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# Photocatalytic core/shell nanocomposites prepared by atomic layer deposition

## PhD thesis summary

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## 1. Introduction

Nowadays, in nanotechnology, a more and more prominent method is atomic layer deposition (ALD), a vapor phase chemical technique for the preparation of thin films. With ALD, it is possible to form coatings with precisely adjustable composition and thickness. During my PhD work, I synthesized core/shell nanocomposites by ALD and studied their usability in photocatalytic test reactions. In the case of composites, the substrate has a significant effect on the specific surface and morphology, as well as the chemical properties. For photocatalysis tests, one of the goals for me was to examine the properties of ALD layers in themselves. Based on this, I have chosen carriers for the depositions where no charge separation is possible between the core material and the coating. One of the most studied ALD coatings is crystalline  $\text{TiO}_2$ <sup>1</sup>. Amorphous  $\text{TiO}_2$  so far has only been used a few times and has always been grown on a highly nanostructured surface (e.g. lotus leaves<sup>2</sup>, fullerene<sup>3</sup>). During my work I synthesized nanoparticles and nanotubes in which the ALD layer consisted of amorphous and crystalline  $\text{TiO}_2$  with the same dimension and morphology. The properties of these have been compared to each other.

As I have described, in photocatalysis charge separation between different semiconductor layers can be used to increase the efficiency of the catalyst. When such nanocomposites are prepared, the outer layer usually consists of  $\text{TiO}_2$ . There are few examples in the literature in which  $\text{TiO}_2$  is used as a core. Thus, my goals included examining nanocomposites in which I grow  $\text{TiO}_2$  on a photocatalytically active semiconductor ( $\text{ZnO}$ ), and then use  $\text{TiO}_2$  as the substrate for the deposition of the other semiconductor ( $\text{ZnO}$ ). Here I studied the effect of changing up the material of the core and the coating on the properties of the composite.

In order to achieve my goals, I first synthesized core/shell  $\text{SiO}_2/\text{TiO}_2$ ,  $\text{SiO}_2/\text{ZnO}$  and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  nanoparticles and a poly(methyl-methacrylate) (PMMA)/ $\text{TiO}_2$  nanocomposite with ALD. The  $\text{TiO}_2$  layer was also grown by sol-gel method on  $\text{SiO}_2$  to be able to compare the two different techniques. Poly(vinyl-alcohol) and poly(vinyl-pyrrolidone) were then coated with  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  with ALD. From the composites, the polymer core was later removed to create amorphous and crystalline metal-oxide nanotubes. Finally, onto  $\text{TiO}_2$  nanofibers, I deposited  $\text{ZnO}$  and  $\text{TiO}_2$  onto  $\text{ZnO}$  fibers with ALD.

(1) Niemelä et al. Titanium Dioxide Thin Films by Atomic Layer Deposition: A Review. *Semicond. Sci. Technol.* 2017, 32 (9), 1–71. <https://doi.org/10.1088/1361-6641/aa78ce>.

(2) Justh et al. Photocatalytic  $\text{C}_{60}$ -Amorphous  $\text{TiO}_2$  Composites Prepared by Atomic Layer Deposition. *Appl. Surf. Sci.* 2017, 419, 497–502. <https://doi.org/10.1016/j.apsusc.2017.04.243>.

(3) Szilágyi et al. Photocatalytic Properties of  $\text{WO}_3/\text{TiO}_2$  Core/Shell Nanofibers Prepared by Electrospinning and Atomic Layer Deposition. *Chem. Vap. Depos.* 2013, 19 (4–6), 149–155. <https://doi.org/10.1002/cvde.201207037>.

## 2. Literature background

Due to the continuous advancement of nanotechnology many methods have been developed to produce a wide variety of nanoparticles. Depending on the raw materials and the manner of synthesis, various nanomaterials can be formed with different physicochemical, structural and morphological properties. They can also be used in diverse applications, eg. electronics, optoelectronics, optics, electrochemistry, environmental protection and biomedicine. Since different physical and chemical properties are advantageous for different applications, it is important that we can accurately control the properties of the nanocomposite formed during the synthesis. This can be accomplished by selecting the appropriate production method or by combining several techniques<sup>4</sup>.

There are two approaches to synthesizing nanoscale materials. The first is the so-called "top-down" approach, where the raw material is produced by breaking down the nanoparticles into fine, nanometer sized ones. The other is "bottom-up", where the desired nanoparticles are built from atoms or molecules<sup>4</sup>. With bottom-up methods, if multiple steps are used, core/shell structure nanomaterials can be developed. In core/shell composites, the core may have two roles: (1) its role is only in the construction of the appropriate structure, e.g. by selecting polymer fibers of different thickness, the specific surface area can be affected by the substrate; (2) the core material also affects the properties, e.g. in photocatalysts by choosing a semiconductor oxide for the core and the coating as well, charge separation is possible, which increases photocatalytic efficiency<sup>5</sup>.

A method for forming a core/shell nanocomposite is atomic layer deposition (ALD)<sup>6</sup>. Due to the size reduction of devices used in the semiconductor industry there is a growing demand for thin and flawless coatings on a variety of substrates, which has contributed to the increase in the popularity of ALD. ALD is a technique that can meet the above-mentioned expectations with nanometer accuracy even on highly nanostructured surfaces. During ALD depositions, the volatile reagents and precursors are alternately pulsed into the reactor, where they are chemisorbed onto the surface of the template

