chosen to measure the photo(electro)catalytic efficiency of the coil-type microreactor with different configurations and the microreactor with eight photocatalytically active units. The experimental set-up is shown in Figure 22.

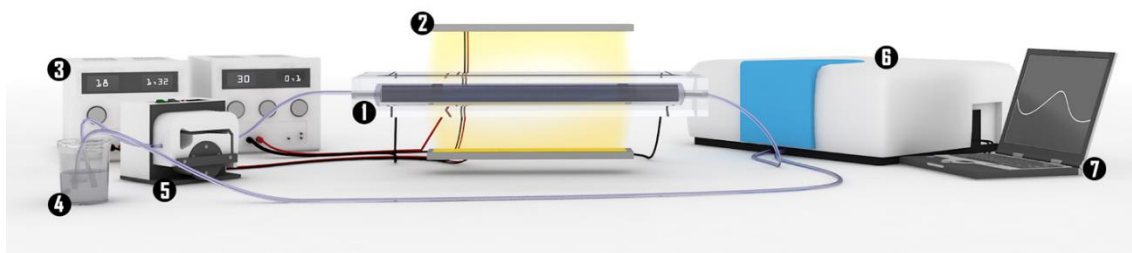


Figure 22: Analytical assembly for measuring the photo(electro)catalytic activity of our microreactor (1) with the four different configurations shown in Fig.1. The components of our system are: (2) UV LED lights, (3) DC power supplies, (4) beaker with caffeine solution, (5) peristaltic pump, (6) high-precision UV-Vis-IR spectrophotometer, and (7) computer.

The inlet of the microreactor was connected to a peristaltic pump (IDEX Health & Science) with fluorinated ethylene propylene tubing (internal diameter of 0.5 mm, Vici AG International). The outlet of the microreactor was connected to a high-precision UV-Vis-IR spectrophotometer (PerkinElmer Lambda 950), as shown schematically in Figure 23. In the schematic representation, the electronic circuit diagram of the most photocatalytically active configuration (configuration d) of our coil-type reactor is included. The UV absorption spectra were measured continuously in a 31-mL, flow-through cuvette (Hellma Analytics) without the need for any sample collection. The solution of caffeine with an initial concentration of app. 40 mg/L was continuously circulated through the system at a volumetric flow rate of 10 mL/min, as it was returned to the beaker with the initial solution after passing the spectrophotometer. The solution volume was 1 mL, and the measurement was made up to seven times during a period of 2 h.

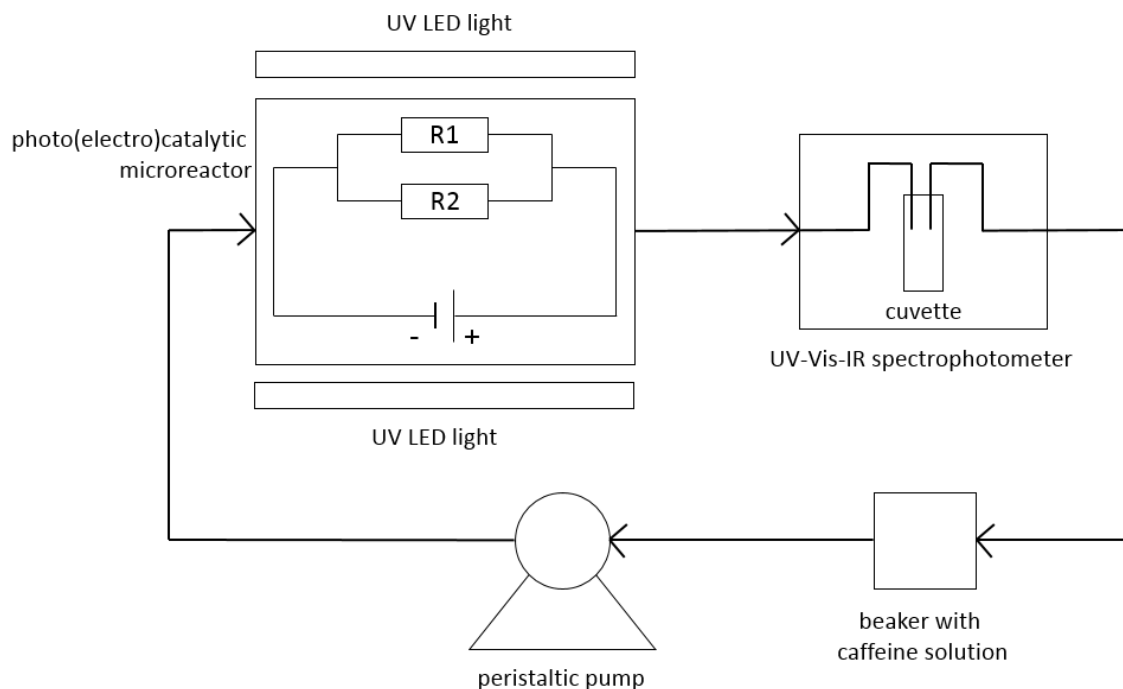


Figure 23: Schematic representation of Figure 22. The electronic circuit diagram of the most photocatalytically active configuration (configuration d) of our photo(electro)catalytic reactor is shown. The solution of caffeine was continuously circulated through the system in the direction of the arrows.

3.3.5.2 HPLC measurements

Phenol degradation was monitored by the HPLC measurements.

The inlet of the microreactor was connected to a syringe pump (Aladdin, World Precision Instruments, Sarasota, USA) with fluorinated ethylene propylene tubing (internal diameter: 0.5 mm, Vici AG International). The initial phenol (99.9%, Sigma-Aldrich) concentrations of app. 10.8 ppm, 23.5 ppm or 46.5 ppm were continuously pumped through the reactor at a volumetric flow rate in the range 7–600 $\mu\text{L min}^{-1}$. Deionized water was used to dissolve the phenol before all the measurements. For the electrocatalytic and photoelectrocatalytic experiments, the electrolyte conductivity was varied with sodium chloride and sodium nitrate. The applied potential was in the range 4–30 V. For the photocatalytic and photoelectrocatalytic experiments, the anode coil was illuminated from the top and the bottom as can be seen in Figure 24. The light intensity of the UV lights was set from 0.1 to 2.8 mW cm^{-2} by changing the operating potential of the lights.

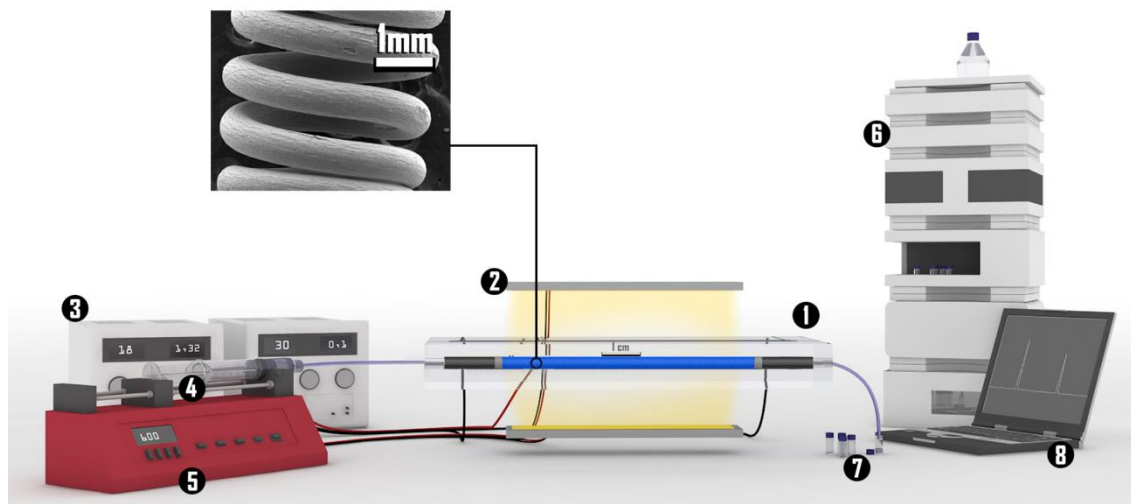


Figure 24: The experimental set-up for measuring the photoelectrocatalytic activity of the coil-type microreactor (1) with an anodized titanium coil as the photocatalytically active unit. Other components of the system are: (2) UV LED lights, (3) DC power supplies, (4) glass syringe, (5) syringe pump, (6) high-performance liquid chromatography (HPLC) system, (7) vials for sample collection and (8) computer.

Before collecting the samples for the individual experimental conditions, 1 mL of the phenol solution was pumped through the microreactor to clean the products of the previous experiment. The experiments were performed at room temperature (25 °C). For each experiment, three samples were collected at the outlet of the microreactor and analyzed with a high-performance, liquid-chromatography apparatus (HPLC, Agilent 1100 Series, Agilent, Santa Clara, CA). The degradation of the phenol and the amounts of the intermediates produced were determined from the calibration curves, which were made for the model degradation compound and all the intermediates that were detected by the HPLC. The method was the same as in a previous study [151]. The HPLC was equipped with a UV–Vis detector (G1315A) and a solvent-delivery pump (G1312A) with a Phenomenex (Torrance, CA) Synergi™ 4-l Hydro-RP 80 Å analytical column (250 × 4.6 mm², 4-μm packing), with a 70:30 (vol:vol) Milli-Q water and acetonitrile mixture as the solvent. The species in question were analyzed at 254 nm. The retention times for the phenol, hydroquinone and benzoquinone were 8.8, 7.4 and 5.3 min.

Chapter 4

Results and Discussion

4.1 Anodic Oxidation of Titanium

4.1.1 XRD analysis of TiO₂ nanotubes array

The TiO₂ nanotube layer grown by anodic oxidation is amorphous, and only the diffraction peaks corresponding to metal titanium substrate can be observed. Annealing at 450 °C for 1 h already transforms the amorphous phase polycrystalline nanotube walls into anatase phase. The most intense diffraction peaks of anatase are the ones of the crystal planes (101), (103), 200) and (105). The diffraction peaks corresponding to rutile phase start to appear after annealing at 620 °C for 1 h. The most intense are the ones of the crystal planes (110), (101), (211) and (002). The diffraction peaks of anatase crystal planes are more intense than the ones of rutile even at the highest annealing temperature of 700 °C.

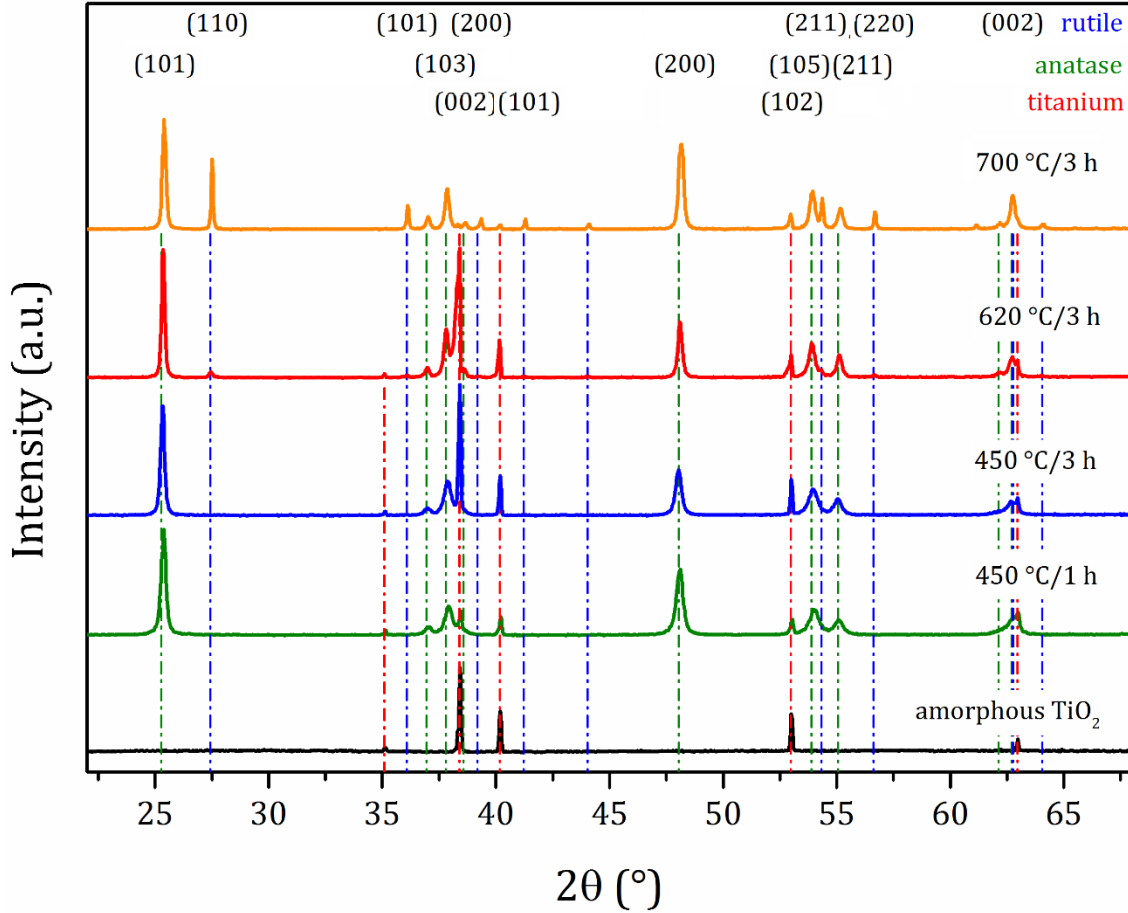


Figure 25: XRD patterns of anodized titanium foils (60 V/3 h) annealed at different temperatures and for different times.

