Effect of titanium source and sol-gel TiO$_2$ thin film formation parameters on its morphology and photocatalytic activity

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TiO$_2$ thin films with different surface structure have been prepared from alkoxide solutions by the sol-gel method using different cationic precursors and heat treatment techniques. The effect of using titanium isopropoxide as well as titanium butoxide as a titanium source on the surface structure and photocatalytic activity of the resultant thin films was studied. Significant differences in the rate of hydrolysis and condensation reactions during the sol-gel synthesis were observed for these titanium precursors. This had a direct influence on the morphology of the as-prepared TiO$_2$ films. Higher quality oxide coatings were obtained from titanium isopropoxide. They were characterized by a smaller grain size, improved surface roughness and uniform coverage of the glass substrate. A beneficial effect of calcination process after each sol application cycle in contrast to single step calcination after all dip-coating cycles was observed. Photocatalytic degradation tests showed that methyl orange was decolorized in the presence of all prepared TiO$_2$ films by exposing their aqueous solutions to UV light ($\lambda = 254$ nm). The highest photocatalytic activity had the TiO$_2$ layer produced using titanium isopropoxide.

Keywords: *TiO$_2$ thin film; sol-gel; photocatalysis*

1. Introduction

Environmental pollution is one of the main problems in the contemporary world. The currently used purification techniques of water or air require considerable financial outlays and often do not lead to a complete decomposition of pollutants [1, 2]. One of the proposed alternative methods for purifying of water or air that combines low cost of the process and the ability to complete mineralization of organic contaminants is photocatalysis and the most popular photocatalyst is TiO$_2$ [3, 4]. However, conventional powder catalysis results in many disadvantages, e.g. technological problem of mixing the powder and solution during the reaction and separation of the photocatalyst after the reaction. One of the methods to overcome these disadvantages is preparation a photocatalysts in the form of thin layer on various kinds of substrates. Additionally it has extended the application of TiO$_2$, apart from catalysis, to other industrial applications, e.g. solar cells, self-cleaning materials

and corrosion protection [5–12]. Currently, several techniques for producing thin semiconductor layers [13–17] are known. The most popular, from the industrial point of view, is a sol-gel method combined with dip-coating or spin-coating techniques. The sol-gel technology can be considered as one of the key technologies for the twenty-first century. The advantages of this method are the simplicity, low cost and the fact that TiO$_2$ can be easily applied on the surface with complicated shapes and large area. On the other hand, the sol-gel technique is very sensitive to synthesis parameters. To obtain oxide coatings with high photocatalytic activity, the thickness of the films, its structure and morphology e.g. thickness uniformity, grain size should be very precisely controlled. In contrast to powder TiO$_2$ there are very few papers focusing on the influence of sol-gel processing parameters on morphology and photocatalytic properties of thin TiO$_2$ films.

One of the key parameters of the sol-gel process is the type of substrates used for the synthesis. It has been shown that using TiCl$_4$ as titanium precursor, thin films with different crystal structure and

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physical properties can be obtained [18–20]. Due to the fact that it is a highly corrosive material, alternative sources of titanium in sol-gel method are of practical interest. Currently, TiO$_2$ coatings are most commonly made from alkoxide solutions, using titanium(IV) isopropoxide as a cation precursor. There is very little information on the use of other kinds of compounds, e.g. titanium butoxide in the process of TiO$_2$ thin films formation and its properties [21–23]. A major challenge in this case is the formation of a sol with appropriate rheological properties enabling to apply multiple layers of titanium dioxide for a long time. It is known from the research published by Alzamani et al. [24] that the presence of acidic catalyst such as H$_2$SO$_4$, HNO$_3$ and HCl during the preparation of the sol using titanium(IV) isopropoxide plays an effective role in controlling hydrolysis and condensation reactions. In addition, other methods for stabilizing such solutions are known, e.g. the use of cation complexing agents such as diethanolamine [25, 26]. The use of such chemical agents makes it necessary to apply a higher calcination temperature in order to obtain oxide layers, which negatively affects the quality of photocatalytic layers. The heating rate has a strong influence on the grain growth and the resultant crystalline phase of TiO$_2$ thin layers [27–29]. Kenanakis et al. [30] reports that the most optimal annealing temperature to obtain the best photocatalytic properties of TiO$_2$ films on glass is 500 °C, but this is strictly related to the type of substrates used during the sol-gel process.