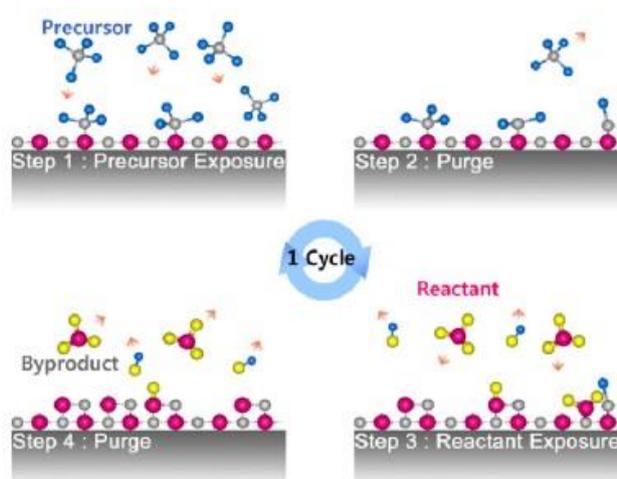


Figure 1.: ALD cycle<sup>6</sup>

(4) Gleiter, H. Nanostructured Materials: Basic Concepts and Microstructure. *Acta Mater.* 2000, 48 (2000), 1–29. [https://doi.org/10.1016/S1359-6454\(99\)00285-2](https://doi.org/10.1016/S1359-6454(99)00285-2)

(5) Szilágyi, et al. Photocatalytic Properties of WO<sub>3</sub>/TiO<sub>2</sub> Core/Shell Nanofibers prepared by Electrospinning and Atomic Layer Deposition. *Chem. Vap. Dep.* 2013, 19 (4-6), 149-155. <https://doi.org/10.1002/cvde.201207037>.

(6) Kim, et al. Applications of Atomic Layer Deposition to Nanofabrication and Emerging Nanodevices. *Thin Solid Films* 2009, 517 (8), 2563–2580. <https://doi.org/10.1016/j.tsf.2008.09.007>.

and react with each other, the by-products are removed by inert gas purging (Figure 1). Thus, the film by built atomic or molecular layers<sup>6,7</sup>.

TiO<sub>2</sub> is one of the most widely researched materials in the field of atomic layer deposition, and it is used in many different applications: e.g. making biocompatible or superhydrophobic coatings, producing photonic crystals, photocatalysis, etc. TiO<sub>2</sub> can be prepared from a variety of precursors. Titanium-containing precursors can be divided into four major groups: halides, alkoxides, alkylamides and heteroleptic precursors. Frequently used reagents are TiCl<sub>4</sub> and Ti(OiPr)<sub>4</sub> (TTIP). ALD can also produce amorphous and crystalline TiO<sub>2</sub>, which is dependent on the deposition temperature<sup>1</sup>.

A popular application of TiO<sub>2</sub> is heterogeneous photocatalysis<sup>8,9</sup>. Photocatalysis is defined as the acceleration of a chemical reaction either directly by light or by illumination of a catalyst which reduces the activation energy of the reaction. The semiconductors, due to their electron structure (filled valence band and empty conduction band), are excellent for these light induced redox processes. When a photon reaches the surface of the semiconductor (Figure 2.),

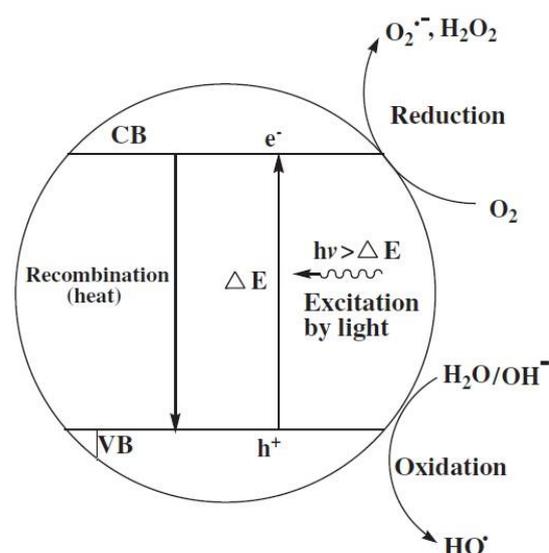


Figure 2.: Mechanism of semiconductor photocatalysis whose energy ( $h\nu$ ) is equal to the energy difference ( $\Delta E$ ) corresponding to the bandgap or exceeds it, an electron ( $e^-$ ) from the valence band (VB) of the semiconductor is excited to the conduction band (CB), leaving behind a hole ( $h^+$ ). Conduction band electrons are strong reducing agents and the holes in the valence band are strong oxidizing agents. The photodegradation reaction of most organic materials utilizes the strong oxidizing effect of the holes. It has already been shown, that a wide range of compounds (e.g., alcohols, carboxylic acids, phenols, organic dyes, simple aromatic compounds) are degradable by photocatalysis. The efficiency of the degradation of the compounds is essentially determined by the composition, structure and specific surface area of the catalyst. With ALD, these parameters can be easily tuned, so this process can be applied to the development of photocatalysts.

(7) Johnson et al. A Brief Review of Atomic Layer Deposition: From Fundamentals to Application. *Mat. Today*. 2014, 17 (5), 236-246. <https://doi.org/10.1016/j.mattod.2014.04.026>.

(8) Hashimoto et al. A. TiO<sub>2</sub> Photocatalysis: A Historical Overview and Future Prospects. *Jpn. J. Appl. Phys.* 2005, 44 (12), 8269–8285. <https://doi.org/10.1143/JJAP.44.8269>.

(9) Pattanaik et al. TiO<sub>2</sub> Photocatalysis: Progress from Fundamentals to Modification Technology. *Desalin. Water Treat.* 2014, 52 (34–36), 6567–6590. <https://doi.org/10.1080/19443994.2013.822187>.

