Irina Levchuk

TITANIUM DIOXIDE BASED NANOMATERIALS FOR PHOTOCATALYTIC WATER TREATMENT

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium of MUC, Mikkeli University Consortium, Mikkeli, Finland on the 5th of August, 2016, at noon.

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Abstract

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Water treatment using photocatalysis has gained extensive attention in recent years. Photocatalysis is promising technology from green chemistry point of view. The most widely studied and used photocatalyst for decomposition of pollutants in water under ultraviolet irradiation is TiO_2 because it is not toxic, relatively cheap and highly active in various reactions.

Within this thesis unmodified and modified TiO_2 materials (powders and thin films) were prepared. Physico-chemical properties of photocatalytic materials were characterized with UV-visible spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectrometry (XPS), inductively coupled plasma optical emission spectrometry (ICP-OES), ellipsometry, time-of-flight secondary ion mass spectrometry (ToF-SIMS), Raman spectroscopy, goniometry, diffuse reflectance measurements, thermogravimetric analysis (TGA) and nitrogen adsorption/desorption. Photocatalytic activity of prepared samples in aqueous environment was tested using model compounds such as phenol, formic acid and metazachlor. Also purification of real pulp and paper wastewater effluent was studied. Concentration of chosen pollutants was measured with high pressure liquid chromatography (HPLC). Mineralization and oxidation of organic contaminants were monitored with total organic carbon (TOC) and chemical oxygen demand (COD) analysis. Titanium dioxide powders prepared via sol-gel method and doped with dysprosium and praseodymium were photocatalytically active for decomposition of metazachlor. The highest degradation rate of metazachlor was observed when Pr-TiO_2 treated at 450°C (8h) was used. The photocatalytic LED-based treatment of wastewater effluent from plywood mill using commercially available TiO_2 was demonstrated to be promising post-treatment method (72% of COD and 60% of TOC was decreased after 60 min of irradiation). The TiO_2 coatings prepared by atomic layer deposition technique on aluminium foam were photocatalytically active for degradation of formic and phenol, however suppression of activity was observed. Photocatalytic activity of $\text{TiO}_2/\text{SiO}_2$ films doped with gold bipyramid-like nanoparticles was about two times higher than reference, which was not the case when gold nanospheres were used.

Keywords: titanium dioxide, gold nanoparticles, dysprosium, praseodymium, LEDs, thin films, powder photocatalysts.

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List of publications

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- I. Levchuk, I., Rueda-Márquez, J.J., Suihkonen, S., Manzano, M.A., and Sillanpää, M. (2015). Application of UVA-LED based photocatalysis for plywood mill wastewater treatment. *Separation and Purification Technology*, 143(25), pp. 1-5.
- II. Levchuk, I., Guillard, C., Dappozze, F., Parola, S., Leonard, D., and Sillanpää, M. (2016). Photocatalytic activity of TiO₂ films immobilized on aluminum foam by atomic layer deposition technique. *Journal of Photochemistry & Photobiology, A: Chemistry*, 328, pp. 16-23.
- III. Levchuk, I., Sillanpää, M., Guillard, C., Gregori D., Chateau D., Chaput F., Lerouge, F., Parola, S. (2016). Enhanced photocatalytic activity through insertion of plasmonic nanostructures in porous TiO₂/SiO₂ hybrid composite films. *Journal of Catalysis*, Submitted
- IV. Levchuk, I., Sillanpää, M., Guillard, C., Chateau, D., Gregori, D., Vadcard, F., Parola, S. (2016). TiO₂/SiO₂ porous composite thin films: role of TiO₂ areal loading and modification with gold nanospheres on the photocatalytic activity. *Applied Surface Science*, 383, pp.367-374.
- V. Kralova M., Levchuk I., Kasperek V., Sillanpää M., Cihlar J. (2015). Influence of synthesis conditions on physical properties of lanthanide-doped titania for photocatalytic decomposition of metazachlor. *Chinese Journal of Catalysis*, 36, pp. 1679-1684.

Author's contribution

Irina Levchuk is the principal author and investigator in papers I – IV. In paper V, Dr. Kralova was the corresponding author and Irina Levchuk participated in the experimental work.

1 Introduction

Freshwater is a crucial source for human well-being and socio-economic development [1]. It is well known that major part of the freshwater is concentrated in glaciers, permanent snow cover and in a few lakes around the world. Most of the freshwater in not frozen condition is located in a few lakes in Africa (for example, Lake Victoria), Russia (Lake Baikal) and North America (Great Lakes in USA and Canada contain about 18% of the world's freshwater supply [2]) [3]. The total surface area of lakes with freshwater is about $8.45 \times 10^3 \text{ km}^2$, while the volume of water retained in these lakes is about $1.3 \times 10^5 \text{ km}^3$ [3]. Nowadays worldwide, access to safe water of about 3.5 billion people are not fulfilled, nearly 2.5 billion people do not have admittance to improved sanitation and around 768 million people do not have admittance to improved source of water [1]. According to some estimation, through 2050 more than 40% of global population will live in conditions of severe water stress [1]. The population growth, economic development and urban expansion will increase demand of freshwater in the future, which in turn will affect water-intensive industries.

Among the most water-intensive industries, thermal power plants, steel plants and pulp and paper are dominating. For instance, according to different sources pulp and paper industry can require from 5 to 20 m^3 of water per ton of product [4] and in some cases up to 1000 m^3 per ton of product, while in sugar industry about 15 m^3 is needed per ton of sugar [5]. It is worth making a point that during recent decades environmental impact of pulp and paper industry on water, air and soil was reduced by 80 - 90% [6]. However, environmental policy regarding quality of discharged wastewater is tightening, leading to necessity of new solutions for water treatment not only for pulp and paper industry but for all water-intensive industries as well as industries discharging hazardous wastewater.

Advanced oxidation processes (AOPs) are promising techniques, which can be used as alternative processes or polishing step in wastewater treatment. Nowadays, AOPs are under extensive interest of many researchers mainly due to non-selectivity regarding the contaminant oxidation, possibility of complete mineralization of pollutants, and lack of solid waste formation during majority of AOPs. Photocatalysis as one of AOPs has gained an extensive attention in last decades for water treatment. The most widely used photocatalytic material for the removal of pollutants from the aqueous environment under UV is TiO_2 . Among main advantages of titanium dioxide its relatively low cost, non-toxicity and high photocatalytic activity should be mentioned [7-9]. The main drawback is limited photocatalytic activity in the visible region. Therefore, under solar irradiation, in which content of UV light is about 3 – 6% (based on energy and not on photon number) [10], the photocatalytic activity of TiO_2 significantly decreases. For the practical application of TiO_2 under solar irradiation, the extension of photocatalytic activity towards longer wavelengths is very important. However, enhancement of TiO_2 photocatalytic activity in UV region is critical as well since it can be applied for indoor water treatment using artificial irradiation sources, such as light-emitting diodes (LEDs), which can be an environmentally friendly alternative for commonly used UV

lamps since they have longer life time, do not contain toxic elements, have better mechanical stability, compact size, higher energy efficiency, *etc.* [11].

Mainly two different approaches such as doping TiO_2 with metals and non metallic elements are generally used to extend its photocatalytic activity [12]. Modification of titanium dioxide with noble metals benefits from relative stability of these metals under UV and aerated atmosphere [13]. As a result, TiO_2 doping with noble metals, especially with gold, is widely studied in order to extend photocatalytic response of TiO_2 into the visible area or enhance its activity in UV region [12, 14-16]. In spite of numerous studies conducted in the field of advanced materials for photocatalysis, many questions are still open and effect of some parameters on photocatalytic activity is underestimated or even neglected in many works. Hence, further investigations are needed in order to find out ways to improve photocatalytic activity of TiO_2 and study effect of different parameters on its performance.

The main aim of this study was to synthesize advanced materials for photocatalytic water treatment. In order to achieve set aim following goals should be accomplished:

- To study photocatalytic activity of commercially available TiO_2 standard (P25) using model contaminants and real industrial effluent (**Paper I**).
- To evaluate feasibility of TiO_2 coatings prepared by Atomic Layer Deposition (ALD) technique on porous aluminum foam substrate for photocatalytic application using model compounds (**Paper II**), and compare performance with commercial standard TiO_2 powder (P25).
- To modify TiO_2 thin films using gold nanoparticles of different shapes, study effect of gold nanoparticles on photocatalytic activity using model pollutant and investigate effect of some critical parameters for coatings on comparison of photocatalytic activity. (**Paper III-IV**)
- To study effect of doping TiO_2 powder with Lanthanides on its photocatalytic activity (**Paper V**) using model contaminant.

2 Treatment of wastewater containing organic matter

2.1 Industrial and sewage wastewater – current situation

The total amount of wastewater (sewage, industrial and agricultural) globally discharged to water bodies is tens of millions of cubic meters per day [17, 18]. According to some estimation, about 80 – 90 % of all wastewater in developing countries is not treated [19]. For instance, an estimated treatment capacity for sewage generated in major cities in India is only about 30 % [20]. Whereas in EU about 82 % of all generated urban wastewaters have received secondary treatment in 2009-2010 [21]. Amount of industrial wastewater varies significantly from country to country. It should be noted that in general almost all water utilized for industrial purposes ends up as wastewater. In developing countries quantities of wastewater generated by the same type of industry are generally higher. For instance, in developed countries steel industry consumes 8 – 10 times lower amount of water per ton of steel than in India [18]. The highest contribution to generation of industrial wastewaters is made by water-intensive industries [18]. The thermal power plants, steel plants and pulp and paper industry were reported to be the most water-intensive industries [18, 19].

Thus, pulp and paper industry is one of the biggest industrial sectors in the world with main producers located in Europe and North America [22]. According to some sources, the NORSCAN countries (U.S., Canada, Sweden, Finland and Norway) supply about 65% of the world pulp market [23, 24]. It is known to be one of the main exporting industries in Finland with about 23 paper mills, 15 pulp mills and 18 mills producing mechanical or semi-mechanical pulp and 13 paperboard mills [25, 26]. It was reported that generally amount of wastewater discharged from different mills varies from 5 to 20 m³ per ton of paper and paper board [4]. Usually before discharge wastewater is treated by primary clarification followed by biological process [27]. Tertiary/advanced treatment is not often applied due to high cost of the processes [28]. Despite applied treatment, wastewater effluent is characterized by high concentration of organic materials, high adsorbable organic halogens (AOX), suspended solids, metal ions, tannins, lignin and derivatives, fatty acids, etc [29]. Very often COD value of pulp and paper wastewater effluent exceeds discharging limits and/or recommendations in EU. Thus, according to best available techniques published by the European commission the mean COD value is 103 mg L⁻¹ [30]. While reported values of COD in pulp and paper effluents varies significantly starting from 592 mg L⁻¹ up to 9065 mg L⁻¹ depending on the type of the process [29, 31-33]. Hence, additional treatment should be applied in order to reach discharging limits and/or recommendations and minimize and/or prevent negative effect to the environment.

2.2 Advanced oxidation processes

In recent decades Advanced Oxidation Processes (AOPs) gained attention as alternative techniques for post-treatment of industrial effluents. Recalcitrant organic compounds are generally decomposed or transformed into biodegradable form during AOPs, which allows to avoid secondary loadings of contaminants to the environment. Therefore, AOPs are considered as “clean technologies” [34]. According to the accepted theory, AOPs involve formation and use of highly reactive oxidizing species, such as hydroxyl radicals ($\text{HO}\cdot$). Hydroxyl radicals are known as powerful (electrochemical oxidation potential $E_0=2.80\text{ V}$) and non-selective species responsible for decomposition of organic pollutants which cannot be destroyed by conventional oxidants (oxygen, ozone and chlorine) [35]. When hydroxyl radicals react with dissolved organic pollutants, series of oxidation reactions is initiated. In ideal case, after application of AOPs contaminants are degraded to CO_2 , water and inorganic ions. If complete decomposition of pollutants and generated intermediates is achieved after AOPs, post-treatment of water is not needed [34]. It should be noted that AOPs are not recommended for treatment of water with COD value higher than 5000 mg L^{-1} [36]. As a general rule, in order to obtain complete mineralization relatively high energy and/or chemicals consumption is required. Hence, AOPs are often integrated into water treatment train with main purpose to decompose specific recalcitrant compounds and/or decrease water toxicity and increase biodegradability of organic compounds. As an example final treatment step at the Leo J. Vander Lans Water Treatment Facility (California) can be considered also known as *golden standard* for advanced recycled water treatment. In order to prevent infiltration by seawater, treated urban wastewater effluent is pumped to the local groundwater aquifer where it is mixed with potentially potable underground water. Therefore, such recalcitrant compounds as N-nitrosodimethylamine (NDMA), 1,4-dioxane, etc. should be removed from water prior it pumped to local aquifer. For this purpose UVC/ H_2O_2 process is implemented after microfiltration and reverse osmosis (TrojanUVPhox™).

Figure 2.1: UV oxidation equipment produced by TrojanUVphox™ located in Orange County (California, USA) [37]

Applied AOP treatment in this case leads not only to degradation of target pollutants but also to water disinfection [38]. It should be mentioned that water toxicity is of high importance and should be determined especially after AOP treatment since generated by-products and residual oxidants can significantly increase toxicity [39].

Conventional AOPs can be divided on homogeneous and heterogeneous based on reactive phase [40]. Among homogeneous conventional AOPs Fenton based process (Fenton, Fenton like, Sono-Fenton, Photo-Fenton, Electro-Fenton, Sono-electro-Fenton, Photo-electro-Fenton, Sono-photo-Fenton) and O_3 based processes (O_3 , $O_3 + UV$) and H_2O_2 based processes ($H_2O_2 + UV$) and their combination can be emphasized. Photocatalysis, catalytic wet peroxide oxidation, catalytic ozonation, etc. are heterogeneous conventional AOPs. Depending on the way of hydroxyl radical generation chemical, electro-, sono- and photo-chemical AOPs can be distinguished [40]. However, there are also alternative AOPs such as supercritical water oxidation, pulsed electron beam, γ -ray irradiation and microwaves [34].

3 Photocatalysis

Heterogeneous photocatalysis is widely studied phenomenon especially in energy-related issues, purification of water and air, etc. Only in last ten years the number of scientific papers containing word photocatalysis or photocatalyst in the title exceeds 9000 [41]. And each year number of articles devoted to photocatalysis is increasing [41]. It is not surprising because photocatalytic properties of some semiconductors are successfully used worldwide for self-cleaning and antifogging surfaces [42], cancer therapy, outdoor air purification, deodorization of indoor air, wastewater purification, etc [43]. For instance, the Taiyo Kogyo Corporation, leading company for tent production in the world, offers self-cleaning warehouse tents coated with TiO_2 [44]. As an example of self-cleaning properties of titanium dioxide coatings the photo of car mirror, half of which was coated with TiO_2 in presented in Figure 3.1.

Figure 3.1: A car mirror, half of which is coated with TiO_2 [45]

Interestingly there are some debates regarding term “photocatalysis” despite relatively long history of research conducted in this field [46]. Photocatalysis can be defined as a chemical reaction induced by absorption of photons by solid material known as photocatalyst [47]. It should be mentioned that photocatalyst does not undergo any chemical changes during and after reaction. In the literature term catalyst is often used instead of photocatalyst. Probably it occurs because some photocatalysts are sometimes used in catalytic reactions as catalysts. But, from thermodynamic point of view the concept of catalysis and photocatalysis is different. Thus, energy-storing reactions can be driven by photocatalysis ($\Delta G > 0$) while catalysis is limited to thermodynamically

possible reactions ($\Delta G < 0$) [10]. Absolute or relative reaction rate in the field of photocatalysis is usually referred as photocatalytic activity [47].

Photocatalytic process in water can be divided on five steps [48]:

1. Transfer of reactants in water to the surface of photocatalysts
2. Adsorption of reactants on the surface
3. Photonic activation of surface of photocatalyst and reaction in the adsorbed phase
4. Desorption of reaction products
5. Elimination of reaction products from the interface region.

Generally accepted explanation of the main principle of photocatalysis with TiO_2 is often presented as shown in Figure 3.2.

Figure 3.2: Simplified scheme of TiO_2 photocatalysis [49]

As shown in Figure 3.2, when photocatalyst (in present case TiO_2) absorb the light with energy equal or greater than band gap energy of photocatalyst, formation of electron-hole pairs occurs. The last dissociate into positively charged holes (h^+) in valence band (VB) and electrons (e^-) in conduction band (CB). These charge carriers in the CB and VB reduce and oxidize compounds adsorbed on the surface of photocatalyst, respectively. However, recombination of these charge carriers can occur (Figure 3.3) causing absence of chemical reaction. Often in the literature decrease or increase of photocatalytic activity is explained by enhanced or suppressed electron-hole recombination, respectively [50]. As it was mentioned in recent review [50] no direct confirmation of electron-hole recombination during heterogeneous photocatalysis was

reported, which may appear surprising. However, detection of electron-hole recombination is not easy because it proceeds with heat liberation.

Figure 3.3: Simplified diagram of electron-hole (e^-/h^+) recombination [50]

There are five main physical parameters which are known to influence photocatalytic activity [49]. Reaction rate as a function of these parameters is shown in Figure 3.4.

Figure 3.4: Effect of (I) mass of photocatalyst, (II) wavelength, (III) initial concentration, (IV) temperature and (V) radiant flux on photocatalytic activity [49]

As it was reported, initial rates of photocatalytic reaction are directly proportional to mass of photocatalyst till certain value after which the function $r = f(m)$ reach plateau (full absorption of photons). Optimal mass of photocatalyst (m_{opt}) depends on operating conditions and reactor geometry [48]. Photocatalytic activity strongly depends on the wavelength of the irradiation source (Figure 3.4 II). For instance, for TiO_2 with band energy 3.20 eV the irradiation with $\lambda \leq 400$ nm is required. Generally kinetics of photocatalytic reactions is described in literature using Langmuir-Hinshelwood mechanism, probably due to its usefulness in modelling process:

$$r = K \frac{KC}{1+KC} \quad (3.1)$$

where r is true rate constant, K is the constant of adsorption at equilibrium and C is the momentary concentration. However, it was demonstrated that rate constants of Langmuir-Hinshelwood mechanism have no physical meaning for photocatalysis

[51]. The optimum temperature range for photocatalytic reactions (Figure 3.4 IV) is between 20°C and 80°C [48]. At very low temperatures photocatalytic activity decreases and desorption of final product becomes rate limiting step. At elevated temperatures (above 80°C) exothermic adsorption of reactant is becoming rate limiting step and activity is decreasing [48]. Hence, photocatalytic reactions in aqueous media are attractive since no heating is required. As presented in Figure 3.4 (V), the photocatalytic activity is proportional to radiant flux (Φ) till certain value. This value significantly varies depending on experimental conditions. For instance, when Philips HPK 125 UV lamp was used critical flux was estimated to be 25 mW/cm² [48, 53]. Interestingly, under solar irradiation critical flux is about 2 – 3 mW/cm² [51]. After this value reaction rate is proportional to square root of radiant flux ($\Phi^{1/2}$). Thus, the optimal use of irradiation corresponds to area where photocatalytic activity is proportional to radiant flux.

3.1 Advanced materials for photocatalysis

3.1.1 Desired properties and design of photocatalysts

As it was reported previously [7], ideal photocatalyst should be chemically and biologically inert, stable in photocatalytic reactions, easy to produce and use, cheap, not dangerous for humans and environment and efficient under sun irradiation. Thus, titanium dioxide, the most studied material for photocatalytic applications [54], is almost ideal photocatalyst. Moreover, TiO₂ (P25) is used as reference photocatalyst. Many excellent review papers were devoted to titanium dioxide and its photocatalytic properties [9, 10, 55-58]. However, photocatalytic activity of TiO₂ and other photocatalytic materials is limited leading to low quantum yields ($\leq 10\%$) [59]. Generally the main limiting factors are [59]:

- recombination of electron-hole (e^-/h^+) pairs;
- requirement of ultraviolet light (UV) at a wavelength shorter than ca. 390 nm [60];
- low rates of mass transport between active centers of TiO₂ and organic pollutants.

Numerous attempts to design photocatalytic materials with activity higher than that of TiO₂ were made recently [61-68]. Lin et al. suggested that efficient photocatalyst can be designed by combination of n-type semiconductor (with good electron conductivity) with hole-accepting semiconductor with relatively high structure openness degree [61]. In order to prove this suggestion Bi₂O₃ (n-type semiconductor) was combined with BaTiO₃ (dielectric and ferroelectric material) and enhanced photocatalytic activity of this material was reported for decomposition of methyl orange and methylene blue. The improvement of photocatalytic activity was associated with electric-field-driven electron-hole separation. Other coupled semiconductors or heterojunctions such as

SnO₂/TiO₂ [69], TiO₂/ZrO₂ [70], CdSe/TiO₂ [71], BiVO₄/TiO₂ [72], BiOCl/BiOI [73], Bi₂S₃/TiO₂ and CdS/TiO₂ [74] etc. were studied for photocatalytic applications.

Another way to design photocatalytic materials is to use metal nanoparticles with surface plasmon resonance (SPR) as co-catalysts [62]. The metal nanoparticles with SPR can absorb light in the semiconductor and possibly enhance photocatalytic activity. Depending on desired SPR particle size, shape and dielectric environment should be modified. The most used co-catalysts for this purpose is gold and silver nanoparticles because of intense optical absorption and scattering properties. Thus, many scientists reported enhanced photocatalytic activity of TiO₂ modified with Au nanoparticles in UV and/or visible light region [13, 14, 20, 75-80].

An interesting approach for design of advanced photocatalytic materials were reported by Yu et al. [63]. In this work electronic band structures and density of states for TiO₂ nanosheets, nanotubes and nanoparticles were calculated using density functional theory (DFT). After that TiO₂ nanosheets, nanotubes and nanoparticles were synthesized and tested for decomposition of 4-chlorophenol. Experimentally obtained band structures and photocatalytic activities of prepared materials were in agreement with theoretical calculations. Thus, photocatalytic activity ranks in order of nanosheets > nanotubes > nanoparticles.

To summarise the definition of term “design” should be refreshed. According to Oxford English Dictionary design is a plan produced to show workings of something before it is made [81]. Hence, strictly speaking possibility to “design” highly active photocatalyst is questionable nowadays [82]. For this purpose more deep understanding of phenomena of photocatalysis is needed.

3.1.2 Preparation of photocatalytic materials

In aqueous photocatalytic reactions materials are generally used in two main forms: highly dispersed powder and coatings deposited on support. Despite all advantages, highly dispersed photocatalyst is not widely used for practical applications in treatment of water. It can be explained by problems arising during separation step. Therefore, filming of photocatalyst can considerably simplify the separation process and improve the photocatalytic performance. Methods used for preparation of photocatalytic materials can be divided on solution routes and gas phase techniques. Widely used methods for preparation of both types of photocatalysts are briefly presented below.

Solution routes

Solution routes are widely used for synthesis of thin photocatalytic films. Among main advantages of liquid-phase techniques are control over stoichiometry, preparation of homogeneous materials, formation of composite materials etc. Possible drawbacks of solution routes may be long time of synthesis, contamination of prepared photocatalysts with carbon, expensive precursors, etc [7]. One of the most commonly used solution

routes for preparation of photocatalytic materials is sol-gel method, which was discovered in 1846 by Ebelmann [83]. Sol-gel is categorized as wet chemical method based on hydrolysis and polycondensation of precursors. Two types of sol-gel process can be distinguished: the alkoxide and non-alkoxide route. Inorganic salts and alkoxides are used as starting materials in non-alkoxide and alkoxide routes, respectively. One of the main drawbacks is high temperature of calcination at final step of material preparation. Advantages of sol-gel process are homogeneity, purity, stoichiometry control, simplicity of performance, composition control, etc. It should be mentioned that sol-gel process is highly beneficial for coating of large and complex surfaces [7]. Example of TiO_2 thin films prepared via sol-gel method is shown in Figure 3.5.

Figure 3.5: SEM image of TiO_2 thin film deposited on borosilicate glass substrate by sol-gel dip coating method

However, for synthesis of bulk materials precipitation method is widely used [84]. This method is based on (co)precipitation of precursors by addition of basic solutions followed by thermal treatment. Such factors as supersaturation, pH, temperature, nature of reagents, and presence of impurities are crucial for morphology and texture of final materials [84]. Despite the simplicity of this method, control of the particle size and distribution is tedious [7].

