SELF-CLEANING PROPERTIES OF THIN PRINTED LAYERS OF TITANIUM DIOXIDE
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1 INTRODUCTION

Environmental pollution is becoming more and more serious. The green house effect is brought about by increasing in carbon dioxide concentration in the atmosphere. This, as well as the acid rain, is closely related to the use of fossil fuels. In order to solve such environmental and energy resource problems, photocatalysis has been attracting a great deal of attention.\textsuperscript{i}

Among the semiconductors, titanium dioxide (TiO \textsubscript{2}) is one of the most popular and promising materials as a photocatalyst because it is stable in various solvents under photoirradiation, available commercially and easy to prepare in the laboratory and has a potent ability to induce various types of redox reactions.

Since the start of its commercial production in the early twentieth century, titanium dioxide (TiO \textsubscript{2}) has been widely used as a pigment, in paints, toothpaste, and sunscreens, etc. In 1972, Fujishima and Honda discovered the photocatalytic splitting of water on TiO \textsubscript{2} electrodes under ultraviolet light.\textsuperscript{ii} Since this date, enormous efforts have been made to the research of TiO \textsubscript{2} material, which has led to many promising applications in areas ranging from photovoltaic to photocatalysis.\textsuperscript{iii} These applications can be roughly divided into “energy” and “environmental” categories, many of which depend not only on the properties of the TiO \textsubscript{2} material itself but also on the modifications of the TiO \textsubscript{2} materials host (e.g., with inorganic and organic dyes) and on the interactions of TiO \textsubscript{2} materials with the environment.\textsuperscript{iv}

As a promising photocatalyst, TiO \textsubscript{2} materials are expected to play an important role in helping to solve many environmental and pollution challenges; water and air purification, prevention of staining, and disinfection. Many approaches to improve the photocatalytic activity of TiO \textsubscript{2} have been tested. These studies proved that TiO \textsubscript{2} activity depends generally on its morphology, crystal composition, crystallinity and surface area.\textsuperscript{v}

Ultraviolet radiation has been used for disinfection purposes since the early 20\textsuperscript{th} century. Nowadays, wastewater and drinking water disinfection are important technical applications of direct UV irradiation in the wavelength range between 240 nm and 290 nm. Other significant contributions of UV disinfection include the photo-inactivation of surface bound or airborne microorganisms by using TiO \textsubscript{2} based photocatalytic techniques or solar photocatalytic disinfection of water, which is of importance in tropical developing countries.\textsuperscript{vi}

Titanium dioxide photocatalysts consists of nanometer scale particles which are either suspended or immobilized into the reactor. So far, mostly suspended systems have been used to investigate the degradation of a variety of components. However, the major drawback of suspended systems in practical applications is the costly separation step necessary after the purification. Therefore, an immobilized system is preferred for an efficient reactor scalable to industrial sizes, especially since the efficiency of the immobilized system can be comparable to that of the suspended system.\textsuperscript{vii}
2 THEORETICAL PART

2.1 PHOTOCATALYSIS

Photocatalysis, i.e., catalysis under light radiation, is a reaction in the presence of a catalyst which causes the acceleration of the whole process. The main difference between the catalyst and photocatalyst is that a catalyst contains active sites on which substrate is converted into a product whereas no active sites are present on a photocatalyst (Fig. 1). Photocatalysis can be homogenous or heterogeneous. The homogenous photocatalysis is taking place in homogenous phase. The heterogeneous is carrying out at the interfacial boundary between two phases (solid-liquid, solid-gas, liquid-gas).

![Fig. 1 Difference in concepts of catalytic and photocatalytic reaction](image)

The basic principles of heterogeneous photocatalysis can be summarized as follows. A semiconductor’s electronic shell consists of valence band (vb), it is the highest occupied energy band, and of conduction band (cb), it is the lowest empty band. These energy bands are separated by a band gap. It is the region of forbidden energies.

![Fig. 2 Simplified diagram of the heterogeneous photocatalytic process occurring on an illuminated semiconductor particle](image)

The initial process for heterogeneous photocatalysis of organic and inorganic compounds by semiconductors is the generation of electron–hole pairs in the semiconductors particles. When a photon, with energy higher or equal to the band gap energy, is absorbed by a semiconductor
particle, an electron from vb goes over to the cb with simultaneous generation of hole (h\(^+\)) in the vb. The electrons and holes are not localized in the valence and conduction bands. Therefore electrons and positives holes can migrate within a crystal. These electrons and holes can be trapped at the surface where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle. In this way, anodic or cathodic redox reactions can be initiated (Fig. 2). On the other hand, next the trapping of the species, electrons and holes can recombine on the surface or in the bulk of the particle in a few nanoseconds; the energy is dissipated as heat. In a real system recombination occurs and concentration of electrons and holes on the surface is not equal. Obviously, this recombination is detrimental to the efficiency of the semiconductor photocatalyst. Modifications to semiconductors surfaces such as addition of metals, dopants, or combinations with other semiconductors are beneficial in decreasing the electron and hole recombination rate and thereby increasing the quantum yield of the photocatalytic process.