Diffraction peaks at $2\theta = 25.3^\circ, 36.9^\circ, 37.8^\circ, 38.6^\circ, 48.0^\circ, 53.9^\circ, 55.1^\circ, 62.1^\circ$ and 62.7° correspond to the (101), (103), (004), (112), (200), (105), (211), (213) and (204) crystal planes of anatase-phase TiO_2 . The diffraction peaks at $2\theta = 27.4^\circ, 36.1^\circ, 39.2^\circ, 41.2^\circ, 44.0^\circ, 54.3^\circ, 56.6^\circ, 62.8^\circ, 64.0^\circ$ and 65.5° correspond to the (110), (101), (200), (111), (210), (211), (220), (002), (310) and (221) crystal planes of rutile-phase TiO_2 . The diffraction peaks at $2\theta = 35.1^\circ, 38.4^\circ, 40.2^\circ, 53.0^\circ$ and 63.0° correspond to the (100), (002), (101), (102) and (110) crystal planes of the titanium substrate (Figure 25).

4.1.2 Morphology of TiO_2 nanotube arrays

Morphology of the TiO_2 nanotube arrays, i.e. top view, bottom view and side view, were studied by field-emission scanning electron microscopy (FSEM). It was observed that the surface morphology of the anodized TiO_2 nanotubes depends on the anodization time (Figure 26). While shorter anodization times (Fig. 26a) yield more compact and even surface of the TiO_2 array, longer anodization times (Fig. 26b,c) increase the surface roughness. Also, longer anodization times more efficiently remove the very thin, more compact, TiO_2 surface layer and thus expose regions of titania nanotubes array where one can observe discrete nanotubes (Fig 26d). This may well be a consequence of constant etching by the fluoride ions during longer anodization times. On the other hand, the wall thickness of nanotubes increases with longer anodization times. The average outer diameter of a single TiO_2 nanotube was measured to be between 150 and 200 nm regardless of anodization parameters, while the inner diameter is app. 50 nm for short anodization times (3 h) and increases for longer anodization times.

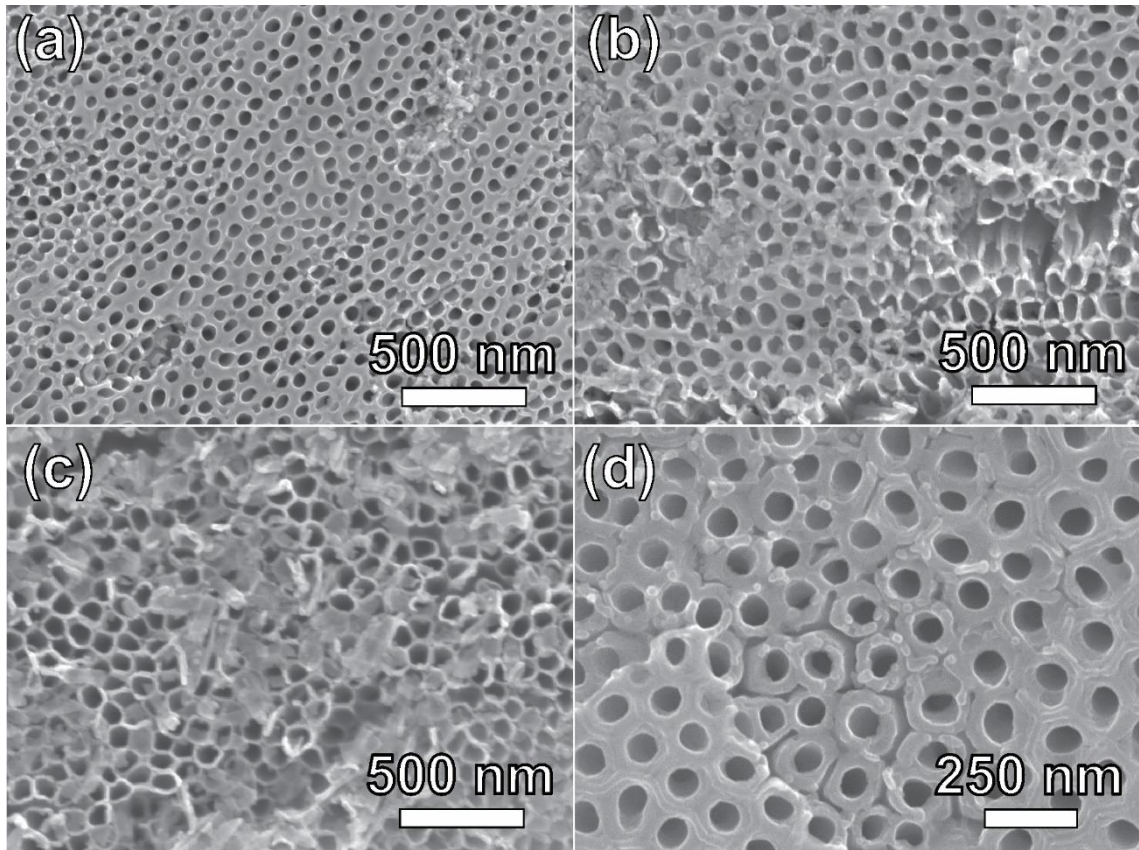


Figure 26: The top surface of the TiO_2 nanotube films after anodization for 3 h (a), 6 h (b) and 9 h (c). (d) TiO_2 nanotube region with discrete titania nanotubes.

If TiO_2 nanotube array is detached from the titanium metal support one can clearly observe that the nanotubes at the bottom are closed (Figure 27). Also, the imprints of the contact of nanotubes with the metal support can clearly be seen on the surface of the detached metal titanium.

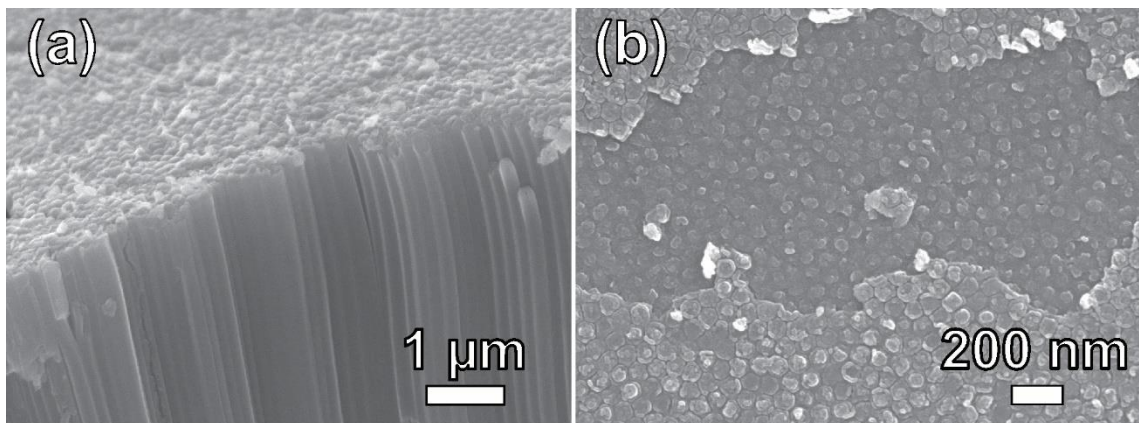


Figure 27: (a) SEM micrograph of detached bottom surface of closed TiO_2 nanotubes. (b) The corresponding imprints of detached TiO_2 nanotubes seen in the metal substrate surface.

SEM side-view imaging was used to determine the length of TiO_2 nanotubes and to investigate the morphology of the nanotubes (Figure 28). The length of the nanotubes was

determined on crushed particles of the TiO_2 nanotube thin films that were oriented perpendicular to the electron beam as shown in Figure 28. The error in the length determination using SEM calibrated marker was app. $\pm 5\%$.

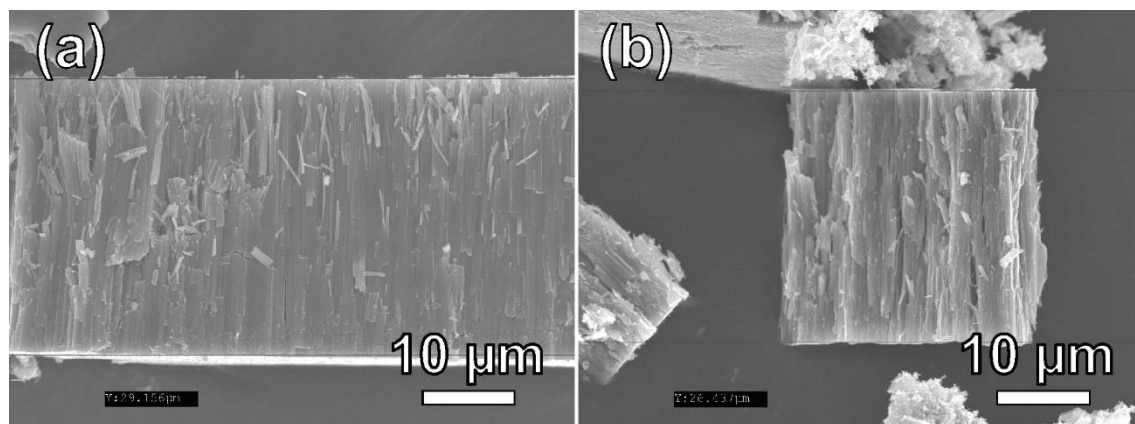


Figure 28: Side views imaging of TiO_2 nanotubes array films that were used for determination of the TiO_2 nanotubes film thickness.

Higher magnification, side-view imaging of TiO_2 nanotubes additionally revealed that they exhibit the so-called bamboo structure which is characteristic when 2 vol.% of water is added to the anodization electrolyte (Figure 29a). High-resolution FSEM images additionally confirm that the observed nanotubes are polycrystalline after annealing at 450 $^{\circ}\text{C}$, 1 h. The estimated size of grains, comprising individual nanotube, is below 10 nm which is important for the photocatalytic activity which is increased due to nano-sized grains.

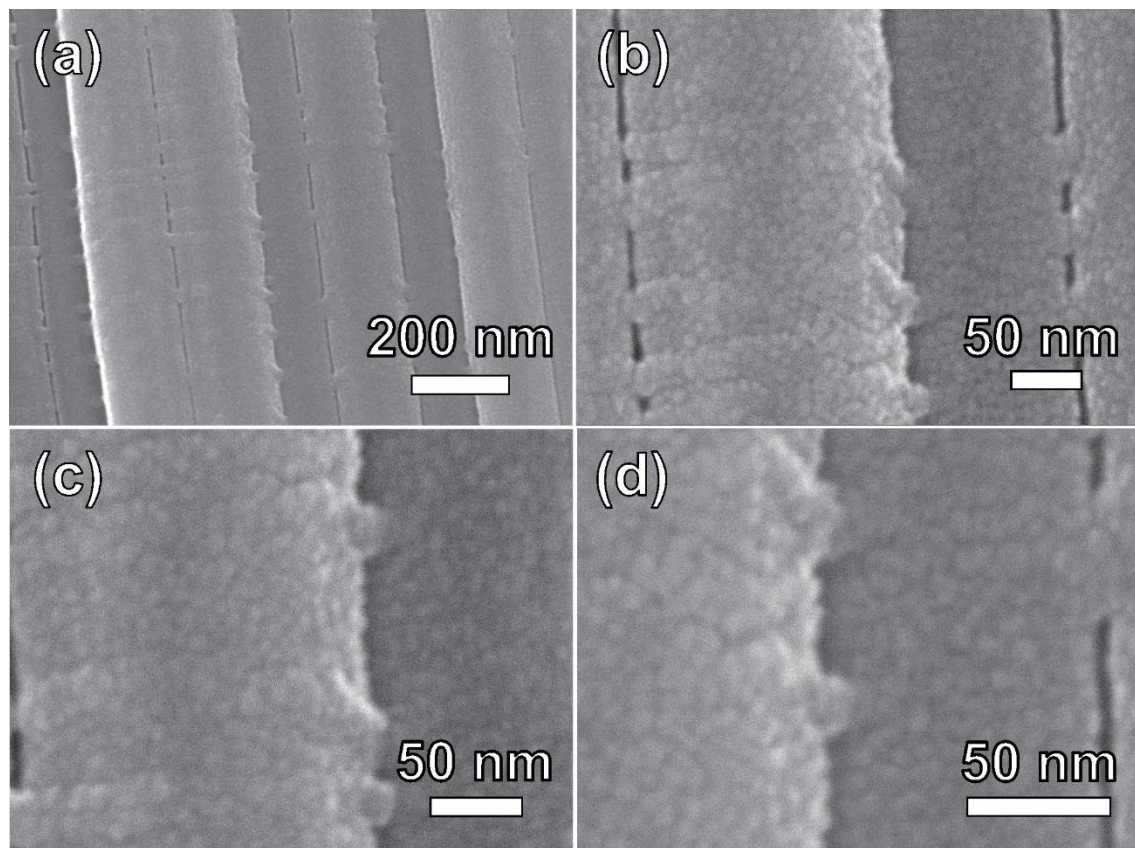


Figure 29: Cross-sectional SEM micrographs of annealed polycrystalline TiO_2 nanotubes. (a) Lower magnification revealing bamboo structure. (b-d) Higher magnification images

revealing nano-sized polycrystalline nature of individual nanotubes (b: 300.000×; c: 400.000×; d: 500.000×).

SEM investigations also showed that while the morphology of TiO₂ nanotubes arrays was dependent on the anodization parameters and annealing temperature, it was independent from the choice of metal titanium form (wire, foil, mesh).