### 3. Experimental methods

First, SiO<sub>2</sub> was prepared by sol-gel method from tetraethyl-orthosilicate (TEOS) and PMMA by emulsion polymerization from methyl-methacrylate monomer. The nanoparticles were coated by ALD with TiO<sub>2</sub>. TiO<sub>2</sub> was grown from titanium-tetraiopropoxide (TTIP) and water reagents in 250 cycles at 80 °C and 300° C. Al<sub>2</sub>O<sub>3</sub> and ZnO were also deposited at 80 °C and 250 °C onto SiO<sub>2</sub>. Al<sub>2</sub>O<sub>3</sub> was prepared from trimethyl-aluminum, ZnO from diethyl-zinc and water precursors in 100 cycles. In the ALD cycles, the precursor/purge time was 0.5 s/15 s in each case. SiO<sub>2</sub> was also coated with a TiO<sub>2</sub> layer by sol-gel method, tetra-n-butyl-orthotitanate was used to prepare the TiO<sub>2</sub> sol. 50 mg of the SiO<sub>2</sub> was stirred (50 °C, 5 hours) in 10 ml of the TiO<sub>2</sub> sol to coat the particles, and then the excess sol was removed by centrifugation. The sample was dried at room temperature. The samples were finally subjected to heat treatment at 450 ° C.

I also produced core/shell nanofibers using poly(vinyl-alcohol) (PVA) and poly(vinyl-pyrrolidone) (PVP) fibers, that were electrospun from aqueous solutions. These were coated with Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> by ALD at 50 °C. For the Al<sub>2</sub>O<sub>3</sub>, the precursors used were trimethyl-aluminum and water. In the ALD cycle, the precursor/purge time was 0.15 s/0.5 s and 100 cycles were used. Titanium-tetrachloride and water precursors were used for the TiO<sub>2</sub> layer. In the ALD cycle, the precursor/purge time was 0.2 s/3 s. The TiO<sub>2</sub> layer was grown in 1400 ALD cycles. From the polymer/metal oxide nanocomposites, in one case the core was dissolved in 60 °C water and in the other removed by heating at 550 °C (in air) to form metal oxide nanotubes.

Finally, I synthesized the PVP/TTIP and PVP /zinc acetate fibers by electrospinning and then I prepared TiO<sub>2</sub> and ZnO nanofibres by annealing the composites (550 °C, air). TiO<sub>2</sub> fibers were coated by ALD with ZnO at 200 °C in 25 cycles using diethyl-zinc and water precursors. In the ALD cycle, the precursor/purge time was 1 s/30 s. Onto the ZnO fibers the TiO<sub>2</sub> layer was grown at 300 ° C in 130 cycles from TTIP and water reagents. The ALD cycle was consistent with that used in the ZnO deposition.

The structure and morphology of the pure carriers and nanocomposites were studied by FT-IR, ATR-IR, Raman, SEM, HR-SEM and TEM measurements. The composition was investigated by EDX, the crystalline phases by XRD and ED and the thermal properties by TG/DTA-MS. The specific surface area was determined by the evaluation of N<sub>2</sub> adsorption isotherms. Photocatalytic activity was measured in quartz cuvettes using 1 mg of catalyst to degrade 0.04mM methyl orange dye (MO) under UV light irradiation. The photocatalytic reactions were followed by UV-Vis spectroscopy.

## 4. Results

### 4.1. Core/shell SiO<sub>2</sub>/metal-oxide and PMMA/TiO<sub>2</sub> nanocomposites

During my work, first I prepared two types of substrate particles for ALD that did not interact with the TiO<sub>2</sub> coating during photocatalytic reactions. Spherical SiO<sub>2</sub> with a diameter of 100-150 nm was synthesized by sol-gel method and 50-70 nm poly(methyl-methacrylate) (PMMA) nanoparticles by emulsion polymerization. Based on XRD measurements, both materials were amorphous. Before the particles were coated, some tests were carried out to select the appropriate ALD deposition temperatures. Onto the PMMA only TiO<sub>2</sub> was grown at 80 °C, owing to that I had to work under its glass transition and softening point. After the growth of the film, the presence of all the oxides (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO) was confirmed by EDX measurement in each sample. Based on the recorded XRD diffractograms the TiO<sub>2</sub> grown at 80 °C onto the PMMA and SiO<sub>2</sub> was amorphous and at 300 °C it was crystalline (anatase). The Al<sub>2</sub>O<sub>3</sub> coating on the SiO<sub>2</sub> was amorphous and the ZnO was crystalline (zinc) at both temperatures (80 and 250 °C). Based on the TEM images (Fig. 3/a-d.) the composites containing SiO<sub>2</sub> all had a core/shell structure, the coating was about 20 nm thick after the deposition of all three oxides. In the case of the PMMA/TiO<sub>2</sub> (Fig. 4/a-c.) no core/shell structure was formed, the polymer softened during the ALD, even though I worked at the lowest possible temperature and a porous nanocomposite was created.

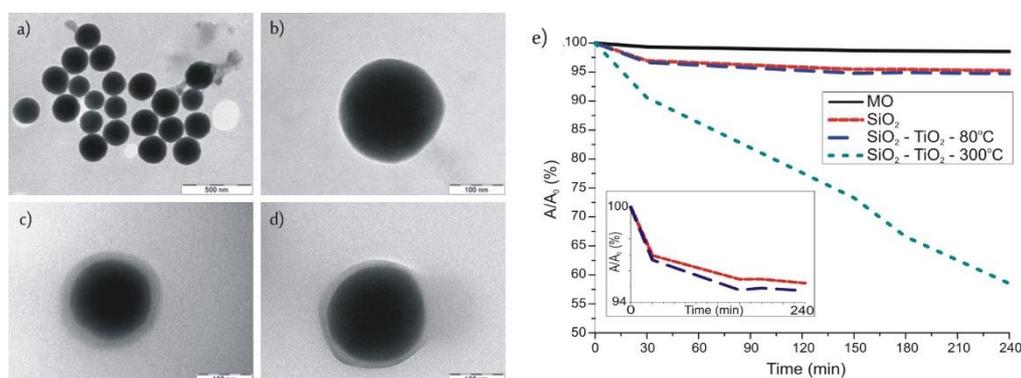


Figure 3.: TEM images of a-b) SiO<sub>2</sub>, c) SiO<sub>2</sub>/TiO<sub>2</sub> - 80 °C, d) SiO<sub>2</sub>/TiO<sub>2</sub> - 300 °C and e) the photocatalytic activity of the SiO<sub>2</sub>/TiO<sub>2</sub> nanocomposites