2.2 METHODS OF TITANIA PREPARATION

Generally, two forms of TiO\(_2\) in photocatalysis have been widely used; highly dispersed fine particles or suspended particles in liquid medium and thin films on supporting materials. The main disadvantage of using the powder form of TiO\(_2\) is the suspension instability in time. This instability is monitored by sedimentation due to the aggregation. The other very important disadvantage is the energy consumption for catalyst removal and recovery. Due to these reasons, it is obvious that the use of active immobilized photocatalyst is more popular than using of this catalyst in powder form.

The photocatalyst can be immobilized onto a suitable inert support. In this case there is no need to remove the catalyst. Unfortunately, when the catalyst in immobilized, there is a decrease in the available surface area for the reaction since the catalyst must adhere to the solid support.\(^{\text{xii}}\) We have to point out, that in the case of immobilized photocatalyst, layer thickness is very important property of prepared films. When the photocatalyst films are too thick, most of the electrons and holes are generated deep in a semiconductor and never get up to the surface. So they are unable to participate in the reaction. On the other side, when the layers are too thin, semiconductor can absorb only a very small amount of incident photons. The efficiency of photocatalytic process decreases as well.\(^{\text{xii}}\)

There are many methods of synthesizing TiO\(_2\) nanostructures. Generally these methods can be divided to two main groups; solution routes and gas phase methods. The advantages of solution route are the control over the stochiometry, production of homogenous materials, ability to coat complex shapes and preparation of composite materials. The disadvantages include the use of expensive precursor, long processing times and the presence of carbon as an impurity. In the case of gas phase methods, the synthesis can be of chemical or physical nature.

**Sol-gel method**

Sol-gel processing is one of the most common methods to produce photocatalyst TiO\(_2\) in both forms; coating and powder. This process is categorized as a wet chemical method based on the hydrolysis and polycondensation of precursor.
In a typical sol-gel process, a colloidal suspension, or a sol, is formed by the controlled hydrolysis and polycondensation reaction of precursors, which are usually inorganic metal salts or organometallic compounds. In this process, the liquid sol is transformed into a solid gel phase during the complete polymerisation and loss of solvent. The thin layers on the substrate can be produced by various coating techniques such as spin-coating or dip-coating.

TiO$_2$ nanomaterials have been synthesized with the sol-gel method by the hydrolysis of titanium precursor. This process normally proceeds via an acid-catalyzed hydrolysis step of titanium(IV) alkoxide followed by condensation. The development of Ti–O–Ti chains is supported by a low content of water, low hydrolysis rates, and excess titanium alkoxide in the reaction mixture. Three-dimensional polymeric skeletons with a close packing result from the development of Ti–O–Ti chains. The formation of Ti(OH)$_4$ is favoured with high hydrolysis rates for a medium amount of water. The presence of a large quantity of Ti–OH and insufficient development of three-dimensional polymeric skeletons lead to loosely packet first-order particles. Polymeric Ti–O–Ti chains are developed in the presence of a large excess of water. Closely packed first-order particles are yielded via a three-dimensionally developed gel skeleton.

The strong reactivity of the alkoxide towards water often results in an uncontrolled precipitation and limits the use of the sol-gel technology. These problems can be eliminated with the aid of chelating agents, such as acetyl acetone (AcAc) and acetic acid. These chemical additives react with alkoxides and modify the ligand structure, enabling the hydrolysis and polycondensation reactions to be controlled.

The interest in application of sol-gel method is due to its many advantages, such as:

- Possibility of preparation homogenous films
- Ease of composition control
- Low processing temperature
- Large area coatings
- No special equipment with low cost
- Preparation of films with high photocatalytic activity

**Hydrothermal treatment**

Hydrothermal synthesis is widely used in industry to manufacture ultra-fine powders and particles. The process is usually realized in a steel pressure vessel called autoclave with or without Teflon or glass liners under controlled temperature and/or pressure with the reaction in aqueous solutions. The temperature can be elevated above the boiling point of water at standard conditions, reaching the pressure of vapoour saturation. The temperature and the amount of solution added to the autoclave largely determine the internal pressure produces. It is a method that is widely used for the production of small particles, for the preparation of TiO$_2$ nanoparticles TiO$_2$ nanorods nanowires and nanotubes.

The initial step in hydrothermal synthesis is the precipitation of the precursor solution, usually consisting of titanium alkoxide or halide. Prepared precipitate is mixed into aqueous slurry,
possibly with the addition of a surfactant. The precursor slurry is then placed into an autoclave and heated to a given temperature over some period time. The precipitate formed is then collected either by filtration or centrifugation, washed with an appropriate solvent and dried. With this relative simplicity, hydrothermal reaction leads to the synthesis of various TiO$_2$ nanomaterials simply by varying the experimental parameters.

The hydrothermal method of preparation TiO$_2$ particles has many advantages. A major advantage of using the hydrothermal process is the ability to produce different crystalline phases without the need of following heat treatment as it provides the capacity to grow good-quality crystals and to control the crystalline composition simultaneously. The other very important feature is that the hydrothermal synthesis favours a decrease in agglomeration between particles, narrow particle size distributions, phase homogeneity, and controlled particle morphology. It also offers uniform composition, purity of the product, monodispersed particles, a control over the shape and size of the particles, and so on. The hydrothermal method has been evaluated as one of the best techniques to prepare TiO$_2$ particles of desired size and shape with homogeneity in composition and a high degree of crystallinity.