Synthesis in aqueous and organic media (methanol, toluene, 1,4 butanol, etc.) at relatively low temperatures ($< 250^\circ\text{C}$) and under self-produced pressure are known as hydrothermal and solvothermal methods, respectively [7]. Usually calcination of prepared photocatalysts is performed after synthesis. Hydrothermal method is widely applied in industrial scale for production of ultra-fine particles and particles and it has been reported as one of the best method for synthesis of homogeneous TiO_2 particles

with required shape and size and high degree of crystallinity [85]. Desired size and morphology of particles, crystalline phase and surface chemistry can be obtained in hydro- and solvothermal methods by controlling such parameters as temperature, pressure, composition of solution, solvent and ageing time [7].

Microemulsion is the solution with two immiscible liquids stabilized by surfactant. Microemulsions are optically isotropic and stable from thermodynamic point of view [7]. There have been only few promising reports on use of microemulsion method for synthesis of photocatalytic materials [86-88]. Another method for synthesis of photocatalysts via solution route is so called combustion synthesis, which is rapid (1-2 min) heating (temperature of the reaction is about 650°C) of solution containing redox groups [7]. As it was reported highly crystalline particles with large surface area can be obtained by this method [89].

Gas phase methods

Gas phase methods are mostly utilized for preparation of coatings. However, powder materials can be synthesized as well. One of widely applied gas phase methods is Chemical Vapor Deposition (CVD) technique. The CVD can be defined as complex process of solid thin films deposition onto substrate through chemical reactions of gaseous precursors at high temperature (about 1000°C) [90]. Uniform, conformal and high purity thin films are usually obtained using CVD technique, which makes it attractive for industry and academy [91]. However, there are some drawbacks of CVD process such as relatively high cost of precursors, which can be also toxic, corrosive and/or explosive. Atomic layer deposition (ALD) technique, a modification of CVD method, is also often used for preparation of photocatalytic materials [92-96]. One of the benefits of ALD process is that it is performed below decomposition temperature of precursors, which allows to avoid such problem as contamination of thin films as it often occurs during CVD.

Another gas phase method is physical vapor deposition (PVD) technique. The main difference of PVD from CVD is that films are deposited from gas phase but with absence of chemical reaction. Hence, stability of substances in gaseous phase used for PVD is required. The most widely used PVD method is thermal evaporation. The electron beam (E-beam) evaporation can be more beneficial than CVD in terms of conductivity, smoothness, crystallinity and presence of impurities. However, E-beam evaporation is more slow and tedious method than CVD [7].

3.1.3 Activation and reuse of photocatalysts

Often the last step in synthesis of photocatalytic materials is calcination at relatively high temperature [97-100]. However, when the low-temperature synthesis is performed activation of photocatalysts may be needed. For instance, photocatalytic activity of $\text{TiO}_2/\text{SiO}_2$ hybrid thin films was increased two times after applied phototreatment (UV irradiation) which was attributed to partial photocatalytic decomposition of CH_3 groups leading to formation of porosity [101].

Another point of concern is decrease of photocatalytic activity during operation (deactivation) which was reported in many studies [102-104]. Reversible and irreversible deactivation of photocatalyst can be distinguished [105]. Generally deactivation of photocatalysts was mostly observed in single-pass fixed bed photoreactors [106]. It was reported that generally there are two possible explanations for photocatalyst deactivation [104]:

1. accumulation of reaction by-products resistant to photocatalytic decomposition on the surface of photocatalyst;
2. formation of surface species with higher adsorption ability than reactants.

Interestingly, not many studies were devoted to such an important practical application of photocatalysis topic as regeneration of photocatalytic materials. However, some researchers suggested efficient strategies allowing multiple use of photocatalysts such as:

- alkaline treatment with NaOH and NH_4OH [107];
- thermal regeneration [7];
- photocatalytic regeneration (exposure to UV light in water) [101];
- oxidation of intermediates adsorbed on the surface of photocatalyst by H_2O_2 /UV treatment [107];
- deionized water [108].

In recent work [107] such approaches as thermal, alkaline and H_2O_2 /UV treatment were applied for regeneration of TiO_2 immobilized photocatalyst and compared based on photocatalytic degradation of emerging contaminants. Among tested regenerated methods thermal and H_2O_2 /UV treatment were more efficient for regeneration of TiO_2 . It was observed that after NaOH treatment TiO_2 was partially removed which unflavoured photocatalytic activity.

3.1.4 Modified and unmodified TiO₂ based materials

Numerous materials such as TiO₂, ZnO, Fe₂O₃, WO₃, CdS, ZrO₂, MoS₂, etc were tested for photocatalytic application [109]. Some of these materials were reported to have high photocatalytic activity. Despite this fact, titanium dioxide is the most widely studied photocatalyst. Three polymorphs of TiO₂ can be found in nature: anatase, rutile and brookite. Commercially available titanium dioxide (Degussa P25), which is often used as reference photocatalyst in many reactions, is a mixture of anatase (70-80%) and rutile (20-30%). It was reported that TiO₂ was used in about 67% of the articles on photocatalysis (2008 - 2012) [62]. The main advantages of TiO₂ are its relatively low price, non-toxicity and high photoactivity, which make it very attractive [7, 9, 110]. However, practical application of photocatalysis using solar light is restricted since content of UV light is about ca. 3 – 5 % (based on energy of light) [60]. Hence, many researchers attempted to enhance photocatalytic activity of TiO₂ towards visible area (wavelengths 390 – 700 nm [111]) by various modification methods (Figure 3.6).

Figure 3.6.: Modification pathways of TiO₂ [112]

Modification of TiO₂ can lead to desired photocatalytic activity under visible light. One of the most efficient photocatalysts active under visible light is titanium dioxide doped with N [113]. Doping of TiO₂ with N and Au enhanced photocatalytic activity of TiO₂ towards visible light as well [114]. Also activity under visible light was reported for TiO₂ modified with W and N [115], N and F [116], Au [13], etc. However, it is not always the case [14].

3.2 Photocatalytic experiment in aqueous media

As it was mentioned in the beginning of this chapter the number of publications on photocatalysis is high and it is increasing every year. From one hand much knowledge has been gained in recent decades. From the other hand, as it was reported, some of scientific articles on photocatalysis are based on illusions and/or misconceptions [49, 60]. Therefore, crucial factors for photocatalysis are briefly discussed in following subchapters.

3.2.1 Crucial factors determining photocatalytic experiment

A very important question, which one should consider when performing experiments on photocatalysis is: how it can be proved that reaction is photocatalytic? According to generally accepted idea, the reaction can be identified as photocatalytic in copresence of three factors such as photoirradiation, photocatalyst and reaction substrate (usually organic pollutant). However, in some cases copresence of abovementioned factors does not mean that performed reaction is photocatalysis [60].

Many researchers test photocatalytic activity of prepared materials using organic dyes. This fact can be easily explained taking into consideration that dye concentration is usually measured by UV-Vis spectrometry, which is simple, fast and readily available analytical method. In recent study [117] feasibility of methylene blue (MB) as a test molecule for photocatalytic reactions was examined. Results suggests that methylene blue is inappropriate probe molecule for photocatalytic reactions since photosensitization may occur, which is difficult to distinguish from photocatalysis. Photosensitization initiated by photoexcitation of MB adsorbed on the surface of photocatalyst, after which photoexcited electron in MB molecule is injected into solid material leading to decomposition of MB. Thus, in described case reaction is not photocatalytic. Therefore, organic dyes are not recommended as a probe compounds for testing photocatalytic activity, especially in visible light [60, 118]. As it was suggested by group of professor Ohtani, measurements of action spectra can be an appropriate tool for confirmation of photocatalytic activity in visible light [60, 117]. The main idea of action spectra measurements is demonstrated in Figure 3.7.

Figure 3.7.: Schematic presentation of action spectra measurements [10]

As it can be seen from the Figure 3.7, the photocatalytic reaction is initiated by monochromatic light at various wavelengths and results are plotted as a function of apparent quantum efficiency (number of incident photons is considered) from the wavelength.

Some crucial factors determining truly photocatalytic regime were summarized and suggested for examination as follows [49]:

- optimization of mass of photocatalyst should be performed in each study since this value varies with photoreactor geometry;
- over-powered lamps should not be utilized in photocatalytic tests due to decrease of photocatalytic activity and heating by the lamp;
- non-truly photocatalytic systems (for example based on dye decolorization) should be avoided;
- analytical techniques (such as HPLC, LC-MS, GC-MS, TOC, etc.) appropriate to prove decomposition of organic pollutants should be used. It is highly recommended to determine not only degradation of parent compound but also by-products and mineralization;

3.2.2 Interpretation and comparison of experimental results

In spite of large number of new photocatalysts reported by different scientists, it is still very difficult to compare results of various studies. This is because standard photocatalytic test is lacking. International standards organisation (ISO) prepared series of standards related to semiconductor photocatalysis [119-126]. Two of these standards are devoted to testing photocatalytic activity of materials in water. According to ISO 10678, visible light photocatalytic activity of surfaces can be checked using methylene blue aqueous solution as shown in Figure 3.8.

Figure 3.8: Experimental set up for photocatalytic decomposition of Methylene Blue (MB)

As shown in Figure 3.8, glass cylinder with diameter 3 – 4.7 cm is fixed onto substrate (about 10 cm²) coated with photocatalyst. Glass cover (UV transparent) is located on the top of cylinder filled with 35 mL of MB solution (10⁻⁵ M). The intensity of UVA irradiation is 1.0 mW cm⁻². The irradiated solution should be mixed each 20 min. Photocatalytic test is performed during 3h at temperature 23 ± 2°C. Concentration of MB is measured by means of UV-vis spectrophotometry and photonic efficiency is calculated [58]. Described above photocatalytic procedure is very simple and can be performed in nearly every laboratory. However, some disadvantages of this test were reported such as [127]:

- purity of MB solution; commercially available MB demonstrate significant variations in purity [128];
- limitations for coatings with relatively low photocatalytic activity ($\xi_{\text{MB}} \leq 0.1\%$);
- initial pH of MB solution is not suggested by standard, which can cause differences in adsorption of MB by photocatalyst surface;

- use of organic dye molecules is not recommended for photocatalytic tests as discussed in previous subchapter;
- it is not clear why visible light photocatalytic activity test is performed under UVA irradiation.

The other ISO standard (10676) devoted to photocatalytic water treatment can be performed with materials deposited or attached to substrate using dimethyl sulfoxide (DMSO) as a probe molecule. It should be mentioned that this test is designed only for checking photocatalytic activity under UV light only (not under visible irradiation) [124]. The schematic experimental set up for discussed standard test is demonstrated in Figure 3.9.

Figure 3.9: Experimental set up for ISO standard 10676

The experimental procedure is performed as shown in Figure 3.9. The aqueous solution of DMSO (initial concentration 10ppm) is pumped (5 mm deep solution flow) over tested material (about 10 cm²) under UV irradiation (2 mW cm⁻²) during 5h at temperature 20 - 25°C. Concentration of DMSO is analysed by means of ion or gas chromatography [127]. Among the advantages of this standard test are unambiguity, low possibility of pollutant adsorption and monitoring of some generated by-products. Main drawbacks are the choice of probe compound and relatively sophisticated analytical methods.

It is difficult to speculate the role of suggested ISO standard tests for existing necessity of standardized way to compare results of different studies, other than to note that some improvements are still needed. Suggestions regarding standardization of photocatalytic tests were reported [49]. It should be mentioned that comparison of photocatalytic activity of various materials within one study can be also challenging. Often commercial TiO_2 known as Degussa (Evonik) P25 is used as a reference material for comparison with newly prepared photocatalysts. The photocatalytic activity of P25 is relatively high in many reactions and it is not always easy to synthesize material with higher than P25 photocatalytic activity. A very important point which is not often taken into consideration in papers devoted to photocatalysis is experimental error. The total error of photocatalytic experiment may include errors of analytical measurements (it can be roughly estimated as 1-3% when HPLC is used), sampling time, UV irradiation measurements, calculations, etc. Thus, the total error might be as high as 10%.

In summary it should be emphasized that there is lack of general agreement in the field regarding standard procedures and the way to compare photocatalytic efficiency of different materials [46]. However, it is recommended to evaluate such parameter as quantum yield or apparent quantum yield [49] because it allows to compare photocatalytic activity of different materials in the same reaction, estimate relative feasibility of various reactions and estimate energetic yield of reactions.

4 Materials and methods

4.1 Photocatalytic materials

4.1.1 Synthesis

Sol-gel technique and atomic layer deposition (ALD) were used for preparation of photocatalytic materials (**Paper II - V**). Thin films of TiO_2 were deposited on aluminium foam substrate (thickness 3.2 mm, bulk density 0.2 g cm^{-3} , purity 98.5 % and porosity 93%) by ALD (**Paper II**). Before deposition, surface of the substrates was cleaned ultrasonically in water and ethanol and dried at 100°C . Thin films were deposited on $7.5 \text{ cm} \times 2.5 \text{ cm}$ substrate using TFS 200 ALD reactor (BENEQ). As a precursor TiCl_4 was used, H_2O was a source of oxygen. The ALD reactor was operated under pressure of about 1 mbar and at temperature 300°C with nitrogen as a carrier and purging gas. Thin film of Al_2O_3 with thickness about 40 nm was deposited on aluminum foam prior TiO_2 in order to avoid corrosion of substrate. The surface of aluminum foam was uniformly coated allowing maintaining the porosity and gas permeability of the support.

Thin films of TiO_2 in silica matrix modified with gold nanoparticles of spherical and bipyramid-like shapes were prepared using sol-gel method and deposited on Si wafers (**Papers III and IV**). Silica matrix was chosen as a binding and protective layer. Firstly hybrid silica sol was prepared by hydrolysing methyltriethoxysilane (MTEOS) in acidic conditions (H_2O at pH 3.5 using hydrochloric acid) in a round bottom flask with a short distillation column. The molar ratio water/precursor was equal to 14. During 1h mixture was stirred at room temperature and heated to 130°C . Distillation of formed ethanol was continued till the mixture turn to white colour indicating separation of water and hybrid silica sol. Five minutes after colour change, oil bath was removed and mixture was cooled down by introducing 40 mL of ice cold water. In order to extract sol from the mixture, diethylether (90 mL) was slowly added. After five minutes, stirring was stopped and water was discarded. Then, diethylether was evaporated and substituted with ethanol. Dried solid residue of the silica sol was 30% in mass. Hybrid silica sol can be stored for a few months at temperature -24°C . More details regarding hybrid silica sol synthesis can be found elsewhere [101, 129, 130]. Silica sol synthesized according to described procedure was utilized for preparation of thin films in **Papers III and IV**. Pastes of TiO_2 with gold nanospheres (**Paper IV**) and gold bipyramid-like nanoparticles (**Paper III**) were dispersed in ethanol and added to hybrid silica sol in the way that concentration of TiO_2 and SiO_2 was 10%. Various concentrations of gold nanoparticles were tested, being 0.05%, 0.5%, 1.25% and 5% for gold nanospheres (**Paper IV**) and 0.1%, 0.5% and 1% for bipyramid-like gold nanoparticles (**Paper III**).

Titanium dioxide powders doped with lanthanides were prepared with sol-gel technique (**Paper V**). Titanium propoxide was added dropwise to isopropanol under continuous stirring. Acetylacetone was utilized as stabilizing agent. Oxides of dysprosium and

praseodymium were dissolved in nitric acid, after which the solutions were dispersed in TiO_2 sol. Sols of TiO_2 doped with dysprosium and praseodymium were aging during seven days until gel structure was formed. After that sols were heated at 120°C in order to form xerogels. Finally, various temperatures (450°C , 550°C , 650°C) and time (4 h, 8 h and 12 h) were applied to xerogels (**Paper V**).

4.1.2 Characterization

The morphology of TiO_2 thin films deposited on aluminium foam was characterized by means of scanning electron microscopy (SEM) (ZEISS LEO 1550). Identification of TiO_2 phase was performed with X-ray diffraction (XRD) method using Bruker D8 Advance A25 diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). ToF-SIMS measurements were conducted with Physical Electronics TRIFT III ToF-SIMS instrument (Physical Electronics, Chanhassen, USA) operated with a pulsed 22keV Au^+ ion gun (ion current of about 2nA) rastered over a $300\mu\text{m} \times 300\mu\text{m}$ area. An electron gun was operated in pulsed mode at low electron energy for charge compensation. Ion dose was kept below the static conditions limits. Data were analyzed using the WinCadence software. Mass calibration was performed on hydrocarbon secondary ions (**Paper II**).

Mean areal loading of titania was measured for TiO_2 films deposited on aluminium foam and $\text{TiO}_2/\text{SiO}_2$ coatings doped with gold nanospheres and bipyramid-like nanoparticles using inductively coupled plasma optical emission spectrometry (ICP-OES). For this purpose “Activa” Jobin Yvon equipment was utilized. Sample preparation consisted of dissolving coatings in a mixture of H_2SO_4 , HNO_3 and HF at 120°C (**Papers II, III and IV**).

The presence of gold in thin films of $\text{TiO}_2/\text{SiO}_2$ doped with gold nanospheres and bipyramid-like nanoparticles (**Papers III and IV**) was confirmed with X-ray photoelectron spectroscopy (XPS). Measurements were conducted with Thermo Fisher Scientific ESCALAB 250Xi spectrometer under vacuum $\sim 10^{-7}$ mbar. Al $\text{K}\alpha$ radiation was used as X-ray source (1486.6 eV). For calibration of binding-energy scale the positions of Ag 3d, Au 4f and Cu 2p peaks were measured. The size and shape of gold nanoparticles (**Papers III and IV**) were evaluated using TOPCON EM002B transmission electron microscope (TEM) operating at 200 kV. Prior TEM analysis, films were scrapped and fragments were directly deposited of onto a microscopy copper grid coated with a holey carbon film. The surface plasmon resonance (SPR) for $\text{TiO}_2/\text{SiO}_2$ coatings doped with gold bipyramid-like nanoparticles (**Paper III**) was recorded using PerkinElmer Lambda 750 UV/VIS/NIR spectrometer. Morphology of thin films was observed with scanning electron microscopes (SEM) Zeiss SUPRA 55 VP (**Paper III**) and ZEISS LEO 1550 (**Paper IV**). Porosity and thickness of $\text{TiO}_2/\text{SiO}_2$ doped with gold nanospheres (**Paper IV**) were analysed by means of SOPRA Ellipsometer EP5 (Semilab) equipped with CCD array detector (190 nm – 870 nm) and tactile method (Form Talysurf Series 2 PGI), respectively. The band gap of $\text{TiO}_2/\text{SiO}_2$ doped with gold nanospheres and bipyramid-like nanoparticles (**Papers III and IV**)

was evaluated based on diffused reflectance measurements. For this purpose fiber UV-Vis spectrometer AvaSpec-2048 (Avantes) equipped with AvaLight-DHS deuterium (UV) and halogen lamps (Vis region) was used. Measurements of contact angle (**Papers III and IV**) were conducted at room temperature ($22\pm 2^\circ\text{C}$) with GBX Digidrop Goniometer connected with digital camera.

Powder TiO_2 modified with dysprosium and praseodymium (**Paper V**) was characterized by thermogravimetric analysis (TGA; Seiko Instruments 6300 TG-DTA), XRD (X-ray diffractometer SmartLab, Rigaku), Raman analysis (Renishaw inVia), SEM (Carl Zeiss Ultra Plus), nitrogen adsorption/desorption analysis (BET) and diffused reflectance measurements (AvaSpec-2048).

4.2 Matrices of treated water and analytical methods

4.2.1 Model solutions and wastewater

Model solutions were utilized for experiments carried out for **Papers I – V**. Formic acid, phenol and metazachlor were used as a model contaminants. Formic acid (CHOOH) is relatively simple organic molecule, which is often found among by-products after degradation of more complex organic compounds. Normally, no stable intermediates are formed during photocatalytic degradation of formic acid [99, 131, 132]. Therefore, formic acid is often used as model contaminant in order to compare photocatalytic activity of novel materials. Phenol ($\text{C}_6\text{H}_5\text{OH}$) is an aromatic organic compound widely used in industry. Phenol is often found in wastewaters of different industries such as refineries, coal processing, manufacture of petrochemicals, pharmaceutical, pulp and paper, *etc.* Acute toxicity and bio-recalcitrant nature of phenol are well known. Phenol was chosen as a representative of wide family of phenolic pollutants present in aquatic environment. Main by-products of phenol degradation were followed as well. Metazachlor ($\text{C}_{14}\text{H}_{16}\text{ClN}_3\text{O}$) is organochlorine pesticide and it was reported to be the fifth most utilized herbicide in Czech Republic in 2010 [133]. Metazachlor is moderately toxic to aqueous organisms such as daphnia, carp and bluegill sunfish [134]. To the best of our knowledge, photocatalytic degradation of metazachlor was not reported earlier. The initial concentrations of formic acid, phenol and metazachlor were 50 mg L^{-1} , 10 mg L^{-1} and 10 mg L^{-1} , respectively.

The feasibility of LED-based photocatalytic treatment was tested using real plywood mill wastewater effluent (**Paper I**). After filtering through filters with pore size $20\text{ }\mu\text{m}$, concentration of tannic acid, TOC and COD were analysed. Since the effluent contained high concentration of organic matter ($\text{COD} = 2200\text{ mg O}_2\text{ L}^{-1}$), it was decided to dilute effluent ten times using tap water ($\text{TOC} = 2\text{ mg L}^{-1}$) in order to decrease time of the experiment. Diluted effluent was characterized using COD ($220\text{ mg O}_2\text{ L}^{-1}$), TOC (70 mg L^{-1}), concentration of tannic acid ($8.8\cdot 10^{-3}\text{ mM}$), turbidity (5.2 NTU), suspended solid concentration (5.6 mg L^{-1}), conductivity (1.1 mS cm^{-1}) and pH (7.4).

4.2.2 Analytical procedures

Changes in concentration of formic acid (**Paper II - IV**) were monitored with High Performance Liquid Chromatograph (HPLC) VARIAN ProStar equipped with column COREGEL-87H3 (300 × 7.8 mm) and UV-Vis detector ($\lambda = 210$ nm). Sulfuric acid ($C = 5 \times 10^{-3}$ mol L⁻¹) was utilized as a mobile phase with flow rate 0.7 mL min⁻¹. In **Paper I** Shimadzu LC-20 with RSpak KC-811 column (300 × 8.0 mm) and UV-Vis detector SPD-20AV ($\lambda = 210$ nm) was used for formic acid analysis. Column temperature was 40°C and 0.1% phosphoric acid aqueous solution was used as mobile phase (flow rate 1 mL min⁻¹).

Measurements of phenol (**Paper II**) its intermediate compounds (hydroquinone, catechol and benzoquinone) were conducted using Shimadzu Ultra Fast Liquid Chromatograph (UFLC) with EC 250/4.6 NUCLEOSIL 100-5 C18 column (porosity – 100 Angstrom and particle size - 5µm) and diode-array detector SPD-M20A ($\lambda = 222$ nm). In **Paper I** phenol, benzoquinone and catechol were measured with Shimadzu LC-20 equipped with Luna 5u C18 (2) 100A (250 × 4.6 mm) column and UV-Vis detector SPD-20AV ($\lambda = 222$ nm). In both cases water (85%) and acetonitrile (15%) were used as an eluent with flow rate 1 mL min⁻¹.

Concentrations of metazachlor (**Paper V**) were determined by means of HPLC Shimadzu LC-20 equipped with UV-Vis detector SPD-20AV ($\lambda = 210$ nm) and Luna 5u C18 (2) 100A (250 × 4.6 mm) column. Water and acetonitrile (50:50, v) was used as eluent with flow rate 1.8 ml/min. Column temperature was 40°C.

Tannic acid analysis was performed using method for formic acid measurements (**Paper I**). Mineralization (**Paper I**) in terms of TOC and COD was followed with Shimadzu TOC – V_{CPH} analyzer in non-purgeable carbon (NPOC) mode and standard method 5220B [135], respectively. Concentration of suspended solids (**Paper I**) was determined using standard method 2540B [135]. Conductivity, turbidity and pH of water (**Paper I**) were analyzed with WTW inolab pH/cond 740 set and Hach 2100P iso turbidimeter, correspondently.

4.3 Experimental setup

4.3.1 Reactor design

For experiments performed with coatings and powder photocatalysts different types of reactor were used. Powder photocatalysts were tested in batch mode with recirculation (**Paper I, V**) using tubular glass reactors (borosilicate glass, inner diameter 0.6 cm) attached to the LEDs. The total volume of tubular reactors was 10.7 mL. The volume of model solutions or effluents treated using this reactor design was chosen according to experimental time, required volume and number of samples. An equation (4.3.1) was used for calculation of contact time.

$$t_{cont} = \frac{(V_r \cdot t)}{V_w} \quad (4.1)$$

Where t_{cont} is contact time (min), V_r – volume of the reactor (mL), t – sampling time (min) and V_w – volume of the water in the system at certain sampling point.