Based on this knowledge, our study is focused on detailed investigation and comparing the influence of selected parameters of TiO$_2$ thin film formation by sol-gel method using different titanium precursors: titanium(IV) isopropoxide and titanium(IV) butoxide on its morphology and photocatalytic activity. The influence of the factors, such as: cationic precursors, H$_2$O to titanium molar ratio as well as the temperature of heat treatment on the properties of powders and thin TiO$_2$ layers, was investigated. Moreover, this paper presents the effect of high-temperature treatment method, i.e. one-step and multi-step calcination after each sol-application cycle on the morphology and photocatalytic properties of the products.

2. Experimental

2.1. Chemicals

All chemicals used in the current study are presented in Table 1. The reagents were used without further purification.

2.2. Preparation

Preparation of precursor solutions for TiO$_2$ thin film formation

Titanium(IV) isopropoxide was dissolved in anhydrous ethanol in the volume ratio 1:10. The obtained solution was stirred (500 rpm) for 2 h at room temperature. After this time, the mixture of water and ethanol in appropriate proportion was added dropwise with a burette under stirring. The resultant alkoxide solution was left standing at room temperature for 2 h for hydrolysis reaction, resulting in the TiO$_2$ sol. All syntheses were also repeated with the addition of HCl (0.5 ml). A concentrated hydrochloric acid was added to the solution to obtain a pH value ≈ 1.3 in order to avoid precipitation. In analogous way, the synthesis of TiO$_2$ was carried out using another titanium precursor, i.e. titanium(IV) butoxide.

Preparation of TiO$_2$ thin films

Formation of TiO$_2$ thin films on the glass substrate comprised of three steps:

I – Substrate preparation. Glass plates (25 mm × 75 mm × 1 mm) were washed in distilled water with detergent and then they were washed with acetone. Analogically, glass plates which were additionally subjected to etching in the solution of nitric acid with water in the ratio of 1:10 were also prepared.

II – Formation of TiO$_2$ films. The TiO$_2$ films on the glass substrates were prepared from the TiO$_2$ sol solution by dip-coating technique. The withdrawal speed was 1 mm·s^{-1}. The thickness of the TiO$_2$ films was controlled by repeating the dip-coating cycles. In the present study six dip-coating cycles were applied.

III – High temperature treatment. High-temperature treatment of TiO$_2$ films was carried out in two series:

Table 1. Chemicals used in the current study.

Chemical	Producer	Purity [%]
$Ti[OCH(CH_3)_2]_4$	Sigma-Aldrich	>98
$Ti(OCH_2CH_2CH_2CH_3)_4$	Fluka Chemical	>97
CH_3CH_2OH	POCH S.A.	99.8
CH_3COCH_3	POCH S.A.	99
HCl	POCH S.A.	35-38
HNO_3	POCH S.A.	65
$C_{14}H_{14}N_3NaO_3S$	POCH S.A.	−

- After each dip-coating cycle, the plate was subjected to drying at 120 °C to evaporate the solvent and then another layer was applied. After the formation of six layers the plate was subjected to calcination at 500 °C for 2 hours to obtain a crystalline product.

- After applying each layer of oxide, the plate was subjected to drying at 120 °C to evaporate the solvent and then calcined at 500 °C for 1 h. Subsequently, after cooling to ambient temperature another layer was applied.