Several authors studied in details the influence of different parameters like temperature, process duration, pressure (percentage fill), solvent type, pH and the starting charge on the final products of the hydrothermal treatment. In all cases, this product was TiO$_2$ but with various ratio of rutile and anatase. Nevertheless, the rutile phase is more dominant in the resultant product, the presence of a small amount of anatase persisted except when the experimental temperature is approximately 200 °C. The creation of a pure phase (pure anatase or pure rutile) required the proper selection of pH of the media and the crystallization temperature. When the pH of the medium is low (pH equals 1 to 2), only rutile phase was formed. When the pH is kept even lower, i.e., in the negative range, the final TiO$_2$ contains also a small amount of anatase. As the pH of the medium is increased, the product contained essentially anatase with very little part of rutile. With the addition of KOH or NaOH, the formation of anatase phase is favoured. With a further increase of the pH, i.e., above the twelve, only amorphous TiO$_2$ is obtained.

Similarly, control over the temperature, time and pH of the medium helps in the preparation of a desired particle shape and size. When the reaction temperature and time increase, it causes the formation of faceted grains of bigger size.

### 2.3 METHODS OF LAYERS PREPARATIONS

**Chemical / physical vapour deposition**

Vapour deposition refers to any process in which materials in a vapour state condenses to form a solid phase material. These processes are normally used to form coatings to alter the mechanical, electrical, thermal, optical, corrosion resistance, and wear resistance properties of various substrates. They are also used to form free-standing bodies, films, and fibers and to infiltrate fabric to form composite materials. If no chemical reaction occurs, this process is called physical vapour deposition (PVD); otherwise, it is called chemical vapour deposition (CVD).
In CVD process, precursor is delivered into a reaction chamber at a suitable determined temperature. As they pass through a reactor this precursor (in gaseous phase) come into contact with a heated substrate. It can react and form a solid layer deposited onto the surface of the substrate. Usually, an inert gas, such as Ar or N₂, is used as a diluting gas. The depositing temperature and pressure are the critical parameters. Whole process can be summarized as follows:

- Mass transport of precursor (in gas phase) to environs of substrate
- Diffusion of gaseous reactant through the boundary layer to the substrate surface or homogenous chemical reactions to form intermediates
- Adsorption of reactant species or intermediates on substrate surface
- Surface migration, heterogeneous reaction, creation of layers on the substrate surface, formation of by-product species
- Desorption of by-products from the substrate
- Diffusion of by-products to the bulk gas
- Transport of by-product gaseous species away from reaction chamber (exhaust)

![Diagram of CVD process](image)

**Fig. 3  Model of CVD process**

CVD method carries a lot of advantages but also many disadvantages. Main advantages are:

- Possibility of formation uniform thickness of layer
- Possibility of using quiet wide range of chemical precursors
- This method requires relatively low deposition temperature
- Ability to control the crystal structure, stoichiometry, surface morphology
- It is also possible prepare epitaxial film

To main disadvantages belong:

- Precursors are usually reactants which are extremely toxic, corrosive, explosive and also quite expensive
• By-precurors can be also very explosive, flammable, toxic and it is necessary their trapping and their treatment before being released to the atmosphere.

CVD methods are generally classified and categorized into seven main types of fabrication. The parameters used to characterize a CVD process include temperature, pressure, wall/substrate temperature, precursor nature, depositing times, gas flow state and activation manner.

**Spin-coating**

Spin-coating is a process used to apply uniform thin films to flat substrates. This method is very simple where an excess amount of precursor solution is placed on the substrate. Consequently the substrate rotated at a high speed to spread the fluid by centrifugal force and create of wet films. The thickness of the final film depends on the angular velocity of substrate rotation, concentration and viscosity of precursor and evaporation rate. Range of thickness which can be created by this method is from 100 nm to 200 μm.

**Dip-coating**

During the dip-coating process, a substrate is dipped into a liquid coating solution and then it is withdrawn from the solution at a controlled speed. The thickness of coated films generally increases with higher withdrawing speed. The thickness is determined by the balance of forces at the stagnation point on the liquid surface. A higher withdrawing speed pulls more liquid up onto the surface of the substrate before it has time to flow back down into the solution. The thickness of prepared films depends on viscosity and density used sols and on surface tension.

**Material printing:**

Up to this date, material printing has become another very important and very popular method of coating. For this purpose, a conventional inkjet printer can be used. During the coating small droplets of low viscosity ink are ejected from a print head and fall onto printed substrate. The movement of the printed head and the substrate is precisely controlled by computer, also the volume of eject droplets and their loading per unit area can be changed by the computer. The printer and also prepared sol of precursor have to fulfil certain requirements in order to be employed as a thin layer deposition tool. The printer has to be able to handle rigid media so that solid materials can be used as layer support. The precursor must be of a very low viscosity (less than 20 mPa⋅s) to prevent damage of the printer. If solid particles are present in the precursor, their diameter has to be well below the print head nozzle diameter and their aggregation must be prevented. Despite these limitations, inkjet printing has been successfully used for the deposition of a wide variety of functional liquids so far, such as conducting polymers, metallic nanoparticles dispersion, etc.