4.2 Photocatalytic Activity of TiO₂ Nanotube Arrays

4.2.1 Influence of anodization potential and time

The most suitable anodization time and applied potential were determined according to the photocatalytic activity of the resulting TiO₂ nanotube arrays. Caffeine was used as model organic compound for determination of photocatalytic activity.

The anodic oxidation of the titanium foils was performed at anodization potentials of 60 V and 120 V. The latter anodization potential requires specific additives to the electrolyte that prevent the dielectric oxide breakdown [152]. This is why we added lactic acid when using a potential of 120 V. The diagram in Figure 30 illustrates the degradation of the caffeine after a reaction time of 180 min for different anodization potentials and times of anodization. All the anodized foils were heat treated in the same way after the anodization. The best photocatalytic performance, i.e., a degradation of app. 63% of the initial caffeine concentration during a UV illumination period of 3 h, was obtained when the foil was anodized at 120 V for 30 min. This is consistent with the results of Kontos et al. [153], who showed that longer TiO₂ nanotubes exhibit better photocatalytic performance. This was also true in our case, since the anodization potential of 120 V for 30 min led to the formation of the longest TiO₂ nanotubes, as compared to other anodizing conditions.

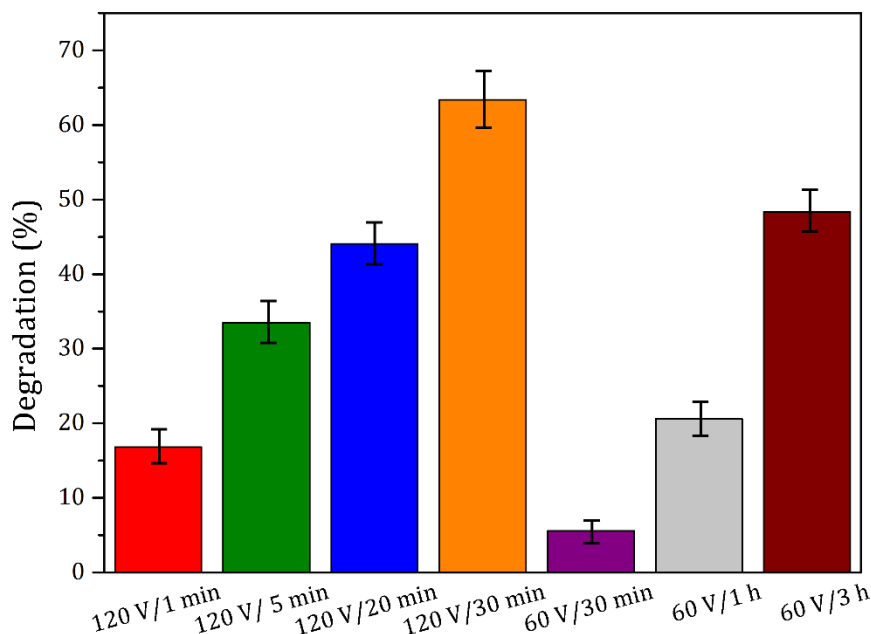


Figure 30: Photocatalytic degradation of caffeine for the reaction time of 180 min by TiO₂ nanotubes grown at different anodization potentials and periods.

However, there is a difference between the different anodized titanium forms in their photocatalytic activity. The most photocatalytically active TiO₂ nanotubes will grow inside

the titanium form with the most microscopically flat surface. The surface of titanium foil is in this regard better than the surface of drawn titanium wire.

In any case, an optimal length of the nanotubes exists which results in the best photocatalytic activity. The length increases with the anodization time and was measured after the anodization for 3 hours, 6 hours and 9 hours at 60 V. The length of the nanotubes is shown in Figure 31 together with their photocatalytic activity. The measured lengths were $26 \pm 1 \mu\text{m}$, $40 \pm 1 \mu\text{m}$ and $49 \pm 1 \mu\text{m}$. The corresponding photocatalytic degradations of 10 mg L^{-1} caffeine were $8 \pm 1\%$, $36 \pm 3\%$ and $11 \pm 1\%$. The lengths of the TiO_2 nanotubes were measured from nanotubes' cross-sections in the FSEM. It is evident that the length of the nanotubes significantly influences their photocatalytic activity and that their growth rate (nm/time) reduces with the increasing anodization time. The maximum photocatalytic activity achieved for app. $40 \mu\text{m}$ -long nanotubes means that this long nanotubes capture the incident illumination the most efficiently.

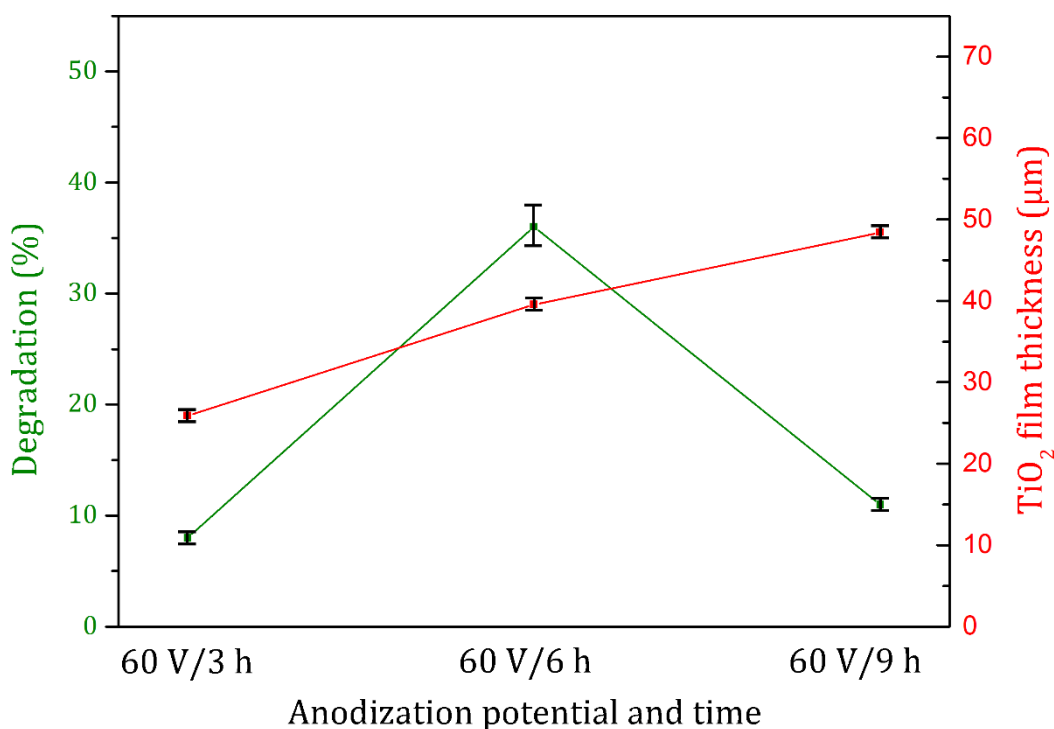


Figure 31: The influence of TiO_2 nanotubes film thickness on its photocatalytic activity. The titanium foils were anodized for different times and tested for the photocatalytic degradation of caffeine.

4.2.2 Choice of the anodization cathode material

Three different inert conductive materials were used as anodization cathode materials in anodization cell, and the photocatalytic activity of the resulting TiO_2 nanotube films was tested. It was found that the most commonly used platinum cathode can be easily replaced by graphite-foil or stainless-steel cathodes with no resulting loss in the photocatalytic performance of the obtained TiO_2 films (Figure 32). Accordingly, I used stainless-steel cathodes in all of our subsequent anodization processes involving either foils, perforated foils and/or titanium wires/coils.

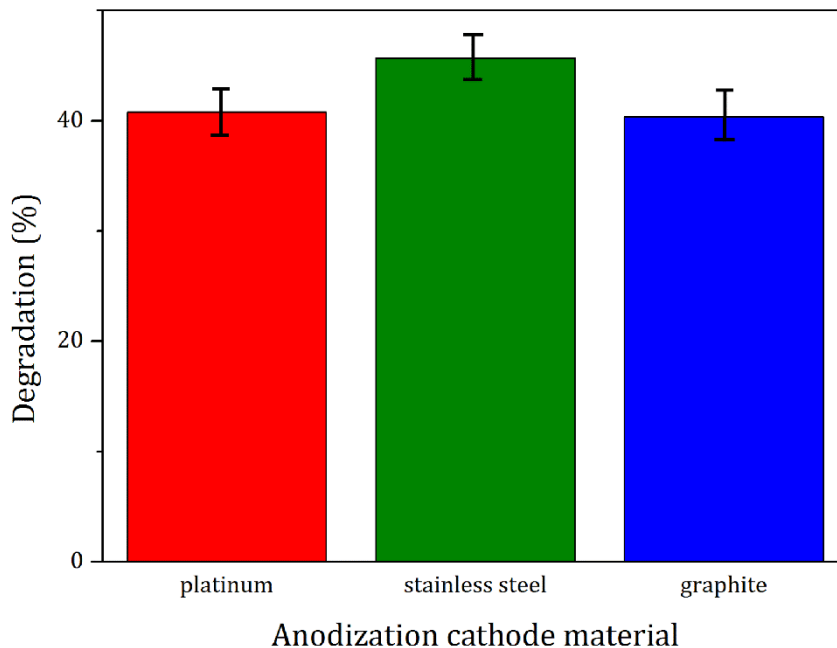


Figure 32: Photocatalytic degradation of caffeine in the microreactor at the reaction time of 120 minutes for different cathode materials used for the anodization process.

4.2.3 Influence of annealing temperature and time

A thermal treatment of the anodized foils also has a significant influence on the resulting photocatalytic activity of the TiO₂ nanotubes (Figure 33). The influence of the annealing temperature, as well as the period of the annealing, were extensively studied because of the many applications of TiO₂ nanotubes. By annealing the TiO₂ nanotubes at a temperature higher than 280°C the anodized amorphous TiO₂ nanotubes were transformed into anatase and/or rutile with varying ratios between the two crystal modifications [96,154]. Some authors have suggested that the mixture of anatase and rutile is the best when using TiO₂ in photocatalytic applications [155,156]; however, our results for caffeine degradation (Figure 33) showed that the most suitable annealing temperature was 450°C with an annealing period of 1 h. The XRD analysis confirmed that only anatase was present in the polycrystalline TiO₂ nanotubes under these annealing conditions (Figure 25). Lower efficiency at shorter annealing time of 30 min was attributed to not yet complete crystallization of amorphous titania to anatase. On the other hand, lower efficiencies at longer annealing times (2 h, 3 h) are most likely due to the nanograins coarsening process within individual polycrystalline titania nanotubes, which consequently reduces the overall grain boundaries surface area which represents a high-diffusivity path for charge carriers.

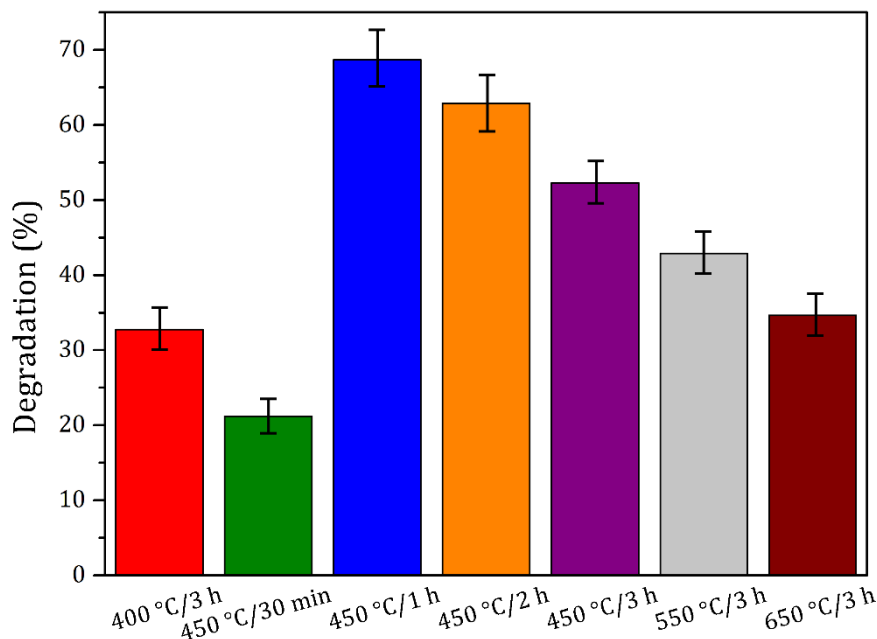


Figure 33: Photocatalytic degradation of caffeine by anodized titanium foils annealed at different temperatures and times. The photocatalytic reaction time was 180 min.

4.3 Characteristics of a Coil-Type Microreactor

4.3.1 Photocatalyst surface to microreactor volume ratio

The photocatalytic surface-to-volume ratio plays a crucial role in the overall efficiency of a photocatalytic reactor because smaller distances between the surface of the photoactive TiO_2 and the reactor housing mean a shorter and therefore a faster diffusion path for the organic compounds to the photoactive surface, where the photocatalytic reaction takes place.

The photocatalytic surface-to-volume ratio was changed by adjusting the coil density on a 1-cm-long glass rod, as described previously. For 30 coils cm^{-1} , the calculated photocatalytic surface-to-volume ratio was app. $6350 \text{ m}^2 \text{ m}^{-3}$, which was based on the assumption that the distance between the coil turns is sufficient for the UV light to also reach the inner surface of the coil. In order for this to be true, the glass rod should be more or less transparent to the UV radiation. In this way, UV light in the channel can reach the larger surface area of the anodized titanium coil, which increases the efficacy of the microreactor. This was tested for two different coil densities, and for the coil density of 30 coils cm^{-1} , this was app. 60%, as opposed to the 40 coils cm^{-1} (close packed), where only app. 40% of the caffeine was degraded (Figure 34).