The photocatalytic activity of thin films synthesized in this work was examined using batch cylindrical reactor with total volume 100 mL and diameter of optical window (quartz) 4 cm (**Papers II - IV**). The irradiation source was located under the reactor. Cooling water cell with cut-off filters was situated between lamp and reactor in order to avoid heating of the solution. Graphical representation of this experimental setup can be found in **Paper II**. The volume of treated model solution was 30 mL (**Papers II - IV**).

4.3.2 Characteristic of lamps

Different lamps were used for photocatalytic experiments. More detailed characterization can be found below.

The UVA light emitting diode (LED) lamp was constructed in the Department of Micro- and Nanosciences, Aalto University School of Electrical Engineering in frame of the TEKES funded DELETE project. The emission spectrum of LED lamp (30 x 8 cm) with peak at 370 nm was very narrow with full width half maximum 10 nm. The maximum optical power density of 22 mW cm⁻² is produced by LED. The UVA LED lamp used for photocatalytic studies (**Paper I, V**) are presented in Figure 4.1.

Figure 4.1: The UVA-LED irradiation source

High pressure mercury lamp (Philips HPK 125 W) with different optical filters was used also as an irradiation source in photocatalytic studies (**Papers II-IV**). For instance, for experiments reported in **Paper III**, O-52 and Pyrex filters were utilized in order to cut UVC and UVB irradiation, the UVA intensity at the bottom of the reactor was $7 \pm 0.2 \text{ mW cm}^{-2}$. For experiments reported in **Papers II and IV** only Pyrex optical filters were utilized and the UVA intensity at the bottom of the reactor was $9.1 \pm 0.2 \text{ mW cm}^{-2}$ (**Paper IV**) and $8.3 \pm 0.2 \text{ mW cm}^{-2}$ (**Paper II**). Spectra of HPK lamp and cut-off filters are presented in Figure 4.2.

Figure 4.2: Spectra of HPK lamp, and cut-off filters (Quartz, Pyrex and O-52)

For photocatalytic experiments conducted in visible light (**Paper III**), visible LED lamp with two Pyrex optical filters was used. This LED was emitting at 447 and 555 nm with intensity 42 and 114 mW cm^{-2} . The spectrum of the Vis LED is shown in Figure 4.3.

Figure 4.3: Spectrum of the Vis LED lamp with Pyrex cut-off filters

It should be noted that all optical filters were washed in 37% HCl before each experiment in order to avoid the errors coming from contamination of filter surface.

Intensity of the lamps was measured using VLX-3W radiometer with a CX-365 (UVA) and CX-312 (UVB) detectors. Spectra of the lamps were recorded with the UV-Vis spectrometer AvaSpec-2048 (**Papers II-IV**). In order to estimate accuracy of measurements for both devices, immediate values of irradiance were measured 50 times with 10 sec intervals at intensity 9 mW cm⁻². The standard deviation was calculated according to the equation 4.2.

$$\sigma = \sqrt{\sum \frac{(x-\bar{x})^2}{n}} \quad (4.2)$$

Results are presented in the Table 4.1:

Table 4.1. Results of irradiance measurements

Name of the device	Interval of irradiance measurements, nm	Mean value and standard deviation
VLX-3W radiometer	365 ± 10 nm	9.2 ± 0.2 mW cm ⁻²
AvaSpec-2048 (UV-Vis)	350 – 400 nm	7.7 ± 0.2 mW cm ⁻²

5 Results and discussion

5.1 Photocatalytic activity of modified and unmodified TiO₂ powder

Commercial TiO₂ Degussa P25 (without modifications) under UVA irradiation (LEDs) was found to be feasible for posttreatment of pulp and paper wastewater received from local plywood mill (**Paper I**). Formic acid was a model compound for optimization of experimental parameters because it is often found as one of the final intermediates of degradation of more complex organic pollutants [99, 131, 136]. Optimal mass of photocatalyst was defined as 0.5 g L⁻¹ based on photocatalytic tests performed with formic acid as demonstrated on Figure 5.1.

Figure 5.1: Initial rate of formic acid degradation as a function of mass of TiO₂

Initial rates of formic acid degradation were estimated according to zero order kinetics for 1 min of contact time. From the Figure 5.1 it was concluded that absorption of efficient photons was reached at loading of TiO₂ 0.5 g L⁻¹. Optimal mass of TiO₂ obtained in this work is in agreement with other studies conducted with model compounds [137-139] and real pulp and paper industrial wastewaters [27, 31, 140, 141].

Therefore, this optimal mass of photocatalyst was used in further experiments with phenol and plywood mill wastewater. In optimal conditions initial degradation rate of phenol was $0.033 \text{ mmol L}^{-1} \text{ min}^{-1}$ and it was almost completely eliminated after 6 min under irradiation. Detected by-products of photocatalytic phenol decomposition were hydroquinone, benzoquinone, catechol and formic acid. Formation of hydroquinone, benzoquinone and catechol during phenol decomposition using TiO_2/UV system was reported earlier [142-144]. According to some studies [142] there are about 20 by-products generated during photocatalytic decomposition of phenol. Results of TOC measurements confirmed that not all intermediates were determined (Figure 5.2).

Figure 5.2: TOC results of photocatalytic phenol degradation

As can be seen from Figure 5.2, after 6 min of irradiation amount of phenol was about 0.7%, while amounts of benzoquinone, catechol, hydroquinone and formic acid were 20%, 7.9%, 6.2% and 2.9%, respectively. Thus, amount of organic carbon corresponding to detected by-products after 6 min of contact time was equal to 37.7%, which means that rest 62.3% of TOC is unidentified intermediates. After 13 min of contact time mineralization in terms of TOC and COD was 74% and 69%, respectively. Apparent quantum yields (QY) for phenol and formic acid degradation under optimal conditions were estimated to be 0.98% and 0.8% , respectively. Achieved values of QY are in agreement with reported earlier values of about 1% for majority of photocatalytic reactions in aquatic environment [46, 49].

The tannic acid present in plywood mill wastewater effluent (initial concentration 0.0088 mM) was fully decomposed after 43 min of contact time. Due to

photosensitization properties of humic substances (like tannic acid) [145], about 45% of this compound was eliminated after 60 min of photolysis. Mineralization of organic pollutants presented in wastewater in terms of TOC and COD is demonstrated on Figure 5.3.

Figure 5.3: Mineralization of organic pollutants in plywood mill wastewater effluent as a function of contact time. Insert – degradation of tannic acid vs contact time

As shown in Figure 5.3, after 60 min of photocatalytic wastewater treatment TOC and COD removal reach values 60% and 72%, respectively. During first 30 min of contact time average TOC removal per power unit of LEDs emission was about 0.14 mg TOC/W. With the increase of contact time this value increased up to 1 mg TOC/W and then declined. Calculated average oxidation state of carbon atoms (AOSC) confirmed oxidation of organic compounds in wastewater leading to changes in AOSC value from -0.8 in the beginning of photocatalytic test to +0.7 in the end. Thus, UVA-LED based photocatalytic treatment can be considered as promising technique for advanced treatment of post-treatment of industrial pulp and paper wastewater effluents.

Titanium dioxide powders doped with dysprosium (Dy) and praseodymium (Pr) synthesized by sol-gel method was found to be active for degradation of metazachlor in water under UVA (LEDs) irradiation (**Paper V**). The highest photocatalytic activity was attributed to the TiO_2 sample doped with Dy and Pr and treated during 8h at temperature 450°C (Figure 5.4).

Figure 5.4: Initial degradation rates of metazachlor for TiO₂ doped with Dy and Pr

Based on the obtained SEM images for TiO₂ doped with Dy and Pr (Figure 5.5) it was suggested that increased photocatalytic activity for samples treated 8h at 450°C can be attributed to the formation of smaller aggregates leading to higher specific surface area.

Figure 5.5: SEM images of TiO₂ samples doped with Dy and Pr

It should be noted that all prepared samples were pure anatase (Figure 5.6) meaning that doping of TiO₂ with Dy and Pr suppressed formation of rutile. These results are in agreement with literature [146].

Figure 5.6: XRD pattern obtained for TiO_2 doped with Dy and Pr and treated 4h at 650°C

Among doped sample, Dy-TiO_2 treated 4h at 450°C was found to be less active. Therefore, this sample was chosen for investigation of time required for full decomposition of metazachlor (Figure 5.7).

Figure 5.7: Degradation of metazachlor using Dy-TiO_2 treated 4h at 450°C

As shown in Figure 5.7, 50 min of contact time was needed for complete elimination of metazachlor. This result is in agreement with literature [147]. It worth making a point

that photocatalytic activity of doped samples was compared with that of undoped TiO_2 prepared under same conditions and commercial standard P25. Higher or similar activity of doped samples was observed suggesting that doping of TiO_2 with Dy and Pr enhanced photocatalytic activity. Possibly it can be explained by the fact that the transitions of $4f$ electrons of rare earth elements are responsible for optical absorption of a doped material and support the separation of photogenerated e^-/h^+ pairs. Lanthanide ions are scavengers of excited electrons from the titania conduction band [148].

5.2 Photocatalytic activity of modified and unmodified TiO_2 films

Titanium dioxide thin films deposited on aluminium foam substrates were found to be photocatalytically active for decomposition of formic acid and phenol in aqueous media (**Paper II**). Based on XRD measurements of prepared coatings, the anatase crystalline phase of TiO_2 was determined (Figure 5.8).

Figure 5.8: XRD pattern of aluminum foam coated with 40 nm of Al_2O_3 and 100 nm of TiO_2 above; * sign corresponds to anatase and ♦ corresponds to substrate

Results of SEM analysis (Figure 5.9) demonstrate that TiO_2 thin films are not porous and not uniform, which can be explained by surface of aluminium foam.

Figure 5.9: SEM images of TiO_2 thin films deposited on aluminium foam

Results of photocatalytic degradation of formic acid in aqueous solution are shown in Figure 5.10.

Figure 5.10: Photocatalytic degradation of formic acid using TiO_2 thin films

During the first photocatalytic test (cycle one) formic acid was completely decomposed after 180 min of contact time. Interestingly, photocatalytic activity of TiO_2 thin film

significantly decreased during the second tests (cycle 2). In order to identify the reason for such behaviour ToF-SIMS spectra of TiO_2 surface before and after photocatalytic tests were done (Figure 5.11). Before photocatalytic test the spectrum was dominated by Ti isotopic pattern with main peak at $m/z = 48$. Presence of aluminium (Figure 5.12, zoom at $m/z = 27$) is hardly detectable. However, after photocatalytic test spectrum of coating is dominated by Al^+ peak ($m/z = 27$). Considering the fact that particles were observed in water after the first photocatalytic test, it can be suggested that decrease of photocatalytic activity of TiO_2 coating occurs due to possible detachment of TiO_2 from substrate.

Photocatalytic activity of TiO_2 thin films for decomposition of formic acid was compared with commercially available powder TiO_2 (P25). The amount of titanium dioxide deposited on aluminium foam was determined by ICP-OES and was equal to 0.07 g L^{-1} . Hence, this mass of powder P25 was used in reference experiment. Based on calculated initial degradation rates of formic acid photocatalytic activity of commercial TiO_2 was about 2.5 times higher than that of thin film. This result is in agreement with previous studies dealing with comparison of photocatalytic activity of powder and immobilized TiO_2 [149-151]. However, some controversial results were reported as well [152]. Lower photocatalytic activity of thin films might be due to presence of TiO_2 adsorbing reaction substrate, but not working because of hindrance by aluminium foam framework. The difference in crystalline structure of P25 and thin films deposited by ALD technique should be taken into consideration. It was reported that photocatalytic activity of pure anatase or rutile is lower than mixture of these phases [153]. However, recent study suggested that synergetic effect of anatase and rutile copresence (in case of P25) is myth [154]. It is difficult to explain differences in photocatalytic activity of tested P25 and thin film based on their physico-chemical properties. Many publications attempted to establish effect of physico-chemical features of photocatalysts on photocatalytic activity [98, 155, 156]. In spite of this the correlations between physico-chemical properties of photocatalytic materials and their activity are not well known [82]. One reason can be that it is difficult to study effect of one property of material on photocatalytic activity because often when one property is changed it causes modification of other properties as well. Successful attempt to find correlations between physico-chemical properties of photocatalysts and their activity was reported by group of B.Ohtani [157]. In this work [157] 40 commercial TiO_2 were tested in five photocatalytic reactions (acetic acid decomposition, oxygen liberation along with silver deposition, acetaldehyde decomposition and synthesis of pipecolic acid from L-lysine, methanol dehydrogenation) and six physico-chemical properties of photocatalysts were determined (specific surface area (BET), density of defective sites (DEF), primary particle size (PPS), secondary particle size (SPS) and existence of anatase (ANA) and

rutile (RUT) phases). Based on results of statistical analysis correlations between photocatalyst properties and activity was established for 35 samples. Interestingly, highest photocatalytic activity was attributed to three samples: P25 (Degussa – Nippon Aerosil), TIO-4 (Catalysis Society of Japan) and ST-F4 (Showa Titanium) [157].

Another important point is that procedure of photocatalytic activity comparison of powder and film materials is not established. Thus, caution should be applied. For instance, amount of photons absorbed by surface of P25 and TiO₂ thin film varies because thin film is located at certain distance from the bottom of photoreactor. While in case of P25 many nanoparticles are located on the bottom of reactor. Intensity of UVA irradiance measured (using radiometer) at the bottom of photoreactor and at the level of thin film was $8.3 \pm 0.2 \text{ mW cm}^{-2}$ and $6.7 \pm 0.2 \text{ mW cm}^{-2}$, respectively. Apparent QYs for formic acid degradation using P25 and TiO₂ thin films were calculated to be 2.2% and 2.7%. These results may suggest that comparison of photocatalytic activity of powdered and coated materials using degradation rate of probe molecule is not always realistic.

Figure 5.11: Positive ion ToF-SIMS spectra from TiO_2 films ($m/z = 0 - 200$); A – before photocatalytic test, B – after photocatalytic test

Figure 5.12: Positive ion ToF-SIMS spectra from TiO_2 films ($m/z = 26.5 - 27.5$); A - before photocatalysis and B - after photocatalysis

Similar behaviour of TiO_2 thin films deposited on aluminium foam was observed for photocatalytic removal of phenol from aqueous solution (**Paper II**). After the first test activity was decreased. The initial disappearance rate of phenol obtained with prepared by ALD films was compared with P25 (Figure 5.13).

Figure 5.13: Photocatalytic degradation of phenol and formation of byproducts (HQ - hydroquinone, BQ - benzoquinone, cath - catechol) with P25 (a) and TiO_2 on aluminum foam (b)

By-products of photocatalytic phenol decomposition such as hydroquinone (HQ), benzoquinone (BQ) and catechol were detected on the course of experiments. The initial rate of phenol decomposition using TiO_2 thin film and powder were $0.0011 \text{ mmol L}^{-1} \text{ min}^{-1}$ and $0.0043 \text{ mmol L}^{-1} \text{ min}^{-1}$, respectively. When TiO_2 thin film was used complete degradation of phenol was not achieved after 6h of contact time. In case of P25 phenol and monitored intermediates were almost completely eliminated after 6h. The maximum concentration of intermediates was detected at 33% of the time needed for full phenol decomposition, which is in agreement with earlier results [143]. Apparent QYs for phenol degradation using TiO_2 thin film and P25 were estimated to be 0.4% and 0.7%, respectively. In order to check if all intermediate compounds of phenol decomposition were detected in this study the intermediate conversion rate (ICR) was plotted as a function of global conversion rate (GCR) as shown in Figure 5.14. As it can be seen from Figure 5.14, the faster mineralization can be recognized when experimental data fit to the diagonal line. Thus, it can be summarized that not all by-products were determined. Interestingly, degradation of phenol using P25 and coating prepared by ALD follow the same mechanism.

Figure 5.14: ICR vs GCR plots with TiO₂ on aluminum foam and TiO₂ nanoparticles

Recent publications demonstrated promising results with TiO₂ doped with Au nanoparticles (NP) [13, 14, 75, 79]. However, in most of the studies these materials were synthesized in powder form, which cause difficulties for practical applications. In this work Au modified TiO₂ thin films in silica matrix were synthesized, characterized and tested for photocatalytic degradation of formic acid (**Paper III and IV**).

As demonstrated in Figure 5.16 porous TiO₂/SiO₂/Au thin films were synthesized (**Paper IV**). Porosity of TiO₂/SiO₂ and TiO₂/SiO₂ thin films doped with 0.05%, 0.5%, 1.25% and 5% were 14.3%, 7.7%, 11%, 9.7% and 14.1%, respectively. It should be mentioned that presented values of thin film porosity were obtained after UVC pretreatment. The size of spherical Au NP was estimated to be 5 – 7 nm based on TEM image (Figure 5.15).

Figure 5.15: TEM images of TiO₂/SiO₂ film doped with Au NP (5% wt.)

Figure 5.16: SEM images of prepared thin films, A - reference, B - $\text{TiO}_2/\text{SiO}_2/\text{Au}$ 0.05%, C - $\text{TiO}_2/\text{SiO}_2/\text{Au}$ 0.5%, D - $\text{TiO}_2/\text{SiO}_2/\text{Au}$ 1.25%, E - $\text{TiO}_2/\text{SiO}_2/\text{Au}$ 5%

Presence of Au NP in thin films was also confirmed by detected Au 4f signal in XPS analysis (Figure 5.17).

Figure 5.17: XPS spectrum of $\text{TiO}_2/\text{SiO}_2$ thin film doped with Au NP (1.25%)

The photoinduced super-hydrophilicity of $\text{TiO}_2/\text{SiO}_2/\text{Au}$ coatings was observed. This phenomenon is well known and directly affects photocatalytic activity [158]. Photocatalytic activity of prepared $\text{TiO}_2/\text{SiO}_2/\text{Au}$ thin films was calculated per cm^2 of thin film in order to avoid errors caused by deviations in geometrical area of the coatings (Figure 5.18).

Figure 5.18: Initial degradation rate of formic acid per cm^2 of coating

As indicated in Figure 5.18 elevated photocatalytic activity of $\text{TiO}_2/\text{SiO}_2$ thin films doped with 0.5% and 1.25% of Au NP was found. It is difficult to speculate if the enhanced photocatalytic activity is connected with wt% of doped Au NP. As it is well known, the mass of photocatalyst plays a crucial role [49]. Therefore, TiO_2 loading was determined for all samples (Table 5.1).

Table 5.1. Thickness and mean areal TiO_2 loading of prepared samples

Sample name	Mean thickness, nm	Mean areal loading of TiO_2 , mg cm^{-2}
$\text{TiO}_2/\text{SiO}_2$ (Reference)	470 ± 33	0.085
$\text{TiO}_2/\text{SiO}_2/\text{Au}$ 0.05%	520 ± 30	0.064
$\text{TiO}_2/\text{SiO}_2/\text{Au}$ 0.5%	860 ± 115	0.112
$\text{TiO}_2/\text{SiO}_2/\text{Au}$ 1.25%	700 ± 75	0.118
$\text{TiO}_2/\text{SiO}_2/\text{Au}$ 5%	220 ± 14	0.024

Significant variations of TiO_2 loading were observed, suggesting that comparison of photocatalytic activity of thin films taking into consideration geometrical area may not be representative. Hence, in order to compare activity of prepared samples, optimal TiO_2 loading of undoped $\text{TiO}_2/\text{SiO}_2$ thin films should be identified in chosen experimental conditions. For this purpose undoped $\text{TiO}_2/\text{SiO}_2$ coatings with different thickness and areal loading of TiO_2 were prepared and tested (Figure 5.19).

Figure 5.19: Initial disappearance rate of formic acid as a function of TiO₂ loading for TiO₂/SiO₂ and TiO₂/SiO₂/Au thin films

With increase of the TiO₂ areal loading for TiO₂/SiO₂ the initial rate of formic acid disappearance increase as well. Significant increase of the rate can be observed in the interval of TiO₂ areal loading from 0.004 mg cm⁻² to 0.04 mg cm⁻² (attributed to thickness interval up to about 300 nm). While in the range of TiO₂ areal loading from 0.04 mg cm⁻² to 0.13 mg cm⁻² (mean thickness from 300 nm to 900 nm) photocatalytic activity of TiO₂/SiO₂ films increased slightly which can be attributed to the fact that for thicker films UV absorption may limit utilization of active sites in the depth of the film [159]. Hence, for studied TiO₂/SiO₂ thin films critical thickness is about 300 nm. This result is in agreement with earlier study, in which critical thickness of TiO₂ coatings prepared by sol-gel method was reported to be 360-430 nm [160]. However, photocatalytic activity of titanium dioxide thin films prepared by atomic layer deposition (ALD) technique was reported to increase with thickness of the film up to 100 - 130 nm, above which only minor effect on photocatalytic activity was observed [161]. Results of later study were in a good agreement with [161], showing maximum photocatalytic activity at film thickness of 150 nm [95]. It is worth making a point that physico-chemical properties of the coatings depend on the preparation method, leading to significant deviations in critical film thickness for photocatalytic applications. Experimental conditions such as type of irradiation source, light intensity and tested model compound have significant influence on critical film thicknesses as well [110,

160]. Obtained results of this study are in agreement with the investigation of Grégori et al. [101], where photocatalytic activity of similar $\text{TiO}_2/\text{SiO}_2$ coatings with different thicknesses (various TiO_2 areal loading) were tested using the same experimental set up. In spite of this, initial degradation rates of formic acid for similar $\text{TiO}_2/\text{SiO}_2$ coatings in the study of Grégori et al. were lower than in present work. It can be attributed to the fact that for establishing dependence between formic acid degradation rate and thickness of the coatings, Grégori et al. used $\text{TiO}_2/\text{SiO}_2$ films not preliminary treated in UV. It can be observed from Figure 5.20, that photocatalytic activity of thin films doped with Au NP is not higher than that of undoped coatings. This fact can be possibly explained by the changes in the amount of adsorbed on the surface oxygen and water or surface hydroxyl groups when Au NPs are introduced to the films. Apparent QYs for all tested films were estimated (Table 5.2).

Table 5.2. Results of quantum yield estimations

Sample name	Initial reaction rate, sec^{-1}	A_{irr} , cm^2	$\varphi_{\text{app,in}}$ %
$\text{TiO}_2/\text{SiO}_2$	$1.90267 * 10^{15}$	8.41	1.27
$\text{TiO}_2/\text{SiO}_2/\text{Au}$ 0.05%	$1.89518 * 10^{15}$	8.27	1.29
$\text{TiO}_2/\text{SiO}_2/\text{Au}$ 0.5%	$2.59300 * 10^{15}$	8.05	1.81
$\text{TiO}_2/\text{SiO}_2/\text{Au}$ 1.25%	$2.82775 * 10^{15}$	8.52	1.87
$\text{TiO}_2/\text{SiO}_2/\text{Au}$ 5%	$2.09032 * 10^{15}$	7.85	1.50

Results of this study (**Paper IV**) suggest that photocatalytic activity of $\text{TiO}_2/\text{SiO}_2$ was not improved by doping of spherical Au NP with size 5 – 7 nm. Importantly, it was suggested that thickness and/or areal loading of photocatalyst are very important parameters and it should be taken into account when comparing photocatalytic activity of coatings in order to avoid erroneous conclusions.

Similar porous $\text{TiO}_2/\text{SiO}_2$ thin films were doped with bipyramid-like (BP) Au NPs for enhancing of photocatalytic activity (**Paper III**). This shape of Au NPs was chosen because the surface plasmon resonance (SPR) of these NP is in accordance with spectrum of solar irradiation. Obtained coatings were very similar to those doped with spherical Au NPs in morphology. Presence of Au NPs was confirmed by XPS, TEM (Figure 5.20) and UV-vis spectroscopic measurements (Figure 5.21).

Figure 5.20: TEM photograph of a drop of pure AuBP solution. **b.** TEM photograph of the 1% AuBP doped film. The white arrow points to a gold bipyramid

Figure 5.21: Reflectance spectra of reference film and doped film with 1% AuBP. Insert shows the difference of reflectance between the two films. **b.** Comparison of AuBP solution spectra and the difference of absorbance between reference film and 1% AuBP doped film

Longitudinal SPR around 610 nm and transverse SPR band at 520 nm shown in Figure 5.21 confirm presence of Au BP in doped coating. In comparison with spectrum of pure Au BP solution (Figure 5.21b) the transverse SPR was red-shifted and longitudinal – blue-shifted. It was reported that when morphology of NPs is similar, shift of SPR can be attributed to differences in optical properties of the matrix [162, 163]. Therefore, elevated refractive index of coatings (about 1.8) in comparison with Au BP solution (about 1.3) can explain the red-shift of transversal SPR [163]. The longitudinal SPR was

expected to be red-shifted as well. But instead of red-shift, blue-shift was observed, which can be probably explained by sensitivity of Au BP tips to oxidation.