One of the inherent advantages of this method is the possibility of direct control the amount of the deposited sol by changing the grey-scale level of the printed image. In the case of inkjet printing, a combination of amplitude modulation screening and frequency modulation screening is used: ink droplets of varying size are placed at different pitch.
The second possibility how to create the thin layer of TiO$_2$ by material printing is using a specialized device, such as the Dimatix material printer (Fig. 4). This printer allows deposition of liquid materials on A4 substrate, utilizing disposable piezo inkjet cartridge. This printer can create and define patterns over an area of about 200 $\times$ 300 mm and handle substrates up to 20 mm thick with an adjusted Z height.xxiv

The temperature of the vacuum platen, which secures the substrate in place, can be adjusted up to 60 °C. Holder of print head can be turned in the range from 0° to 90°. It allows continuous changing of print resolution (from 100 dpi to 5080 dpi). The mechanical movements are extremely precise and they enable very precise work (resolution 5 µm) and reproducibility of printing.xxv

The Dimatix material printer offers a variety of patterns by employing a pattern editor program. Additionally, a waveform editor and a drop-watch camera system allows the manipulation of the electronic pulses to the piezo jetting device for optimization of the drop characteristics as it is ejected from the nozzle. There is a built-in cleaning station with a program editor that includes an automatic capping mechanism. This system thereby enables easy printing of structures and samples for process verification and prototype creation.

Fig. 4 Commercial inkjet printer Epson R220 and Dimatix material printer 2800

2.4 PHOTODEGRADATION OF WATER POLLUTANTS

Wastewater treatment is a very important for the removal of organic pollutants. Large amount of organic pollutants consumed in the industries are being released into the eco-system and constitute a serious treat to the environment. As chemical and agricultural wastes, these contaminants are frequently carcinogenic and toxic to the aquatic system because of their aromatic ring structure, optical stability and resistance to biodegradation. In past decades, the traditional physical techniques for the removal of organic pollutants from wastewaters have included adsorption, biological treatment, coagulation, ultrafiltration and ion exchange on synthetic resins.xxvi xxvii Those methods have not always been effective and they may not actually break down the pollutants in wastewater. For example, adsorption technology does not degrade the contaminants, but essentially transfers the contaminants from one medium to another, hence, contributing the secondary pollution. Moreover, such operations are expensive because the
pollutants are treated before the adsorption process while the adsorbent medium has to be regenerated for reuse. Traditional biological treatments are often ineffective in removing and degrading pollutants because the molecules, being mostly aromatic, are chemically and physically stable. Hence, biodegradation of organic pollutants is usually incomplete and selective. In fact, some of the degradation intermediates may be more toxic and carcinogenic than the original pollutants.

Heterogeneous photocatalysis has been successfully used in the oxidation, decontamination or mineralization of organic and inorganic contaminants in wastewater without generating harmful by-products. A large amount of chemical substrates that have already been subjected to photodegradation experiments in water with or without auxiliary oxidants or photocatalyst. Many authors presented extensive lists of organic compounds that have been treated according to H₂O₂-UV, O₃-UV and TiO₂-UV procedures. Richard and Grabner published work concerning the photodegradation of phenol and of its derivates in aqueous solution. Phenolic compounds are systematically introduced into the environment via several house-hold and industrial activities. A lot of fungicides, insecticides are based on this structural element. Hence, this class of organic compounds represents big toxicological risk because most of them are water soluble and highly toxic. They were detected in ground water reservoirs. Photocatalytic degradation of phenol derivates represents an alternative method for biological detoxification.

**Formic acid**

Carboxylic acids occur in natural waters at varying concentrations depending on origin, aqueous solubility, and biological activity. Formic acid has become the most investigated organic molecules on single-crystalline surface. The absorption of formic acid on TiO₂ surface is one of the best examined organic systems at this point.

During the degradation of formic acid, this compound undergoes direct mineralization to water and carbon dioxide without the creation of any stable intermediate species. Moreover, it also represents a possible final step in the photodegradation of more complex organic compounds.

**Organic dye**

Dyes have relatively large photoabsorption (extinction) coefficients and therefore measurements of their concentrations in solutions are easy even if the concentrations are very low. However, the fact that dyes absorb visible light indicates that a photoreaction might be induced by visible-light photoabsorption (dye sensitization) as well as by photoabsorption of a photocatalyst. Organic dyes are inappropriate as a model compound, particularly for testing visible light-induced photocatalytic activity. There are three reasons for its inappropriate:

- Dye molecules absorb photons, especially in the visible light range, and thus photo-excited electrons may be injected into photocatalytic particles.
- The absolute molar amount of dye contained in the reaction system can be much smaller than that of solid photocatalysts. The concentration of the dye in the solution should be relatively low since the absorption coefficient is large.
• The mechanism of dye degradation is so complicated that efficiency of the photocatalytic reaction, e.g., quantum efficiency, cannot be measured.

Advantage of using dye is:

• Measuring the consumption (decrease) of a dye during photo-irradiation requires only a spectrophotometer.

If dyes are used as model compounds, care must be taken in the interpretation of experimental results. Photocatalytic degradation of many organic compounds been reported, including noxious compounds such as polychlorobiphenyls (PCB), dioxin, dichlorodiphenyltrichloroethane (DDT). Among them the chlorophenolic compounds have been studied extensively, because these compounds are toxic, water-soluble and used for synthesis of other chemicals.