2.3.   Characterization

The as-synthesized materials were analyzed via a powder X-ray diffraction with a CuKα source on an X'Pert Philips instrument, in 2θ range of 10° to 90° with a step size of 0.01°. The identification of the material was made according to a JCPDS Card. The crystallite size was calculated by Scherrer equation:

$$D = (k\lambda)/(\beta cos\Theta) \tag{1}$$

where D is the crystallite size of TiO_2, k is a constant (0.95), λ is the wavelength of X-ray, β is the measured full width at half maximum (FWHM) of the peak and Θ is the Bragg diffraction angle in degrees. Thermal analysis (TG/DTG-DTA curves) in the temperature range of 20 °C to 1000 °C was performed using TA Instruments SDT 2960 with a heating rate of 20 °C·min^{-1}. The SEM images of the microstructure and morphology of obtained materials were taken with a HITACHI TM-3000 instrument. The surface morphology was measured with an atomic force microscope (AFM) in semi-contact mode using a NTEGRA Aura-NT-MDT

system. The photocatalytic activity of the materials was tested in the decomposition reaction of methyl orange in water with a concentration of 2 mg/dm^3. The experiments were carried out in a dark and closed box with UV radiation source, 12 W low-pressure mercury lamp (Krüss Optronic) with a wavelength of 254 nm. The scheme of the experiment is presented in Fig. 1. Before turning on the light source, photocatalysts was moistened with a solution of methyl orange in a dark for 60 min to achieve adsorption equilibrium. The samples were taken regularly at 120 minute intervals. The concentration of the dye was measured by UV-Vis Specord 205 Analytik Jena spectrophotometer.
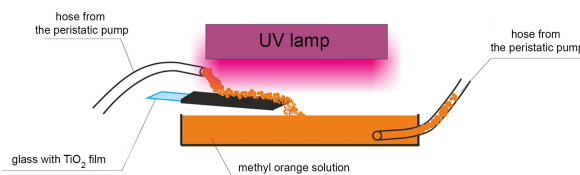

Fig. 1. The scheme of photocatalytic test of TiO_2 thin films.

3.   Results and discussion

3.1.   Sol-gel chemistry and precursors

The solution from which the TiO_2 films are prepared by dip-coating technique should have suitable rheological properties. To find the most optimal chemical composition of the mixture, the effect of parameters such as the type of titanium precursor, the stoichiometric ratio of Ti:H_2O and the influence of the stabilizer addition was investigated.

A series of syntheses were performed in which the titanium(IV) butoxide and titanium(IV) isopropoxide were used respectively as a source of titanium. In order to investigate the influence of molar ratio of water to titanium, the reactions with the molar ratios of 1:1, 1:3.5 and 1:5 were carried out. With the increasing amount of water, hydrolysis occurred faster. It was also noted that the hydrolysis reaction took place much faster when titanium butoxide was used as a cation precursor. It was characterized by a clouding rate of the solution and a change in color to milky white after adding a few drops of a solution containing water. In addition, the viscosity of the fluid significantly increased as a result of addition of water, which precluded the deposition of titanium dioxide thin films using a dip-coating technique. In the case of titanium(IV) isopropoxide, slight cloudiness was noted after addition of a few drops of a solution comprising water and after adding the entire contents of the burette, the color of the solution turned to milky white. The resulting sol solution was characterized by a much lower viscosity enabling deposition of TiO$_2$ on the glass substrate in contrast to earlier solution. All prepared solutions gelled within several dozen minutes, making it impossible to apply a multiple layers of titanium dioxide. These observations are very similar to other authors' in this area [31, 32]. It is known from the research conducted by Alzamani et al. [24] that the presence of acidic catalyst such as HCl during the preparation of the sol from titanium(IV) isopropoxide, plays an effective role in controlling hydrolysis and condensation reactions. In this part of the study, the influence of the presence of a stabilizer in the form of hydrochloric acid on the gelation process using different titanium precursors was investigated. The analogous reaction as described above was carried out except that, for each solution of titanium(IV) isopropoxide as well as titanium(IV) butoxide with anhydrous alcohol, 0.5 ml of hydrochloric acid was added and then the hydrolysis reaction was carried out. The addition of the concentrated hydrochloric acid stabilized the solutions (pH value $\approx$ 1.3) and prevented the negative precipitation process. Regardless of the amount of added water, the hydrolysis reaction proceeded similarly in all cases. None of

the solution has transformed into gel even after two months. The solutions were characterized by excellent rheological properties enabling the application of thin layers of TiO$_2$ by dip-coating technique.