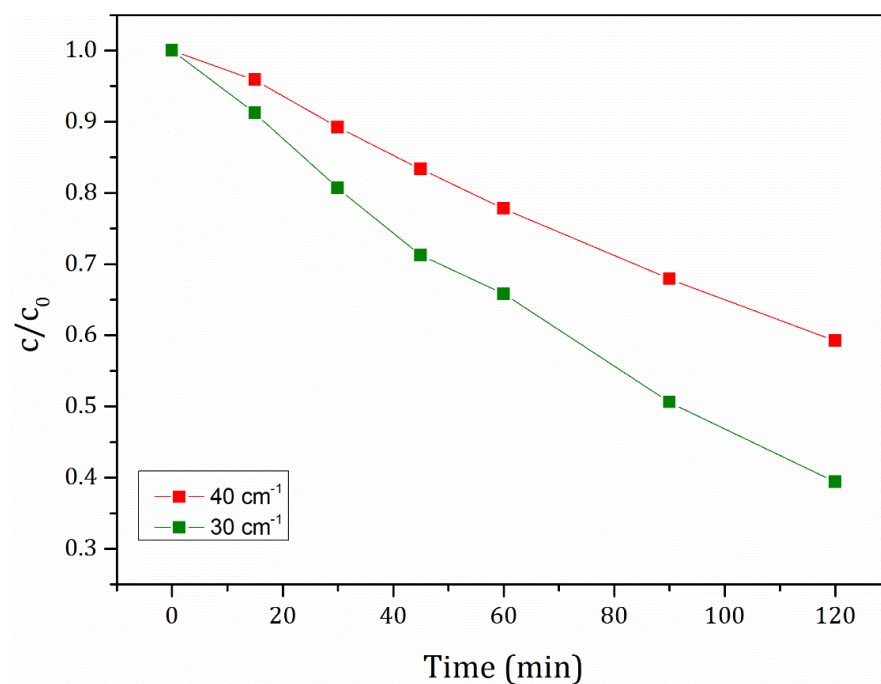


Figure 34: Photocatalytic degradation of caffeine in the microreactor at different reaction times for two different anodized coil densities.

4.3.2 Influence of the cathode material

Configuration b from Table 1 was used to determine the influence of the cathode material on the degradation efficiency of the caffeine. For these experiments titanium and copper wires of the same diameter and surface area were placed inside the glass tube in the microreactor, and the photoelectrocatalytic activity of both systems was measured at two different applied potentials, i.e., at 2 and 4 V. It was found that the best results were obtained for the titanium cathode with an applied potential of 4 V, as shown in Figure 35. After 2 h of reaction time, the initial concentration of app. 40 mg/L of caffeine was reduced to app. 1.1 mg/L, which corresponds to an app. 97% degradation of the initial concentration.

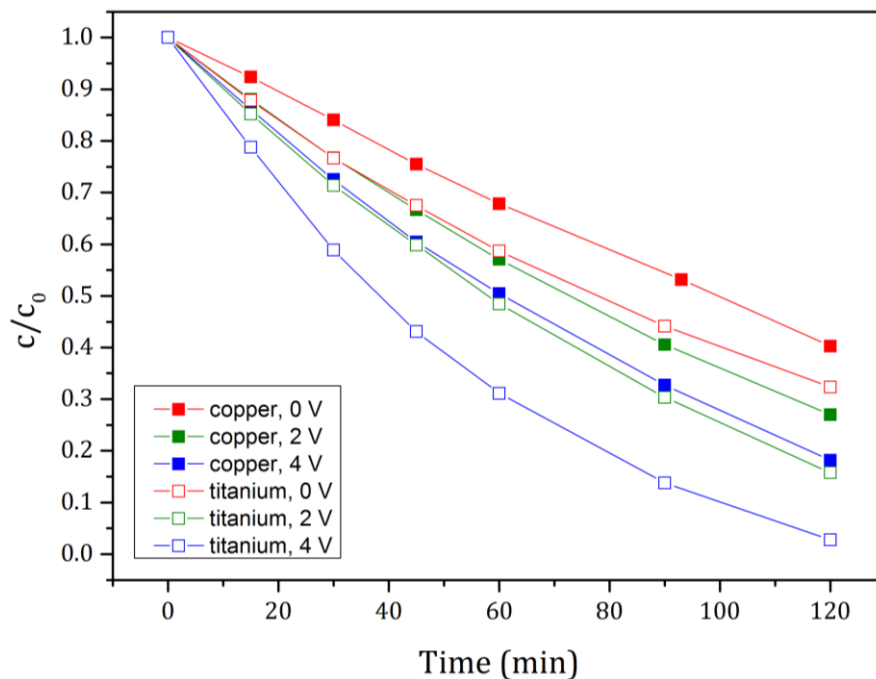


Figure 35: Photoelectrocatalytic degradation of caffeine in the microreactor at different reaction times for two different cathode materials and two different applied external voltages in the photoelectrocatalytic reactor (configuration b).

4.4 Degradation of Organic Compounds with a Coil-Type Microreactor

4.4.1 Degradation of caffeine

The coil-type photocatalytic microreactor is very suitable for use as a photoelectrocatalytic microreactor because it is made of a photocatalytically active coil that can be easily connected to a power supply. In order to change the photocatalytic microreactor into the photoelectrocatalytic microreactor we added one or more cathodes in the form of a metal coil and/or wire into the microreactor's reaction chamber. The various configurations of the cathode and anode coils in our photoelectrocatalytic coil-type microreactor are shown in Figure 18 and described in the Fabrication and Assembly of Photo(electro)catalytic Reactors subsection of this thesis. The same anode coil with a maximum coil density of 40 coils/cm was used for all the photoelectrocatalytic experiments. The anode coil was anodized at 100 V for 30 min in an anodization cell with a stainless-steel cathode.

We investigated several parameters that influence the performance of a photoelectrocatalytic coil-type microreactor, such as the caffeine solution's conductivity, the position and the shape of the cathodes, the surface area of the cathode material, and the applied potential.

4.4.1.1 Influence of the caffeine solution's conductivity

Of all the parameters influencing the performance of a photoelectrocatalytic coil-type reactor, the caffeine solution's conductivity was the most important, as the photoelectrocatalytic process does not work without the presence of a conductive electrolyte (Figure 36). The measurements of the photocatalytic degradation were first made without

an applied external potential, but with the connected cathode, for two caffeine solutions with different electrical conductivities. Although there was no electrical potential applied, the degradation rate of the caffeine in a solution containing drinking water with a conductivity of $270 \mu\text{S cm}^{-1}$ was significantly higher than the one in a solution containing deionized water with a conductivity of $1 \mu\text{S cm}^{-1}$. In the first case, app. 68% of the initial caffeine was degraded, whereas in the second case this was only app. 33% (Figure 36). This result shows that the photoelectrocatalytic process is present immediately after placing two different electrode materials in a conductive solution. Configuration b from Table 1 was used for this experiment.

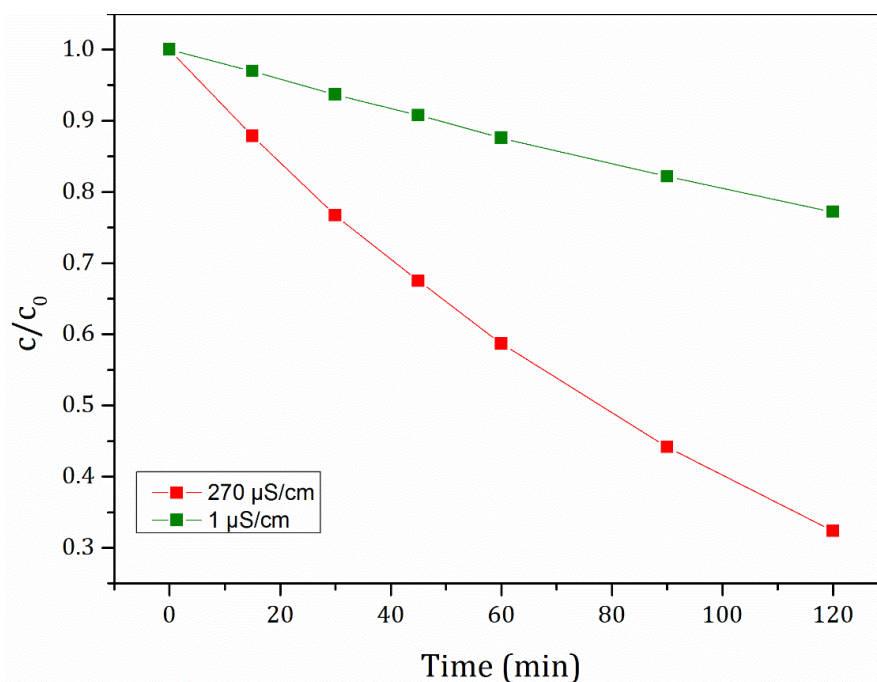


Figure 36: Photoelectrocatalytic degradation of caffeine in the microreactor at different reaction times for two different caffeine solution conductivities.

4.4.1.2 Influence of the external bias potential

Microreactor's design was changed in two different ways in order to determine the most appropriate position and surface area of the cathodes, the most appropriate applied potential, and the separate contribution of the photocatalysis and electrocatalysis. As we can see from Figures 37 and 38, the performance of a photoelectrocatalytic process is much better than the sum of the photocatalytic and electrocatalytic processes, which indicates the synergistic effect of both processes is very strong, as was already reported by other authors [157-159]. Configuration c of the microreactor showed a better photocatalytic reaction rate than configuration b, but significantly lower than configuration d. The reason for the much higher photocatalytic efficiency of configuration d is the reduced reactor volume, as the glass tube in the reaction chamber was replaced by a glass rod, and the larger cathode surface area compared to the one in configuration c. The influence of the applied potential showed the same trend in both configurations c and d. The rate of the photoelectrocatalytic reaction increased up to 4 V of the applied potential. A further increase of the potential to 8 V slightly lowered the photocatalytic activity of the system. The reason for this behavior was the insufficient UV-light intensity that did not generate enough electron-hole pairs. Besides the higher applied voltage, there was also an increase

in the rate of the water-electrolysis process, which does not contribute to the photoelectrocatalytic degradation. By applying a negative bias potential of -4 V to the photocatalyst in configuration c (Figure 37), the degradation rate was only slightly higher than in the case of no applied potential, which tells us that the hole-driven reaction pathway is much more efficient for the caffeine degradation. In the same diagram, we also see that there is no degradation reaction going on, as well as there is no adsorption of caffeine when no external potential is applied, and the photocatalyst is not illuminated. The shortest time for complete caffeine degradation was 55 min when an anodic bias potential of 4 V was applied to the photoelectrocatalytic coil-type configuration d microreactor (Figure 38).

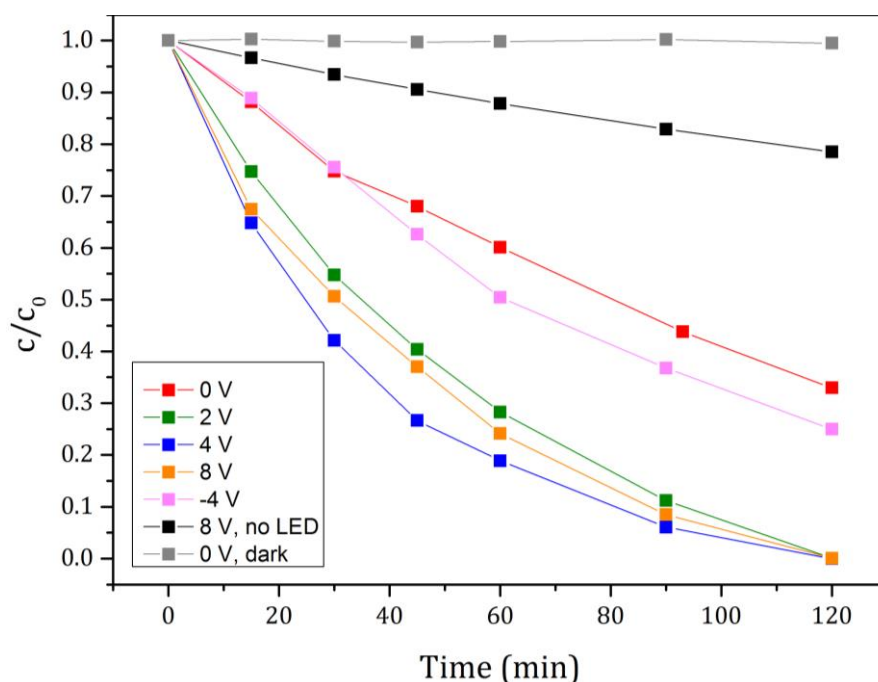


Figure 37: Photoelectrocatalytic degradation of caffeine in a photoelectrocatalytic microreactor (configuration c) at different reaction times for different applied potentials.