Many dyes are decolorized and ultimately mineralized by photocatalysis. In the degradation of azo dye, the degradation rate decreases in the order monoazo–diazo–triazo. Three processes including oxidation and reduction are considered to occur simultaneously in the photocatalytic degradation of dye (Fig. 5). The photocatalytic degradation of organic compounds is the first process. Spectral sensitization is the second process. One moiety of dye molecule serves in last process as the electron acceptor, suppressing recombination between electron and positive hole.

Fig. 5  Photocatalytic degradation mechanism of dye

3  AIM OF THE EXPERIMENTAL WORK

The aim of this work is the preparation of thin layers of titanium dioxide on the solid substrates. The preparation of TiO₂ thin layers are performed by two different methods; by materials printing
and by chemical vapour deposition. TiO₂ for material printing is prepared by two methods; by sol-gel and by hydrothermal treatment. Photocatalytic activity of all prepared TiO₂ is investigated and the most active samples are evaluated.

**Sol-gel method**

Titanium tetraisopropoxide (TTIP) is used as a precursor, acetyl acetone (AcAc) as a chelating agent, and ethanol is used as a solvent in sol-gel preparation. The sol deposition is realized by inkjet material deposition. Different amount of PEG are added to each prepared sol. PEG is used as anti-cracking agent. The influence of different sol loading on physical properties and final photocatalytic activity of prepared TiO₂ thin films is examined.

**Hydrothermal treatment**

Titanium oxochloride (TiOCl₂) is used as a precursor, KOH as a precipitation agent and water is used as solvent. Hydrothermal synthesis is performed under various conditions. The influence of process temperature and time of hydrothermal treatment on final physical properties of prepared sols is studied. Subsequently, the best conditions of preparation for final activity are evaluated. These sols are deposited onto the substrates by material printing and again the photocatalytic activity of thin titania layers is evaluated.

**Chemical vapour deposition**

Titanium tetraisopropoxide (TTIP) is used as a precursor and nitrogen is used as carried and also dilution gas. Deposition is performed in cold-wall reactor. The final photocatalytic activity of thin titania layers is evaluated and compared with photocatalytic activity of titania thin film prepared by hydrothermal treatment.

4 **CHOSEN METHOD FOR PREPARATION OF TITANIUM DIOXIDE**

4.1 **SOL-GEL METHOD**

Thin layers of titanium dioxide were immobilized on the soda-lime glass plates by material printing. Titanium(IV) isopropoxide (TTIP) was used as a precursor. Different amounts of PEG with molecular weight of 1500 (0, 1, 4, 16 g×dm⁻³) were added to form the printing solutions. Physical properties of prepared layers were investigated. Photocatalytic activity was studied as a degradation rate of 2,6-dichloroindophenol (DCIP) with initial concentration 2×10⁻⁵ mol·dm⁻³ in the bath reactor (Fig. 6).
4.2 HYDROTHERMAL SYNTHESIS

Titanium oxo-chloride (TiOCl₂) was used as a precursor for preparation the colloidal suspension of TiO₂. The influence of process conditions on final photocatalytic activity was investigated. The efficiency of colloidal slurries was examined as a degradation rate of formic acid in the pyrex reactor (Fig. 7).

Prepared titania colloidal suspensions were immobilized on the soda-lime glass substrates using material printing method. Photocatalytic activity of these thin layers was investigated as a degradation rate of DCIP in a flow reactor (Fig. 8).
4.3 CHEMICAL VAPOUR DEPOSITION

Apart from the material printing, also chemical vapour deposition was chosen as a technique for the preparation of thin TiO$_2$ layers. Glassy carbon was used as substrate and TTIP as a precursor. Whole process was performed in a vertical cold wall CVD reactor. Photocatalytic experiments were performed in a flow reactor on a rotary sample holder as well as in previous case. Photocatalytic activity was again evaluated as a degradation rate of DCIP. The activity of these samples was compared with the results for hydrothermal printed layers. Reactivity of TiO$_2$ was calculated for 1 gram of photocatalyst.

5 MAIN RESULTS

5.1 SOL-GEL METHOD

5.1.1 Optical microscopy

The quality of prepared titania films was studied by optical microscope in polarized light, with the magnification 10×. We found out that all prepared layers adhered well to the soda-lime glass after the calcinations process and all were optically transparent.
The surface topology of prepared layers was studied by AFM analysis. Using this method, the influence of added PEG amount on the final roughness of prepared films was investigated. We

5.1.2 Atomic force microscopy

The surface topology of prepared layers was studied by AFM analysis. Using this method, the influence of added PEG amount on the final roughness of prepared films was investigated. We
compared the sample without PEG (PEG 0) and the sample with the highest amount of PEG (PEG 16). We discovered that PEG causes an increase of surface roughness (surface roughness of the sample PEG 0 was 0.28 nm; surface roughness of PEG 16 was 0.41 nm). The obtained records are shown in the following figure (Fig. 9).

5.1.3 Photocatalytic activity

The photocatalytic activity was evaluated as a degradation rate of DCIP realized in bath reactor. DCIP was chosen due to its very easy detection in VIS range and a very low absorption at 360 nm wavelength. We discovered that a dependence of logarithm of concentration on time is linear (Fig. 10) so it means that photochemical degradation of DCIP runs according to first order kinetics.

Fig. 9  *Comparison of the roughness; a) PEG 0; b) PEG 16*

Fig. 10  *Dependence of logarithm of concentration on time*
We compared the influence of PEG and sol loading on final photocatalytic activity of prepared TiO$_2$ in this part of study. We discovered that samples with PEG have higher activity than the sample without PEG (Fig. 11). This can be accounted for the higher roughness of the thin layers surface, which is created by the present of PEG.