To investigate the photocatalytic efficiency of the samples I studied the degradation of methyl orange (MO) dye under UV light irradiation. The results obtained for the reference Al<sub>2</sub>O<sub>3</sub> and ZnO layers corresponded with the expectations: while Al<sub>2</sub>O<sub>3</sub> did not decompose the dye, the crystalline ZnO showed good activity, the conversion was close to 50 %. I have also grown amorphous and crystalline TiO<sub>2</sub> layers onto the SiO<sub>2</sub> and was the first to compare their properties to each other. The crystalline TiO<sub>2</sub> coating decomposed more than 40% of the methyl orange, the efficiency of the composite was 2.5 times higher than that of the reference

P25 TiO<sub>2</sub>. In addition, a small effect was clearly observable in the case of the amorphous TiO<sub>2</sub> coating (on SiO<sub>2</sub> and PMMA) as well. The degree of decomposition has increased compared to the photolysis and to when the clear substrates were used (Fig. 3/e. and 4/d.).

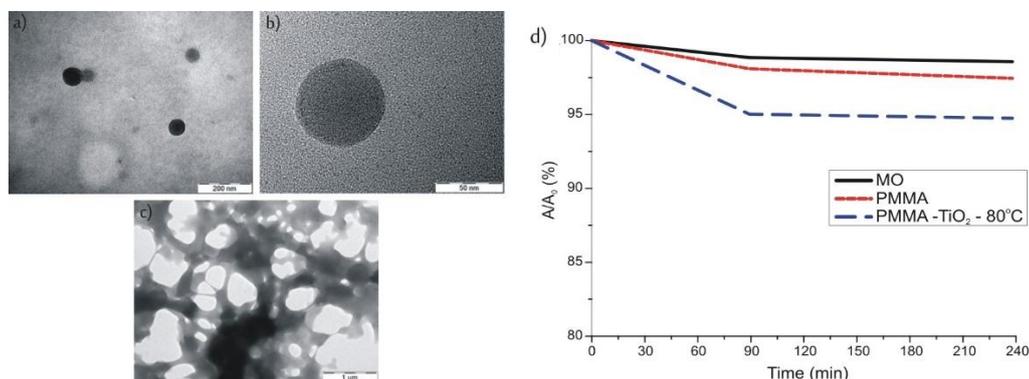


Figure 4.: TEM images of a-b) PMMA, c) PMMA/TiO<sub>2</sub> - 80 °C és d) the photocatalytic activity of the PMMA/TiO<sub>2</sub> nanocomposite

The SiO<sub>2</sub> nanoparticles were also coated with TiO<sub>2</sub> by sol-gel method to be able to compare the ALD coating with a thin layer produced by another method. SiO<sub>2</sub>/TiO<sub>2</sub> samples either just centrifuged or heat-treated after centrifugation contained nearly the same amount of TiO<sub>2</sub> as the sample prepared by ALD (~10 m/m%). The thickness of the layer was about 20-30 nm (Fig. 5/a-d.). Based on the XRD diffractograms, the TiO<sub>2</sub> was slightly crystalline even before the heat treatment, and after the annealing highly crystalline anatase layer was formed. I found that the ALD prepared sample had a higher photocatalytic activity; the conversion was almost twice as high as in the case of the sol-gel sample (Fig. 5/e.). This can be explained by the high temperature (450 °C) heat-treatment that is needed to create a crystalline layer after the sol-gel synthesis. This temperature is much higher than the one used for the ALD reactions (300 °C), thus the sintering of the particles is higher in the sol-gel sample. This significantly reduces the useful specific surface area, and the photocatalytic activity of the sample.

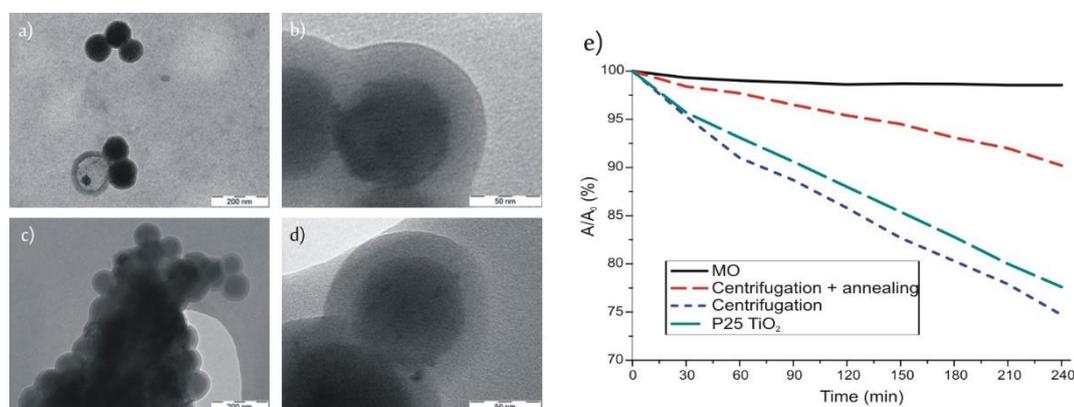


Figure 5.: TEM images of the sol-gel a-b) SiO<sub>2</sub>/TiO<sub>2</sub> (centrifugation), c-d) SiO<sub>2</sub>/TiO<sub>2</sub> (centrifugation and heat-treatment) and e) the photocatalytic activity of the sol-gel SiO<sub>2</sub>/TiO<sub>2</sub> nanocomposites