3.2. Influence of process parameters

In order to determine the optimum calcination temperature for obtaining a crystalline TiO$_2$ with appropriate polymorphic form and particle size, the produced sol from titanium(IV) isopropoxide was dried at 120 °C for 12 h and obtained powder was calcined in air at temperatures of 400 °C, 500 °C and 600 °C for 2 h, respectively. According to the thermal analysis of the dried sol powder shown in Fig. 2, a calcination temperature in the range from 400 °C to 600 °C is the most optimal to obtain pure TiO$_2$ in the anatase form, using the described substrates in the sol-gel process. The thermal decomposition of most organic substrates takes place around 200 °C, as evidenced by the TG/DTG curves. The obtained material was analyzed by X-ray powder diffraction for the phase composition and the crystallite size was calculated using Scherrer formula. The results for each temperatures are presented in Table 2 to Table 4.
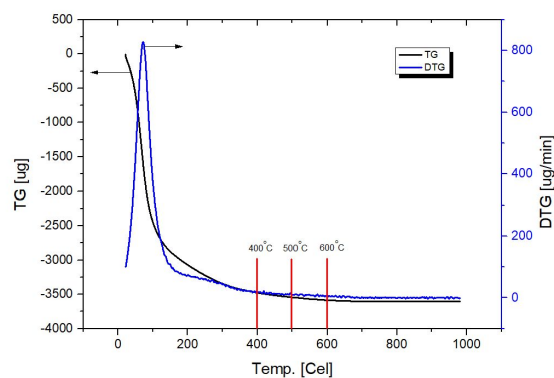

Fig. 2. TG/DTG curves of TiO$_2$ dried sol powder.

The influence of calcination temperature on the particle size of the TiO$_2$ is clearly visible. Materials which have been subjected to calcination at higher temperature have a well-formed crystalline planes, and are characterized by greater size of the crystallites which is confirmed by diffraction reflections

Table 2. Results of XRD analysis and weight loss of powders subjected to calcination at 400 °C.

Ti:H$_2$O molar ratio	Weight before calcination [g]	Weight after calcination [g]	Δm [g]	Anatase [%]	Rutile [%]	Crystallite size [nm]
1:1	0.707	0.622	0.085	100	0	150
1:3.5	0.804	0.589	0.215	100	0	150
1:5	0.695	0.628	0.067	100	0	160
1:1 (+HCl)	0.910	0.625	0.285	100	0	60
1:3.5 (+HCl)	0.718	0.626	0.092	100	0	40
1:5 (+HCl)	0.812	0.548	0.264	100	0	60

Table 3. Results of XRD analysis and weight loss of powders subjected to calcination at 500 °C.

Ti:H$_2$O molar ratio	Weight before calcination [g]	Weight after calcination [g]	Δm [g]	Anatase [%]	Rutile [%]	Crystallite size [nm]
1:1	0.700	0.606	0.094	93	7	190
1:3.5	0.800	0.574	0.226	96.6	3.4	140
1:5	0.700	0.589	0.111	100	0	110
1:1 (+HCl)	0.799	0.598	0.301	100	0	110
1:3.5 (+HCl)	0.712	0.612	0.100	100	0	80
1:5 (+HCl)	0.808	0.553	0.255	100	0	105

with lower half-width and greater intensity. Moreover, the effect of the addition of hydrochloric acid on the crystallite size of produced materials is evident. Regardless of the of calcination temperature, the product with a smaller particle size was obtained when HCl was used (Fig. 3).
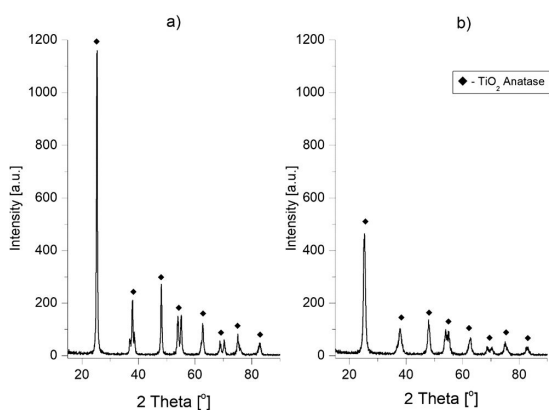

Fig. 3. X-ray powder diffraction patterns for powders obtained at a molar ratio of titanium isopropoxide(IV) to water of 1:3.5, subjected to calcination at 400 °C (a) without addition of HCl, (b) with addition of HCl.