Based on conclusions of **Paper IV** it was decided to measure TiO_2 loading for thin films doped with Au BP and figure out optimal loading for reference samples. Results are presented in Figure 5.22.

Figure 5.22: Initial rate of formic acid decomposition as a function of TiO_2 loading

From results presented in Figure 5.22 it can be concluded that optimum loading of TiO_2 for undoped coatings was $0.04 - 0.09 \text{ mg cm}^{-2}$. Amount of TiO_2 for thin films doped with Au BP was analysed by means of ICP-OES (Table 5.3).

Table 5.3. Loading of TiO_2 for $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ thin films

Sample	TiO_2 loading, mg cm^{-2}
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 0.1%	0.044
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 0.5%	0.088
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 1%	0.061

Since the TiO_2 loadings of doped coatings were in optimum range, the initial degradation rates of formic acid obtained for doped samples were compared with that of reference sample (with TiO_2 loading in range $0.04 - 0.09 \text{ mg cm}^{-2}$). Mean values of initial degradation rates are shown in Figure 5.23.

Figure 5.23: Initial disappearance rates of formic acid for $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ thin films and reference

As it can be seen from Figure 5.23, increase of photocatalytic activity was observed with increase of Au BP concentration. The highest activity was attributed to coatings doped with 1 wt% of Au BP, which was about two times higher than that of reference samples. This can be possibly explained by the fact that gold nanoparticles act as electron traps and promote electron-hole separation [14, 20, 76]. Similar results were reported in literature for decomposition of acetic acid in aqueous solution by TiO_2 modified with Au NP (2 wt.%) [80]. The apparent QYs were calculated for all tested samples (Table 5.4) and increase of QYs with increase of Au BP was observed.

Table 5.4. Apparent quantum yields for $\text{TiO}_2/\text{SiO}_2$ films doped with Au BP

Sample name	Apparent QY, %
$\text{TiO}_2/\text{SiO}_2$	2.5
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 0.1%	2.6
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 0.5%	3.5
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 1%	4.7

The coatings with higher photocatalytic activity were tested three times and no suppression of activity was observed. Also $\text{TiO}_2/\text{SiO}_2$ films doped with 1 wt% of Au BP were tested for formic acid degradation under visible light only. However, no changes of formic acid concentration were detected on the course of experiment, suggesting absence of visible light photocatalytic activity for chosen reaction. A plausible reason can be absence of direct contact of TiO_2 surface and Au BP [79], which was demonstrated by XPS measurements.

6 Conclusion

Photocatalysis is an efficient method which can address environmental issues such as purification of water and air. The field of photocatalysis is constantly developing. Scientists are preparing new photocatalytic materials in order to improve photocatalytic activity of titanium dioxide known as benchmark material. In spite of this fact, titanium dioxide is one of the most studied photocatalysts nowadays. This work was devoted to preparation and testing of TiO_2 and modified TiO_2 materials for photocatalytic water treatment. Materials were prepared in the form of powders and thin films. Main outcomes of this work are presented below:

- Feasibility of UVA-LED based photocatalytic treatment of plywood mill wastewater effluent was demonstrated (**Paper I**). Commercially available TiO_2 (Degussa P25) was used as a photocatalyst. Results suggest that photocatalysis can be successfully applied as post-treatment method for industrial effluents (pulp and paper, refinery, textile, etc.) containing organic compounds some of which can be recalcitrant. Use of LEDs as irradiation source is promising (especially in countries with poorly available solar irradiation) and can solve an environmental problem arising when conventional lamps containing hazardous mercury are utilized. It should be mentioned that high power LEDs are more expensive in comparison with conventional UV lamps, but they have longer life time, better mechanical stability, compact size and they are more energy efficient.
- The Pr- TiO_2 powder sample treated 8 h at 450 °C demonstrated the highest photocatalytic activity, which was attributed to formation of smaller aggregates during synthesis. Moreover, all doped samples were more active or similar for the degradation of metazachlor than Degussa P25 and undoped TiO_2 prepared in a similar way. Hence, it was concluded that doping of TiO_2 with Dy and Pr enhance photocatalytic activity.
- Titanium dioxide (anatase) thin films deposited on aluminum foam by ALD technique were photocatalytically active for decomposition of formic acid and phenol in aquatic environment (**Paper II**). Performance of thin films was compared with commercially available Degussa P25 for decomposition of both probe molecules. Degussa P25 was found to be more efficient than prepared thin films. This fact was explained by significant differences in specific surface area of TiO_2 nanoparticles (P25) and coatings. It was also demonstrated that the number of incident photons varied, leading to difficulties of such comparison. Apparent quantum yields were calculated for degradation of formic acid (2.2% - film and 2.7% - P25) and phenol (0.4% - film and 0.7% - P25). Intermediates of phenol decomposition such as hydroquinone, benzoquinone and catechol were

detected. However, based on intermediate conversion rate plotted as a function of global conversion rate it was concluded that not all by-products of phenol degradation were measured. Interestingly, it was demonstrated that decomposition of phenol using thin films and P25 follows the same mechanism. Suppression of photocatalytic activity of prepared thin films was observed after the first photocatalytic tests in case of formic acid and phenol degradation due to detachment of TiO_2 from the surface of thin film.

- Composite porous $\text{TiO}_2/\text{SiO}_2$ thin films modified with gold nanoparticles of different shapes (sphere and bipyramid-like) were photocatalytically active for degradation of formic acid in water (**Papers III and IV**). An increase of photocatalytic activity evaluated as rate of formic acid degradation per cm^2 of film was observed for thin films doped with 0.5% and 1.25% of Au nanospheres (**Paper IV**). However, detailed investigation of TiO_2 areal loading and thickness of thin films doped with Au nanospheres lead to conclusion that enhanced photocatalytic activity of samples doped with 0.5% and 1.25% of Au nanospheres was more likely attributed to elevated TiO_2 areal loading than presence of Au nanoparticles. It was suggested that such crucial parameters as thickness and/or areal loading of photocatalyst should be taken into consideration when doped thin films are tested. Unlike Au nanospheres, bipyramid-like Au nanoparticles implemented into TiO_2 thin films enhanced photocatalytic activity under UV irradiation in comparison with undoped coatings. As Au bipyramid-like nanoparticles loading increase so did photocatalytic activity of doped coatings. The most efficient doped films were ones doped with 1wt% of Au bipyramid-like nanoparticles demonstrating activity two times higher than reference sample. Durability of Au bipyramid-like doped TiO_2 thin films was demonstrated. However, only visible irradiation did not had significant effect on photocatalytic properties of Au doped thin films, which was attributed to absence of electronic contact between TiO_2 and Au bipyramid-like nanoparticles.

The photocatalytic activity of some materials prepared within this thesis exceeded that of TiO_2 benchmark (Degussa P25). However, preparation of photocatalytic materials with higher activity than P25 is not easy mainly due to lack of understanding of fundamentals of photocatalysis. Hence, more research should be done in order to understand fully fundamentals of photocatalysis. This will leads to possibility to design more efficient low cost photocatalytic materials and use renewable solar irradiation for photocatalysis in the future.

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Paper I

Application of UVA-LED based photocatalysis for plywood mill wastewater
treatment

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Application of UVA-LED based photocatalysis for plywood mill wastewater treatment

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ABSTRACT

The batch mode UVA-LED photocatalytic reactor with recirculation was tested for formic acid (0.22 mM) and phenol (0.1 mM) degradation using commercially available titanium dioxide. Decomposition of model molecules was monitored by means of high pressure liquid chromatography (HPLC), total organic carbon analyzer (TOC) and chemical oxygen demand (COD). Apparent quantum yields for formic acid and phenol were estimated to be 0.8% and 0.98%, respectively. Also, plywood mill effluent treatment was performed using chosen reactor. Primary degradation of tannic acid, as well as TOC and COD removal were monitored in the course of an experiment. About 72% and 60% of COD and TOC removal was achieved, respectively, after 60 min of irradiation at TiO₂ loading 0.5 g L⁻¹. The evolution of average oxidation state of carbon atoms was estimated for plywood mill wastewater.

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1. Introduction

The majority of pulp and paper producing companies in the world are located in North America and Europe [1]. In 2006, the market share of European pulp and paper industry was 31% [1]. The pulp and paper is known to be the major exporting industry in Finland [2]. In Finland there are 23 paper mills, 13 paperboard mills, 15 pulp mills and 18 mills producing mechanical or semi-mechanical pulp [3].

Large amount of water is used in pulp and paper industry causing the formation of wastewater. For different mills amount of wastewater varies but generally from 5 to 20 m³ of wastewater is discharged per ton of paper and paper board [4]. Usually, wastewater treatment on pulp and paper mills consists of primary clarification followed by biological process [5].

In spite of this, the effluent can be characterized by high chemical oxygen demand (COD) concentrations, color and presence of different organic compounds, some of which can be toxic. When discharged, the pulp and paper wastewater effluents may lead to anoxic conditions in the water and sediments, toxicity, mutagenicity, and eutrophication [6–8]. Tannic acid is present in most surface and ground waters and in industrial wastewater streams from paper and pulp board mills, tanneries, coir and cork factories [9]. It is known to be toxic to the aquatic organisms [10]. Hence, it is

necessary to apply effective methods in order to minimize concentration of tannic acid in drinking water or water discharged from companies. The negative effect of the pulp and paper mills effluent discharge into the Finnish surface water was reported [11–13].

Therefore, an effluent post-treatment is desired in order to decrease negative effect to the environment. Photocatalytic treatment of pulp and paper wastewater was more efficient than UV, UV/H₂O₂ and UV/H₂O₂/TiO₂ for total organic carbon (TOC) and toxicity removal [14]. The successful photocatalytic treatment of pulp and paper wastewaters was reported [5,15,16]. For instance, it was observed by Rodrigues et al. [15] that at optimal TiO₂ (Degussa P25) loading of 0.5 g L⁻¹ the performance of tested AOPs was following: UV < UV/H₂O₂ < UV/TiO₂ < UV/TiO₂/H₂O₂. However, UV/TiO₂/H₂O₂ process did not differ significantly from UV/TiO₂. The COD values after coagulation (initial COD = 1303 ± 25 mg L⁻¹), 2 h of photocatalysis and 4 h of photocatalysis were 514 ± 14, 204 ± 7 and 205 ± 6 mg L⁻¹, respectively [15].

In this regard, it was decided to study feasibility of photocatalytic treatment of local pulp and paper effluent under light-emitting diode (LED) UVA irradiation using commercially available titanium dioxide as photocatalyst. Also, degradation of model compounds such as formic acid and phenol was studied. The LED lamp was chosen as an eco-friendly alternative for traditional UV irradiation sources since it does not contain toxic elements [17]. It should be noted that in comparison with conventional UV lamps high power LEDs are more expensive but show longer life time

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(up to 50,000 h) and better mechanical stability, also they are more energy efficient and have compact size [18].

2. Experimental section

2.1. Materials

Commercial titanium dioxide Aeroxide® (Evonic Degussa GmbH) with specific surface area $36\text{--}65\text{ m}^2\text{ g}^{-1}$, mean particle size 21 nm and point of zero charge around 5.5 was purchased from Sigma Aldrich (Helsinki, Finland). The reagent grade formic acid, phenol (>99%), benzoquinone (>98%), catechol (>99.5%) hydroquinone (>99%) and tannic acid (ACS reagent) were purchased from Sigma-Aldrich. When needed ultrapure water with conductivity $18\text{ M}\Omega\text{ cm}^{-1}$ was used. All chemicals were used without further purification.

2.2. Wastewater

In order to study the effect of TiO_2 concentration (from 0.05 to 1 g L^{-1}) on rate of photocatalytic reaction, Milli-Q water with formic acid (0.22 mM) was used. The formic acid was chosen as a model pollutant because it is known to be an intermediate compound during photocatalytic decomposition of more complex organic molecules [19–21]. Also, the degradation of phenol (0.1 mM) in Milli-Q water and its main byproducts was followed with the chosen concentration of TiO_2 . Phenol was selected as a representative of phenolic contaminants in wastewaters. Finally, feasibility of suggested system was checked for primary degradation of tannic acid in effluent from pulp and paper plant as well as its mineralization.

When received, the pulp and paper mill effluent was filtered using filters with pores size of $20\text{ }\mu\text{m}$ and analyzed. In accordance with reference documents on the best available techniques (BREF) published by the European commission [22] the annual average value of COD is 103 mg L^{-1} , when activated sludge and bio-filtration are applied for the treatment. For this reason and in order to decrease experimental time, it was decided to use effluent diluted 10 times with tap water ($\text{TOC} = 2\text{ ppm}$). Main parameters of prepared for experiment wastewater are shown in Table 1.

2.3. Analytical procedures

Water samples after treatment were analyzed within three days and were kept in the dark place at temperature $5\text{ }^\circ\text{C}$. Concentrations of phenol, benzoquinone, catechol, tannic acid and formic acid were analyzed using Shimadzu LC-20 High Performance Liquid Chromatograph (HPLC). Tannic and formic acids analysis was performed with RSpak KC-811 column ($300 \times 8.0\text{ mm}$) and UV-Vis detector SPD-20AV ($\lambda = 210\text{ nm}$) was utilized, 0.1% phosphoric acid aqueous solution was used as a mobile phase with flow rate 1 mL min^{-1} at column temperature $40\text{ }^\circ\text{C}$. Measurements of phenol, benzoquinone and catechol concentrations in water samples were conducted with Luna 5u C18 (2) 100A ($250 \times 4.6\text{ mm}$)

Table 1

The main characteristics of diluted effluent from pulp and paper mill.

Parameter (unit)	Value
COD ($\text{mg O}_2\text{ L}^{-1}$)	220
TOC (mg C L^{-1})	70
Tannic acid concentration (mM)	8.8×10^{-3}
pH	7.4
Turbidity (NTU)	5.20
Suspend solids (mg L^{-1})	5.6
Conductivity (mS cm^{-1})	1.1

Fig. 1. Experimental set up; 1 – reservoir, 2 – peristaltic pump, 3 – tubular borosilicate reactors, 4 – UVA LEDs.

column and UV-Vis detector SPD-20AV ($\lambda = 222\text{ nm}$). Mixture of water and acetonitrile in ratio 85:15 was used as mobile phase with flow rate 1 mL min^{-1} at column temperature $40\text{ }^\circ\text{C}$.

Rate of mineralization was followed by total organic carbon (TOC) and chemical oxygen demand (COD) measurements. For TOC determination Shimadzu TOC – V_{CH}TOC analyzer was used in non-purgeable carbon (NPOC) mode. The COD and suspended solids (SS) concentrations were determined using standard methods of analysis 5220B and 2540B, respectively [23]. Turbidity, conductivity and pH were measured using Hach 2100P is turbidimeter, WTW inolab pH/cond 740 set, correspondently.

2.4. Photocatalytic experiment

All photocatalytic tests were conducted using experimental set up presented in Fig. 1.

As it is shown in Fig. 1, tests were done in batch mode with recirculation glass tube (borosilicate glass, inner diameter 0.6 cm) reactor under UVA-LED (370 nm) irradiation. The emission spectrum of LED lamp ($30 \times 8\text{ cm}$) was very narrow with full width half maximum 10 nm. The LEDs produced optical power density of 22 mW cm^{-2} at distance 1 cm. Tubular glass reactors were attached to the LEDs. The volume of the aqueous solutions used in experiments was 60 mL (100 mL for wastewater effluent), volume of the mixing reactor was 40 mL and the flow rate was 1 mL s^{-1} . Samples were taken at different time intervals, filtered (pore size $0.45\text{ }\mu\text{m}$) and analyzed.

3. Results and discussion

3.1. Photocatalytic degradation of formic acid

It is well known that in heterogeneous photocatalysis, the loading of TiO_2 is directly proportional to overall reaction rate till certain point after which rate becomes independent on mass of TiO_2 [24]. This point varies for reactors with different geometry and working conditions [25]. It was demonstrated in earlier studies with model pollutants [26–28] and real pulp and paper industrial wastewater [5,14,15,29] that optimal loading of TiO_2 is about $0.5\text{--}0.75\text{ g L}^{-1}$ both for photocatalysis and disinfection. Hence, it was decided to test photocatalytic activity of TiO_2 in the range from 0.05 to 1 g L^{-1} using formic acid as a model compound. Formic acid (FA) with initial concentration 0.22 mM was chosen as a contaminant mainly due to the fact that it is one of the last byproducts found after photocatalytic degradation of more complex organic molecules [19–21] and as it was reported [30] it may have refractive character and in some cases cannot be completely oxidized.

Direct photolysis and adsorption tests were conducted in order to confirm the occurrence of photocatalytic reaction. Samples were taken at certain time intervals and analyzed by means of HPLC after filtration. Concentration of formic acid as a function of contact time at different TiO_2 loadings is presented in Fig. 2A, not all loadings are shown for the sake of clarity. Adsorption and direct photolysis of FA were negligible. As it can be seen from Fig. 2A, dependence of formic acid concentration on contact time is linear, suggesting zero order kinetics in tested interval. Initial rates of formic acid degradation were evaluated for 1 min of contact time and plotted as a function of TiO_2 loading (Fig. 2B).

It was observed that for photocatalyst concentrations 0.05 and 0.1 g L^{-1} no significant difference for initial disappearance rate of formic acid occurs. Probably, minimum concentration of TiO_2 required for starting photodegradation in tested conditions is close to value 0.1 g L^{-1} , after which significant increase of disappearance rate can be noticed. The initial FA degradation rates are increasing with TiO_2 concentration till the value 0.5 g L^{-1} . Further increase of photocatalyst concentration did not affect significantly the initial FA degradation rate, therefore it was decided that in chosen operational conditions total absorption of efficient photons was reached at TiO_2 loading 0.5 g L^{-1} . Slight decrease of reaction rates with increase of TiO_2 loading after 0.75 g L^{-1} can be explained by increase of turbidity leading to decrease of UVA light penetration and screening effect of TiO_2 particles excess [25]. Similar observations were reported in the study of Ghaly et al. [5] devoted to photocatalytic treatment of paper mill wastewater, where resembling photoreactor configuration was used. It was demonstrated that after increase of TiO_2 loading higher than 0.75 g L^{-1} , no significant changes in reaction rate were detected. Decrease of TiO_2 photocatalytic activity for pulp and paper wastewater treatment with increasing TiO_2 concentration after 0.75 g L^{-1} was reported by Kumar et al. [29]. The optimal TiO_2 loading for treatment of pulp and paper wastewater was reported to be 0.5 g L^{-1} in study of

Rodrigues et al. [15]. Based on obtained experimental results and the literature discussed above, it was decided to choose TiO_2 loading of 0.5 g L^{-1} for further experiments.

3.2. Photocatalytic degradation of phenol

Phenol was chosen as a model compound for photocatalytic test as a representative of phenolic pollutants in wastewaters. The mechanism of photocatalytic degradation of phenol was discussed in excellent review [31]. It was reported that at least 20 intermediates are formed during photocatalytic degradation of phenol [31]. However, it is well known that main byproducts of phenol degradation using TiO_2/UV are hydroquinone, benzoquinone and catechol [31–33]. Hence, in this study, the concentrations of the intermediates such as hydroquinone, benzoquinone, catechol and formic acid were monitored during decomposition of phenol. The results of phenol removal as a function of contact time are presented in Fig. 3.

As it can be seen from the plot, the decrease of phenol concentration during adsorption was negligible. Almost complete elimination of phenol was achieved after 6 min of contact time under UVA irradiation. Initial phenol degradation rate was $0.033 \text{ mmol L}^{-1} \text{ min}^{-1}$. Carbon balance was estimated for all detected byproducts during the reaction and results are shown in Fig. 4.

According to Fig. 4, formation of intermediate compounds such as hydroquinone, benzoquinone, catechol and formic acid was observed on the course of photocatalytic experiment. Results shown in Fig. 4 suggest mineralization of phenol and its intermediates. After 6 min of contact time amount of phenol, BQ, catechol,

Fig. 2. (A) Results of formic acid degradation with different loadings of TiO_2 . (B) Dependence of initial degradation rate of FA on TiO_2 loading.

Fig. 3. Photocatalytic degradation of phenol.

Fig. 4. Mineralization of phenol.

HQ and FA was 0.7%, 20%, 7.9%, 6.2% and 2.9%, respectively. The sum of all compounds was 37.7%, assuming 100% for initial phenol concentration. While after 13 min of contact time no phenol was detected and sum of all determined intermediates was 16.8%. However, the TOC measurements indicate that there was about 26% of organic matter in the system after 13 min, confirming the fact that there were undetected byproducts. According to measured TOC and COD values, the mineralization achieved 74% and 69%, correspondently.

3.3. Apparent quantum yield estimation

In order to compare performance of different photocatalytic experimental set ups, the apparent quantum yield should be evaluated. The apparent quantum yield, known to be the ratio of number of molecules of pollutant degraded per second to the number of photons entering the reactor, was evaluated for formic acid and phenol according to Eq. (1) [34].

$$\varphi_{app} = \frac{\left\{ \frac{dN_i}{dt} \right\}_m}{\int_{\lambda_1}^{\lambda_2} \frac{R A_{irr} d\lambda}{hc}} \quad (1)$$

where R is the irradiation intensity ($\text{W m}^{-2} \text{nm}^{-1}$); A_{irr} is the irradiated area of the reactor (optical window, m^2); h the Planck's constant ($6.62 \times 10^{-34} \text{ J s}^{-1}$); the speed of light in vacuum ($2.997 \times 10^8 \text{ m s}^{-1}$); λ_1 the lower wavelength of the spectrum in the range of interest (350 nm) and λ_2 the higher wavelength of the spectrum in the range of interest (400 nm); $\left\{ \frac{dN_i}{dt} \right\}_m$ is the initial rate of photoconversion of i species molecules.

The apparent quantum yields of FA and phenol removal at optimal TiO_2 loading were estimated to be 0.8% and 0.98%, correspondently. Earlier studies demonstrated that quantum yields for most of photocatalytic reactions in aquatic environment are about 1% [35,36].

3.4. Photocatalytic treatment of plywood mill effluent

During the photocatalytic treatment, parameters such as degradation of tannic acid, TOC and COD were monitored. Results of tannic acid primary degradation are shown in Fig. 5.

As it can be seen from the plot, during photocatalytic test complete removal of tannic acid was achieved after 43 min of contact time. It should be noted that about 45% of tannic acid was removed during 60 min of photolysis, which can be ascribed to photosensitization properties of humic substances in water environment [37]. Adsorption of tannic acid was negligible. Mineralization of wastewater effluent during photocatalysis, photolysis and adsorption are presented in Fig. 6.

Fig. 5. Primary degradation of tannic acid as a function of contact time.

Fig. 6. Mineralization of wastewater effluent.

Level of COD and TOC removal during photolysis reach the values of 15% and 2%, respectively. It is obvious that COD removal during photolysis was relatively fast before 8 min of contact time, after which no changes were observed. On the contrary, during photocatalysis, TOC and COD removal was relatively slow in the beginning and faster in the end of the experiment. It can be explained by the formation of more simple intermediates, which can be mineralized easier.

The average oxidation state of carbon atoms (AOSC) was calculated according to Eq. (2) [38].

$$\text{AOSC} = 4 - 1.5 \frac{\text{COD}}{\text{TOC}} \quad (2)$$

The AOSC is a parameter, which allows to indicate the oxidation degree of carbon in complex solutions taking values from -4 (CH_4) to $+4$ (CO_2). Results of AOSC calculations for wastewater effluent during photocatalysis, photolysis and adsorption are shown in Fig. 7.

According to Fig. 7, during photolysis, AOSC changed from -1.6 to -0.8 after 10 min of contact time. This indicates that change of chemical composition of organic compounds occurs not leading to mineralization. With further increase of contact time no oxidation was registered. During first 30 min of adsorption test, AOSC was changed from -1.6 to -0.8 , which can be explained by sorption of some organic compounds on the surface of TiO_2 .

In the photocatalytic test, the residual organic molecules are oxidized, increasing values of AOSC from -0.8 to $+0.7$ with a 60 min of contact time. These results suggest oxidation of organic compounds, confirmed also by mineralization (Fig. 6).

Fig. 7. The AOSC for plywood mill effluent during photocatalysis, photolysis and adsorption.