#### 4.2. Core/shell polymer/metal-oxide nanofibers and metal-oxide nanotubes

I prepared polymer/metal-oxide nanocomposites that contained polymer fibers synthesized by electrospinning. In these, the polymer core was poly(vinyl alcohol) (PVA) with a diameter of 200-300 nm and 500-700 nm polyvinylpyrrolidone (PVP). The polymer nanofibers were first coated with ALD  $\text{Al}_2\text{O}_3$  at a low temperature (50 °C). Based on TEM measurements, the fibrous structure was maintained after the deposition, the polymers did not soften during the ALD reactions. From these composites, the polymer core was successfully removed by two different methods: dissolution and annealing. This enabled me to create  $\text{Al}_2\text{O}_3$  nanotubes with a wall thickness of 50 nm. The structure of the tubes was not damaged during either dissolution or annealing. 100 nm thick  $\text{TiO}_2$  film was also grown from  $\text{TiCl}_4$  precursor onto the polymers at 50 °C. The polymer core was again removed from PVA/ $\text{TiO}_2$  and PVP/ $\text{TiO}_2$  nanocomposites. Based on XRD and TEM measurements, by the dissolution in 60 °C distilled water amorphous and by annealing at 550 °C crystalline, anatase  $\text{TiO}_2$  nanotubes (Fig. 6/a-d.) were successfully prepared.

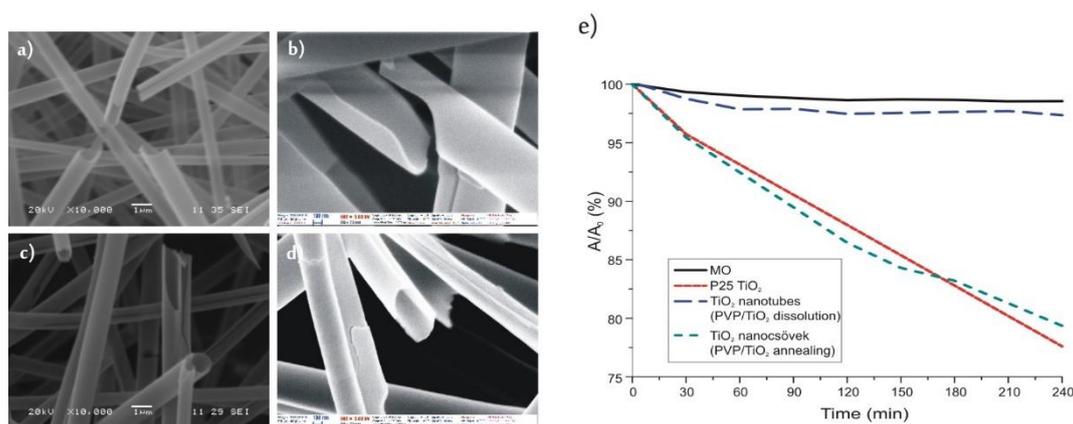


Figure 6.: TEM images of the  $\text{TiO}_2$  nanotubes prepared from the PVP/ $\text{TiO}_2$  composite by a-b) dissolution, c-d) annealing and e) the photocatalytic activity of the  $\text{TiO}_2$  nanotubes

The photocatalytic properties of amorphous and crystalline  $\text{TiO}_2$  nanotubes with the same dimension and morphology were compared to each other and as reference to P25  $\text{TiO}_2$ . The highest amount of dye (20 %) was degraded by the anatase  $\text{TiO}_2$  nanotubes made from the composite containing PVP, it showed similar activity to the P25  $\text{TiO}_2$ . The amorphous  $\text{TiO}_2$  nanotubes prepared from PVP/ $\text{TiO}_2$  core/shell fibers had a small, but clearly detectable effect in decomposing the methyl orange (Fig. 6/e.). The photocatalytic effect of amorphous  $\text{TiO}_2$  was thus found in both  $\text{SiO}_2/\text{TiO}_2$ , PMMA/ $\text{TiO}_2$  composites and  $\text{TiO}_2$  nanotubes. This phenomenon could have three explanations: (1) some residue remains in the  $\text{TiO}_2$  layer from the precursor used in the ALD depositions, (2) there are nanocrystalline domains in the sample, or (3) the substrate interacts with the coating during the photocatalytic reactions. In the synthesis of  $\text{SiO}_2/\text{TiO}_2$  and PMMA/ $\text{TiO}_2$  nanocomposites, I used a TTIP precursor, which could leave small

amounts of carbon contamination in the TiO<sub>2</sub>, but this was not the case with the TiCl<sub>4</sub> precursor used for TiO<sub>2</sub> nanotubes. In addition, no crystalline part was detected in the samples either on the XRD diffractograms or on the electron diffraction patterns investigated during the TEM measurements. Amorphous SiO<sub>2</sub> and PMMA have no effect on photocatalytic reactions and for the TiO<sub>2</sub> nanotubes there is no substrate, so it cannot influence the photocatalysis. Therefore it is difficult to give a clear explanation, and an extensive computational chemical study would help in interpreting these results, but it is beyond the scope of the present work.

#### 4.3. Core/shell metal-oxide/metal-oxide nanofibers

Finally, I have synthesized core/shell nanofibers in which both the core and coating consisted of photocatalytically active metal-oxides. The PVP/TTIP and PVP/ZnAc nanofibers were formed by electrospinning, and by annealing them pure metal-oxide nanofibers could be prepared. In the case of PVP/TTIP nanofibers, the heat-treatment determines the formation of the crystalline phases, therefore the thermal decomposition of these fibers has been examined in detail. The TTIP-containing composite was heated in an inert (nitrogen) and oxidative (air) atmosphere in a TG/DTA device and the evolved gases were analyzed by mass spectrometry. Evolved gas analysis of PVP/TTIP nanocomposites prepared by electrospinning has not been performed in the literature so far. I found that at 550 °C anatase and at 900 °C mostly rutile TiO<sub>2</sub> nanofibers are formed. In addition, using Raman measurements (Fig. 7.), I also discovered that when nitrogen atmosphere was used, the sample contained a small amount of carbon residue left over from the polymer. Doping TiO<sub>2</sub> with carbon can extend light absorption to the visible range. Thus by annealing the sample in inert atmosphere, the carbon content is easily adjustable, and it can be useful in photocatalysis.