The presence of acid during the sol-gel process caused that the hydrolysis reaction did not occur rapidly, which enabled us to obtain a material with a smaller crystallite size. Furthermore, addition of acid resulted in an increase of the temperature of TiO$_2$ phase transition from anatase to rutile [24]. In the case of synthesis of titanium dioxide, in which the hydrochloric acid was used, the relationship between crystallite size and the molar ratio of water to titanium used during the sol-gel synthesis was also observed. Smaller grains were obtained when the molar ratio of water to titanium was higher.

The observed weight loss of the material after calcination process confirms the presence of organic remains of the precursor of titanium and some solvent particles. The magnitude of this weight loss has significant influence on the preparation of titanium dioxide thin films because it affects the quality of the produced films. The smallest weight loss after calcination process in all tested temperatures, had the sample with the addition of hydrochloric acid as a stabilizer, when the molar ratio of water to titanium was 1:3.5.

Table 4. Results of XRD analysis and weight loss of powders subjected to calcination at 600 °C.

Ti:H_2O molar ratio	Weight before calcination [g]	Weight after calcination [g]	Δm [g]	Anatase [%]	Rutile [%]	Crystallite size [nm]
1:1	0.727	0.622	0.105	59.2	40.8	210
1:3.5	0.807	0.581	0.226	39.4	60.6	190
1:5	0.711	0.575	0.136	69.3	30.7	180
1:1 (+HCl)	0.905	0.608	0.297	87	13	130
1:3.5 (+HCl)	0.725	0.608	0.117	96.6	3.4	120
1:5 (+HCl)	0.806	0.523	0.283	10.2	89.8	130

In this part of the study the influence of the method of preparing the glass substrate, titanium precursors, molar ratio of titanium to H_2O in the sol-gel process as well as high-temperature processing conditions on the quality of titanium dioxide thin films was investigated. TiO₂ thin films were applied on glass substrates by dip-coating technique. In each case, a six-fold repetition of the dip-coating gel application cycle was used. Prepared coatings were dried at 120 °C for 12 hours.

In Fig. 4 photomicrographs of TiO₂ thin films deposited on the glass substrates that have been earlier subjected to a treatment in nitric acid and without acid etching is shown.
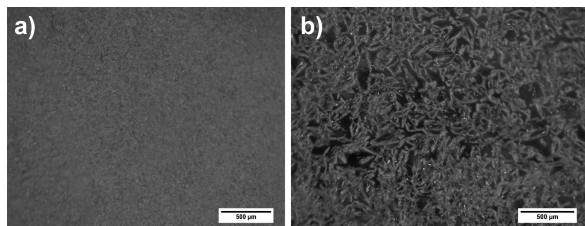

Fig. 4. Photomicrographs of TiO₂ thin films prepared from the sol with a molar ratio of 1:3.5 (+ HCl), deposited on glass slides (a) without HNO₃ treatment; (b) with HNO₃ etched.

The obtained layers were markedly different from each other in terms of morphology. Texture of the layers on the glass, which were subjected to etching in nitric acid are characterized by uneven distribution of material on the substrate. The areas which are not covered with the oxide layer are clearly visible. It has a negative effect on photocatalytic activity of the material due to a small contact area of catalyst with the reactants. The layers formed on the glass substrate that has not been etched in the acid, is characterized by a uniform covering of surface without the texture effect.