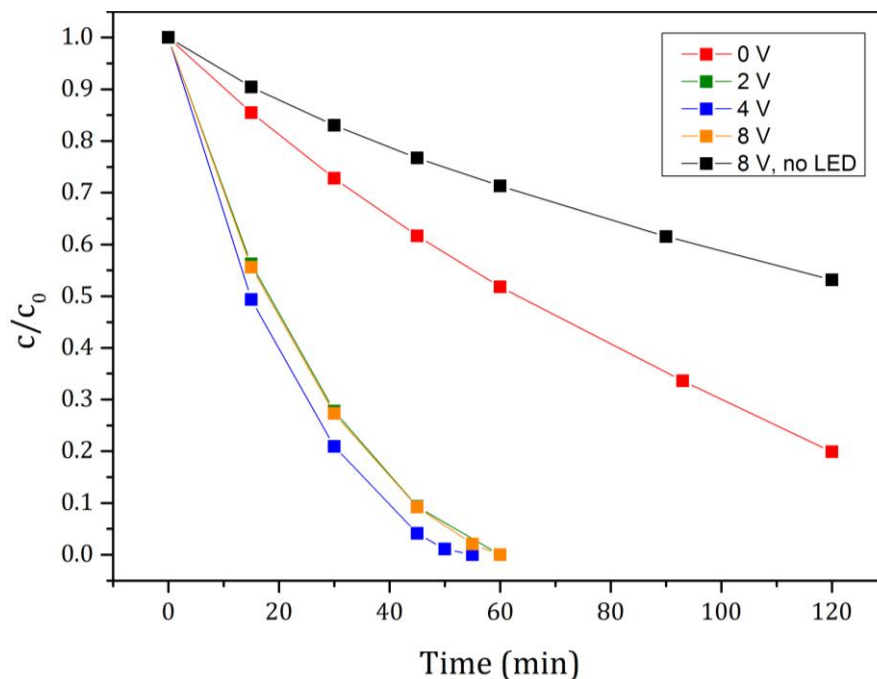


Figure 38: Photoelectrocatalytic degradation of caffeine in a photoelectrocatalytic microreactor (configuration d) at different reaction times for different applied potentials.

4.4.1.3 Scale-up process

The simple structure of the coil-type microreactor makes possible a quick and easy assembly process, wherein each part of the microreactor can be made separately and then put together into a highly efficient photoelectrocatalytic reactor. Another great advantage of such a system is the quick and simple replacement of the active parts. In order to prove this concept I assembled a coil-type photoelectrocatalytic microreactor with eight, 55-mm-long active units were placed. The initial caffeine concentration was 25 mg L^{-1} and NaCl was added to the caffeine solution to provide the desired conductivity, which was $275 \text{ } \mu\text{S cm}^{-1}$. The microreactor was operated under a continuous flow with an applied voltage of 4 V.

The initial reaction rates (R_i) and photonic efficiencies (ζ) for the microreactor were calculated from the initial slopes of the caffeine degradation at an initial concentration of 25 mg L^{-1} . While the initial reaction rate of the coil-type microreactor was $6.1 \text{ mmol L}^{-1}\text{h}^{-1}$, the photonic efficiency value was 0.52%. The results of the photoelectrocatalytic degradation of caffeine at different hydrodynamic residence times (τ), calculated from V/q_v^{-1} , where V is the reactor volume, and q_v is volumetric flow rate, are shown in Figure 39. All the initial caffeine is degraded at the volumetric flow rate of 100 mL min^{-1} .

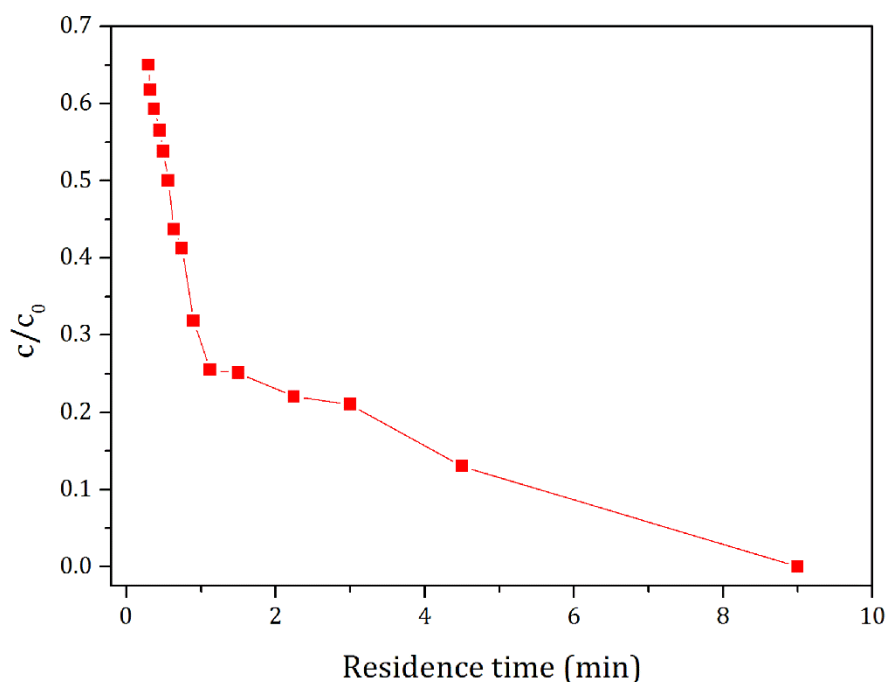


Figure 39: Photoelectrocatalytic degradation of caffeine in a scaled-up microreactor for different residence times.

4.4.2 Degradation of phenol

4.4.2.1 Phenol decomposition

Phenol (Ph) adsorbs onto the TiO_2 catalyst, where it reacts with the hydroxyl radicals and decomposes to benzoquinone (Bq) and simultaneously to acids, CO_2 and H_2O . The benzoquinone also decomposes to acids, CO_2 and H_2O . Hydroquinone was only detected in two experiments, both at the highest voltage of 30 V, the highest UV-light intensity of app. 2.8 mW cm^{-2} and for very short residence times (at flow rates of 200 and $600 \text{ }\mu\text{L min}^{-1}$). Since it is a rapidly decomposed intermediate, it was not specifically treated in the model (Figure 40).

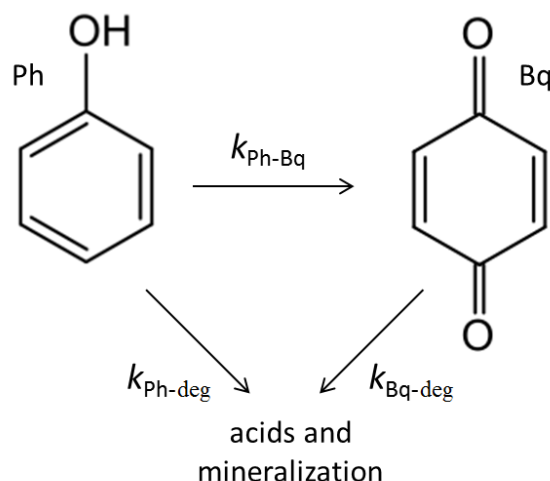
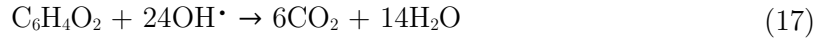
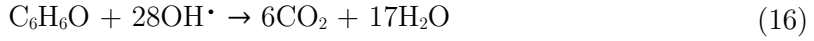
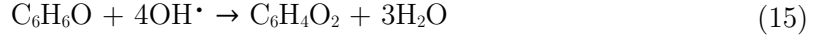


Figure 40: The mechanism of phenol degradation that applies to the current investigation.

The reactions inside the reactor take place at the TiO_2 surface, where the electron-hole pairs induce the oxidation reactions. Phenol decomposes to benzoquinone with the aid of

four hydroxyl radicals, while total mineralization is achieved with 28 hydroxyl radicals. Benzoquinone requires 24 hydroxyl radicals for complete mineralization. Water and CO₂ are formed in the process.



4.4.2.2 The proposed model

The partial differential mass-balance equations (with the transient, convection and diffusion terms in cylindrical coordinates) were solved using the finite difference method. The finite difference scheme for the solution of the partial differential mass balance equations (Equations 18–20) can be seen in Appendix A. Grid independence was achieved at a $41 \times 40 \times 10^5$ discretization of the computational domain (radial $\times$ longitudinal $\times$ time dimensions). At higher phenol conversions, a finer discretization of the time dimension was required. The solution was obtained when the calculations converged to the steady state. For the parameter estimation, a regression analysis was performed using the trust-region-reflective algorithm.

$$\frac{\partial c_{Ph}}{\partial t} = -\nu(r) \frac{\partial c_{Ph}}{\partial x} + D_i \left(\frac{\partial^2 c_{Ph}}{\partial x^2} + \frac{\partial^2 c_{Ph}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{Ph}}{\partial r} \right) \quad (18)$$

$$\frac{\partial c_{Bq}}{\partial t} = -\nu(r) \frac{\partial c_{Bq}}{\partial x} + D_i \left(\frac{\partial^2 c_{Bq}}{\partial x^2} + \frac{\partial^2 c_{Bq}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{Bq}}{\partial r} \right) \quad (19)$$

$$\frac{\partial c_{O_2}}{\partial t} = -\nu(r) \frac{\partial c_{O_2}}{\partial x} + D_i \left(\frac{\partial^2 c_{O_2}}{\partial x^2} + \frac{\partial^2 c_{O_2}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{O_2}}{\partial r} \right) \quad (20)$$

where c_i are the species' concentrations, t represents the time, ν is the linear velocity, x is the axial dimension, r is the radial dimension, and D_i are the diffusion coefficients. ν is dependent on the radial position, due to the formation of a parabolic laminar velocity profile. The domain in the radial direction extends from R_1 , which is 1.625 mm, to R_2 , which is 1.95 mm. The reaction takes place on the TiO₂ catalyst, which is positioned on the inner channel wall at R_1 .

Since the catalyst consists of TiO₂ nanotubes and the phenol concentrations are small, the saturation of the catalyst surface was not considered to be a restrictive factor governing the overall kinetics. The boundary conditions and the reaction-rate expressions on the catalyst surface are therefore dependent on the adsorption coefficients of each individual species (K_i), and on the kinetic constants (k_{i-i}):

$$r_{Ph-Bq} = k_{Ph-Bq} K_{Ph} c_{Ph} c_{OH\cdot} \quad (21)$$

$$r_{Ph-deg} = k_{Ph-deg} K_{Ph} c_{Ph} c_{OH\cdot} \quad (22)$$

$$r_{Bq-deg} = k_{Bq-deg} K_{Bq} c_{Bq} c_{OH\cdot} \quad (23)$$

During photocatalysis, the reduction of oxygen on the catalyst surface removes the e^- and allows for OH $\cdot$ generation on the holes. The rate expression is:

$$r_{O_2} = I_{UV}^{nl_1} k_{red} K_{O_2} c_{O_2} \quad (24)$$

The boundary conditions and the mass balance for the hydroxyl radicals involved in photocatalysis at the catalytic wall are:

$$-D_{O_2} \frac{dc_{O_2}}{dr} = -r_{O_2} \quad (25)$$

$$-D_{Ph} \frac{dc_{Ph}}{dr} = -r_{Ph-Bq} - r_{Ph-deg} \quad (26)$$

$$-D_{Bq} \frac{dc_{Bq}}{dr} = r_{Ph-Bq} - r_{Bq-deg} \quad (27)$$

$$\frac{d c_{OH\bullet}}{dt} = r_{O_2} - 4r_{Ph-Bq} - 28r_{Ph-deg} - 24r_{Bq-deg} \quad (28)$$

During photoelectrocatalysis the UV light excites the electrons, and the electrical current moves them to the cathode. The $OH\bullet$ radicals are produced from water on the available holes. Dissolved oxygen does not play a part in the degradation of the phenol since the applied electrical current suppresses the recombination and enables the holes on the photocatalyst surface to produce the $OH\bullet$. The rate expression can be written as:

$$r_{elect.} = (I_{UV}^{nl_2} + I_0) I_{current}^{nc} k_{elect.} \quad (29)$$

The boundary conditions and the mass balance for the hydroxyl radicals at the catalytic wall for the photoelectrocatalysis are:

$$-D_{Ph} \frac{dc_{Ph}}{dr} = -r_{Ph-Bq} - r_{Ph-deg} \quad (30)$$

$$-D_{Bq} \frac{dc_{Bq}}{dr} = r_{Ph-Bq} - r_{Bq-deg} \quad (31)$$

$$\frac{d c_{OH\bullet}}{dt} = r_{elect.} - 4r_{Ph-Bq} - 28r_{Ph-deg} - 24r_{Bq-deg} \quad (32)$$

A zero concentration-gradient boundary condition was imposed on the R_2 boundary (non-catalytic outer wall) for all the species. The diffusion coefficients were determined using the correlation provided by Siddiqi and Lucas [160] from the molar volumes of the liquid solutes at their normal boiling points. The diffusion coefficient of the oxygen was calculated using the Wilke–Chang correlation [161]. The kinetic parameters were obtained by a simultaneous regression analysis of all the experimental data and are presented in Table 4. The reaction and adsorption constants are coupled in the reaction–adsorption constant.

Table 4: The kinetic parameters for photocatalysis and photoelectrocatalysis obtained using the regression analysis of the experimental data.

<i>parameters</i>	<i>value</i>
$k_{\text{Ph-Bq}} K_{\text{Ph}} \text{ (L s}^{-1} \text{ mol}^{-1}\text{)}$	9.51×10^{-2}
$k_{\text{Ph-deg}} K_{\text{Ph}} \text{ (L s}^{-1} \text{ mol}^{-1}\text{)}$	1.48×10^{-3}
$k_{\text{Bq-deg}} K_{\text{Bq}} \text{ (L s}^{-1} \text{ mol}^{-1}\text{)}$	1.36×10^{-4}
nl_1	0.91
$k_{\text{red}} K_{\text{O}_2} \text{ (mW cm}^{-2}\text{)}^{-nl_1} \text{ s}^{-1}\text{)}$	1.18×10^{-5}
$I_0 \text{ (mW cm}^{-2}\text{)} nl_2$	0.25
nl_2	0.94
Ne	0.96
$k_{\text{elect}} \text{ ((mW cm}^{-2}\text{)}^{-nl_2} \text{ mA}^{-ne} \text{ mol L}^{-1} \text{ s}^{-1}\text{)}$	1.18×10^{-8}

All the experiments were performed under laminar flow conditions. The highest Reynolds number at the highest flow rate of $600 \mu\text{L min}^{-1}$ was less than 1. The electrical current (I_{current} in mA) measured was $0.153 \text{ mA V}^{-1} \times \text{electrical potential (U in V)}$. A detailed discussion follows in the subsequent sections.