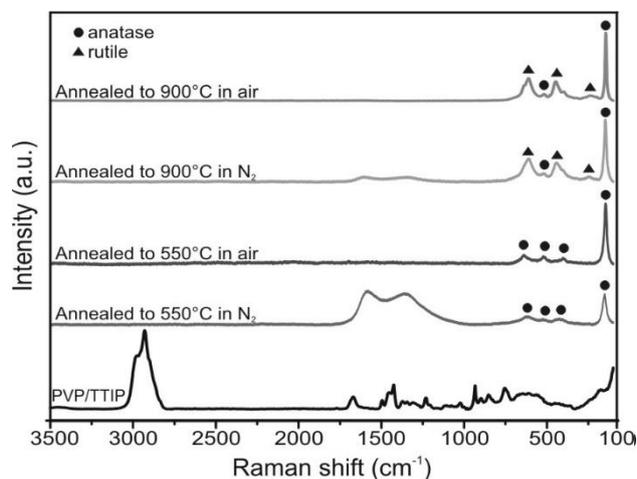


Figure 7.: Raman spectra of the TiO<sub>2</sub> nanofibers prepared by annealing

After the thermal studies, for the preparation of the TiO<sub>2</sub> nanofibers that were used in the ALD deposition s, I selected the 550 °C annealing in air atmosphere, since previously I mostly investigated samples containing anatase TiO<sub>2</sub>. ZnO fibers were also synthesized using 550 °C annealing temperature. For both metal oxide fibers, a low heating rate of 1 °C/min was chosen to avoid damaging the structure. The as-prepared TiO<sub>2</sub> and ZnO fibers had a diameter of about

200-300 nm. TiO<sub>2</sub> fibers were coated at 200 ° C by ALD with an 8-10 nm thick crystalline ZnO layer and ZnO was covered with a 2-3 nm thick crystalline TiO<sub>2</sub> film at 300 ° C (Figure 8/c-d.).

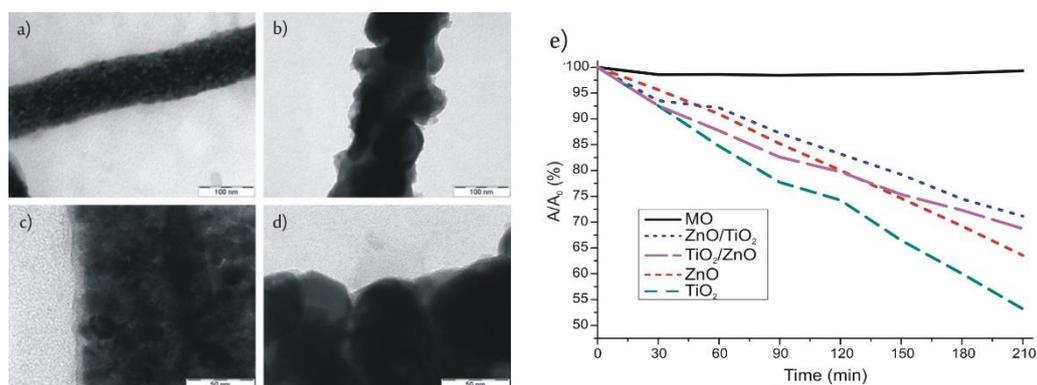


Figure 8.: TEM images of the a) TiO<sub>2</sub>, b) ZnO, c) TiO<sub>2</sub>/ZnO, d) ZnO/TiO<sub>2</sub> nanofibers and e) the photocatalytic activity of all the samples

In the photocatalytic test reactions, the pure metal-oxide nanofibres decomposed 10-15% more dye than metal-oxide/metal-oxide composite fibers. The highest conversion (47%) was obtained for the TiO<sub>2</sub> nanofibers (Fig. 8/e.). Based on the TEM images, this can be explained by the fact that the surface of the TiO<sub>2</sub> and ZnO fibers both of which consisted of smaller nanoparticles was coated with a smooth, uniform ALD layer, and it has reduced the specific surface area and thus the photocatalytic activity. In the case of the core/shell nanofibers, the composite in which TiO<sub>2</sub> was the core and the ZnO was the shell material showed higher activity. All four samples that were prepared decomposed 30-50% of the methyl orange, which was higher than the conversion achieved with the reference P25 TiO<sub>2</sub> (Figure 8/e.).

## 5. Application

The photocatalytic effect of semiconductor materials and nanocomposites containing them was tested in many field: water and air purification is in the first place<sup>10</sup>, but they have also been shown to be useful in destroying microorganisms, decomposing organic pollutants, or even in the preparation of self-cleaning surfaces<sup>11</sup>. The efficiency of the photocatalysis depends on many of its properties. In atomic layer deposition by selecting the appropriate substrate a high specific surface can be achieved, also the thickness and composition of the coating can be precisely controlled by adjusting the precursor pulses, and the crystallinity can be influenced by the deposition temperature. For this reason, ALD is an excellent method for the preparation of photocatalysts, and in my work, I have also shown that ALD also allows the use of heat-sensitive substrates that are accessible at a relatively low cost.

(10) Baruah, et al, K. Perspectives and Applications of Nanotechnology in Water Treatment. Environ. Chem. Lett. 2016, 14 (1), 1–14. <https://doi.org/10.1007/s10311-015-0542-2>.