Similar effects were observed for TiO₂ films made from a solution where different mole ratios of water to titanium were used. Photomicrographs of TiO₂ thin films which were made at Ti:H_2O molar ratios 1:5 and 1:3.5 are shown in Fig. 5. The films were deposited on glass substrates without etching in nitric acid.
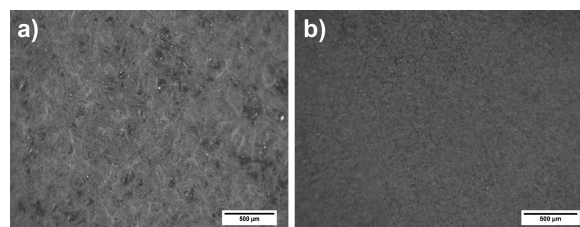

Fig. 5. Photomicrographs of TiO₂ thin films deposited on glass slides prepared from the sols (+ HCl) with molar ratios of (a) 1:5 (+HCl); (b) 1:3.5 (+HCl).

The presented TiO₂ films, obtained both at a molar ratio of 1:5 and 1:3.5 have similar degree of surface coverage. But they are significantly different from each other in terms of morphology. For 1:5 titanium to water molar ratio, the obtained layer is characterized by non-uniform surface and inhomogeneous glass coverage. Areas with a negligible coverage of the oxide layer are clearly visible. This is due to the large mole ratio of water to titanium during the sol-gel synthesis, which caused that the hydrolysis reaction in this case occurred much more faster than in the sample prepared at

1:3.5 ratio, leading to the formation of large particles with nonuniform shapes. These observations are similar to the results for the powder material presented earlier in this paper, where, in spite of maintaining similar synthesis conditions the obtained materials had different crystallite size. TiO_2 films prepared at a molar ratio of titanium ions to water of 1:3.5 were characterized by a better coverage of the glass and lower surface roughness.

3.3. Influence of calcination process

In order to obtain crystalline titanium dioxide films with photocatalytic activity, the produced materials were subjected to calcination in air at 500 °C. The effect of high-temperature processing on the layer formed on the glass substrate from a sol solution with HCl at a molar ratio Ti to H_2O of 1:3.5, without etching in nitric acid, was presented. Calcination process was performed in two series, i.e. after application of all layers, and after each applied layer of TiO_2. High-temperature treatment process significantly affected the quality of the titanium dioxide thin films. Fig. 6 presents a SEM image of amorphous TiO_2 film prepared from the sol by six time repetition of dip-coating cycle and subjected to drying at 120 °C to evaporate the solvent. Uniform coverage of the glass substrate by the coated material is clearly visible. The thin film is not transparent and is characterized by a plate-like structure with a grain size in the range of 5 μm to 10 μm.
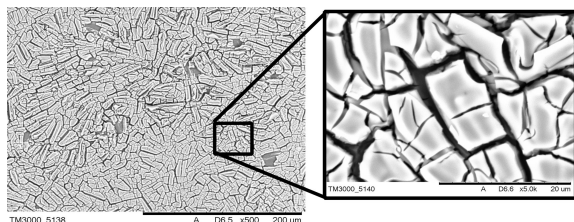

Fig. 6. SEM micrographs of TiO_2 thin films prepared from the sol with a molar ratio of 1:3.5 (+ HCl) coated on glass slides before the calcination process.

Subjecting such materials to high temperature processing at 500 °C in air for 2 h has led to crystallization of TiO_2 and decomposition of organic

elements from the titanium precursor. The morphology of the film has changed significantly. The SEM images of such TiO_2 film is shown in Fig. 7.
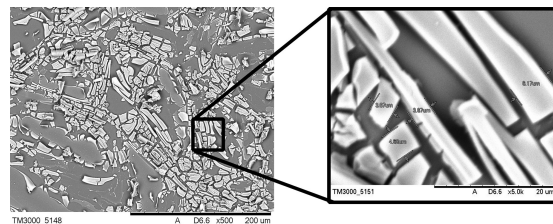

Fig. 7. SEM micrographs of TiO_2 thin film prepared from the sol with a molar ratio of 1:3.5 (+ HCl) deposited on glass slides after 6 dip-coating cycles, subjected to one step calcination at 500 °C.