4. Conclusion

The UVA-LED based photocatalytic degradation of formic acid, phenol and organic compounds in plywood wastewater using commercially available titanium dioxide as a photocatalyst was investigated. The main conclusion of this work can be summarized as follows:

- Based on literature and experimental results performed with formic acid as a model compound, the optimal concentration of TiO_2 for tested discontinuous mode LED – reactor was defined to be 0.5 g L^{-1} .
- Photocatalytic degradation of phenol with initial concentration 0.1 mM at TiO_2 loading 0.5 g L^{-1} was studied. After 6 min of irradiation time, phenol was almost completely eliminated. During the reaction, formation of hydroquinone, benzoquinone, catechol and formic acid was detected. However, it was confirmed that unidentified byproducts of phenol degradation were present in the system. Phenol mineralization was monitored using TOC and COD. After 13 min of irradiation time, removal of TOC and COD reach the level of 74% and 69%, correspondently.
- The apparent quantum yields for formic acid and phenol photocatalytic degradation were estimated to be 0.8% and 0.98%, respectively.
- The feasibility of chosen experimental set up was also tested for plywood mill wastewater treatment. It was observed that tannic acid with initial concentration 0.0088 mM was completely removed after 43 min of irradiation. Mineralization of wastewater on the course of the experiment was monitored using TOC and COD measurements. The decrease of TOC and COD after 60 min of irradiation was 60% and 72%, respectively. The AOSC was calculated as well and it increases from -0.8 to $+0.7$, which confirms oxidation of organic compounds.
- Based on obtained results it was suggested that UVA-LED based photocatalysis is a promising post-treatment method for effluents from pulp and paper industry.

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Paper II

Photocatalytic activity of TiO₂ films immobilized on aluminum foam by
atomic layer deposition technique

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Apparent quantum yield

ABSTRACT

The aim of this work was to study feasibility of titanium dioxide thin films prepared by atomic layer deposition (ALD) technique on aluminum foam substrates for photocatalysis and compare performance of thin films with commercially available AEROXIDE[®] TiO₂. Formic acid and phenol photocatalytic decomposition was monitored using high-pressure liquid chromatography (HPLC). The morphology and thickness of TiO₂ films were characterized by scanning electron microscopy (SEM) and their structure was determined by X-ray diffraction (XRD). Surface of the thin films was characterized with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The amount of TiO₂ deposited on aluminum foam was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). It was observed that initial rates of formic acid and phenol degradation were 0.007 and 0.001 mmol L⁻¹ min⁻¹, respectively. The apparent quantum yields for formic acid using immobilized and reference TiO₂ powder (AEROXIDE[®] TiO₂ P25, Evonik) were 2.2 and 2.7%, correspondingly. While for phenol apparent quantum yield was equal to 0.4% when TiO₂ thin film was used and 0.7% in the case of reference powder. A decrease of the photocatalytic activity of TiO₂ films deposited on aluminum foam was observed after the first cycle for both model compounds. It was suggested from this study that suppression of activity occurs due to detachment of TiO₂ from the surface of thin film.

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1. Introduction

Titanium dioxide is well known as an efficient photocatalyst [1]. It is also the most commonly used one, mainly due to its nontoxicity, sufficiently high photocatalytic activity, large scale availability and relatively low price [1]. Numerous studies have been devoted to the photocatalytic activity of TiO₂ in slurry systems [2–7]. However, the main challenge arising when slurry reactor design is used is the separation of photocatalyst from treated water, which is costly operation [8,9]. Hence, since 1993 the idea of using titanium dioxide or other photocatalyst deposited on inert support became widely accepted [9]. The most studied supports for photocatalytic coatings are glass [8,10–15], activated carbon [16,17], silica gel [18–20] and polymers [21–23]. Other materials such as cellulose [24], and stainless steel [25,26]

have been studied for the immobilization of photocatalysts as well. However, relatively few studies on photocatalytic activity of titanium dioxide deposited on reticulated substrates such as foams have been reported [27–33]. Macroscopic three-dimensional pore structure of foams makes them promising materials for immobilization of photocatalysts due to their large interface for reaction and possibility for liquid to flow through foam quite efficiently [29]. Also lightweight of these materials is beneficial when used as support for photocatalyst.

To the best of our knowledge, there was only one study devoted to photocatalytic activity of TiO₂ thin films deposited by ALD technique on reticulated substrates such as porous steel fiber [32]. In this investigation it was demonstrated that photocatalytic degradation of methyl orange was enhanced by using TiO₂ film on porous steel fiber substrate with specific surface area of 41.88 m² g⁻¹ in comparison with flat TiO₂ film.

Atomic layer deposition (ALD) is a chemical gas phase thin film deposition technique, which can be considered as a modification of

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the chemical vapor deposition (CVD) method [34]. In comparison with other deposition techniques, ALD is extremely beneficial due to easy control of composition and thickness of the films, as well as exceptional conformality on substrates of complex shapes [34]. Hence, ALD was chosen as an optimal method for coating porous foam substrate.

The aim of present study was to investigate feasibility of TiO₂ thin films deposited on aluminum foam substrate using ALD technique for photocatalysis, compare their performance with powder TiO₂ and to study their stability. For testing photocatalytic activity of prepared thin films, two common contaminants were selected. The first model compound was formic acid (FA) which is often one of the ultimate compound obtained during degradation of the different pollutants, photocatalytic degradation of which normally follows a single mechanism without formation of any stable intermediates [35–37]. The second model compound used in photocatalytic tests was phenol, which is representative of the common family of phenolic pollutants. Reference tests were performed using commercially available TiO₂ (AEROXIDE TiO₂ P25, Evonik) with both model contaminants.

2. Experimental

2.1. Chemicals

Commercial standard of titanium dioxide (P25, anatase – 72%, rutile – 28%) with surface area 50 m² g^{−1} was purchased from Evonik. The formic acid was purchased from Acros Organics (99%). Phenol, benzoquinone (BQ), hydroquinone (HQ) and catechol with purity >98% were purchased from Aldrich. In all experiments ultrapure water with conductivity 18 MΩ cm^{−1} was used. All chemicals were used without further purification.

2.2. Deposition of TiO₂ thin films on Al foam substrate

Aluminum foam with thickness 3.2 mm, bulk density 0.2 g cm^{−3}, purity 98.5% and porosity 93% was purchased from Goodfellow Cambridge Ltd. and used as substrate for TiO₂ thin films. Before coating, substrates were treated ultrasonically in water and ethanol and dried at 100 °C in order to clean the surface. Titanium dioxide films with thickness 100 nm were deposited on 7.5 cm × 2.5 cm substrate using TFS 200 ALD reactor (BENEQ) with thermal 2D reaction chamber (diameter = 200 mm and height = 6 mm). The reactor was operated under pressure of about 1 mbar and at temperature 300 °C. Carrier and purging gas was nitrogen. TiCl₄ as a precursor and H₂O as source of oxygen were used for deposition of TiO₂ films. Film of Al₂O₃ with thickness 40 nm was deposited on aluminum foam prior TiO₂ (similar reactor and operational conditions were applied) in order to avoid corrosion of substrate. For deposition of Al₂O₃ film trimethylaluminum (TMA) and H₂O were used as precursors. The surface of aluminum foam was uniformly coated, which allowed to maintain the porosity and gas permeability of the support.

2.3. Characterization

Morphology of thin films was observed using scanning electron microscopy (SEM) (ZEISS LEO 1550). In order to identify phase of TiO₂, X-ray diffraction (XRD) analysis was performed with Bruker D8 Advance A25 diffractometer with Cu-Kα radiation (λ = 1.54184 Å). Amount of Ti loaded on the substrate and concentration of Ti in samples after photocatalytic tests was determined by means of inductively coupled plasma optical emission spectrometry (ICP-OES) using “Activa” Jobin Yvon machine. Before analysis TiO₂ coatings were dissolved in a mixture of H₂SO₄, HNO₃ and HF and left overnight at the oven at 120 °C. ToF-

SIMS measurements were carried out using a Physical Electronics TRIFT III ToF-SIMS instrument (Physical Electronics, Chanhassen, USA) operated with a pulsed 22 keV Au⁺ ion gun (ion current of about 2 nA) rastered over a 300 μm × 300 μm area. An electron gun was operated in pulsed mode at low electron energy for charge compensation. Ion dose was kept below the static conditions limits. Data were analyzed using the WinCadence software. Mass calibration was performed on hydrocarbon secondary ions.

2.4. Photocatalytic activity

Photocatalytic activity of TiO₂ films with thickness about 100 nm deposited on aluminum substrate was estimated using experimental set up presented in Fig. 1. As it can be seen from Fig. 1, batch cylindrical reactor with total volume of 100 cm³ and diameter of quartz optical window 4 cm was used. Samples of TiO₂ deposited on aluminum foam with dimensions 2.5 cm × 3 cm were located in the reactor (on the top of glass peaks) and covered by 3 cm × 3 cm glass substrate preventing floating of the sample.

Formic acid and phenol were used as model pollutants. Concentration of formic acid was measured with VARIAN ProStar High Performance Liquid Chromatograph (HPLC) equipped with column COREGEL-87H (300 × 7.8 mm) purchased from TRANSGENOMIC[®] and UV-vis detector (λ = 210 nm) using H₂SO₄ (C = 5 × 10^{−3} mol L^{−1}) as a mobile phase with flow rate 0.7 mL min^{−1}. Limit of detection (LOD) and limit of quantification (LOQ) for FA were 0.004 mM and 0.012 mM, respectively. Shimadzu Ultra Fast Liquid Chromatograph (UFLC) was applied for phenol analysis (LOD = 0.004 mM and LOQ = 0.011 mM) and its intermediate compounds hydroquinone (LOD = 0.008 mM and LOQ = 0.025 mM), catechol (LOD = 0.012 mM and LOQ = 0.038 mM) and benzoquinone (LOD = 0.008 mM and LOQ = 0.023 mM), EC 250/4.6 NUCLEOSIL 100-5C18 column (porosity – 100 Å and particle size – 5 μm) and diode-array detector SPD-M20A (λ = 222 nm) were used, water (85%) and acetonitrile (15%) were used as an eluent with flow rate 1 mL min^{−1}.

Irradiation was provided with high pressure mercury lamp (Philips HPK 125W). Owing to circulation water cell with Pyrex filters, no infrared and UVC beams reach the reactor. The radiant flux measurements were conducted before each experiment using VLX-3W radiometer with a CX-365 (UVA) and CX-312 (UVB) detectors. Spectrum of the lamp, measured with the UV-vis spectrometer AvaSpec-2048 (Avantes) is shown in Fig. 2.

Results of irradiance measurements at the level of the thin film and at the bottom of the reactor are shown in Table 1.

Magnetic stirrer with “+” shape was used for mixing 30 mL solution with speed of about 600 rpm. Samples were taken after

Fig. 1. Set up for photocatalytic experiments.

Fig. 2. Spectrum of HPK lamp after circulation water cell with Pyrex filters.

regular intervals and concentration of formic acid and phenol (initial concentration of FA 1.09 mM and phenol 0.53 mM) were measured with HPLC. Photocatalytic tests were performed at least three times. Adsorption test and photolysis were carried out with each pollutant as well. For confirmation of photocatalytic activity of TiO_2 deposited on aluminum foam, photocatalytic tests with aluminum foam coated only with 40 nm Al_2O_3 were conducted. Because the photocatalytic activity is relative value [38], reference tests were performed using commercially available titanium dioxide.

3. Results and discussion

Titanium dioxide thin films were deposited using ALD technique onto aluminum foam. The materials were first structurally characterized before evaluation of their photocatalytic properties.

3.1. Characterization of photocatalytic material

XRD spectrum of TiO_2 thin film deposited on aluminum foam is shown in Fig. 3.

As it can be seen from Fig. 3, peak of anatase was detected at 2θ equal to 25. Other peaks were attributed to the substrate. Characteristic diffraction pattern of the support were extremely intense, and the representative peak of anatase was relatively weak (shown in insert in Fig. 3).

SEM images of TiO_2 thin film deposited on aluminum foam are shown in Fig. 4.

From Fig. 4 it can be seen that uneven surface of substrate is coated with rather uniform film of TiO_2 . It can be also concluded that prepared coatings are not porous. The thickness of thin film was evaluated by bending coated substrate and checking profile widths with SEM (Fig. 4E). Measured thickness of thin film was 146 nm, which is very near to expected value 140 nm (40 nm of Al_2O_3 film and 100 nm of TiO_2 film).

Positive ion mode ToF-SIMS spectra of TiO_2 surface before and after photocatalytic test are shown in Figs. 5 and 6. As it can be seen from Fig. 5A, the spectrum of the thin film before photocatalytic experiment was dominated by the Ti isotopic pattern (main peak at $m/z=48$). Zoom around $m/z=27$ (see insert in Fig. 6A)

demonstrates that presence of aluminum is hardly detectable (the main peak is related to C_2H_3^+ – exact m/z of C_2H_3^+ is 27.0235). After photocatalytic test (Fig. 5B) spectrum of the thin film is dominated by Al^+ peak $m/z=27$ (see insert in Fig. 5B – exact m/z of Al^+ is 26.9815). These results can suggest loss of TiO_2 during photocatalytic test.

Amount of titanium coated on $2.5\text{ cm} \times 3\text{ cm}$ substrates was measured with ICP-OES before photocatalytic tests and it was $1.24 \pm 0.04\text{ mg}$.

3.2. Photocatalytic activity

3.2.1. Photocatalytic degradation of formic acid

It is known that critical thin film thickness depends on factors such as preparation technique, experimental set up and organic test substance [39]. It was reported earlier that optimal thickness for TiO_2 thin films prepared by ALD in similar to this study conditions is about 100 nm [40,41]. Therefore, this value was chosen for current study. The amount of TiO_2 coated on substrate corresponds to TiO_2 concentration 0.07 g L^{-1} , therefore, this concentration of P25 was used in reference tests.

Evaluation of photocatalytic activity and aging of prepared thin films was conducted with aqueous solutions of formic acid and phenol. Commercial standard of TiO_2 was used for comparison of photocatalytic activity.

Degradation of formic acid in aqueous solution with initial concentration 1.09 mM was conducted within 3 h, samples were taken after each 30 min and analyzed with HPLC. In order to achieve adsorption equilibrium, first 30 min of each test were carried out under continuous stirring in darkness. Five photocatalytic tests were performed with one sample in order to check if there is change in activity. No treatment of TiO_2 film deposited on aluminum foam was applied between tests. After each run, sample was rinsed with Milli-Q water, dried with air and used in next experiment. Results of FA decomposition using TiO_2 film deposited on aluminum foam are shown in Fig. 7.

As it can be seen from Fig. 7, adsorption, photolysis and test with aluminum foam coated with 40 nm of Al_2O_3 lead to negligible decrease of FA concentration. During the first photocatalytic run, FA was fully decomposed after 180 min under irradiation. After the first test photocatalytic activity of TiO_2 thin film deposited on Al foam decreased almost two times. Results of ICP analysis demonstrated that there was no dissolved titanium after photocatalytic tests. However, particles were observed in the water after photocatalytic test suggesting possible detachment of TiO_2 . The ToF-SIMS measurements clearly show domination of aluminum on the surface of films after photocatalytic test, which can be ascribed to loss of TiO_2 . This fact can explain significant decrease of the thin film activity after first photocatalytic test.

Degradation of FA was performed using commercial TiO_2 powder as a reference. Since the loading of TiO_2 in a reference test was relatively low, it was decided to follow initial FA disappearance rates with different TiO_2 concentrations. Results are shown in Fig. 8.

From Fig. 8 it can be seen that at chosen experimental conditions, initial FA disappearance rate does not change with increase of TiO_2 loading above 0.4 g L^{-1} . It can be explained by full absorption of emitted photons [42].

Table 1
Results of irradiance measurements (UVA).

Parameter	At the level of the film	At the bottom of reactor
Irradiance from 355 to 375 nm, mW/cm^2 (radiometer)	6.7 ± 0.2	8.3 ± 0.2
Irradiance from 350 to 400 nm, mW/cm^2 (UV–vis)	5.5 ± 1.3	7.7 ± 1.6

Fig. 3. XRD pattern of aluminum foam coated with 40 nm of Al_2O_3 and 100 nm of TiO_2 above; * sign corresponds to anatase and ♦ corresponds to substrate.

Photocatalytic degradation of FA using TiO_2 powder with loading equal to amount of TiO_2 in thin film deposited on aluminum foam (0.07 g L^{-1}) was significantly faster than that using thin film. The initial disappearance rates of FA using TiO_2 powder (0.07 g L^{-1}) and TiO_2 film on aluminum foam were calculated to be 0.017 and $0.007 \text{ mmol L}^{-1} \text{ min}^{-1}$, correspondently. Thus, the initial

rate of FA decomposition using commercial TiO_2 was about 2.5 times higher than that using TiO_2 film deposited on aluminum foam. In previous studies dealing with comparison of photocatalytic activity of powdered TiO_2 and immobilized one, using different deposition techniques (sol-gel, PMTP, sputtering), higher activity of powdered TiO_2 has also been observed [8,43,44]. However, some reports are controversial and present more efficient photocatalytic degradation of organic compounds when immobilized titanium dioxide is used. Thus, Ochuma et al. [45] reported that photocatalytic oxidation of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was more efficient when titanium dioxide deposited on aluminum foam was used in comparison with P25 with equal loading of photocatalyst. It is worth making a point that also in this study at optimal concentration of P25, performance of slurry system exceeds that of immobilized one [45].

It should be noted also that P25 is mixture of anatase and rutile, while samples prepared for this study were pure anatase. It was reported that pure anatase or rutile is less efficient than the mixture of these phases [46,47].

However, feasibility of comparison between powder and thin film is under scrutiny and caution should be applied in the interpretation of data. It is likely that in case of powdered TiO_2 almost all surface was illuminated and in case of thin film only one side was exposed to the irradiation source. Another point is difference in amount of photons received by nanoparticles and TiO_2 film, since the thin film was located at the certain distance from the bottom of the reactor and significant amount of nanoparticles were at the bottom. An attempt was made to estimate photon flux received by the surface of photocatalysts and results are shown in Table 1. It should be noted that measurements were performed inside the reactor in absence of FA solution. As it can be seen from Table 1, the photon flux at the bottom of the reactor is higher than that at the level of thin film. The quantum yields were calculated for more adequate comparison of prepared sample with the reference.

3.2.2. Photocatalytic degradation of phenol

When photocatalysis is applied for the removal of complex organic compounds it is not always easy to follow degradation pathway and detect all formed byproducts. As it was reported in recent review, at the first step of phenol photocatalytic degradation intermediates such as hydroquinone (HQ) and catechol are formed

Fig. 4. SEM micrographs of coated aluminum foam (A, B, C and D); E – SEM micrograph of bended substrate.

Fig. 5. Positive ion ToF-SIMS spectra from TiO_2 films ($m/z = 0\text{--}200$); A – before photocatalysis; B – after photocatalysis.

[48]. Also in some studies, presence of benzoquinone (BQ), HQ *etc.* was detected [48]. Therefore, in present study during the photocatalytic degradation of phenol using TiO_2 films deposited on aluminum foam and TiO_2 nanoparticles, concentrations of phenol and its main byproducts such as HQ, BQ and catechol were analyzed at each sampling point with HPLC.

Results of photocatalytic degradation of phenol using TiO_2 thin film deposited on aluminum foam and TiO_2 commercial standard are represented in Fig. 9 as well as results of experiments performed in darkness and under irradiation in absence of photocatalysts.

As it can be seen, the decrease of phenol concentration during adsorption and photolysis tests was negligible as well as during photocatalytic tests of aluminum foam coated with 40 nm of Al_2O_3 . Prior to each photocatalytic tests adsorption equilibrium was achieved during 30 min in darkness, which is indicated in Fig. 9 as “UV off”. After adsorption period photocatalyst was irradiated during period of 360 min, indicated in Fig. 5 as “UV on”. Phenol with initial concentration of 0.53 mM totally disappeared only after 330–360 min of irradiation using P25 with loading 0.07 g L^{-1} , while only about 70% of phenol can be degraded under similar conditions using fresh TiO_2 film deposited on aluminum foam. After the first run significant decrease of photocatalytic activity of TiO_2 film was observed leading to only 20–25% of phenol decomposition. Similar behavior was observed for degradation of formic acid, which can be possibly explained by loss of TiO_2 and

Fig. 6. Positive ion ToF-SIMS spectra from TiO_2 films ($m/z = 26.5\text{--}27.5$); A – before photocatalysis and B – after photocatalysis.

degradation of intermediates which can be chemisorbed on the surface of film [49,50].

The initial disappearance rates for phenol with P25 and TiO_2 film were estimated to be 0.0043 and $0.0011\text{ mmol L}^{-1}\text{ min}^{-1}$, respectively. Thus, initial degradation rate of phenol using TiO_2 powder is about four times faster than using immobilized TiO_2 .

In Fig. 10 results of phenol degradation and formation of BQ, HQ and catechol are shown for test with fresh TiO_2 film on aluminum foam and powdered TiO_2 . Changes of phenol concentration after adsorption were negligible and therefore this part of experiment was not shown in Fig. 10.

The attempts to understand the mechanism of phenol degradation under UV irradiation in presence of TiO_2 were made by many researchers [32,51,52]. It is generally agreed that when TiO_2 is used for phenol degradation under UV, the primary oxidation species responsible for phenol removal are hydroxyl radicals [48]. As it was expected, considering that $^{\bullet}\text{OH}$ concur *ortho* and *para* positions in the phenol aromatic ring, byproducts of photocatalytic degradation of phenol in both cases were HQ and catechol, which is also in agreement with literature [53].

It should be noted that when TiO_2 nanoparticles were used as a photocatalyst, formation of byproducts started in the beginning of experiment and by the end of the test almost all intermediates were decomposed as well as phenol. The maximum concentration of byproducts was detected at 33% of the time, required for full phenol degradation, which is in agreement with results reported elsewhere [51]. In case of immobilized TiO_2 , monitored intermediates started to appear in the solution after 120 min of irradiation when the concentration of phenol was about 0.4 mM.

Fig. 7. Photocatalytic degradation of formic acid and aging of TiO_2 thin film.

Fig. 8. Influence of TiO_2 concentration on initial disappearance rate of FA degradation.

Complete degradation of phenol and its byproducts was not achieved after 6 h of irradiation when TiO_2 deposited on aluminum foam was used.

The intermediate conversion rate (ICR) as a function of global conversion rate (GCR) of phenol was calculated using Eqs. (1) and

(2) and plotted in Fig. 10 in order to evaluate if all byproduct of phenol degradation were determined [54].

$$\text{ICR} = \frac{[\text{HQ}] + [\text{BQ}] + [\text{Ct}]}{[\text{Ph}]_0} \quad (1)$$

$$\text{GCR} = \frac{[\text{Ph}]_0 - [\text{Ph}]}{[\text{Ph}]_0} \quad (2)$$

where $[\text{HQ}]$, $[\text{BQ}]$, $[\text{Ct}]$, and $[\text{Ph}]$ are concentrations of hydroquinone, benzoquinone, catechol and phenol at different time, respectively. And $[\text{Ph}]_0$ is concentration of phenol at time 0.

On Fig. 11, the faster mineralization can be recognized when data is maximum fit to the diagonal line. From obtained curves, it can be concluded that not all intermediates of phenol degradation were determined. However, it can be seen that photocatalytic degradation of phenol using commercial TiO_2 and prepared sample follow the same mechanism.

3.2.3. Evaluation of apparent quantum yield

It is challenging to estimate primary and overall quantum yields for heterogeneous photocatalytic systems correctly, mainly due to problems arising when number of photons absorbed by photocatalyst should be measured, detailed discussion can be found elsewhere [55,56]. The apparent quantum yield is a parameter, which is usually defined as the ratio of converted reactant molecules over the number of photons entering the reactor [57] and therefore, easier to evaluate [58]. In this work an attempt to estimate apparent quantum yields for tested photocatalysts (TiO_2 thin films and P25 with concentration 0.07 g L^{-1}) from an equation presented below was made [57].

$$\phi_{\text{app.in}} = \frac{\left\{ \frac{dN_i}{dt} \right\}_{\text{in}}}{\int_{\lambda_1}^{\lambda_2} \frac{RA_{\text{irr}} \lambda d\lambda}{hc}} \quad (3)$$

where R is the irradiation intensity ($\text{W m}^{-2} \text{ nm}^{-1}$), A_{irr} is the irradiated catalyst area (m^2); h the Plank's constant ($6.62 \times 10^{-34} \text{ J s}^{-1}$); the speed of light in vacuum ($2.997 \times 10^8 \text{ m s}^{-1}$); λ_1 the lower wavelength of the spectrum in the range of interest (300 nm) and λ_2 the higher wavelength of the spectrum in the range of

Fig. 9. Photocatalytic degradation of phenol with TiO_2 on aluminum foam and P25.