(11) Hoffmann et al. Environmental Applications of Semiconductor Photocatalysis. Chem. Rev. 1995, 95 (1), 69–96. <https://doi.org/10.1021/cr00033a004>

## 6. Thesis statements

1. Using SiO<sub>2</sub> substrate prepared by the sol-gel method, I synthesized core/shell structured SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>/ZnO and SiO<sub>2</sub>/TiO<sub>2</sub> nanoparticles by atomic layer deposition (ALD) and investigated their possible application in photocatalysis. I was the first to compare the photocatalytic activity of core/shell nanoparticles that contained equivalent thick outer amorphous or crystalline TiO<sub>2</sub> layers. I have shown that under the given conditions greater conversion can be achieved with the SiO<sub>2</sub>/anatase TiO<sub>2</sub> and SiO<sub>2</sub>/zincite ZnO composites in the degradation of methyl orange dye than with the reference P25 TiO<sub>2</sub>. These nanocomposites may therefore be useful in the development of photocatalysts. In addition, I have also demonstrated that the amorphous TiO<sub>2</sub>, deposited by ALD onto SiO<sub>2</sub> and onto poly(methyl-methacrylate) (PMMA) synthesized by emulsion polymerization, also has a small, but detectable photocatalytic activity. [4.]
2. I compared the photocatalytic properties of similar crystalline TiO<sub>2</sub> coatings synthesized by ALD and sol-gel method. The core/shell nanoparticles contained nearly the same amount of TiO<sub>2</sub>, and in both cases the thickness of the TiO<sub>2</sub> layer was 20-30 nm. I have shown that among the two coatings, the ALD-grown TiO<sub>2</sub> is more active in degrading the methyl orange. This could be explained by that, in contrast to the sol-gel method, a highly crystallized TiO<sub>2</sub> layer can be formed without heat-treatment by ALD, thus the decrease in the specific surface resulting from the sintering of the sample is smaller.
3. I have successfully prepared poly(vinyl-alcohol) (PVA)/Al<sub>2</sub>O<sub>3</sub>, poly(vinyl-pyrrolidone) (PVP)/Al<sub>2</sub>O<sub>3</sub>, PVA/TiO<sub>2</sub> and PVP/TiO<sub>2</sub> core/shell nanofibers by electrospinning and ALD. The fibrous structure was maintained after the ALD depositions. Later I have removed the polymer core from the nanocomposites by two different methods: dissolution and annealing, and by this I could fabricate Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> nanotubes. I have determined the heating program used for annealing the polymer/oxide composites based on thermal studies. [2.]
4. I was the first to compare the photocatalytic properties of amorphous and crystalline TiO<sub>2</sub> nanotubes with the same dimension and morphology that were synthesized by electrospinning and ALD. I have shown that the anatase TiO<sub>2</sub> nanotubes have similar efficiency to the reference P25 TiO<sub>2</sub> in the degradation of the dye, so it may also be useful to study their application in photocatalysis. The measurements also confirmed that the amorphous ALD TiO<sub>2</sub> in itself has also decomposed a small amount of the methyl orange.

5. I have carried out a detailed thermal analysis of the PVP/TTIP nanocomposite that was prepared by electrospinning, which I also supplemented with evolved gas analysis. I examined the effect of annealing temperature and atmosphere on the composition of the TiO<sub>2</sub> nanofibers that were formed. I have shown that by heating the fibers in nitrogen atmosphere anatase-rutile mixed-phase composite TiO<sub>2</sub> fibers can be produced that are doped with a small amount of carbon, and UV-Vis measurements have confirmed that the light absorption of the nanocomposite was extended to the visible range. [3.]
  
6. I synthesized TiO<sub>2</sub>/ZnO and ZnO/TiO<sub>2</sub> core/shell nanofibers by electrospinning and ALD. I investigated the effect of coating the pure nanofibers and the exchange of the core and the shell material on the photocatalytic properties. I have demonstrated that under the given circumstances, the best conversion can be achieved in the degradation of the methyl orange dye with the pure TiO<sub>2</sub> fibers, so these metal-oxide nanofibers formed by electrospinning can also be used in photocatalysts. In the case when the two semiconductor oxides were used core/shell nanocomposites, it was better when TiO<sub>2</sub> was the core and ZnO was the shell material. [1.]

## 7. Publications

### Publications related to the dissertation:

1. S. I. Boyadjiev, O. Kéri, P. Bárdos, T. Firkala, F. Gáber, Zs. K. Nagy, Zs. Baji, M. Takács, I. M. Szilágyi, TiO<sub>2</sub>/ZnO and ZnO/TiO<sub>2</sub> core/shell nanofibers prepared by electrospinning and atomic layer deposition for photocatalysis and gas sensing, *Applied Surface Science*, 2017, 424 (March), 190-197., doi: 10.1016/j.apsusc.2017.03.030 (IF 2017: 4,439, independent citations: 8)
2. O. Kéri, E. Kocsis, Zs. K. Nagy, B. Parditka, Z. Erdélyi, I. M. Szilágyi, Preparation of Al<sub>2</sub>O<sub>3</sub> coated PVA and PVP nanofibers and Al<sub>2</sub>O<sub>3</sub> nanotubes by electrospinning and atomic layer deposition, *Revue Roumaine de Chimie*, 2018, 63 (5-6), 401-406. (IF 2017/2018: 0,37)
3. O. Kéri, P. Bárdos, S. Boyadjiev, T. Igricz, Zs. K. Nagy, I. M. Szilágyi, Thermal properties of electrospun polyvinylpyrrolidone/titanium tetraisopropoxide composite nanofibers, *Journal of Thermal Analysis and Calorimetry*, 2019, doi: 10.1007/s10973-019-08030-0 (IF 2017/2018: 2,209)
4. O. Kéri, L. Kócs, Z. Hórvölgyi, Zs. Baji, K. László, I. M. Szilágyi, Photocatalytic amorphous and crystalline TiO<sub>2</sub> prepared by atomic layer deposition, *Periodica Polytechnica Chemical Engineering*, **2019**, ACCEPTED, doi: 10.3311/PPch.13873 (IF 2017: 0,877)

### Manuscripts in preparation:

- O. Kéri, E. Kocsis, Zs. K. Nagy, B. Parditka, Z. Erdélyi, I. M. Szilágyi, Photocatalytic and amorphous TiO<sub>2</sub> nanotubes prepared by electrospinning and atomic layer deposition
- Kéri, Á. Patak, L. Kócs, E. Albert, Z. Hórvölgyi, I. M. Szilágyi, Photocatalytic SiO<sub>2</sub>/TiO<sub>2</sub> core/shell nanoparticles prepared by sol-gel method