Consequently, we investigated the influence of sol loadings on the titania photocatalytic reactivity. We found out that the samples with 100% sol loading were the most photocatalytically active (Fig. 11). It can be explained by presence of higher amount of photocatalysts with increasing sol loading.

![Graph showing photocatalytic activity of prepared TiO$_2$](image)

**Fig. 11  Photocatalytic activity of prepared TiO$_2$**

### 5.2 HYDROTHERMAL SYNTHESIS

Firstly twelve samples were prepared by hydrothermal synthesis with varying process conditions, especially pH, temperature or duration of process. We investigated the stability of prepared colloidal solution after 1 day of leaving in a rest using gravimetric analysis. The obtained results are shown in Fig. 12. We discovered that with increasing time of hydrothermal treatment the stability of TiO$_2$ particles increases except the samples prepared at 110 °C in basic pH. These slurries had constant stability.

After the comparison of different pH we found out that samples prepared in acid environment were more stable. When we compared different temperatures, 110 °C in acid pH and 160 °C in basic pH was evaluated as better temperature for preparation hydrothermal titania solutions.
5.2.1 Photocatalytic activity

The photocatalytic activity was evaluated by the degradation rate of formic acid. We compared the rate constant of prepared TiO$_2$ and evaluated the best conditions of hydrothermal treatment for final activity. We investigated the decreasing of FA concentration because of UV radiation by HPLC analysis. A record of this analysis is shown in the Fig. 13. It is the dependence of peak intensity (mAU) on the retention time (min). In this figure we can observe decreasing of FA peak (in the position 11.4 min) which characterized the decreasing of FA concentration. There is also noticeable peak in the position 4.7 min that correspond to the injection peak. The concentration of FA was calculated from the height of the peak.

We examined the decreasing of relative concentration as a function of time. We discovered that the profile of time-dependent photocatalytic reactivity is linear within the studied range so we conclude that our degradation reactions run according to the zero kinetics model. Subsequently,
we calculated the rate constants (k) and their standard errors (SE) for all prepared samples. The comparison of received results is shown in Fig. 14.

![Fig. 14 Comparison of rate constants k (·10^-6 min^-1)](image)

According to this analysis, the best samples were prepared in acid pH at 110 °C. After the comparison of these samples with commercial TiO₂ (P25) we discovered that our best samples (acidic, 110 °C, 24 hours and 48 hours) were comparable with P25.

In this part of work we discovered that the process conditions have the significant influence on the photocatalytic activity and also on the final physical properties of prepared samples. We discovered that acid solutions had better physical properties and also better final photocatalytic activity. Therefore these samples were chosen for further investigation.

5.2.2 Preparation of thin titania films

The colloidal solutions of TiO₂ were prepared by hydrothermal synthesis under the different conditions in acidic environment. These samples were used for formation of printing mixtures. Soda-lime glass substrates were coated using experimental printer FUJIFILM Dimatix.

Different surfactants were used as stabilization agents. Firstly, we tried the neutral (Tween 20). We observed decreasing of aggregation using this compound but this decreasing was not
sufficient. It means that still quite high amount of TiO₂ particles remained in the mesh size syringe filter. Consequently, we tried one anion active surfactant (Abesone) and one cation active surfactant (CTAB). We observed that only in case of anion active surfactant the aggregation of colloidal particles was completely removed.

We prepared TiO₂ one- and two-layers samples by material printing. This part of study focuses on investigation of thickness influence on final physical properties and photocatalytic activity of the prepared samples.

5.2.3 Photocatalytic activity

The photocatalytic activity was evaluated as the degradation rate of DCIP in a flow reactor. The absorption maximum of DCIP was found at wave length 600 nm so the absorbance was recorded each minute at this value. The total time of reactions was 40 minutes because of complete decolonization of DCIP solution.

Subsequently the constant rates for examined samples were calculated. The influence of layers thickness was investigated. The activities of our samples were compared with the photocatalytic activity of common commercial TiO₂ (P25).

We discovered that logarithm dependence of relative concentration on time was linear for all prepared titania layers. So we assumed that reaction runs according the first order kinetics within the studied range. The reaction rate constants (k), their standard errors (SE) and conversion degree were calculated (Table 1).

The analysis was performed with intensity 7.5 mW·cm⁻². We discovered from this measurement that double-layers samples were more active. This result was supposed because of higher presence of TiO₂ in the double-layers, i.e. more photocatalyst and so higher amount of photoactive sites.

Although the amount of deposited TiO₂ in case of double-layers increased twice, we did not observe increasing of photocatalytic activity two times. It means that all titania particles didn’t participate of photocatalytic degradation process. It could be cause by using insufficient intensity for activation of all photocatalysts. Also there could be the influence of a steric effect which could cause adsorption of lower amount of DCIP.