Fig. 10. Photocatalytic degradation of phenol and formation of byproducts (HQ – hydroquinone, BQ – benzoquinone, cath – catechol) with P25 (a) and TiO₂ on aluminum foam (b).

Fig. 11. ICR vs GCR plots with TiO₂ on aluminum foam and TiO₂ nanoparticles.

interest (400 nm); $\{dN_i/dt\}_m$ is the initial rate of photoconversion of *i* species molecules. Results of calculations are shown in Table 2.

As can be seen from Table 2 apparent quantum yield for FA degradation was higher than that of phenol, which can be explained by higher rate of FA degradation. The results of the apparent quantum yields estimations demonstrate that all values are close to values of 1–2%, which is in agreement with [59].

4. Conclusion

Titanium dioxide (anatase) thin films with thickness about 100 nm were deposited on aluminum foam using atomic layer deposition technique (ALD). Photocatalytic activity of prepared thin films was evaluated using formic acid and phenol as a model compounds and compared with the activity of commercially available TiO₂ (P25) in the same conditions. Apparent quantum yields were calculated in order to compare photocatalytic activity of titanium dioxide thin films and commercial standard (P25). For formic acid apparent quantum yields were 2.2 and 2.7% for thin films and P25, respectively. Apparent quantum yields for phenol degradation were 0.4 and 0.7 for thin films and P25, correspondingly. Byproducts of photocatalytic phenol degradation, such as hydroquinone, catechol and benzoquinone were determined. However, calculation and plotting of the ICR as a function of

GCR demonstrated that not all intermediates were detected. Based on this plot, it was concluded that photodegradation of phenol using thin films and P25 follows the same mechanism. Suppression of photocatalytic activity of thin films was observed after the first test for phenol and formic acid. Results of material characterization suggest that it possibly occurs due to detachment of TiO₂ and degradation of intermediates of formic acid and phenol photocatalytic decomposition.

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Table 2
Results of quantum yield estimations.

Compound	Photocatalyst	$\phi_{app,m}$ %
FA	P25	2.7
FA	TiO ₂ on Al foam	2.2
Phenol	P25	0.7
Phenol	TiO ₂ on Al foam	0.4

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Paper III

Enhanced photocatalytic activity through insertion of plasmonic
nanostructures in porous TiO₂/SiO₂ hybrid composite film

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Enhanced photocatalytic activity through insertion of plasmonic nanostructures in porous TiO₂/SiO₂ hybrid composite films

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ABSTRACT: Composite TiO₂/SiO₂ porous thin films prepared using the sol-gel process were doped with dispersion of bipyramid-like gold nanoparticles (AuBP). The impact of the presence of the nanoparticles on the photocatalytic activity during degradation of formic acid in aqueous media was fully investigated and improvement of the efficiency was observed. The films compositions and structures were characterized by means of UV-Vis spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectrometry (XPS), inductively coupled plasma optical emission spectroscopy (ICP-OES), goniometry and diffuse reflectance measurements. The photocatalytic activity was evaluated through decomposition of formic acid and correlated with the structure and the spectroscopic characterizations. The best results in terms of photocatalysis were obtained with thin films doped with 1 wt% of AuBP, more specifically initial degradation rate of formic acid was nearly two times higher in comparison with the undoped reference. It was observed that after three cycles performance of prepared photocatalyst does not undergo significant changes. No photocatalytic activity was detected for any of synthesized thin films under only visible light irradiation. The photocatalytic improvement was correlated with the lowering of the band gap of TiO₂.

1. INTRODUCTION

Titanium dioxide is one of the best photocatalytic materials among semiconductors¹. Also, TiO₂ is known as not toxic and relatively cheap, which makes it very attractive in particular for large scale applications². However, the main drawback is that it has a limited photocatalytic activity in the low visible region and only the UV part of the spectrum can be exploited in the case of sun natural excitation. Therefore, different approaches such as doping TiO₂ with metals and non metallic elements are generally used to extend its photocatalytic activity¹. Modification of titanium dioxide with noble metals benefits from relative stability of these metals under UV and aerated atmosphere³. As a result, TiO₂ doping with noble metals is widely studied in order to

extend photocatalytic response of TiO₂ into the visible area¹. Among these metals, gold has attracted significant attention during last two decades⁴.

Unique properties and high potential of gold nanostructures lead to new applications in different areas such as optoelectronics, sensors, nanocatalysis, nanomedicine *etc.*⁵⁻¹². Mostly, these properties are caused by collective oscillation of electrons when interacting with electromagnetic wave known as surface plasmon resonance (SPR). The size and geometry of gold nanoparticles have critical effect on wavelength and intensity of SPR. In this sense the use of anisotropic gold nanoobject present a real advantage in term of possibility of plasmon control up to the IR wavelength and of intense

local field when the structure exhibit tips such as for bipyramids or stars¹³⁻²⁴.

In most of the works devoted to photocatalytic activity of TiO₂ doped with gold nanoparticles, they are introduced with spherical shape²⁵⁻²⁹. However, recently photocatalytic properties of TiO₂ doped with gold nanorods^{30, 31}, were reported. Tips bearing nanoparticles were explored for fluorescence enhancement of dyes which appeared to be more efficient than when using spherical shapes³². Moreover they were shown to strongly improve nonlinear optical properties when associate to dyes in sol-gel matrices, in a more efficient way than spheres or rods³³⁻³⁵.

To the best of our knowledge, no work demonstrating effect of association of TiO₂ with gold bipyramidal nanostructures on photocatalytic activity was reported. The use of sol-gel method for the preparation of efficient photocatalytic flexible coatings was previously reported³⁶. These films were porous which is of particular interest for efficient photocatalytic activity due to high catalyst/organics surface of interactions. Similar strategy was used here for the preparation of the composite.

Hence, the aim of this work was to study photocatalytic properties of SiO₂/TiO₂ composite films synthesized via sol-gel method and doped with bipyramid-like gold nanoparticles (AuBP). For the study of the photocatalytic activity, formic acid degradation was performed under UV and/or visible light.

2. EXPERIMENTAL

2.1 Chemicals

Méthyltriethoxysilane (MTEOS) was purchased from ABCR, Tetrachloroauric acid trihydrate (99.9%) and silver nitrate were obtained from Alfa Aesar, while CTAB (cetyltrimethylammonium bromide, 99%), CTAC (cetyltrimethylammonium chloride solution 25% in water), 2-methyl-8-hydroxyquinoline (MHQL, 98%) and 8-hydroxyquinoline (HQL, 99%) were received from Aldrich. The 8-hydroxyquinoline was purified by dissolution in refluxing toluene, followed by hot filtration on a silica plug and crystallization. The formic acid was purchased from Acros Organics (99%). Titanium dioxide (P25, anatase – 72%, rutile – 28%) with surface area 50 m²g⁻¹ was purchased from Degussa-Hüls-AG.

2.2 Synthesis and material characterization

2.2.1. Hybrid silica sol preparation. The preparation of silica sol was previously investigated and reported³⁶⁻³⁹. MTEOS (60 ml) was hydrolyzed in acidic medium (H₂O at pH 3.5 using hydrochloric acid) in a round bottom flask equipped with a short distillation column. The hydrolysis molar ratio water/precursor was 14. The mixture was stirred for 1h at room temperature and heated to 130°C (oil bath temperature). The formed ethanol was distilled till the mixture became white, indicating a phase separation between water and hybrid silica sol. Five minute after, oil bath was removed, 40 ml of ice cold water were introduced in the solution and the mixture

was cooled down while maintaining stirring. Ten minutes after, 90 ml of diethyl ether were introduced slowly with strong stirring to extract the sol from the mixture. The stirring was stopped after five minutes, and the aqueous layer was discarded. Then, diethyl ether was evaporated and replaced by ethanol so that the dried solid residue after evaporation of the solvents represented 30% in mass. This prepared sol was stored at -24 °C and kept for several months.

2.2.2. Preparation of gold bipyramids (AuBP) with LSP around 600-650 nm. AuBP were prepared as described elsewhere⁴⁰. Briefly, a growth solution was prepared by mixing 1200 µl of HAuCl₄ (25 mM in water) and 40 ml CTAB (47 mM in water). Then, 1050 µl of aqueous silver nitrate (5 mM) was added, followed by 700µl of 8-hydroxyquinoline (0.4 M in ethanol). The growth solution turned light yellow. 4500 µl of 6-7 nm CTAC-capped gold seeds (0.25 mM in Au³⁺) were introduced into the growth solution under stirring. The mixture was gently stirred for 20 seconds and directly put into an oven at 40-45°C for 45 min.

After one hour of cooling at room temperature, the solution was centrifuged at 8000 rpm for 30 to 60 minutes. The supernatant was discarded and replaced by a 1 mM CTAB solution. The same operation was repeated one more time and the particles were dispersed in half of the initial suspension volume of MilliQ water. The resulted concentrated solution contains approximately 0.3 g l⁻¹ of AuBP.

2.2.3. Preparation of TiO₂/AuBP/hybrid silica sol. 1g of TiO₂ was dispersed in 50 ml of water under sonication and vigorous stirring. Then, the calculated volume of AuBP suspension was added. The dispersion was stirred for 5 minutes and sonicated. The mixture was centrifuged at 10 000 rpm for 20 minutes and the supernatant was discarded. A maximum amount of water was removed. Then, 5 ml of ethanol were added to disperse the precipitate, followed by 5 g of 20% wt MTEOS sol. The mixture was sonicated to give a bluish milky suspension ready for deposition. The reference sol was prepared in similar way except addition of AuBP.

Thin films were deposited using dip-coating technique on Si wafers (3 x 3 cm). The Si wafers were cleaned using following procedure: wafers were wiped with acetone, immersed in TFD4 detergent for 10 min, rinsed with Milli-Q water, immersed in absolute ethanol and dried with air. Coating was performed at dipping and retrieval speed - 50 mm min⁻¹ and dip duration - 10 sec. After deposition, thin films were dried in an oven Memmert 100-800 at 120°C for 20 h.

2.2.4. Material characterization. UV-visible measurements were performed using PerkinElmer Lambda 750 UV/VIS/NIR spectrometer. TEM images were obtained using a TOPCON EM002B transmission electron microscope operating at 200 kV in order to estimate size and shape of gold nanoparticles. Sample preparation for TEM analysis consisted of scrapping of prepared thin films and direct deposition of fragments onto a

microscopy copper grid coated with a holey carbon film. Scanning electron microscope Zeiss SUPRA 55 VP was used for observation of prepared thin films morphology. X-ray photoelectron spectrometer Thermo Fisher Scientific ESCALAB 250Xi was used in order to confirm presence of Au in the coatings.

Concentrations of immobilized TiO_2 were measured using "Activa" Jobin Yvon inductively coupled plasma optical emission spectrometer (ICP-OES). Sample preparation was done by dissolving of $\text{TiO}_2/\text{SiO}_2$ and $\text{TiO}_2/\text{SiO}_2$ -Au NP coatings in a mixture of H_2SO_4 , HNO_3 and HF at 120°C .

The values of contact angle before and after UVC pretreatment were obtained using GBX Digidrop Goniometer connected with digital camera. Milli-Q water droplets with volume of 20 μL were deposited on different places of coatings and recorded immediately. Mean values were calculated using from five to seven measurements per sample.

The band gaps of the prepared materials were evaluated from the diffused reflectance measurements done using the fiber UV-Vis spectrometer AvaSpec-2048 (Avantes) equipped with AvaLight-DHS deuterium (UV) and halogen lamps (Vis region). Barium sulfate was used as a reference. Evaluation of band gaps for all prepared samples was performed^{41, 42}.

2.3 Photocatalytic experiment

In order to test photocatalytic activity of prepared materials, a model solution of formic acid (FA) with concentration 1.09 mM was utilized ($\text{pH}=3.4$). The formic acid was chosen as a pollutant because no stable intermediates are formed during the photocatalytic degradation of this compound⁴³.

Prior to each test, the samples were treated for 1600 min under UVC (4.2 mW cm^{-2}) according to previously reported procedure to ensure final stabilization of the microstructure of the films^{36, 44}. All photocatalytic tests were carried out at room temperature ($22 \pm 2^\circ\text{C}$) utilizing experimental 100 ml batch glass reactor with quartz optical window. The diameter of optical window was 4 cm. Thin films deposited on $3 \times 3 \text{ cm}$ Si wafers were located inside the reactor and covered by glass substrate preventing sample floating. The volume of solution used in all tests was 30 ml, sampling volumes of 0.3 ml were conducted each 30 min. Changes in formic acid concentration were monitored with High Performance Liquid Chromatograph (HPLC) VARIAN ProStar equipped with column COREGEL-87H3 ($300 \times 7.8 \text{ mm}$) and UV-Vis detector ($\lambda = 210 \text{ nm}$). As a mobile phase sulfuric acid with concentration $5 \times 10^{-3} \text{ mol l}^{-1}$ and flow rate 0.7 ml min^{-1} was used. In order to reach adsorption-desorption equilibrium, the first 30 min of each photocatalytic experiment was conducted in darkness. Photolysis in pure water and adsorption tests were performed in order to confirm the photocatalytic degradation of formic acid in the presence of the composite material.

A high pressure mercury lamp (Philips HPK 125 W) was used for all experiments except photocatalytic tests in

visible region only. The lamp was stabilized for at least 30 min before each test. UVC, UVB and infrared beams did not reach the reactor due to circulation water cell with Pyrex and O-52 cut-off filters. For experiments in the visible region, a LED lamp was used ($400 - 800 \text{ nm}$) with maximum peaks at 555 nm and 447 nm with intensity 156 mW cm^{-2} . The VLX-3W radiometer equipped with CX-365 (UVA) and CX-312 (UVB) was used before and after each experiment for radiant flux measurements at the bottom of reactor. The UVA irradiance at the bottom of the reactor was about $7 \pm 0.2 \text{ mW cm}^{-2}$. At the level of the thin film location UVA was $5.2 \pm 0.2 \text{ mW cm}^{-2}$.

3. RESULTS AND DISCUSSION

3.1 Material characterization

The AuBP doped composite films were first analyzed by UV-Vis spectroscopy. Since P25 is rather polydisperse and easily formed aggregates, significant light diffusion occurred. Therefore, the films were analyzed by reflectance and compared with a reference film without gold nanoparticles (Figure 1)

Figure 1. a. Reflectance spectra of reference film and doped film with 1% AuBP. Insert shows the difference of reflectance between the two films. b. Comparison of AuBP solution spectra and the difference of absorbance between reference film and 1% AuBP doped film

The presence of AuBP in the 1% doped films is evidenced by the presence of the longitudinal surface plasmon resonance

(SPR) around 610 nm and the transverse SPR band around 520 nm. Interestingly, compared to the AuBP solutions (Figure 1b), the transverse contribution of the SPR was red-shifted while the longitudinal contribution was blue-shifted. According to earlier studies ^{45, 46}, in the case where morphology of nanoparticles are similar, shift of SPR could be correlated with differences in the optical properties of the matrix. The red-shift of transversal SPR band could probably be explained by an increase of refractive index of thin films (about 1.8) in comparison with solution of AuBP (about 1.3) ⁴⁶. However, expected red-shift of longitudinal SPR was not observed, on contrary, it was blue-shifted. It should be noted that longitudinal SPR is very sensitive to oxidation of AuBP tips, which could probably explain the blue-shift.

The Figure 2a shows a TEM picture of the prepared gold nanobipyramids and Figure 2b shows Au bipyramid (pointed by the white arrow) surrounded by TiO₂ particles inside the silica matrix in the 1% AuBP doped composite film.

Figure 2. a. TEM photograph of pure AuBP. b. TEM photograph of the 1% AuBP doped film. The white arrow points to gold bipyramid

The morphology of the thin films was similar for all samples. Hence, for sake of brevity, only SEM images for TiO₂/SiO₂ doped with 0.1% of AuBP are presented in this work (Figure 3.)

Figure 3. SEM images of TiO₂/SiO₂ doped with 0.1% of AuBP thin film showing the porosity of the films

According to the literature ⁴², the most accepted method for semiconductor's band gap determination is plotting square root of the Kubelka-Munk function multiplied by photon energy versus photon energy, and extrapolating linear part of the rising curve to zero (indirect band gap). Plots for evaluation of band gap are shown in Figure 4 and results are presented in Table 1.

Table 1. Band gap energy evaluation

Sample	Indirect band gap, eV
TiO ₂ /SiO ₂	3.11
TiO ₂ /SiO ₂ /AuBP 0.1%	3.02
TiO ₂ /SiO ₂ /AuBP 0.5%	2.92
TiO ₂ /SiO ₂ /AuBP 1%	2.90

Figure.4. Evaluation of indirect band gap of the thin films

As it can be seen from Table 1, a decrease of the indirect band gap with an increase of the Au nanoparticles concentration was observed. This fact could be attributed to the introduction of energy levels in the band gap of $\text{TiO}_2/\text{SiO}_2$. Similar results were reported earlier when semiconductor was doped with transition metal ions^{26, 42, 47}. In the work of Navio and Hidalgo⁴⁷, ZrO_2 synthesized using sol-gel method was doped with Fe^{3+} leading to materials with highly disordered structure. Observed decrease of band gap with increase of iron content was attributed to defects and impurities in synthesized materials, leading to introduction of energy levels into semiconductor⁴⁷. Decrease of band gap of TiO_2 doped with Au nanoparticles in comparison with TiO_2 due to introduction of energy levels into semiconductor was reported by Centeno et al.²⁶. Loading of gold nanoparticles varied from 0.11% to 1.26%, however, no direct dependence between Au loading and indirect band gap was observed probably due to significant variations of Au NP size in samples with different loading. Interestingly, material with lowest band gap (0.25% Au/ TiO_2 , 2.8 eV) demonstrated the highest activity for phenol degradation in aquatic environment.

The X-ray photoelectron spectroscopy (XPS) measurements were conducted with Thermo Fisher Scientific ESCALAB 250Xi spectrometer under vacuum $\sim 10^{-7}$ mbar. Al K α radiation was used as X-ray source (1486.6 eV). For calibration of binding energy scale the positions of Ag 3d, Au 4f and Cu 2p peaks were measured. The XPS spectra of Ti 2p, O 1s, Si 2p, C 1s and Au 4f for $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ films are presented in Figures 5 and 6. Presence of Au nanoparticles was confirmed by detectable Au 4f signal (Figure 6). The Ti 2p peak indicated that titanium is present in Ti^{4+} state. Interestingly, no significant difference was observed for Ti 2p signals for reference sample (about 8 at%) and $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ (about 8.8 at%). This results suggest that surface of TiO_2 was not in contact with gold nanoparticles. Similar observations were reported elsewhere⁴⁸.

Figure 5. Typical XPS spectrum of $\text{TiO}_2/\text{SiO}_2$ thin film doped with AuBP (0.5%)

Figure 6. Typical XPS spectrum of the Au4f levels of $\text{TiO}_2/\text{SiO}_2$ thin film doped with AuBP (0.5%)

The hydrophilicity of $\text{TiO}_2/\text{SiO}_2$ composites prepared by sol gel method after heat treatment at 500°C was reported earlier^{49, 50} as well as photoinduced hydrophilicity of TiO_2 ⁵¹. In this study, wettability of obtained coatings was checked after heat treatment and after UVC pretreatment and results are summarized in Table 2.

Table 2. Mean contact angle of thin films before and after UVC treatment

Sample name	Before UVC treatment	After UVC treatment
$\text{TiO}_2/\text{SiO}_2$	117.9	9.0
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 0.1%	132.2	8.1
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 0.5%	131.2	4.9
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 1%	127.8	4.9

Obviously, after UVC treatment all samples exhibit hydrophilic properties, while it was hydrophobic before the irradiation. This can be explained by presence of organic groups in the thin films left after the synthesis

since the temperature of the treatment (120°C) is not high enough to remove them. However, after UVC treatment, most of the groups were removed through photocatalytic decomposition. This parameter was rather important since hydrophilicity was required to obtain efficient photocatalytic activity.

3.2 Photocatalytic activity

It is well known that initial photocatalytic reaction rates are directly proportional to the mass of photocatalyst up to a certain limit, which depends on the reactor geometry and operational conditions⁵². Hence, it is important to determine the influence of the photocatalyst mass on initial reaction rate. This was achieved for thin films undoped with Au particles (Figure 7). Pure reference $\text{TiO}_2/\text{SiO}_2$ thin films with different loading of TiO_2 were prepared and pretreated as it was mentioned above. Initial disappearance rates of FA for all samples were measured for 90 min of contact time.

Figure 7. Influence of mass of deposited $\text{TiO}_2/\text{SiO}_2$ on initial disappearance rate of FA

According to Figure 7, the initial reaction rate rises with increase of TiO_2 loading up to maximum value obtained for about 0.04 mg cm^{-2} . In the range about 0.04 to 0.09 mg cm^{-2} no significant changes were observed. It should be noted that due to slight changes in properties of $\text{TiO}_2/\text{SiO}_2$ sols after Au doping, it was extremely important to measure the amount of TiO_2 deposited for all prepared samples in order to compare properly the photocatalytic activity. The TiO_2 loading for thin films doped with AuBP varies in the range 0.044 to 0.088 mg cm^{-2} of TiO_2 (Table 3). In this interval, same initial reaction rates were observed when reference sample (undoped with AuBP) were tested. Finally, the initial reaction rates of the FA decomposition for $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ and $\text{TiO}_2/\text{SiO}_2$ thin films were correlated with TiO_2 loading in range from 0.04 to 0.09 mg cm^{-2} of TiO_2 .

Table 3. Loading of TiO_2 for $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ thin films

Sample name	TiO_2 loading mg cm^{-2}
$\text{TiO}_2/\text{SiO}_2/\text{AuBP } 0.1\%$	0.044
$\text{TiO}_2/\text{SiO}_2/\text{AuBP } 0.5\%$	0.088
$\text{TiO}_2/\text{SiO}_2/\text{AuBP } 1\%$	0.061

The mean values of initial FA disappearance rate determined for $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ thin films are presented in Figure 8.

Figure 8. Initial disappearance rate of FA for $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ films with 3 different doping ratios and the reference without Au nanoparticles

The results shown in Figure 8 demonstrate that with an increase of AuBP loading, the rate rose and photocatalytic activity was improved. The highest initial FA disappearance rate was attributed to $\text{TiO}_2/\text{SiO}_2/\text{AuBP } 1 \text{ wt}\%$, which was about two times higher than that of reference sample with similar TiO_2 loading. Similar observations were reported⁵³ for degradation of acetic acid in aquatic environment under UV irradiation, which was increased by factor of 1.7 when TiO_2 (P25) modified with AuNP (2 wt.%) was compared with bare TiO_2 ⁵³. The photocatalytic degradation of FA when $\text{TiO}_2/\text{SiO}_2/\text{AuBP } 1 \text{ wt}\%$ and $\text{TiO}_2/\text{SiO}_2$ (with TiO_2 loading 0.063 mg cm^{-2}) films were used is shown in Figure 9.

Figure 9. Photocatalytic degradation of FA

As it can be seen from Figure 9, negligible changes in FA concentration were detected during photolysis and adsorption tests. Significant difference in degradation of FA was observed for $\text{TiO}_2/\text{SiO}_2$ and $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ films doped with 1wt% of Au. For instance, after 60 min under UVA+Vis irradiation, 58% of FA was decomposed when AuBP doped film was used, while for reference coating this value was only 24%.

Enhanced photocatalytic activity of thin films doped with AuBP could possibly be explained by the fact that gold nanoparticles act as electron traps and promote electron-hole separation^{25, 30, 31, 54}.

In the work of Okuno et.al.³¹, photocatalytic activity of $\text{TiO}_2\text{-SiO}_2$ doped with Au nanospheres (diameter 7 nm) and nanorods (diameter 7 nm, length from 10 to 400 nm) was compared. Enhancement of photocatalytic activity was observed for the materials doped with Au nanorods. This fact was explained by increase of charge separation between TiO_2 and Au with rise of nanoparticle size³¹. Interestingly, in the study of Kaur and Pal³⁰, where photocatalytic activity of TiO_2 doped with Au NP of different shape and size was examined, activity of TiO_2 doped with Au nanorods (average length 23.6 nm, aspect ratio 2.8) was lower than that of TiO_2 doped with Au nanospheres (3.5 nm).