4.4.2.3 Photocatalytic degradation

The photocatalytic experiments were performed at different flow rates, initial phenol concentrations and light intensities. Figure 41 shows the results for the UV-light intensity of 2.8 mW cm^{-2} . The experimental symbols are the microreactor exit concentrations for the different residence times, which correspond to the appropriate flow rates. During the photocatalysis the phenol was not decomposed to any great extent, i.e., only to 83.7% and 83.3% (experiment and model) at an app. 10.8 ppm initial phenol concentration, to 90.7% and 91.7% of its initial value (experiment and model) at app. 23.5 ppm, and to 92.8% and 95.5% (experiment and model) at app. 46.5 ppm. This was found to be due to the depletion of oxygen inside the microchannel. Oxygen has a determining role in the photodegradation since it consumes the photogenerated electrons and prevents their direct recombination with the holes. In the case of O_2 depletion, extensive recombination stops the photocatalytic activity of the TiO_2 catalyst. From the model, it was determined that one reacted O_2 results in one $\text{OH}^\bullet$ being produced from H_2O at the positive hole, in which case the final experimental conversions matched the final model conversions.

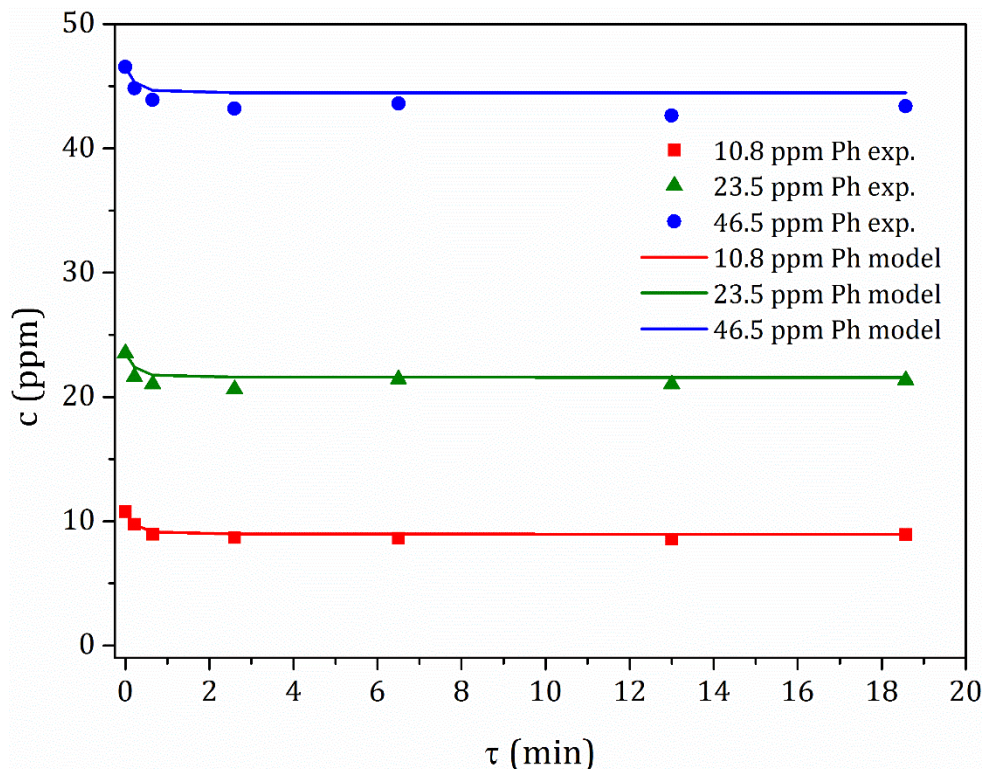


Figure 41: Phenol concentrations at different microreactor residence times for different initial phenol concentrations and at app. 2.8 mW cm^{-2} UV-light intensity. The symbols represent the experimental results, whereas the lines are the results from the model.

The detailed concentration profiles of phenol, benzoquinone and oxygen are presented in Figure 42 (a, b and c) for the 2.1 mW cm^{-2} UV-light intensity and a flow rate of $50 \text{ }\mu\text{L min}^{-1}$. The concentration profiles are presented in ppm along the axial (x) and radial (r) dimensions. The reaction takes place at the boundary for $r = 1.625 \text{ mm}$. At the beginning of the microchannel at the cathode coil, there is no hydroxyl radical generation, and decomposition does not occur. Further along the microchannel at the anode, hydroxyl radicals decompose the phenol into benzoquinone; oxygen is depleted in the process (Figure 42c). After this oxygen depletion, the reactions taking place come to a halt. The initial oxygen concentration corresponds to the saturated oxygen concentration at $25 \text{ }^{\circ}\text{C}$, which is 4.59 mol L^{-1} . The concentration profiles in the radial (r) direction are dependent on the rate of diffusion for each species. Figure 42d presents the average concentration at the exit of the microreactor for different residence times (for flow rates of 7, 10, 20, 50, 200 and $600 \text{ }\mu\text{L min}^{-1}$). The flow rates 7 to $50 \text{ }\mu\text{L min}^{-1}$ yield the same result, since the oxygen was depleted in all cases before reaching the exit of the microreactor.

The majority of the phenol was converted to benzoquinone, which is also expressed in the reaction-adsorption constant $k_{\text{Ph-Bq}}-K_{\text{Ph}}$ of $9.51 \times 10^{-2} \text{ L s}^{-1} \text{ mol}^{-1}$, which is the highest of the constants for the competing reaction pathways. Second is the reaction-adsorption constant for phenol degradation, which is almost two orders of magnitude lower ($1.48 \times 10^{-3} \text{ L s}^{-1} \text{ mol}^{-1}$). Benzoquinone, once formed, does not decompose readily; the reaction-adsorption constant for benzoquinone degradation is one order of magnitude lower than the constant for direct phenol degradation.

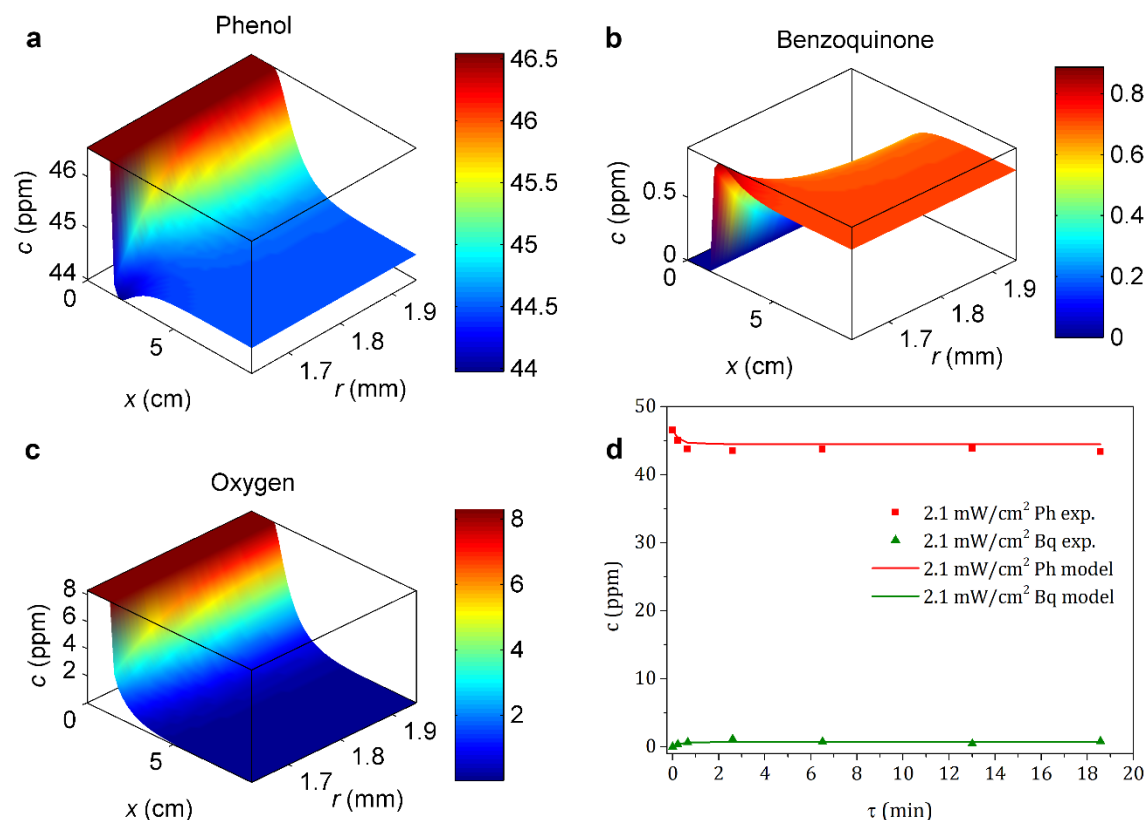


Figure 42: The concentration profiles of (a) phenol, (b) benzoquinone and (c) oxygen along the length and radius of the reactor in ppm for a flow rate of $50 \mu\text{L min}^{-1}$. (d) The average outlet concentrations for various residence times (different flow rates). The light intensity was 2.1 mW cm^{-2} .

The effect of light intensity is presented in Figure 43. Its effect on the kinetic constant, in the studied range from 0 to app. 2.8 mW cm^{-2} , follows an almost linear dependency, with a power law coefficient of 0.91. Nevertheless, higher phenol conversions were not achieved at higher light intensities due to an oxygen deficiency. The model predictions were in good agreement with the experimental results.

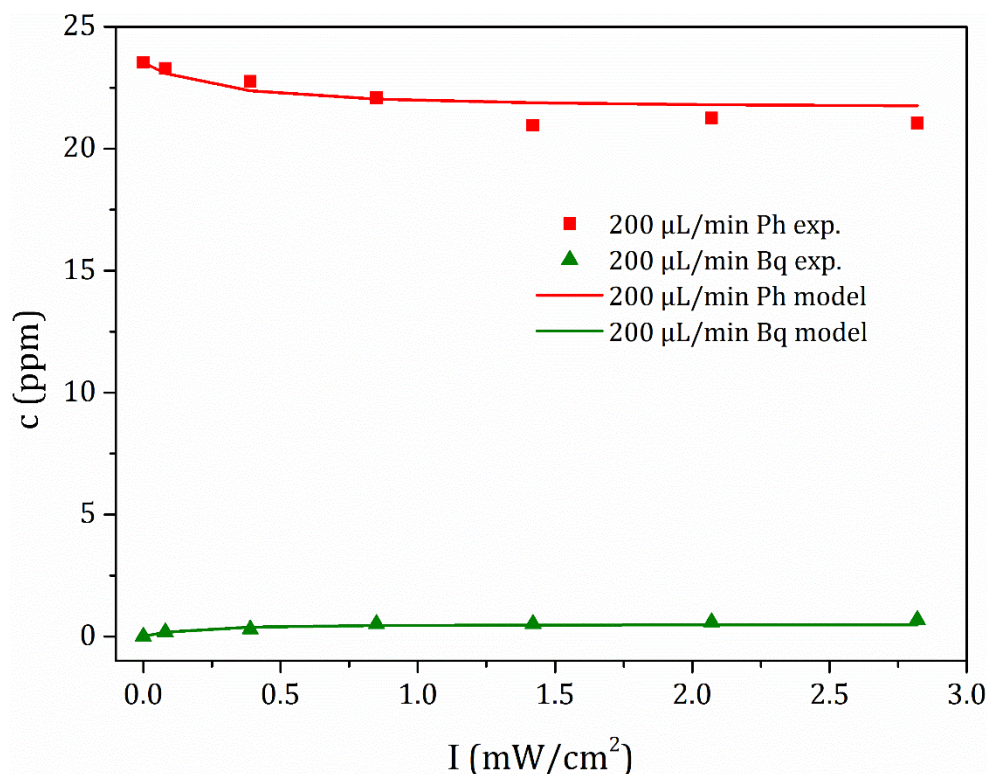


Figure 43: The effect of light intensity on the phenol (red) and benzoquinone (green) concentrations. The symbols represent the experimental, while the lines represent the modeling results for a flow rate of 200 $\mu\text{L min}^{-1}$.

4.4.2.4 Photoelectrocatalytic and electrocatalytic degradation

Photoelectrocatalytic experiments were performed at different flow rates, light intensities, and under an applied electrical potential (U) of 4, 8, and 16 V. The oxygen did not play a decisive role in the phenol degradation; the existence of the positive holes was stabilized by the electrical current. At higher currents, more hydroxyl radicals were generated, which increased the rate of the reaction. Photoelectrocatalysis allowed for a complete degradation of the phenol.

The reaction-adsorption constants were the same as with the photocatalysis (Table 4). Phenol degradation also took place in the dark (0 mW cm^{-2}); without UV illumination, the reactions were undergoing electrocatalysis only. It is presumed that the hydroxyl radicals were electrochemically produced at the anode surface, with chlorine radicals also being generated, because of the presence of chloride ions, which were electrochemically oxidized at the anode surface. Figure 44 shows the effect of the applied electrical potential on phenol degradation for various light intensities. The concentrations depict the average outlet phenol concentration. The expected trend is evident, except in the case of electrocatalysis, at zero illumination and 16 V, when a very high phenol concentration drop can be observed, as compared to the experiments performed at 8 V and 4 V. At app. 1.4, 2.1, and 2.8 mW cm^{-2} and 16 V, the model results are similar, since, at a high reaction rate, the diffusion transport to the catalytic wall becomes the limiting factor. This was not observed for the photocatalytic experiments since the reaction rate was slower. The calculated diffusion coefficients were $7.96 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the phenol and $7.68 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the benzoquinone.