Photocatalytic activities of all samples including P25 per 1 g of photocatalyst are shown in Fig. 15. The final standard error was influenced by the SE of partial measurement (calculation of constant rate and SE of weighting). Final standard error was calculated according the equation (1)xxxviii. When the considered values are independent r is equal to 0. When there is a total dependence r is equal 1. Because rate constant is dependent on the amount of photocatalysts only in a small range and consequently it is independent we considered r equals 0.

\[
\left( \frac{S_{k/m}}{k/m} \right)^2 = \left( \frac{S_k}{k} \right)^2 + \left( \frac{S_m}{m} \right)^2 - 2r \left( \frac{S_k}{k} \right) \left( \frac{S_m}{m} \right)
\] (1)
We discovered that P25 is the best photocatalyst. Most of prepared samples had activity much lower than P25 only TiO$_2$ synthesized for 48 hours at 160 °C showed a comparable efficiency.

This difference between our TiO$_2$ and P25 was probably caused by the different phase of TiO$_2$. In case of P25 there was mixture of anatase and rutile however all our titania were pure rutile. So this result was expected because it is well known that mixture of anatase and rutile is much more active than only pure anatase or pure rutile. So this supposition was confirmed in this part.

Table 1  *Formal 1st order rate constant, their standard errors and conversion degree for experiment took place using intensity 7.5 mW·cm$^{-2}$*

<table>
<thead>
<tr>
<th>Sample</th>
<th>k (min$^{-1}$)</th>
<th>SE (min$^{-1}$)</th>
<th>Conversion degree (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 layer</td>
<td>0.0002</td>
<td>0.0001</td>
<td>51.0</td>
</tr>
<tr>
<td>2 layers</td>
<td>0.0090</td>
<td>0.0005</td>
<td>66.4</td>
</tr>
<tr>
<td>24 h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 layer</td>
<td>0.0049</td>
<td>0.0003</td>
<td>61.6</td>
</tr>
<tr>
<td>2 layers</td>
<td>0.0163</td>
<td>0.0009</td>
<td>74.9</td>
</tr>
<tr>
<td>48 h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 layer</td>
<td>0.0130</td>
<td>0.0007</td>
<td>69.6</td>
</tr>
<tr>
<td>2 layers</td>
<td>0.0212</td>
<td>0.0012</td>
<td>79.2</td>
</tr>
<tr>
<td>160 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 layer</td>
<td>0.0084</td>
<td>0.0005</td>
<td>68.6</td>
</tr>
<tr>
<td>2 layers</td>
<td>0.0083</td>
<td>0.0005</td>
<td>67.4</td>
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<tr>
<td>24 h</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1 layer</td>
<td>0.0122</td>
<td>0.0008</td>
<td>72.8</td>
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<tr>
<td>2 layers</td>
<td>0.0153</td>
<td>0.0009</td>
<td>76.3</td>
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<tr>
<td>48 h</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1 layer</td>
<td>0.0271</td>
<td>0.0015</td>
<td>83.1</td>
</tr>
<tr>
<td>2 layers</td>
<td>0.0313</td>
<td>0.0017</td>
<td>86.0</td>
</tr>
<tr>
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<tr>
<td>1 layer</td>
<td>0.0284</td>
<td>0.0017</td>
<td>84.5</td>
</tr>
<tr>
<td>2 layers</td>
<td>0.0344</td>
<td>0.0019</td>
<td>87.7</td>
</tr>
</tbody>
</table>
Analysis of the given text:

**Fig. 15**  *Photocatalytic activity per gram*

**5.3 CHEMICAL VAPOUR DEPOSITION**

Apart from the material printing, CVD method was used as a second technique for the preparation of thin TiO\textsubscript{2} films. The samples were prepared during two depositions cycles. The duration of vacuum creation and age of precursor were the parameters which were different. We studied the influence of substrate positions and influence of different parameters of CVD on final photocatalytic activity. The position of substrates on susceptor is shown in Fig. 16.

**Fig. 16**  *Position of glassy carbon during CVD processes*

**5.3.1 Photocatalytic activity**

The photocatalytic activity of prepared titania thin layers was examined as a degradation rate of DCIP in a flow reactor. The reactivity of samples was studied for two different intensities (7.5 W·cm\textsuperscript{-2} and 10 W·cm\textsuperscript{-2}). Consequently, the results for intensity 7.5 W·cm\textsuperscript{-2} were compared with the activity of hydrothermal process printed layers. We observed again a linear dependence of relative concentrations logarithm on time. So this result indicates that reaction runs according the first order kinetics within the studied range.
The formal 1st order rate constants (k) and their standard errors (SE) were calculated for both intensities and obtained results are shown in Fig. 17. As we can observe the photocatalytic activity of prepared samples increases with increasing intensity of irradiation. This result was expected because higher intensity can activate more photocatalysts so the degradation reaction runs faster.

In the case of intensity 7.5 mW·cm⁻² the photocatalytic activity for all samples were similar however for 10 mW·cm⁻² we could observe increasing reactivity of samples GC-3 and GC-4.

Subsequently, the activity of TiO₂ layers prepared by CVD method was compared with the activity of samples prepared by material printing from hydrothermally treated sols. The rate constants had to be related to 1 gram of photocatalysts because the amount of deposited TiO₂ was in each case different. The results from this analysis are summarized in Fig. 18. We discovered that only the sol treated at 160 °C for 48 hours was more active and the others had a comparable activity.
Fig. 18 Comparison of photocatalytic activity for samples prepared by hydrothermal treatments and CVD method

6 CONCLUSION

Two methods of thin layers depositions were used in this study: material printing and chemical vapour deposition. Two sols with different precursors (TTIP and TiOCl$_2$) and different preparation (sol-gel method and hydrothermal treatment) were used for material printing. All thin layers were deposited onto the soda-lime glass plates in this case. TTIP was used as a precursor during the CVD process and these layers were deposited onto glassy carbon substrates.