The value of indirect band gap of the sample with the highest photocatalytic activity suggests the possibility of expanding the photocatalytic response into the area of visible light. Hence, $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ doped with 1wt% of Au were tested under only visible light. No photocatalytic activity was detected in this irradiation conditions. Similar behavior (enhanced activity in UV region and no activity in visible light) for TiO_2 composites doped with gold nanoparticles was reported in recent works^{34, 55}. It was suggested that the increase of TiO_2/Au photocatalytic activity in UV region does not require electronic contact between nanoparticles of TiO_2 and Au⁵⁵. Visible-light induced photocatalytic activity of TiO_2 modified with AuNP was also reported⁵³. It should be mentioned that AuNP were attached to the surface of

TiO_2 leading to occurrence of electronic contact between them. The mechanism for photocatalytic activity of TiO_2/Au in visible light suggested by Kowalska et al.⁵³ included absorption of photon by Au NP through LSPR excitation, injection of electron from Au NP into CB of titania and reduction of molecular oxygen adsorbed on the surface of titania, as a result electron deficient gold oxidized organic pollutants. In the present study, no photocatalytic activity under visible light was detected possibly due to absence of crystalline TiO_2/AuBP interface, which is quite reasonable considering the difference of concentration between TiO_2 and AuBP particles (over $10^3\text{-}10^4$ for samples with 1wt% of AuBP). Moreover, the results of XPS measurements confirmed that the surface of TiO_2 was not in contact with AuBP.

The durability of the prepared materials was tested for the sample $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 1 wt% during three cycles of photocatalytic tests. Between each test, the samples were rinsed with water and dried in the air. The results demonstrated that no decrease of photocatalytic activity was observed.

The apparent quantum yields were calculated for the tested samples according to the equation shown below.

$$\varphi_{app,in} = \frac{\left\{ \frac{dN_i}{dt} \right\}_{in}}{\int_{\lambda_1}^{\lambda_2} \frac{RA_{irr}\lambda d\lambda}{hc}}$$

where R is the irradiation intensity ($\text{W m}^{-2} \text{ nm}^{-1}$), A_{irr} is the irradiated area (m^2); h is the Plank's constant ($6.62 \cdot 10^{-34} \text{ J s}^{-1}$); c is the speed of light in vacuum ($2.997 \cdot 10^8 \text{ m s}^{-1}$); λ_1 is the lower wavelength of the spectrum in the range of interest (300 nm) and λ_2 the higher wavelength of the spectrum in the range of interest (400 nm); $\left\{ \frac{dN_i}{dt} \right\}_{in}$ is the initial rate of photoconversion of i species molecules. The values of apparent quantum yields obtained for samples are shown in the Table 4.

Table 4. Apparent quantum yields

Sample name	Apparent QY, %
$\text{TiO}_2/\text{SiO}_2$	2.5
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 0.1%	2.6
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 0.5%	3.5
$\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 1%	4.7

As it can be seen from Table 4, an increase of apparent QY was observed for $\text{TiO}_2/\text{SiO}_2$ thin films doped with AuBP. These values were in agreement with earlier reported results⁵⁶.

4. CONCLUSIONS

In this study, porous $\text{TiO}_2/\text{SiO}_2$ thin films doped with bipyramid-like gold nanoparticles were successfully synthesized by sol-gel method and their photocatalytic activity was investigated. The initial rate of formic acid photocatalytic degradation under UV light was evaluated for samples with different loading of gold. An increase of gold loading led to an improvement of initial rates of formic acid decomposition. The highest photocatalytic activity was attributed to the samples $\text{TiO}_2/\text{SiO}_2/\text{AuBP}$ 1wt%, which is about two times more efficient than the reference. Three cycles of photocatalytic tests were performed using the sample exhibiting the highest photocatalytic activity and no changes in the initial rates of formic acid degradation were observed. Visible irradiation had no significant effect on photocatalytic properties of obtained materials, which can be explained by the fact that electronic contact between TiO_2 and AuBP was not formed.

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Paper IV

TiO₂/SiO₂ porous composite thin films: role of TiO₂ areal loading and modification with gold nanospheres on the photocatalytic activity

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TiO₂/SiO₂ porous composite thin films: Role of TiO₂ areal loading and modification with gold nanospheres on the photocatalytic activity

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ABSTRACT

The aim of the work was to study photocatalytic activity of composite TiO₂/Au/SiO₂ thin films. Coatings were prepared using sol-gel technique. Physicochemical parameters of coatings were characterized using UV–vis spectrometry, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectrometry (XPS), inductively coupled plasma optical emission spectroscopy (ICP-OES), ellipsometry, tactile measurements, goniometry and diffuse reflectance measurements. The photocatalytic activity of the films was tested in batch mode using aqueous solution of formic acid. Changes of formic acid concentration were determined by means of high pressure liquid chromatography (HPLC). Increase of initial degradation rate of formic acid was detected for TiO₂/Au/SiO₂ films with gold nanoparticle's load 0.5 wt.% and 1.25 wt.%. However, deeper insights using more detailed characterization of these coatings demonstrated that the improvement of the photocatalytic activity is more probably attributed to an increase in the areal loading of TiO₂.

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1. Introduction

Photocatalytic water treatment resulting in degradation of organic compounds has gained extensive attention in last decades as a promising option for the development of environmentally friendly technologies. The most commonly used photocatalyst for the removal of harmful compounds from the aqueous environment is titanium dioxide. The advantages of titanium dioxide include its non-toxicity, relatively low cost and high photocatalytic activity [1]. However, the photocatalytic activity of TiO₂ is observed only in UV region [2]. Hence, scientists made a significant effort to expand photoresponse of TiO₂ to visible area [3]. Two approaches are mainly used for improvement of TiO₂ photocatalytic activity in UV and visible range: modification of photocatalyst with metals or non-metallic elements [4–6]. Noble metals are generally applied for this purpose [2,7]. Interestingly, this approach does not necessarily leads to enhancement of photocatalytic activity [8].

Recently, numerous publications demonstrated enhancement of photocatalytic activity of TiO₂ doped with gold [9–13]. Gold nanoparticles possess unique properties, which find application in such areas as optoelectronics, nanomedicine, nanocatalysis, etc. [14–18]. These properties are mostly caused by surface plasmon resonance (SPR). Doping of TiO₂ with Au nanoparticles was reported to cause decrease of charge carrier recombination and change morphological and structural properties [19]. In most of the studies, TiO₂/Au materials are prepared in form of powder. This causes difficulties when the powder photocatalyst should be separated from treated water. Deposition of photocatalysts on substrates in a form of thin films could significantly simplify the separation procedure and enhance the photocatalytic process. This approach has been widely used for titanium dioxide since 1994 [20]. As reported in literature, for improvement of thin film's mechanical properties [21], thermal stability, photoinduced hydrophilicity [22], chemical durability, flexibility [23], etc. titania-silica composite coatings are widely used. Numerous TiO₂/SiO₂ materials were synthesized for various applications [24–29]. For example, teardrop-shape core-shell SiO₂/TiO₂ nanoparticles were synthesized via sol-gel method for photocatalytic application [25]. Antireflective and self-cleaning coatings were prepared using raspberry-like SiO₂/TiO₂ nanoparticles [26]. SiO₂@Au@TiO₂ core

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shell nanoparticles were reported to have high photocatalytic activity under visible light [30]. Significant enhancement of salicylic acid photocatalytic decomposition was observed when Au@SiO₂ core shell structures have been loaded on TiO₂ surface [31]. However, investigations are still required since influence of various factors such as surface area, film thickness, areal loading of TiO₂, etc. on photocatalytic activity is often underestimated or even neglected.

The aim of this work was to study photocatalytic and physicochemical properties of SiO₂/TiO₂ composite thin films prepared using sol-gel method and modified with spherical gold nanoparticles. Formic acid (FA) was chosen as a model compound for photocatalytic tests. Photocatalytic activity of obtained coatings was compared by areal loading of TiO₂ and geometrical thin film area.

2. Experimental

2.1. Reagents and materials

Methyltriethoxysilane (MTEOS) and tetrachloroauric acid trihydrate (99.9%) were purchased from ABCR and Alfa Aesar, respectively. Sodium borohydride (>99.9%) was purchased from Aldrich. The formic acid was received from Acros Organics (99%). Titanium dioxide (P25, anatase – 72%, rutile – 28%) with surface area 50 m²g^{−1} was purchased from Degussa-Hüls-AG.

2.2. Material preparation

The hybrid silica sol was prepared as it was reported earlier [23,33–35]. Firstly, 60 mL of pure MTEOS was hydrolyzed at pH 3.5 during 1 h at room temperature. After, the ethanol was removed by distillation heating the mixture to 130 °C until the solution turned white. The solution was cooled down at room temperature and stirred for about 10 min. Then, 90 mL of diethyl ether was added to the solution under vigorous stirring in order to extract the sol from the mixture. When the stirring was stopped, a phase separation was observed and the aqueous phase was removed. The final step was the evaporation of diethyl ether and addition of ethanol. The final dried solid residue was adjusted to about 30% in weight.

Deposition of gold nanoparticles on TiO₂ was performed by addition of the HAuCl₄ solution (25 mM) to TiO₂ nanoparticles (Degussa P25) suspended in Milli-Q water (C = 10 g L^{−1}) so that TiO₂/Au ratios (wt.%) were 0%, 0.05%, 0.5%, 1.25% and 5%. Gold was reduced by freshly prepared 0.1 M NaBH₄ (NaBH₄/Au = 5 mol mol^{−1}) under vigorous stirring [36]. In the reference sample (TiO₂/Au ratio 0), volume of added NaBH₄ was equal to that in sample with ratio 1.25%. After that, pH of solutions was adjusted to 10 using 1 M NaOH. Obtained suspensions were stirred (650 rpm) in darkness for 3 h. Then the suspensions were centrifuged for 35 min at 10 000 rpm and 14 °C in order to get rid from supernatant, washed a few times with Milli-Q water and centrifuged again. Obtained TiO₂/Au pastes were dispersed in ethanol and added to hybrid silica sol in the way that TiO₂ and SiO₂ concentration were 10% weight for each. The sols were stabilized with acetic acid.

The coatings were prepared on Si wafers (3 × 3 cm) using dip coating method (speed – 50 mm min^{−1} and dip duration – 10 s). Prior to deposition, the Si wafers were wiped with acetone, immersed in TFD4 detergent for 10 min, rinsed with Milli-Q water, immersed in absolute ethanol and dried with air. After deposition, thin films were dried in the oven at 120 °C for 20 h. Before running the photocatalytic test, the films were treated in Milli-Q water under UVC irradiation (4.2 mW/cm²) for 1600 min in order to oxidize organic species present in the matrix according to the previously reported procedure [23,37].

2.3. Characterization of the thin films

The UV–vis measurements were performed with PerkinElmer Lambda 750 UV/VIS/NIR spectrometer. The X-ray photoelectron spectroscopy (XPS) measurements were conducted with Thermo Fisher Scientific ESCALAB 250Xi spectrometer under vacuum ~10^{−7} mbar. Al Kα radiation was used as X-ray source (1486.6 eV). For calibration of binding-energy scale the positions of Ag 3d, Au 4f and Cu 2p peaks were measured. For estimation of size and shape of gold nanoparticles, TEM images were done using a TOPCON EM002B transmission electron microscope operating at 200 kV. Sample preparation for TEM analysis consisted of scraping prepared thin films and direct deposition of fragments onto a microscopy copper grid coated with a holey carbon film.

Morphology and thickness of prepared thin films were studied using scanning electron microscopy (ZEISS LEO 1550) and tactile method (Form Talysurf Series 2 PGI). Porosity of prepared thin films was measured by means of SOPRA Ellipsometer EP5 (Semilab) equipped with CCD array detector (190 nm–870 nm).

The diffused reflectance measurements were used for evaluation of the band gap of synthesized samples. The fiber UV–vis spectrometer AvaSpec-2048 (Avantes) equipped with AvaLight-DHS deuterium (UV) and halogen lamps (Vis region) was utilized in this study. The optical path was built in such a way that one optical fiber was connected to lamps providing illumination and another – to the spectrometer for recording the signal. The band gap calculations were done based on obtained reflectance measurements (from 250 nm–400 nm). Barium sulfate was used as a reference. Calculations of direct and indirect band gaps for all prepared samples were performed following the protocol described below. Firstly, molar absorption coefficient (α) was obtained from the Eq. (1), derived from Kubelka-Munk theory

$$\alpha = \frac{(1 - R)^2}{2R} \quad (1)$$

where R is reflectance and α is molar absorption coefficient. After that, for direct and indirect band gap evaluation (α × h × ν)² and (α × h × ν)^{0.5} were plotted as a function of photon energy (h × ν), respectively. Finally, calculations were performed from extrapolation of molar absorption coefficient to zero [38].

The measurements of contact angle were performed in order to evaluate the wettability of synthesized thin films before and after UVC pretreatment. Measurements were conducted at room temperature (22 ± 2 °C) with GBX Digidrop Goniometer connected with digital camera. Milli-Q water droplets with volume of 10 μL were deposited on the different locations of the sample surfaces and contact angles were recorded immediately. Mean values of contact angle were calculated using WinDrop++ software from five measurements per sample.

Loading of TiO₂ was determined with "Activa" Jobin Yvon inductively coupled plasma optical emission spectrometer (ICP-OES). Sample preparation consisted of dissolving of TiO₂/SiO₂ and TiO₂/Au/SiO₂ coatings in a mixture of H₂SO₄, HNO₃ and HF at 120 °C.

2.4. Photocatalytic tests

Model solution containing formic acid (FA) with a concentration of 50 ppm was used in order to estimate and compare the photocatalytic activity of the materials. High Performance Liquid Chromatograph (HPLC) VARIAN ProStar equipped with column COREGEL-87H3 (300 × 7.8 mm) and UV–vis detector (λ = 210 nm) was used for measurements of the formic acid concentration. Sulfuric acid (C = 5 × 10^{−3} mol L^{−1}) was utilized as a mobile phase with flow rate 0.7 mL min^{−1}.

Table 1
Results of irradiance measurements.

Parameter	At the reactor's bottom	At the level of the film
Irradiance in UVB (mW/cm ²)	0.5 ± 0.2	0.34 ± 0.2
Irradiance in UVA (mW/cm ²)	9.1 ± 0.2	6.5 ± 0.2

Photocatalytic tests were conducted at room temperature ($22 \pm 2^\circ\text{C}$) in a 100 cm³ batch cylindrical reactor wrapped in aluminum foil. The diameter of Pyrex optical window of the reactor was 4 cm. Samples of TiO₂/Au/SiO₂ thin films deposited on silicon wafer with dimensions 3 cm × 3 cm were located in the reactor and covered by 3 cm × 3 cm glass substrate preventing floating of the sample. Detailed description of used experimental set up can be found elsewhere [20]. A magnetic stirrer was used for mixing 30 mL solution with speed of about 600 rpm. Sampling was carried out after each 30 min, volume of the sample was 0.3 mL and changes in FA concentration were monitored with HPLC. First 30 min of each photocatalytic experiment were performed in darkness in order to reach adsorption-desorption equilibrium. It should be noted that each experiment was repeated at least three times.

High pressure mercury lamp (Philips HPK 125 W) was used as a source of irradiation in all experiments. Before starting the experiments the lamp was stabilized for at least 30 min. Owing to circulation water cell with Pyrex filters, no infrared and UVC beams reach the reactor. It should be noted that before each test, optical filters were washed in 37% HCl. Before and after each experiment, the

Fig. 1. Spectrum of high pressure mercury lamp (Philips HPK 125 W).

radiant flux measurements were done with VLX-3W radiometer using a CX-365 (UVA) and CX-312 (UVB) detectors. The spectrum of the lamp was recorded by means of AvaSpec-2048 spectrophotometer (Avantes) (Fig. 1).

The results of irradiance measurements at the level of the thin film in the glass reactor performed using radiometer are shown in Table 1.

The adsorption tests and photolysis were carried out as well. In order to evaluate effect of Au nanoparticles loading on photo-

Fig. 2. SEM images of prepared thin films, A—reference, B—TiO₂/Au/SiO₂ 0.05%, C—TiO₂/Au/SiO₂ 0.5%, D—TiO₂/Au/SiO₂ 1.25%, E—TiO₂/Au/SiO₂ 5%.

Fig. 3. Absorption spectra for $\text{TiO}_2/\text{SiO}_2$ and $\text{TiO}_2/\text{Au}/\text{SiO}_2$ thin films.

Fig. 4. TEM images of $\text{TiO}_2/\text{Au}/\text{SiO}_2$ film (5 wt.%).

catalytic activity, the reference photocatalytic test was conducted. $\text{TiO}_2/\text{SiO}_2$ thin films were used as a reference samples.

3. Results and discussion

3.1. Material characterization

The morphology of the prepared thin films and the microstructure can be seen from the SEM images presented in Fig. 2.

It is worthwhile to note that in all cases, porous thin films with similar morphology to those previously reported by this procedure were prepared [23]. The porosity of $\text{TiO}_2/\text{SiO}_2$ (reference) thin films was measured before and after UVC treatment leading to values of 1.3% and 14.3%, respectively. These data confirm that the porosity of $\text{TiO}_2/\text{SiO}_2$ coatings increases due to degradation of superficial part of the silica methyl groups which in turn increase the porosity and enhance the photocatalytic activity of the coatings [23]. The porous volume of coatings modified with Au nanoparticles was determined after UVC treatment and for coatings with Au loading of 0.05%, 0.5%, 1.25% and 5%. This porosity was 7.7%, 11%, 9.7% and 14.1%, respectively. It should be mentioned that for thinner films quality of the signal was better suggesting more precise porosity estimation.

$\text{TiO}_2/\text{Au}/\text{SiO}_2$ films were coloured from light pink to purple depending on Au loading, while $\text{TiO}_2/\text{SiO}_2$ composites were white.

Therefore, it can be suggested that all $\text{TiO}_2/\text{Au}/\text{SiO}_2$ coatings gave SPR absorption band in the visible area. However, from typical UV–vis spectra of $\text{TiO}_2/\text{SiO}_2$ and $\text{TiO}_2/\text{Au}/\text{SiO}_2$ (Fig. 3) it can be seen that broad absorption band at wavelengths ~ 538 nm (attributed to Au NPs) was detected only for coatings with highest loading of Au. Absence of SPR corresponding to Au NPs in $\text{TiO}_2/\text{Au}/\text{SiO}_2$ coatings with lower Au loading can be possibly explained by the fact that thickness of the films and Au concentration were relatively low.

The Fig. 4 illustrates TEM images of a typical $\text{TiO}_2/\text{Au}/\text{SiO}_2$ composite film. In this case TEM images of coatings with highest Au loading (5 wt.%) have been chosen. The presence of Au NPs is distinguishable because of small size and relatively high electron density. Spherically shaped Au NPs can be observed in $\text{TiO}_2/\text{SiO}_2$ matrix. As indicated in Fig. 3 the size of Au NPs is relatively small, ranging from 5 to 7 nm.

Similar qualitative XPS spectra were obtained for all $\text{TiO}_2/\text{Au}/\text{SiO}_2$ thin films. Typical spectra of $\text{TiO}_2/\text{SiO}_2$ and $\text{TiO}_2/\text{Au}/\text{SiO}_2$ 1.25% coatings are presented in Fig. 5. As can be seen from Fig. 6a two peaks attributed to TiO_2 were detected $\text{Ti}2p\ 3/2$ (459.28 eV) and $\text{Ti}2p\ 1/2$ (465.08 eV). The $\text{Si}2p$ peak with binding energy 103.08 eV (Fig. 6b) corresponds to SiO_2 [23]. The $\text{C}1s$ peak detected at 285.08 eV (Fig. 6c) may be attributed to C–C or C–H bond [23]. The carbon can be presented in the films because organic precursors were used during synthesis. The binding energy

values for Au 4f 7/2 and Au 4f 5/2 (Fig. 6d) were 84.08 eV and 87.68 eV, respectively, which is characteristic for Au⁰ species [39].

Results of direct and indirect band gap calculations achieved using Origin 7.5 software are shown in Table 2. TiO₂ anatase is known to be a semiconductor with indirect band gap. From the results reported in Table 2, it seemed difficult to extract any correlation between the Au amount and the measured band gap. However, in most cases the band gap tended to increase which is not in favor of an improvement of the photocatalytic activity in the UV–vis area.

The photoinduced super-hydrophilicity of TiO₂ thin films is a well-known fact that directly impacts the photocatalytic activity [40]. In previous studies devoted to TiO₂/SiO₂ composites synthesized via sol gel method, superhydrophilicity of the films was observed directly after heat treatment at 500 °C [41]. In the present work changes of hydrophilic properties were studied for all prepared samples before and after UVC treatment by goniometer method. Mean values of contact angle measurements are summarized in Table 3.

The results, shown in Table 3, suggest that before and after UVC treatment all samples exhibit hydrophobic and super-hydrophilic character, respectively. The hydrophobicity of prepared coatings after heat treatment at 120 °C can be explained by the presence of organic groups (methylene) in the thin films, which were used to generate microporosity and flexibility of coatings [23]. As it was reported earlier for TiO₂/SiO₂ thin films during UVC pretreatment photocatalytic degradation of organic groups occurs [23]. Hence, hydrophilicity of coatings drastically increases after phototreatment.

3.2. Photocatalytic activity

The photocatalytic activity of the films was evaluated as the initial rate of FA degradation in batch reactor. The use of simple organic molecules such as FA is preferable due to elimination of any stable byproducts [42–44].

Fig. 5. XPS spectrum of TiO₂/SiO₂ (a) and TiO₂/Au/SiO₂ 1.25% (b).

Table 2
Band gap energy evaluation.

Sample name	Direct band gap (eV)	Indirect band gap (eV)
TiO ₂ /SiO ₂ (Reference)	3.48	3.11
TiO ₂ /Au/SiO ₂ 0.05%	3.66	3.20
TiO ₂ /Au/SiO ₂ 0.5%	3.65	3.17
TiO ₂ /Au/SiO ₂ 1.25%	3.63	3.16
TiO ₂ /Au/SiO ₂ 5%	3.61	2.99

Table 3
Contact angle of thin films before and after UVC treatment.

Sample name	Mean contact angle before UVC treatment	Mean contact angle after UVC treatment
TiO ₂ /SiO ₂ (Reference)	122.3	2.9
TiO ₂ /Au/SiO ₂ 0.05%	128.9	3.2
TiO ₂ /Au/SiO ₂ 0.5%	129.3	2.7
TiO ₂ /Au/SiO ₂ 1.25%	129.3	4.7
TiO ₂ /Au/SiO ₂ 5%	99.7	9.9

Fig. 6. Plots of XPS spectra of TiO₂/Au/SiO₂ 1.25%: (a) Ti 2p, (b) Si 2p, (c) C 1s, (d) Au 4f.

Table 4

Thickness (measured by tactile method), and mean areal TiO₂ loading of prepared samples.

Sample name	Mean thickness (nm)	Mean areal loading of TiO ₂ (mg cm ⁻²)
TiO ₂ /SiO ₂ (Reference)	470 ± 33	0.085
TiO ₂ /Au/SiO ₂ 0.05%	520 ± 30	0.064
TiO ₂ /Au/SiO ₂ 0.5%	860 ± 115	0.112
TiO ₂ /Au/SiO ₂ 1.25%	700 ± 75	0.118
TiO ₂ /Au/SiO ₂ 5%	220 ± 14	0.024

The photocatalytic performance of each sample type was tested at least three times using fresh sample each time. This was done because of the small geometrical area variations of deposited thin films and for statistical evaluations. Therefore, standard deviations for each sample type were deduced from at least three initial FA degradation rates.

In order to simplify comparison of photocatalytic performance of different samples and avoid errors caused by deviations in geometrical area of the samples, the initial FA degradation rates were calculated per cm² of the thin film (Fig. 7).

As indicated in Fig. 7, the initial reaction rates of TiO₂/Au/SiO₂ films with 0.5% and 1.25 wt% of Au NP were higher than that of reference sample and thin films with other loading of Au NP. However, it was difficult to speculate the role of Au NP doping in the increase of the rate constants, other than to note that loading of TiO₂ seemed to be extremely important in this case. Therefore, the areal loadings of TiO₂ were measured for all samples using ICP-OES, and results are reported in Table 4.

As it can be seen from Table 4, the mean areal loadings of TiO₂ vary significantly for TiO₂/Au/SiO₂ thin films. These results suggest that comparison of photocatalytic activity taking into account only geometrical surface area was not representative. Therefore, it was decided to prepare and test TiO₂/SiO₂ thin films with different thicknesses and areal loading of TiO₂.

All TiO₂/SiO₂ thin films were treated in UVC prior to run photocatalytic experiments in similar way to other samples. The initial rates of FA disappearance for TiO₂/Au/SiO₂ films and TiO₂/SiO₂ thin films with different TiO₂ areal are shown in Fig. 8.