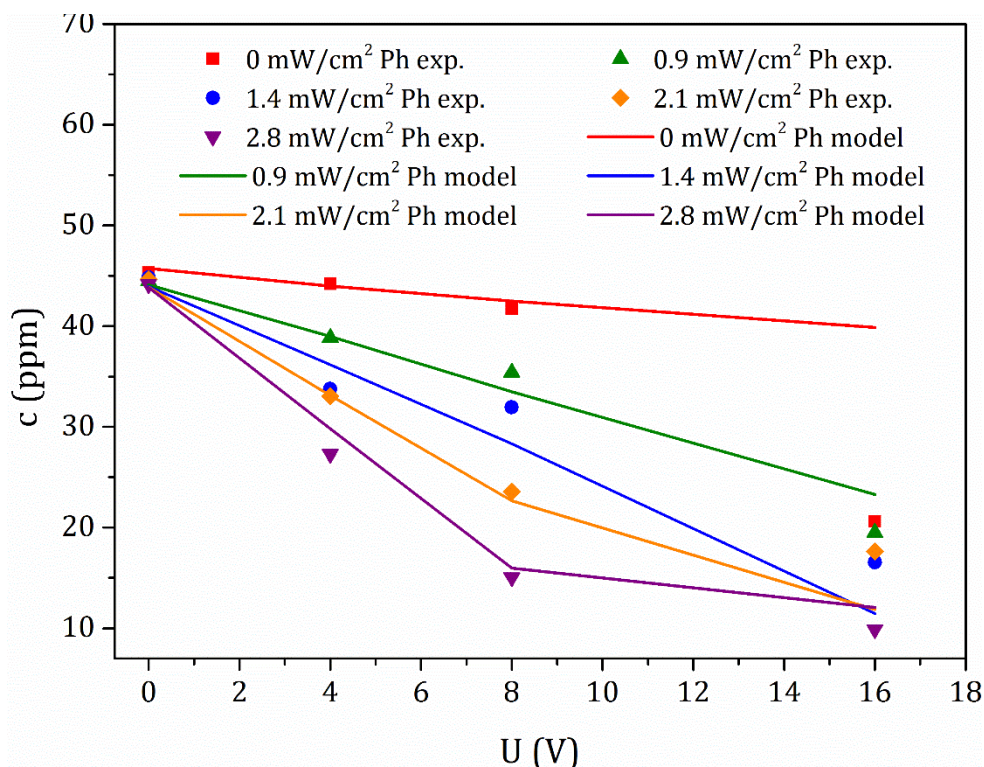


Figure 44: The effect of an applied electrical potential on phenol degradation for various light intensities and an initial phenol concentration of app. 45.7 ppm at a 200 $\mu\text{L min}^{-1}$ flow rate. The 0 mW cm^{-2} demonstrates the results of the electrocatalysis only.

Detailed concentration profiles for the phenol and benzoquinone are presented in Figure 45 for the case of an initial phenol concentration of app. 45.7 ppm, a flow rate of 600 $\mu\text{L min}^{-1}$, a light intensity of app. 2.8 mW cm^{-2} , and an electrical potential of 8 V. In Figure 45a the phenol decomposes to 0 ppm at the inner catalytic wall, while the average outlet concentration is 78.2% of the initial concentration. The diffusion of phenol from the outer to the inner wall is slow, which produces a high concentration gradient in the radial direction. Benzoquinone (Figure 45b) is formed and decomposed at the catalytic wall. These results show that the process would be intensified in a narrower (radial-wise) channel, where the rate of the diffusional transport to and from the catalytic wall would be improved. The velocity profile, presented in Figure 45c, formed between the two walls is parabolic, and the flow was laminar in all the experiments and simulations. The exit phenol and benzoquinone concentrations at 600 $\mu\text{L min}^{-1}$ for different electrical potentials are shown in Figure 45d.

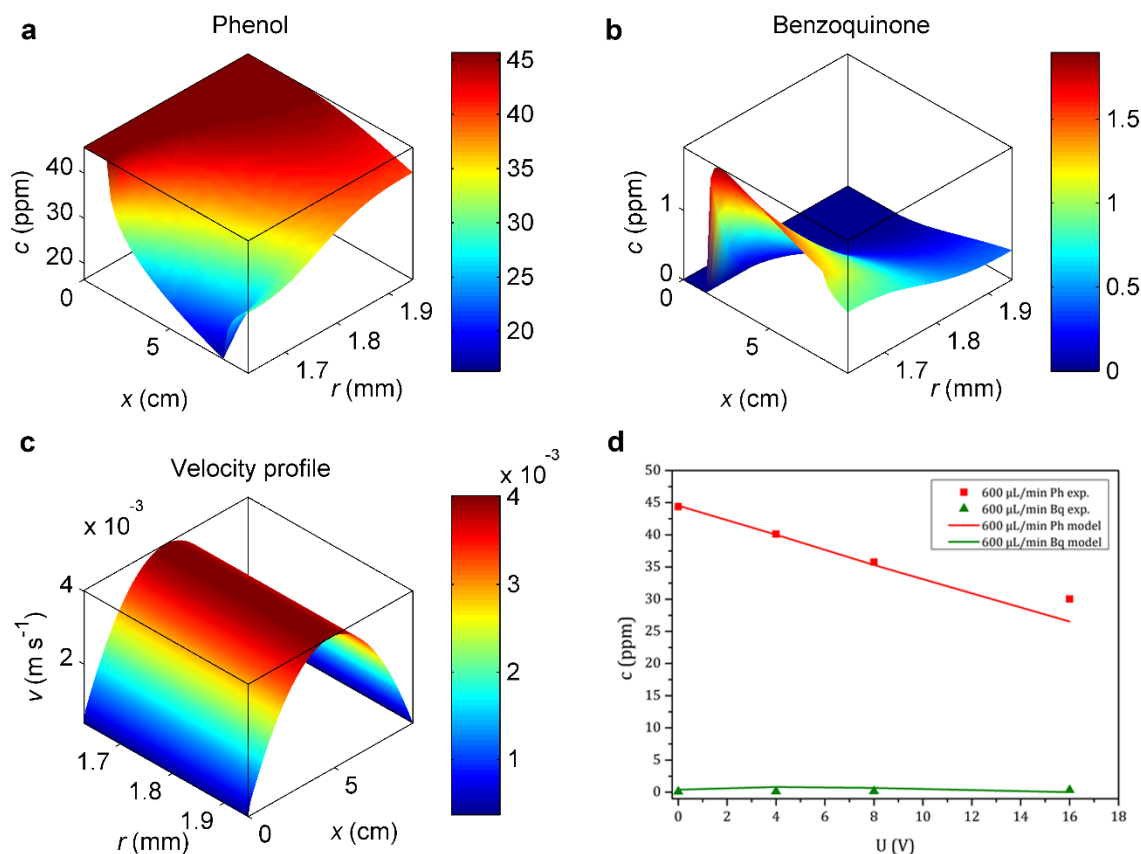


Figure 45: The concentration profiles of (a) phenol, (b) benzoquinone and (c) the velocity profile along the length and radius of the reactor in ppm at a flow rate of $600 \mu\text{L min}^{-1}$, light intensity of 2.8 mW cm^{-2} , and an electrical potential of 8 V. (d) The average outlet concentrations at different electrical currents (0–16 V).

At 16 V there was a large discrepancy between all of the modeling results and the experimental values (Figure 46). Much higher conversions were achieved for low UV irradiation than it could be predicted using the model. This is most pronounced at 0 mW cm^{-2} and a 16 V electrical potential, in which case the phenol concentration dropped to 45.1% of the initial concentration.

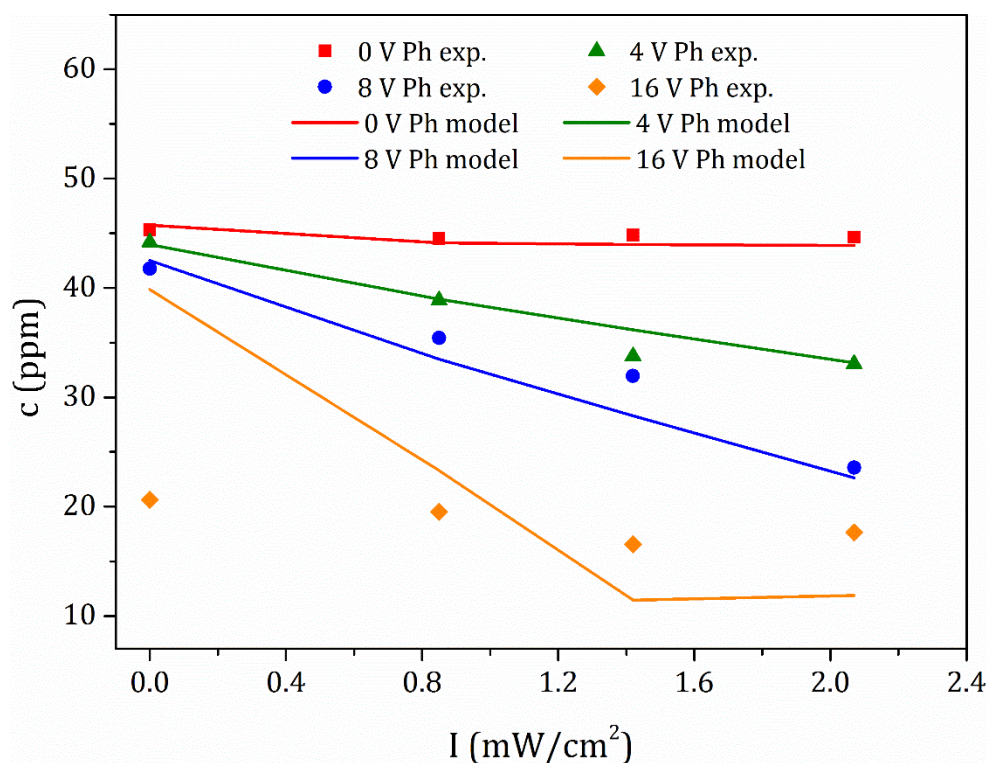


Figure 46: The effect of light intensity on phenol degradation at $200 \mu\text{L min}^{-1}$.

At 16 V it is clear that the light intensity did not have a substantial effect on the phenol degradation. The reason for this was the different reaction mechanism governing the process. The phenol was not only oxidized by the $\text{OH}^\bullet$, but also by the chlorine radicals. In order to verify this assumption, NaNO_3 was added to the phenol solution instead of NaCl . As shown in Figure 47 the change in the inorganic salt plays a significant role in the phenol degradation, which was especially visible at higher applied potentials and higher phenol-solution conductivities. With a high enough Cl^- ion concentration in the solution and a zero applied potential, chloride ions inhibit the phenol degradation (Figure 47b). By increasing the applied electrical potential, more and more chlorine radicals are generated, which contribute to the overall degradation. Water is also split into hydrogen and oxygen at 16 V, but the amount of released gases during degradation is extremely low.

The limiting current density for chlorine evolution is already achieved at the applied potential of 4 V. From this applied potential the NaCl exceeds the performance of the phenol degradation in comparison to NaNO_3 . This can be seen regardless of the NaCl concentration in the phenol solution.

The difference in the degradation rate between both cases, the addition of NaCl or NaNO_3 , is increasing with an increasing applied potential due to the presence of Cl^- ions, which generates additional radicals that further enhance the phenol degradation rate. The main role of the NaNO_3 addition is therefore only to increase the conductivity of the solution and enable the suppression of electron-hole pair recombination with the application of the external electrical potential. Up to a certain applied potential value, the phenol degradation rate is increasing due to the better separation of electron-hole pairs and, consequently, a greater $\text{OH}^\bullet$ generation. The use of NaNO_3 to adjust the solution's conductivity shows that the applied potential of 8 V is enough to suppress the recombination of the electrons and holes generated at a light intensity of app. 2.8 mW cm^{-2} (Figure 47b). All the additional degradation is attributed to the high oxidizing power of the chlorine radicals.

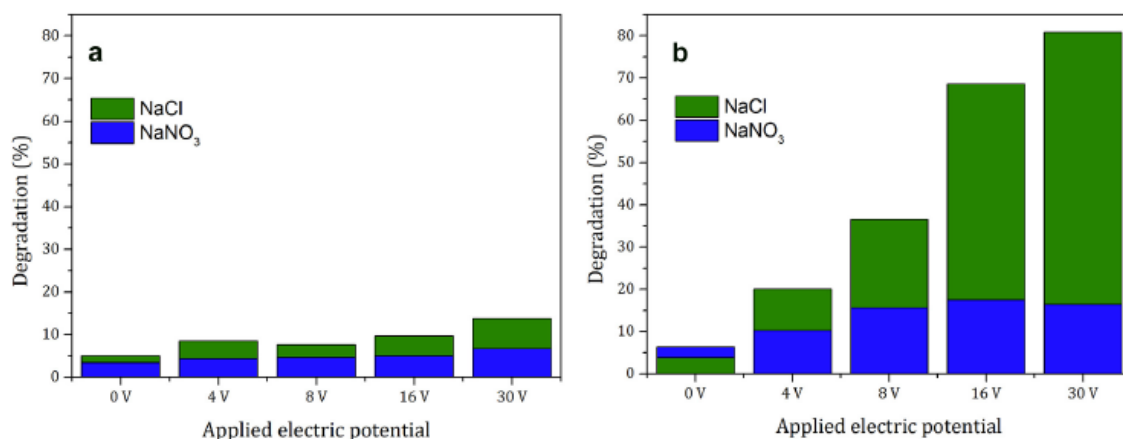


Figure 47: Photoelectrocatalytic degradation of phenol with an initial concentration of app. 46 mg L^{-1} at different applied electrical potentials, a light intensity of app. 2.8 mW cm^{-2} and at a phenol solution conductivity of (a) app. $230 \text{ }\mu\text{S cm}^{-1}$ and (b) app. 10.5 mS cm^{-1} . The phenol solution's conductivity was adjusted with NaCl or NaNO_3 and the flow rate was set to $200 \text{ }\mu\text{L min}^{-1}$ for both sets of experiments.