The layers prepared by sol-gel method were homogeneous and transparent. PEG was used as anticracking agent and we discovered that concentration of 4 g·dm$^{-3}$ caused their complete disappearance. The thickness of prepared layers was investigated by specular reflectance measurement using NanoCalc-2000 and we found out that the thickness of titania films increased with increasing sol loading. The morphology of the layers was examined by SEM analysis and the roughness was evaluated using AFM analysis. We discovered that with increasing amount of PEG the roughness increased. The sessile water drop method was used for studying photoinduced superhydrophilicity. We discovered that after storage the layers in darkness for 10 days all films obtained hydrophobic properties. Nevertheless, these properties were changed back to superhydrophilic after the irradiation by UV light with intensity 15 W/m$^2$ for 10 minutes.

We investigated the influence of process conditions on final properties for the hydrothermally treated sols. We discovered that temperature and duration of hydrothermal synthesis as well as pH of reaction have significant influence on final properties as stability of slurries, crystallite phase and size, and final photocatalytic activity. Acidic environment was evaluated as better so the other study continued only with sols prepared under this condition.

Consequently, acidic sols were deposited onto the soda-lime glass plates by material printing. We discovered that only anion-active surfactants could be used for preparation of stable printing
mixture. All these layers had milky color. Crystallite phase was examined by XRD analysis and we discovered that we prepared pure rutile. This change of crystallite phase from mixture of anatase and rutile to pure rutile was caused by decreasing of pH from value 2 to 1. The morphology and grain size was evaluated by SEM and AFM. We discovered that grain size decreased with increasing of treatment time. As well as for layers prepared by the sol-gel method, we studied the photoinduced superhydrophilic properties for all prepared films. However, we found out that even 30 minutes, what corresponded to exposure dose 180 kJ/m² was not sufficient to reach superhydrophilic properties in this case.

Apart from the material printing, the thin titania layers were deposited also by CVD. The samples were prepared during two processes and the parameters of the reactions were the same while the only differences were in age of precursors and in the time for vacuum creation. Crystallite phase of prepared layers was analysed by XRD method and in both cases we prepared pure anatase. This result was supposed because of the same temperature. The morphology and thickness of prepared layers were examined by SEM. The thickness of the films prepared during the first process was higher than in the second. The topology and roughness of the samples was investigated by AFM.

The aim of this work was to investigate the photocatalytic activity of all prepared TiO₂, to compare different method and evaluated the best conditions or the preparation of the titania thin layers. In case of samples prepared by CVD method we examined the influence of different intensities and positions on the susceptor. We did not observe any significant difference between the photocatalytic activities of the samples for the same intensity. This result indicates that there is not any influence of the samples position and their efficiency. Then we found out that with increasing intensity of irradiation the activity of TiO₂ increase.

We compared the influence of treatment conditions and amount of layers on final activity in case of printed layers prepared by hydrothermal synthesis. We discovered that with increasing amount of layers the photocatalytic activity increases. As the best time for hydrothermal synthesis were evaluated 48 hours. When we studied the influence of temperature we observed higher activity for samples prepared at 160 °C but only in case of one layer. These results were not obtained for two layers. In this case we found out that photocatalytic activities were similar for samples treated for the same time.

The calculation of activity per gram was necessary for the comparison these two method of depositions. We discovered that activity of TiO₂ synthesized at 110 °C for 6 hours was very negligible with the others samples. So these conditions were not satisfactory. The activity of samples treated for times 24 and 48 hours at 110°C were comparable with the activity of samples prepared in CVD process. We evaluated as the best conditions for the preparation time 48 hours and temperature 160 °C.

The photocatalytic activity of titania prepared by sol-gel process could not be compared with the other results because the conditions of the experiment was different. We used different reactor (Fig. 6), different lamp (so different emission spectrum) and also different intensity of irradiation (1 mW/cm²). We discovered from these experiments that activity increased with increasing sol loading. Also we discovered that with increasing amount of PEG the efficiency increased but only up to 4 g·dm⁻³. We observed decreasing of the activity in case of PEG 16.
7 REFERENCES


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**Education and training**

Dates  
July 2008 onwards

Principal subjects/occupational skills covered  
Ph. D. student, specialized at physical chemistry of colloids

Name and type of organisation providing education and training  
Brno University of Technology, Faculty of Chemistry

Dates  
June 2003 – June 2008

Principal subjects/occupational skills covered  
masters degree, title achieved: Ing. physical chemistry, colloid chemistry, technology of consumer chemistry, diploma work:

Name and type of organisation providing education and training  
Brno University of Technology, Faculty of Chemistry

**Personal skills and competences**

Mother tongue(s)  
Czech

Other language(s)  

Self-assessment

European level (*)  

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<th>Writing</th>
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</table>

(*) Common European Framework of Reference for Languages

Social skills and competences  
good communication ability

team work

Technical skills and competences  
measurement of UV-VIS spectra,

measurement crystallite size by photon correlation spectroscopy,

HPLC measurement,

Computer skills and competences  
excellent knowledge on Microsoft Office applications,