Clearly visible reduction of the degree of coverage of the glass substrate is caused by the loss of organic material by thermal decomposition. The material is characterized by nonuniform size and shape of the grains. The thin films after calcination process, due to the large size of crystallites, were also nontransparent to the visible light. The XRD analysis of the as-prepared materials presented in Fig. 8a confirms the formation of crystalline TiO_2 films.
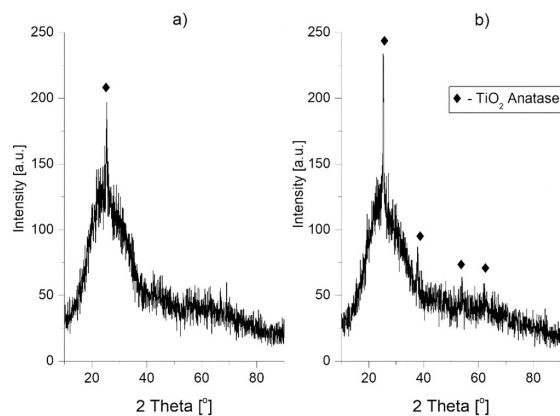

Fig. 8. X-ray diffraction patterns of the TiO_2 thin films coated on glass slides after 6 dip-coating cycles subjected to calcination at 500 °C (a) one step calcination process after application 6 dip-coating cycles, (b) after each dip-coating cycle.

The use of calcination process after each sol application cycle, despite the fact that it is more

time-consuming, allows production of TiO$_2$ coatings with a much better quality. Fig. 9 shows the AFM images of the surface of the oxide layer produced from various titanium precursors, i.e. titanium(IV) isopropoxide and titanium(IV) butoxide. Regardless of the used precursor each layer is characterized by a granular microstructure, flat texture with nanometer grain size and uniform coverage of the substrate. The strong adhesion of the layer to the substrate and the uniform thickness of the coating are clearly visible. The obtained TiO$_2$ films, unlike the previous ones, are completely transparent for visible light, the surface of the oxide layer is very smooth and uniform and free of any visible defects or agglomerates. The layer prepared with the use of titanium(IV) butoxide is characterized by a slightly larger and more differentiated size of grains. This film has also a higher root mean square roughness value – 3.1 nm, compared to the layer prepared from titanium isopropoxide where this value is 1.9 nm. The XRD analysis showed in Fig. 8b confirms that the titanium dioxide is well dispersed on the glass substrate and the crystallite size is suitable for detection by this technique regardless of the used precursor. In comparison with the previous TiO$_2$ layer (Fig. 8a) in which only one diffraction peak is observed, this one shows significantly higher intensity of diffraction reflections corresponding to titanium dioxide. It indicates that there is an improvement in the crystallinity of the material due to the longer high-temperature treatment. The absence of the rutile phase is due to the low annealing temperature (500 °C) used in this work and the addition of HCl as a catalyst in the sol-gel process. In all investigated samples, the broad peak in the 2θ range of 10° to 40° corresponding to amorphous substrate glass is clearly visible.

3.4. Photocatalytic activity tests

Photocatalytic activity tests were carried out on three TiO$_2$ films prepared by six time repeated dip-coating cycle. These layers differed from each other by the used titanium source and by the calcination method, i.e. one-step calcination after all sol-application cycles and a multi-step thermal
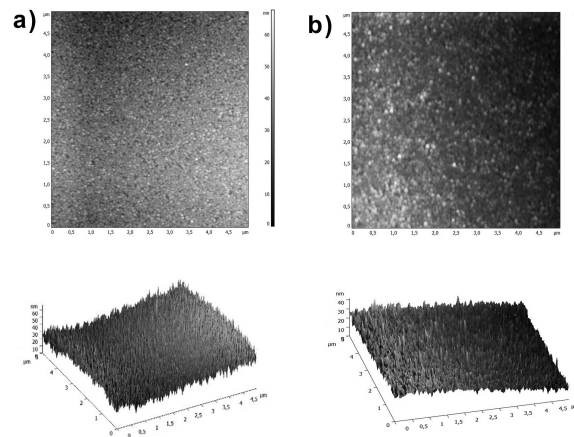