As the TiO₂ areal loading for TiO₂/SiO₂ increased so did the initial rate of FA disappearance (Fig. 8). In the interval of TiO₂ areal loading from 0.004 mg cm⁻² to 0.04 mg cm⁻² (attributed to thickness interval up to about 300 nm), the initial FA disappearance rate significantly increased. While in the range of TiO₂ areal loading from 0.04 mg cm⁻² to 0.13 mg cm⁻² (mean thickness from 300 nm to 900 nm) photocatalytic activity of TiO₂/SiO₂ films increased slightly which can be attributed to the fact that for thicker films UV absorption may limit utilization of active sites in the depth of the film [45]. Thus, from Fig. 8 it can be suggested that critical TiO₂/SiO₂ film thickness is about 300 nm. Various values of critical film thickness were reported in the literature. For instance, photocatalytic activity of titanium dioxide thin films prepared by atomic layer deposition (ALD) technique was reported to increase with thickness of the film up to 100–130 nm, above which only minor effect on photocatalytic activity was observed [46]. Results of later study were in a good agreement with it, showing maximum photocatalytic activity at film thickness of 150 nm [47]. For TiO₂ thin films prepared using sol-gel process values of critical film thickness were reported to be 360–430 nm [48]. It should be noted that physico-chemical properties of the films strongly depend on the method of synthesis, leading to significant deviations in critical film thickness for photocatalytic applications. Also, experimental conditions such as type of irradiation source, light intensity and tested model compound had significant influence on critical film thicknesses [1,48]. Results demonstrated in Fig. 8 are in agreement with work of Grégori et al. [23], where photocatalytic activity of similar TiO₂/SiO₂ coatings with different thicknesses and as a result with various TiO₂

Table 5

Results of quantum yield estimations.

Sample name	Initial reaction rate (s ⁻¹)	A _{irr} (cm ²)	φ _{app, in} (%)
TiO ₂ /SiO ₂	1.90267 × 10 ¹⁵	8.41	1.27
TiO ₂ /Au/SiO ₂ 0.05%	1.89518 × 10 ¹⁵	8.27	1.29
TiO ₂ /Au/SiO ₂ 0.5%	2.59300 × 10 ¹⁵	8.05	1.81
TiO ₂ /Au/SiO ₂ 1.25%	2.82775 × 10 ¹⁵	8.52	1.87
TiO ₂ /Au/SiO ₂ 5%	2.09032 × 10 ¹⁵	7.85	1.50

areal loading was tested. However, FA degradation rates for similar TiO₂/SiO₂ coatings in the study of Grégori et al. were lower than in present work. This can be explained by the fact that for establishing dependence between FA degradation rate and thickness of the coatings, Grégori et al. used TiO₂/SiO₂ films not preliminary treated in UV.

Initial FA disappearance rates for TiO₂/Au/SiO₂ films were plotted on Fig. 8 as well. It is worthwhile to note, that photocatalytic activity of TiO₂/Au/SiO₂ coatings seemed to be not higher than for TiO₂/SiO₂ thin films with similar areal loading of TiO₂.

It is well known that the surface of titania particles strongly affect their photocatalytic activity [2]. Therefore, modification of TiO₂ surface with gold nanoparticles alters the amount of adsorbed on the surface oxygen and water or surface hydroxyl groups, which generate the active titanoxyl radicals [2]. Most of the studies devoted to photocatalysis of TiO₂ modified with spherical Au NP reported enhancement of photoactivity [3,9–13,49,50]. For instance, TiO₂/Au composites prepared by deposition-precipitation method demonstrated higher rate of photocatalytic degradation of phenol than TiO₂ [9]. Mesoporous TiO₂/SiO₂ composites doped with Au nanoparticles enhanced photocatalytic decomposition of methylene blue, which was explained by more efficient charge separation of the electron-whole pairs [10]. Photocatalytic degradation of acetic acid under UV irradiation was 1.7 times greater when P25 was doped with Au nanoparticles, which was explained by the fact that Au acts as co-catalyst for O₂ reduction by photoexcited electrons [51]. However, presence of gold nanoparticles was also reported to cause negative effect on photocatalytic activity of TiO₂ due to reduction of surface titanol groups [52].

It is challenging to estimate primary and overall quantum yields for heterogeneous photocatalytic systems correctly, mainly due to problems arising when number of absorbed by photocatalyst photons should be measured, detailed discussion can be found elsewhere [53,54]. The apparent quantum yield is a parameter, which is usually defined as the ratio of converted reactant molecules over the number of photons entering the reactor [55], and therefore, easier to evaluate [56]. In this work an attempt to estimate apparent quantum yields for tested photocatalysts from an equation presented below was made [55].

$$\phi_{app, in} = \frac{\left\{ \frac{dN_i}{dt} \right\}_{in}}{\int_{\lambda_1}^{\lambda_2} \frac{R A_{irr} \lambda d\lambda}{hc}} \quad (1)$$

where R is the irradiation intensity (W m⁻² nm⁻¹), A_{irr} is the irradiated catalyst area (m²); h the Planck's constant (6.62×10^{-34} J s⁻¹); the speed of light in vacuum (2.997×10^8 m s⁻¹); λ_1 the lower wavelength of the spectrum in the range of interest (300 nm) and λ_2 the higher wavelength of the spectrum in the range of interest (400 nm); $\left\{ \frac{dN_i}{dt} \right\}_{in}$ is the initial rate of photoconversion of i species molecules. Results of calculations are shown in Table 5.

The results of the apparent quantum yields estimations demonstrated that all values were below 2%, which is in agreement with [57]. The highest values of apparent quantum yield were attributed to samples with loading of Au NPs 0.5 wt.% and 1.25 wt.%. Interest-

Fig. 7. Photocatalytic activity per cm² of thin films.

Fig. 8. Initial disappearance rate of formic acid as a function of TiO₂ loading for TiO₂/SiO₂ and TiO₂/Au/SiO₂ thin films.

ingly, the mean areal loading of TiO₂ for these two samples was highest.

4. Conclusions

The photocatalytic activity of composite TiO₂/Au/SiO₂ thin films was studied using formic acid as model contaminant in aqueous media. The effect of different loading of gold nanoparticles in the composite on the photocatalytic activity was evaluated. An increase of the initial degradation of formic acid per cm² of coatings was observed for samples loaded with 0.5% and 1.25% of Au. Detailed investigation of thickness and areal TiO₂ loading of prepared coatings demonstrated significant variations of these values. Hence, reference thin films (TiO₂/SiO₂) with different thicknesses and areal TiO₂ loading were tested for more representative comparison of photocatalytic activity. Results suggest that elevated initial degradation rate of formic acid for samples with 0.5% and 1.25% of Au is due to higher than for other samples areal TiO₂ loading rather than presence or absence of gold nanoparticles. Thus, areal TiO₂ loading and/or thickness of coatings are very important parameters which should systematically be taken into account when comparing photocatalytic activities of thin films.

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Paper V

Influence of synthesis conditions on physical properties of lanthanide-doped titania
for photocatalytic decomposition of metazachlor

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Article

Influence of synthesis conditions on physical properties of lanthanide-doped titania for photocatalytic decomposition of metazachlor

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ABSTRACT

Heterogeneous photocatalysis is a very effective method for the decomposition of a whole range of water pollutants. In this work, the influence of synthesis conditions on the physical properties and photocatalytic activity of lanthanide-doped titanium dioxide photocatalysts was evaluated. Titanium dioxide was prepared via sol-gel synthesis followed by a solid state reaction under different conditions, including different temperatures (450, 550, and 650 °C) and reaction times (4, 8, and 12 h). The crystalline phase of the products was determined to be solely anatase using X-ray diffraction, and this result was confirmed by Raman spectroscopy. The structure, as well as particle size, of the samples was examined using scanning electron microscopy, and their specific surface area was calculated using Brunauer-Emmett-Teller analysis. The band gap energy of the samples was examined using ultraviolet-visible spectroscopy from diffuse reflectance measurements. Doping with lanthanide species, dysprosium and praseodymium, caused the absorption edge to shift towards higher wavelengths and enhanced photocatalytic activity in comparison with pure titania. The photocatalytic activity of the samples was studied in terms of the degradation of the commonly used herbicide metazachlor. The decomposition was carried under UV light and the decrease in metazachlor concentration was measured using high performance liquid chromatography. The best performance was obtained for samples treated at 550 °C for 8 h during the solid state reaction step.

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1. Introduction

Metazachlor belongs to the organochlorine pesticide group and was the fifth most used herbicide in the Czech Republic in 2010, with a consumption of nearly 200 000 kg [1]. Generally, residues of various pesticides and herbicides are able to leach from agricultural soil to deeper ground or to ground water, where they can remain for long time owing to their nondegradable properties. Consequently, such species can cause different serious problems even at very low doses of nanograms per cubic decimeter [2]. Metazachlor has been

found to be moderately toxic to different aqueous organisms, especially daphnia, carp, and bluegill sunfish. The highest sensitivity was discovered in trout, where it can cause damage to liver or kidneys [3]. Because of its toxicity, metazachlor, as with many other pesticides, belongs to large group of endocrine disrupting chemicals (EDCs) [4]. Many of these compounds pass through wastewater treatment plants [5,6] that are not designed for removing such contaminants [7], and therefore many of them reach the surface water unchanged [8].

Many different techniques have been studied in the effort to remove micropollutants from water, from physical processes,

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such as sorption or membrane filtration, to biological processes, using bacteria or enzymes [9]. Nowadays, one very promising group of treatment techniques is that based on advanced oxidation processes, particularly heterogeneous photocatalysis. The main feature of this method is the production of hydroxyl radicals, which initiate subsequent reactions that lead to the decomposition and removal of organic compounds [10]. This technology is also non-selective and versatile, which are useful and necessary in wastewater treatment [11]. Titanium dioxide is one of the most commonly used photocatalysts because of its high activity, biological and chemical inertness, high photostability, excellent optical and electrical properties, and nontoxicity. However, its absorption only in the UV region and quite narrow band gap energy, which brings about fast back recombination of the electron-hole pair, are its main disadvantages. Many authors have attempted either to shift the absorption edge of titania towards higher wavelength, or to suppress the recombination process, which may be achieved by doping the titania [12]. Nevertheless, most studies concentrate their photocatalytic investigations on model compounds [13,14] such as phenol or dyes [15,16].

In this work we successfully prepared lanthanide-doped titanium dioxide, which has been reported to exhibit better photocatalytic activity in comparison with that of pure titania [17], and investigated its suitability for the photocatalytic decomposition of metazachlor because of the current need to remove this species from wastewater. Furthermore, we investigated the effects of different process conditions and compared the photocatalytic activity of doped and undoped samples with commercial titania P25.

2. Experimental

2.1. Catalyst preparation

Preparation of lanthanide-doped titanium dioxide was performed by sol-gel synthesis using titanium propoxide as the precursor. The titanium propoxide (0.125 mol) was added dropwise under continuous stirring to isopropanol (0.5 mol), which was used as a solvent. Afterwards, acetylacetone (0.06 mol) was added to the mixture as a stabilization agent. Dysprosium (Dy) and praseodymium (Pr) doped TiO_2 (0.3 mol% [18]) samples were synthesized by first dissolving the oxides of the corresponding elements in nitric acid (20 cm³), and the obtained solutions were poured into the propoxide dispersions. The sols were left to age at room temperature for 7 d to form a gel structure, after which they were heated at 120 °C until xerogels were formed. The xerogels were then subjected to solid state reaction at various temperatures ($T = 450, 550$, and 650 °C) for different time periods ($t = 4, 8$, and 12 h). The obtained lanthanide-doped TiO_2 samples were denoted as Dy- TiO_2 T/t and Pr- TiO_2 T/t .

2.2. Catalyst characterization

Thermogravimetric analysis (TGA) was carried out on the heat-treated powders using a thermoanalyzer (Seiko Instru-

ments 6300 TG-DTA) in an atmosphere of argon-air (volume ratio 1:1). The analysis was performed over the temperature range 35–1000 °C, with a gas flow rate of 400 cm³/min and a temperature ramp rate of 20 °C/min. The crystalline phase of the prepared powders was examined using X-ray diffraction (XRD; X-ray diffractometer SmartLab, Rigaku), using a Cu K_α radiation source and a 2θ scan range of 20°–60°. The results of the XRD measurements were confirmed by Raman analysis (Renishaw inVia), which was carried out using a 633 nm laser at an output power of 30 mW and measured range of 0–1600 cm⁻¹. Crystallite size was calculated from the XRD results using the Scherrer equation $d = B\lambda/(\beta\cos\theta)$, where d is the size of the crystallites in the direction vertical to the corresponding lattice plane, B is a constant equal to 0.94, λ is the wavelength, equal to 0.157 nm, and β is the width of the selected peak at half of its height.

The structure of the prepared powders, as well as their particle size, was investigated using scanning electron microscopy (SEM; Carl Zeiss Ultra Plus). The influence of synthesis conditions on the band gap energy was examined from diffuse reflectance measurements (UV-Vis spectrometer Avaspec-2048). Nitrogen adsorption/desorption analysis was carried out to determine the specific surface area of the samples (BET).

2.3. Photocatalytic experiments

The aim of this study was to determine optimal solid state reaction for the preparation of photocatalytically active nanopowders that could be useful for decomposition of pesticides in water. The photocatalytic experiments were performed on metazachlor. All experiments were carried out in a flow reactor (Fig. 1), which was composed of a borosilicate glass tube with inner diameter of 0.6 cm placed at a distance of 1 cm from the light source. The decomposition reaction was performed using UV-LED (370 nm) irradiation with an optical power density of 22 mW/cm². The flow rate in the reactor was 2.5 cm³/s. Before each experiment, the Dy- TiO_2 or Pr- TiO_2 sample (1 g/L) was dispersed in 70 cm³ of an aqueous solution of metazachlor (10 mg/L), and the resulting suspension was kept in darkness for 6 min under continuous stirring to reach adsorption/desorption equilibrium. 1 cm³-aliquots of the reaction solution were sampled at certain intervals, and the concentration of remaining metazachlor was determined by HPLC (Shimadzu LC-20) after filtration (pore size 0.45 μm). The HPLC conditions were as follows: Luna 5u C18 (2) 100A (250 mm $\times$ 4.6 mm) column, the eluent was a mixture of water-acetonitrile (volume ratio 1:1) with a flow rate of 1.8 cm³/min, column temperature 40 °C, injection volume 0.25 μL , and detector wavelength 210 nm.

Fig. 1. Flow tube reactor. 1, beaker containing reaction mixture; 2, UV-LED source; 3, borosilicate tube; 4, direction of flow.

3. Results and discussion

3.1. Thermogravimetric analysis

TGA experiments on the heat treated powders revealed a mass loss no higher than 3% for all samples. An example TGA/DSC trace is given in Fig. 2. The mass loss in the first temperature interval (35–175 °C) was caused by desorption of water physically adsorbed by the sample from humid air. The mass loss in the second temperature range (175–500 °C) may be a result of oxidation of organic residues, mainly acetylacetone, remaining in the powder owing to slow oxygen diffusion through titania layers during the solid state reaction. A lesser loss of mass was observed in the third temperature interval (500–700 °C), attributed to removal of the last organic residues that had formed a donor-acceptor bond between Ti atoms and the carbonyl group of acetylacetone. The exothermic peak around 650 °C is ascribed to the phase transformation of anatase to rutile.

3.2. Phase composition of nanopowders

The influence of process conditions on the crystalline phase of the obtained samples was evaluated by XRD analysis, as shown in Fig. 3. All the prepared samples were found to be pure anatase, which implies that the Pr and Dy doping suppressed the creation of the rutile phase, which is expected to occur at 650 °C. This result is in good agreement with the literature [19,20]. The crystallite size of the samples was calculated using the Scherrer equation and was found to increase with the temperature of the solid state reaction. In contrast, no influence of synthesis time on crystallite size was observed. Subsequently, the phase composition was studied by Raman analysis,

Fig. 2. Recorded data from the thermogravimetric analysis of sample Pr-TiO₂ 450/4.

which confirmed the results from XRD. All of the obtained results are summarized in Table 1.

3.3. Band gap energy evaluation

The optical properties, especially the band gap energy, of the samples were investigated using UV-Vis spectroscopy by diffuse reflectance measurements. The band gap energy was calculated according to the Kubelka-Munk theory [21] using function $f(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty}$, where $R_{\infty} = R_{\text{sam}} / R_{\text{st}}$. The diffusion reflectance of barium sulfate was used as a standard (R_{st}); R_{sam} is the diffused reflectance of the samples. The relationship between the band gap energy E_g and the absorption coefficient, which can be obtained from the reflectance measurements, is: $ah\nu = C(h\nu - E_g)^2$, where C is a proportionality constant. If the material scatters perfectly, the equation becomes: $[f(R_{\infty})h\nu]^{1/2}$

Fig. 3. XRD patterns (a) and Raman spectra (b) for Pr-TiO₂ 650/4 and Dy-TiO₂ 650/4 samples, indicating the formation of pure anatase.

Table 1
Crystalline phase and crystallite size of the samples.

Treatment conditions (°C/h)	Dy-TiO ₂				Pr-TiO ₂			
	Crystalline phase (XRD/Raman)	Crystallite size (nm)	E_g (eV)	Absorption edge (nm)	Crystalline phase (XRD/Raman)	Crystallite size (nm)	E_g (eV)	Absorption edge (nm)
450/4	anatase	10	3.24	383	anatase	9	3.24	383
550/4	anatase	10	3.11	399	anatase	12	3.12	397
650/4	anatase	31	3.17	391	anatase	20	3.22	385
450/8	anatase	9	3.16	392	anatase	11	3.14	395
450/12	anatase	11	3.11	399	anatase	11	3.20	388

Fig. 4. Kubelka-Munk plots used to calculate band gap energy.

$= C(h\nu - E_g)$ [22]. The band gap energy for each sample was evaluated from relation $(\alpha h\nu)^{1/2} = f(h\nu)$ by extrapolation of the linear part of the curve in Fig. 4. The calculated E_g are summarized in Table 1. Values around 3.2 eV correspond to the anatase crystalline phase. These results confirm the results of the XRD and Raman analyses.

3.4. Particle size and specific surface area

The changes in the morphology of the prepared powders

were examined by scanning electron microscopy, which revealed a difference between the Dy- and Pr-doped titania samples (Fig. 5). The particle size and consequently the size of the aggregates were larger in the samples doped with dysprosium. Although the particle size did not seem to be much affected by the synthesis conditions, the conditions significantly influenced the aggregate size (Table 2 and Fig. 5). The smallest aggregates were formed at a solid state reaction temperature of 550 °C and time of 8 h for both lanthanides. The results of the specific surface area measurements from BET analysis are summarized in Table 2. It can be seen that the specific surface area decreased with increasing aggregate size.

3.5. Photocatalytic activity

Before the photocatalytic experiments, an adsorption was carried out to determine the time needed to achieve adsorption/desorption equilibrium. The results are shown in Fig. 6 and indicate that the required time was 5 min. Within this time, the concentration of metazachlor in the solution decreased from 10 to 8.2 mg/L and then remained nearly constant.

The photocatalytic experiments were performed in a flow reactor. Each experiment lasted 60 min, which corresponded to 10 min of contact time (where the photocatalyst was exposed to the LED source). The decrease in metazachlor concentration determined by HPLC was used to calculate the initial rate of metazachlor decomposition. Metazachlor belongs to the chlo-

Fig. 5. Scanning electron microscopy images of TiO₂ samples doped with dysprosium and praseodymium.

Table 2

Particle size results from SEM and BET analysis.

Treatment conditions (°C/h)	Dy-TiO ₂			Pr-TiO ₂		
	Particles size (nm)	Aggregates size (nm)	Specific surface area (m ² /g)	Particles size (nm)	Aggregates size (nm)	Specific surface area (m ² /g)
450/4	25	750	60.4	20	500	77.5
550/4	25	500	73.6	23	150	89.9
650/4	30	700	66.9	25	400	82.8
450/8	20	300	80.6	20	<100	106.3
450/12	25	500	72.4	22	400	83.1

Fig. 6. Decrease in concentration of metazachlor during the adsorption/desorption test.

roacetamide herbicides, which undergo dechlorination in the first step of photodegradation. This process is subsequently followed by mono- or multi-hydroxylation and cyclization.

The contribution of direct photolysis was subtracted from the observed rate of decomposition. The influence of the solid state reaction temperature and time was examined, and the best performing materials for the decomposition were found to be those prepared at 550 °C and 8 h, both the dysprosium and the praseodymium doped samples. The results are shown in Fig. 7. We conclude that the increased rates were a result of the creation of smaller aggregates (as shown by the SEM results), because smaller particles (or more precisely, smaller aggregates) should have higher specific surface area and hence, more specific sites where reactions can occur. The Pr-doped TiO_2 samples exhibited higher activity than Dy-doped samples prepared under the same synthesis conditions. Moreover, we compared the initial degradation rate of the doped TiO_2 (450/4 and 550/4) with that of undoped TiO_2 prepared under the same conditions and commercial titania Degussa P25, and found that doping increased the photocatalytic activity (Table 3). This can be explained by the fact that the rate of back recombination (e^-/h^+) in pure TiO_2 is quite fast, and consequently its activity is limited. Generally, the transitions of 4f electrons of rare earth elements are responsible for the optical absorption of a doped catalyst and support the separation of photo-generated e^-/h^+ pairs. Lanthanide ions behave as a scavenger of excited electrons from the titania conduction band [23].

Fig. 7. Initial rates of metazachlor degradation over different catalyst samples.

Table 3

Comparison of initial degradation rate ($\mu\text{mol L}^{-1} \text{s}^{-1}$) for doped and undoped TiO_2 samples and commercial titania P25.

Treatment conditions (°C / h)	Pr- TiO_2	Dy- TiO_2	TiO_2	P25
450/4	4.239	4.034	3.712	4.038
550/4	4.573	4.180	3.656	—

Fig. 8. Decrease in metazachlor concentration with time using Dy- TiO_2 450/4.

Dy-doped TiO_2 450/4, the least photocatalytically active sample, was used in further experiments to investigate the time required for total decomposition of metazachlor. We found that 5 h, which corresponded to 50 min of contact time, was sufficient to lower the metazachlor concentration nearly to zero (as shown in Fig. 8). Complete photocatalytic decomposition of metazachlor in water after 1 h of irradiation total is a comparable time to that reported in the literature [24], which indicates that the photocatalysts prepared in this work were efficient and suitable for this purpose. Furthermore, our results indicate that increasing the amount of lanthanides in the sample could lead to lower band gap energy owing to a shift of the absorption edge towards the visible range.

4. Conclusions

Dysprosium and praseodymium doped titania powders were prepared by sol-gel synthesis and subsequent solid state reaction treatment. All prepared samples were found to be suitable for photocatalytic decomposition of metazachlor in water; the best photocatalyst for this purpose was Pr- TiO_2 treated at 450 °C for 8 h. All the prepared photocatalysts were more active than or comparable in activity with commercial titanium dioxide P25. The aggregate size and consequently, the specific surface area, of the photocatalysts very significantly affected their final activity. Moreover, the lower activity of pure TiO_2 prepared under the same conditions confirmed that the Dy and Pr dopants enhanced photocatalytic activity.

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Graphical Abstract

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Influence of synthesis conditions on physical properties of lanthanide-doped titania for photocatalytic decomposition of metazachlor

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Praseodymium-doped titania shows higher photocatalytic activity than P25. The synthesis conditions significantly affected the physical properties of the photocatalysts and consequently their activity, which was mainly dependent on specific surface area.

Cihlarova, who performed the BET analysis, Jan Cupera, who performed the SEM imaging, and Dusan Hemzal, who performed Raman analysis.

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制备条件对稀土掺杂TiO₂物理性质和光催化降解吡啶草胺性能的影响

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摘要: 多相光催化是一种非常有效的降解各种水污染物的方法。本文以稀土(铈和镨)掺杂的TiO₂为光催化剂, 考察了制备条件对其物理性质和光催化性能的影响。采用溶胶-凝胶法和不同条件(反应温度450, 550, 650 °C; 反应时间4, 8, 12 h)的固态反应法制备

了TiO₂样品. 运用X射线衍射分析了该样品的晶相, 发现只存在锐钛矿相, 并得到Raman光谱的证实. 同时采用扫描电镜观察了样品的结构和粒径; 以BET法计算了其比表面积; 运用紫外-可见光漫反射光谱测得了样品的带隙能量. 通过测量紫外光照射下常用除草剂吡啶草胺的降解速率评价了样品的光催化活性, 反应过程中吡啶草胺的浓度用高效液相色谱分析. 结果表明, 稀土掺杂使得TiO₂吸收边红移, 并提高了其光催化活性; 制备时最优的固态反应条件为550 °C反应8 h.

关键词: 稀土掺杂二氧化钛; 铈; 镨; 合成条件; 光催化降解; 吡啶草胺

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