### Other journal papers:

1. K. Gesheva, T. Ivanova, G. Bdurov, I. M. Szilágyi, N. Justh, O. Kéri, S. Bojadjev, D. Nagy, M. Aleksandrova, Technologies for deposition of transition metal oxide thin films: application as functional layers in „Smart windows” and photocatalytic systems, *Journal*

*of Physics- Conference Series*, **2016**, 682 (1) 012011, doi: 10.1088/1742-6596/682/1/012011 (IF: -, independent citations: 2)

2. O. Czoboly, É. Lublóy, V. Hlavička, O. Kéri, I. M. Szilágyi, Gy. L. Balázs, Fibers and fiber cocktails to improve fire resistance of concrete, *Journal of Thermal Analysis and Calorimetry*, **2016**, 128 (3), 1453-1461., doi: 10.1007/s10973-016-6038-x (IF 2016: 1,953, independent citations: 7)
3. T. Firkala, O. Kéri, F. Gáber, L. Kócs, D. Nagy, Z. Hórvölgyi, M. Zaharescu, I. M. Szilágyi, Photocatalytic properties of hexagonal WO<sub>3</sub> nanowires decorated with gold nanoparticles, *Revue Roumaine de Chimie*, **2017**, 62 (10), 767-773 (IF 2017/2018: 0,37)
4. L. Lőrincz, Á. Tóth, L. Kondor, O. Kéri, J. Madarász, E. Varga, E. Székely, Gas antisolvent fractionation based optical resolution of ibuprofen with enantiopure phenylglycinol, *Journal of CO<sub>2</sub> Utilization*, **2018**, 27 (August), 493-499, doi: 10.1016/j.jcou.2018.09.004 (IF 2017: 5,503)

## **8. Conference lectures and posters**

1. Orsolya Kéri, Imre Miklós Szilágyi, Lenke Kócs, Zsófia Baji: Investigation of the photocatalytic activity of amorphous titanium-dioxide, 11th International Conference “Students for Students, 2015. april 22-26., Cluj-Napoca, Romania
2. Orsolya Kéri, Imre Miklós Szilágyi, Tamás Firkala, Fanni Gáber, Dávidné Nagy, Lenke Kócs, Zoltán Hórvölgyi: Photocatalytic properties of hexagonal WO<sub>3</sub> nanofibers doped with Au nanoparticles, XXXVIII. Chemical Lecturer Days, 2015. october 26-28., Szeged, Hungary
3. **Kéri Orsolya: Fotokatalitikus mag/héj nanokompozitok, BME-VBK Tudományos Diákköri Konferencia, Anyagtudomány és Polimerkémia, 2015. november 17., Budapest, 3. helyezés**
4. Orsolya Kéri, Imre Miklós Szilágyi: Thermal analysis of oxide nanofibers prepared by electrospinning, MKE Thermoanalytical Group – Thermoanalytical Seminar, 2015. november 27., Pécs, Hungary

5. Orsolya Kéri, Eszter Kocsis, Lenke Kócs, Levente Kárpáti, Zsófia Baji, Bence Párditka, Zoltán Erdélyi, Imre Miklós Szilágyi: ALD on polymers and inorganic nanoparticles, Vapor Phase Technologies for Metal Oxide and Carbon Nanostructures, 2016. júly 5-9., Velingrad, Bulgaria
6. Orsolya Kéri, Eszter Kocsis, Lenke Kócs, Levente Kárpáti, Zsófia Baji, Bence Párditka, Zoltán Erdélyi, Szilágyi Imre Miklós: Photocatalytic properties of ALD coated polymer and inorganic nanostructures, International Conference of Physical Chemistry, ROMPHYSICHEM 16, 2016. september 21-24, Galati, Romania
7. **Kéri Orsolya: Fotokatalitikus mag/héj nanokompozitok, XXXIII. Országos Tudományos Diákköri Konferencia, Kémia és Vegyipari Szekció, Anyagtudomány I., 2017. március 29-31., Miskolc, 2. helyezés**
8. Orsolya Kéri, Eszter Kocsis, Zsombor Kristóf Nagy, Tamás Igricz, Bence Párditka, Zoltán Erdélyi, Imre Miklós Szilágyi, Preparation and analysis of metal-oxide nanotubes (poszter), JTAC-V4 Conference, 2017. júne 6-9., Budapest, Hungary
9. Orsolya Kéri, Eszter Kocsis, Lenke Kócs, Zoltán Hórvölgyi, Levente Kárpáti, Bence Párditka, Zoltán Erdélyi, Imre Miklós Szilágyi, Preparation and investigation of the photocatalytic properties of core/shell nanocomposites, YUCOMAT, 2017. september 4-8., Herceg Novi, Montenegro
10. Orsolya Kéri, Eszter Kocsis, Zsombor Kristóf Nagy, Tamás Igricz, Bence Párditka, Zoltán Erdélyi, Imre Miklós Szilágyi, Preparation and analysis of metal-oxide nanotubes (poster), Oláh György Doctoral School XV. Conference, 2018. february 1., Budapest, Hungary
11. Orsolya Kéri, Eszter Kocsis, Lenke Kócs, Zoltán Hórvölgyi, Levente Kárpáti, Bence Párditka, Zoltán Erdélyi, Imre Miklós Szilágyi, ALD coated photocatalytic polymer and inorganic nanomaterials, 2018 Spring meeting of the European Materials Research Society, 2018. júne 18-22., Strasbourg, France
12. Orsolya Kéri, Eszter Kocsis, Zsombor Kristóf Nagy, Tamás Igricz, Bence Párditka, Zoltán Erdélyi, Imre Miklós Szilágyi, Preparation of TiO<sub>2</sub> nanofibers and TiO<sub>2</sub> nanotubes, European Symposium on Thermal Analysis and Calorimetry, ESTAC12, 2018. augst 18-22., Brasov, Romania