Fig. 9. AFM images of TiO$_2$ thin films prepared from the sol with different titanium precursors (a) titanium(IV) isopropoxide; (b) titanium(IV) butoxide on glass substrates, after 6 dip-coating cycles, subjected to calcination at 500 °C after each dip-coating cycle.

treatment after each sol-application cycle. The photocatalytic activities of these materials were evaluated by the discoloration of methyl orange solution under UV light irradiation. Before testing the photocatalytic activity of thin TiO$_2$ films, the effect of the photolysis of the dye was determined. The experiment was carried out in the same way as the real photocatalytic test but without the presence of the photocatalyst. Based on these results, it was found that the effect of photolysis on decolorization of the solution is negligible. The results of the experiment are shown in Fig. 10. All TiO$_2$ layers exhibit photocatalytic activity in the investigated reaction. Depending on the preparation method, TiO$_2$ thin films exhibit different rates of decomposition of the organic dye.

The films subjected to one-step calcination after applying six layers by dip-coating were characterized by the lowest photocatalytic activity. It is related with a low degree of surface coating by TiO$_2$. Moreover, a large, heterogeneous crystallites have a small surface area which limits the contact of the catalyst with the reactants. Thin films produced by applying the calcination process after each dip-coating cycle were characterized by more than twice higher photocatalytic activity in the investigated reaction than the previous ones,
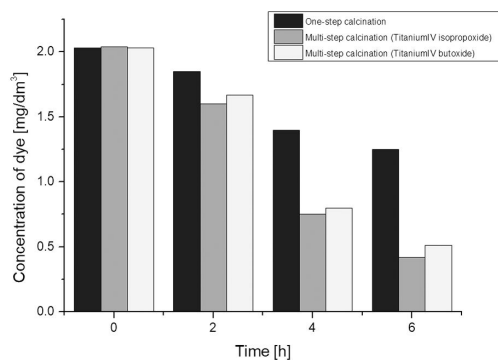
Fig. 10. Decolorization of the methyl orange solution by photocatalysis under UV irradiation.

regardless of the used titanium source. Fine grains of nanometric size and even coverage of the glass surface with a crystalline TiO$_2$ provides a perfect contact of catalyst with organic compound. Small differences in the dye solution discoloration rates were observed for the layers made from different titanium precursors. The layers made with titanium isopropoxide, due to the smaller grain size and lower surface roughness, were characterized by a higher photocatalytic activity than those produced from titanium butoxide.

4. Conclusions

Based on the results of this study the following conclusions can be drawn:

- Using both, titanium(IV) isopropoxide and titanium(IV) butoxide as a source of titanium during the sol-gel synthesis, it is possible to produce a high quality TiO$_2$ layer.

- Higher molar ratio of water to titanium during the hydrolysis reaction results in a larger and more heterogeneous grain size of produced material, both in powder and thin films form.

- The addition of HCl during the sol-gel synthesis controls the hydrolysis and condensation reactions in both isopropoxide and butoxide titanium compounds, which enables the production of TiO$_2$ with nanometric grain size. The presence of acid also

stabilizes the sols whereby the solution does not gel rapidly and it is possible to deposit multiple layers of TiO$_2$ by dip-coating technique.

- Etching the glass substrate by nitric acid affects adversely on the quality of the titanium dioxide thin layers by modifying the surface of the glass.

- The morphology and photocatalytic activity of TiO$_2$ films depend strictly on the method of heat treatment and the used titanium precursor during synthesis.

- In order to obtain transparent oxide films with nanometric grain size and high photocatalytic activity the calcination process should be carried out after each dip-coating cycle at 500 °C in air, regardless of the used titanium precursor.

- The highest photocatalytic activity in the methylene orange discoloration reaction has the TiO$_2$ layer produced using titanium isopropoxide. This layer was characterized by the smallest grain size and surface roughness.

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