Figure 48 shows the concentration profiles of phenol and benzoquinone in Cartesian coordinates for the case of 0.85 mW cm^{-2} UV-light intensity, at 16 V and at a flow rate of $200 \text{ }\mu\text{L min}^{-1}$. The microchannel is divided into 10 planes along the axial direction. The reactions take place at the inner wall, and a nonhomogeneous concentration distribution can be observed at the planes due to the slow molecular diffusion, as opposed to the rate of the chemical reactions.

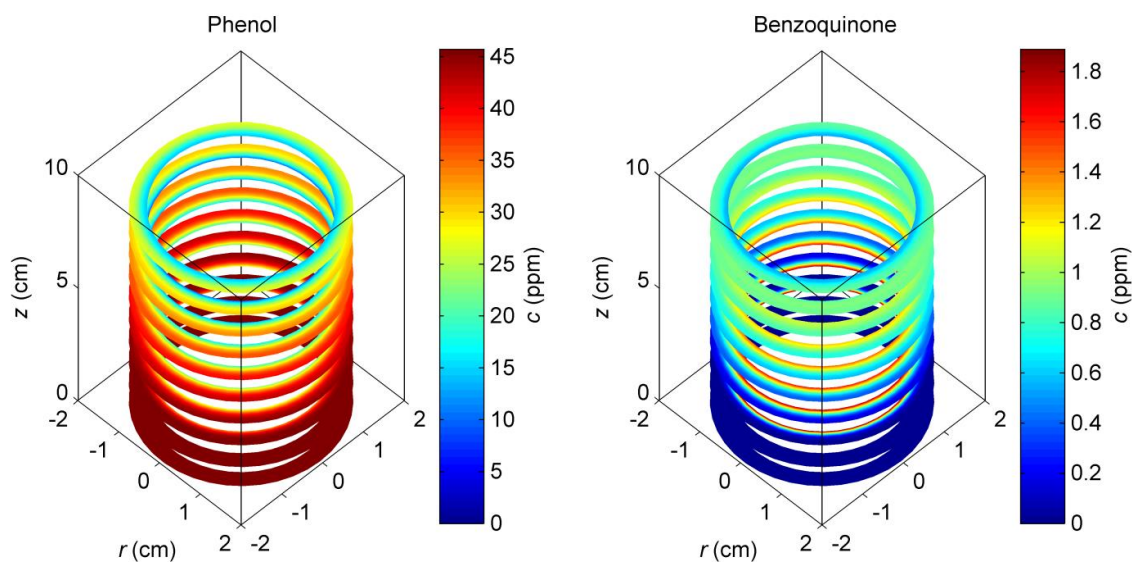


Figure 48: The concentration profiles of phenol and benzoquinone in Cartesian coordinates at 0.85 mW cm^{-2} , 16 V and $200 \text{ }\mu\text{L min}^{-1}$.

With photoelectrocatalysis, 100% degradation was readily achieved. The highest degradation rate of $26.76 \text{ ppm min}^{-1}$ was achieved at 16 V, 2.8 mW cm^{-2} , and $600 \text{ }\mu\text{L min}^{-1}$. The stability of the catalyst was monitored throughout the experimentation process. After 200 h of operation, there was no measurable lowering of the catalytic activity of the TiO_2 -nanotube catalyst.

4.4.2.5 Energy efficiency

During the reactor's operation, the energy consumption of the UV lights and the electrical power needed to apply the external electrical potential were monitored. Our results show that the electrical power consumed by the potentiostat to apply the electrical potential during the photoelectrocatalytic and electrocatalytic measurements is negligible compared to the power consumption for the UV lights. Namely, the power consumption for photocatalytic degradation at a light intensity of 1.4 mW cm^{-2} is 10.7 W, whereas for photoelectrocatalytic degradation at the same light intensity and an applied potential of 16 V it is 10.74 W. However, in the case of photocatalytic degradation some other purification treatment has to be applied afterwards in order to fully degrade the pollutant, or oxygen has to be continuously introduced into the microreactor. In the case of using electrocatalytic water purification alone, the electrical current densities used here are much lower than those normally used in such treatments [142]. When the potential of 16 V was applied, the current density was only 0.26 mA cm^{-2} . Such a current density was high enough to degrade all the 45.7 mg L^{-1} initial phenol concentration when photoelectrocatalytic degradation was used at a flow rate of $50 \text{ }\mu\text{L min}^{-1}$ and a light intensity of app. 2.8 mW cm^{-2} . Usually, a much lower bias is applied for photoelectrocatalysis [162], and some authors state that it is counterproductive to apply electrical potentials larger than 1.229 V because of the water electrolysis reaction [163]. However, our results showed that the application of the relatively low electrical potentials used for photoelectrocatalytic degradation is not only decisive for degradation completion but also negligible compared to the energy consumption needed to power the light-emitting-diode UV lights.

Chapter 5

Conclusions

The R&D work within present thesis was focused on the development of new, highly efficient, photo(electro)catalytic reactors that were used for degradation of model organic compounds. Since TiO₂ nanotube arrays obtained by anodic oxidation process were used as an active photocatalyst material, a systematic study of anodic oxidation process was carried out in order to determine the optimum anodization parameters and annealing conditions to synthesize a highly active TiO₂ photocatalyst. The anodic oxidation process produces a firmly adhered/bounded photoactive material with a metallic titanium substrate which is one of the most important advantages of the anodic oxidation process compared to other procedures that are used for preparation of TiO₂ films on substrates. This is why anodic oxidation is a very promising process for successful and cost-effective industrial applications to produce TiO₂ films on a substrate. Moreover, the anodic oxidation process enables precise control of TiO₂ nanotubes morphology regardless of the choice of the titanium starting form (coil, foil, mesh).

Self-ordered, vertically aligned, TiO₂ nanotubes were grown on a titanium foil by the anodic oxidation process in a viscous organic electrolyte (ethylene glycol). It was found out that the length of TiO₂ nanotubes as well as annealing temperature had a great effect on the photocatalytic activity of the TiO₂ nanotube films. Our results showed that longer TiO₂ nanotubes (app. 40 μm), regardless of the form of the supporting titanium (coils, foils), exhibited better photocatalytic activities compared to shorter TiO₂ nanotubes. Crystallization of amorphous TiO₂ nanotubes after anodization was readily achieved at 450 °C for 1 hour with heating and cooling rates of 5 °C min⁻¹. After annealing fully crystallized TiO₂ nanotubes were obtained with the anatase crystal structure.

The results of systematic investigation of the anodic oxidation process of various metal titanium forms enabled us to design and assemble a new type of a continuous-flow photo(electro)catalytic reactor. The so-called coil-type microreactor was made of anodized titanium coils and was tested for the degradation of caffeine and phenol. The photocatalytic, electrocatalytic, and photoelectrocatalytic degradation of the caffeine was systematically studied under different conditions. It was found that the highest efficiency of the microreactor was obtained when the photoelectrocatalytic process was used for the caffeine's degradation. The best results were obtained for an anodic bias potential of 4 V and with two cathodes placed on each side of the active photoanode (configuration d in Figure 18). The most suitable cathode material was determined to be titanium.

After successful testing of a coil-type microreactor with a single photoactive unit, a scaled-up version of a microreactor with eight active units was assembled in order to increase the flow rate of the microreactor. Due to specific design of a microreactor, scaling-up process turned out to be relatively simple. Larger, scaled-up version of the TiO₂-nanotubes-based, coil-type, photoelectrocatalytic microreactor with one 64 mm-long photocatalytically active unit was used to study the photocatalytic, electrocatalytic, and

photoelectrocatalytic degradation of phenol. The results were used to describe the reaction mechanisms and governing phenomena occurring inside the microreactor with the help of a three-dimensional mathematical model. It was determined that the photocatalytic reaction stops due to the increased electron-hole recombination resulting from an oxygen deficiency. The role of the dissolved oxygen is to react with the photo-generated electrons and therefore enables the holes to react with the water molecules and generate $\text{OH}\cdot$. Our model showed that one reacted O_2 results in one $\text{OH}\cdot$ which is produced from H_2O at the positive hole. In the case of electrocatalytic degradation, there is a huge increase in the degradation rate for external applied potentials higher than 8 V. The reason for such behavior is the high oxidative power of the chlorine radicals that were present because NaCl was used to regulate the phenol solution conductivity. The oxygen-depletion issue was remedied in a photoelectrocatalytic process as the electron-hole recombination was suppressed by the externally applied potential. Only the photoelectrocatalytic degradation completely degraded the phenol. The limiting factor influencing the conversion rate of the photoelectrocatalytic process was the slow diffusion transport of the species to the catalytic wall. Therefore, the most important augmentation of the studied microreactor would be the utilization of a narrower microchannel, which would accelerate the overall phenol degradation process.

Our results of the degradation of caffeine and phenol clearly showed the advantages of the photoelectrocatalytic process over the photocatalytic and/or electrocatalytic process. The results of the photoelectrocatalytic degradation showed a strong synergistic effect between the photocatalytic and electrocatalytic processes. It can be concluded that photoelectrocatalysis can assure a significantly faster degradation process that can be applied for the degradation of a variety of organic compounds that are not easily oxidized otherwise.

Appendix A

Mathematical Model for Photo(electro)degradation

A.1 Finite Difference Scheme

The explicit finite difference scheme for the solution of the partial differential mass balance equations is presented below. The indexes (inside the brackets) are represented with the same letter as the corresponding spatial dimension. NR is the index at the non-catalytic wall.

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= -\nu(r) \frac{\partial c_i}{\partial x} + D_i \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} \right) \rightarrow \\ c_i(x, r, t + 1) &= c_i(x, r, t) \\ &+ dt \left(-\nu(r) \frac{c_i(x, r, t) - c_i(x - 1, r, t)}{\Delta x} \right. \\ &\left. + D_i \left(\frac{c_i(x + 1, r, t) - 2c_i(x, r, t) + c_i(x - 1, r, t)}{\Delta x^2} \right. \right. \\ &\left. \left. + \frac{c_i(x, r + 1, t) - 2c_i(x, r, t) + c_i(x, r - 1, t)}{\Delta r^2} \right. \right. \\ &\left. \left. + \frac{1}{r} \frac{c_i(x, r + 1, t) - c_i(x, r, t)}{\Delta r} \right) \right) \end{aligned}$$

The boundary conditions at the catalytic wall:

$$-D_i \frac{dc_i}{dr} = -\sum r_i \rightarrow c_i(x, 1, t) = c_i(x, 2, t) - \frac{\Delta r}{D_i} \sum r_i$$

$$\frac{dc_{\text{OH}\bullet}}{dt} = -\sum r_i \rightarrow c_{\text{OH}\bullet}(x, 1, t + 1) = c_{\text{OH}\bullet}(x, 1, t) - \Delta t \sum r_i$$

The boundary conditions at the non-catalytic wall:

$$-D_i \frac{dc_i}{dr} = 0 \rightarrow c_i(x, N_R, t) = c_i(x, N_R - 1, t)$$

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Biography

The author of this thesis, Luka Suhadolnik, was born on February 27th, 1989 in Ljubljana, Slovenia. After graduating from Gymnasium Ledina in 2008 he enrolled the bachelor study at the University of Ljubljana, Faculty of Natural and Technical Sciences at the Department of Materials and Metallurgy. He defended his bachelor thesis in 2013 entitled: “Optimization of TiO₂ nanotubes based dye-sensitized solar cells” and was awarded the title Bachelor of Materials Science and Metallurgy.

In 2014, he enrolled into the Jožef Stefan International Postgraduate School, Nanosciences and Nanotechnologies programme. The topic of his research was design and development of TiO₂ nanotubes based photo(electro)catalytic reactors for water and air purification. From October 2015 to May 2016 he spent eight months at Francisco Zaera Surface Group, Department of Chemistry, University of California, Riverside, United States, where he worked on the synthesis of yolk-shell heterogeneous tandem catalyst under the supervision of Distinguished Prof. Francisco Zaera. In 2016, he was awarded the third price in the young researchers’ oral presentation competition at the 24th International Conference on Materials and Technology in Portorož, Slovenia. In the same year he presented his work at the Science Slam and was invited to hold a scientific presentation of his work at the Slovenian National TV. During his PhD studies he collaborated with different industrial partners and was awarded the Climate-KIC accelerator programme in 2016 and 2017. In the framework of Climate-KIC accelerators he promoted both the business and technological part of his technology which was possible due to the Climate-KIC extensive international network, education, coaching, and financial support. In 2017, he won the first prize for his inventive/innovative project entitled NanoAirPur: Nanotubes-based Air Purification System at the 10th International Technology Transfer Conference in Ljubljana, Slovenia. His scientific papers were cited more than 35 times and he has filed two patent applications.