Formation and Research of Properties of Photocatalytic Materials on the Basis of TiO_2 for Water Treatment

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Abstract. The paper describes the sol-gel method for producing photocatalytic materials based on titanium oxide. The temperature-time regimes of heat treatment of the obtained materials are determined. The surface properties of the resulting coatings were studied by scanning electron microscopy and asthmatic force microscopy. The photocatalytic properties of the synthesized coatings and bulk samples were studied on destruction of methylene blue molecules in the developed water purification systems.

Keywords: Sol-gel process · TiO_2 coating · Photocatalytic materials · Photocatalytic properties

1 Introduction

The getter, destructive and dividing technologies existing today only partially solve a water pollution problem as they provide additional neutralization and waste disposal, the sorbents or filters accumulating on a surface in the course of cleaning. The photocatalytic method stands out against the background of these technologies and has a set of positive properties. The application of this method reduces the amount of pollution oxidizers such as chlorine and ozone, eliminates the need for waste neutralization as its implementation is not associated with the accumulation of pollutants that require subsequent disposal [1, 2].

The method, that allows the formation of high-purity nanostructured materials, differs from the most promising technological approaches to the creation of photocatalytic fissile materials on the basis of sol-gel oxides of refractory metals. Based on the deposition of metal oxyhydroxides or ethoxides with the subsequent crystallization of oxides during heat treatment, this method allows varying the physical and chemical properties of the obtained materials over a wide range.

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2 Preparation of Materials

When carrying out the hydrolysis of various titanium compounds (mainly ethoxides and propoxides) in aqueous and anhydrous solutions, the primary products at low pH values are the main salts of variable composition. At higher pH values, hydrated forms of titanium dioxide are formed. They are consistent with the formula $Ti(OH)_2$ or $TiO_2 \cdot nH_2O$ where n depends on the aging and drying conditions [3].

Freshly precipitated hydrated titanium dioxide has a high adsorption capacity with respect to cations and anions. This paper suggests using titanium ethoxide as starting alcohol compounds to prepare film-forming solutions. The hydrolysis of these compounds in an organic solvent with the addition of a well-defined amount of ultrapure water and a catalyst under mild conditions leads to the formation of a stable solution.

To prepare film-forming solutions, the required amount of titanium ethoxide was mixed with anhydrous isopropyl alcohol. Then an aqueous hydrochloric acid solution was added to the mixture and stirred. The hydrolysis reaction in systems based on titanium alkoxides takes a long time, therefore the prepared solution was kept at room temperature for 2–3 days. The finished film-forming solutions were coated with brass mesh structures by dipping. The immersion process is optimally suitable for the formation of thin coatings on substrates with a complex structure. The immersion in the solution should be smooth and uniform, without the formation of bubbles. The sample must be completely coated with the solution and maintain the same position, which helps to obtain a uniform layer on the complex mesh structure of the substrate. To study the surface properties of the materials obtained by immersion, coatings were formed on the surface of silicon wafers.

The distinctive features of the formation of titanium dioxide films are polymorphism and the parallel flow of dehydration and polymerization during heat treatment. Therefore, the composition of film-forming sols in the synthesis of powders and the deposition of functional coatings based on highly dispersed titanium dioxide are very important. In the sols based on hydrated titanium dioxide, the nuclei of nanoparticles are formed of only one polymorphic modification of TiO_2 – anatase in the form of spherical nanoparticles of hydrated titanium dioxide. The removal of alkoxititanium hydrolysis products is carried out only at temperatures above 300 °C [4].

Heat treatment of the resulting coatings was carried out step by step in air at temperatures from 100 °C to 600 °C. The heat treatment process during the gel-oxide transition can be divided into three stages:

- complete removal of physically adsorbed water and organic solvent residues (up to 100–200 °C);
- final hydrolysis of film-forming solutions, decomposition of intermediate hydrolysis products and organic residues (200–400 °C);
- complete dehydration and final oxide formation, glass formation in multicomponent films (above 400 °C) (Fig. 1 a).

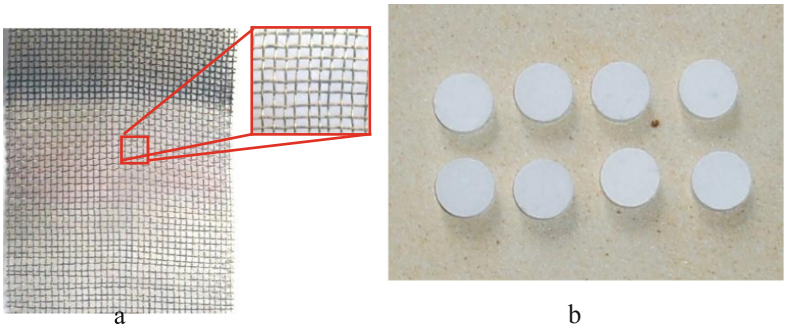

Fig. 1. Samples of materials for use in the water purification systems: **a** coatings on mesh structures, **b** volume photocatalytic materials

To get bulk photocatalytic materials the solution, used to obtain the coating, was evaporated to a gel state. Then the gel was dried in an oven at a temperature of 80 °C for 5 days. The round billets were formed from the obtained fine powder using a manual hydraulic press. The initial solution was taken as a binder. As a result, the round billets (diameter 15 mm, height 7 mm) were obtained (Fig. 1 b). A series of samples was made at annealing temperatures of 500 °C, 600 °C, 700 °C and 800 °C to study the effect of annealing temperature on the photocatalytic properties of the obtained materials.

3 Results and Discussion

To get a fuller picture of the obtained coatings structure, the studies were carried out using scanning electron microscopy and atomic force microscopy. Figure 2 presents the research results of the coating surface using a TESCAN MIRA 3 LM Scanning Electron Microscope. The surface of the coating is characterized by the presence of the chains consisting of partially immersed spherical formations with a base diameter of 150–200 nm. It should be noted that an increase in the annealing temperature of the obtained samples leads to the coating compaction and a slight decrease in spherical formations by 5–7% in the surface volume. The effect of the spherical structures formation is observed due to the crystallization of the amorphous phase and the formation of TiO2 in the form of a metastable polymorphic modification - anatase [4].

The presence of spherical formations on the coating surface is confirmed by the research of the surface using an NT-MDT SOLVER P47-PRO atomic force microscope (Fig. 3).

The research results of the surface by the AFM method confirm the presence of spherical particles on the coating surface. The data analysis confirms that the diameter of the particles at the base is 150–200 nm, and their height varies from 70 to 100 nm.

The installation for water treatment was made to study the photocatalytic properties. The results of a comparative quantitative assessment of catalytic activity on the photo degradation reaction of dye – methylene blue showed that volume samples have

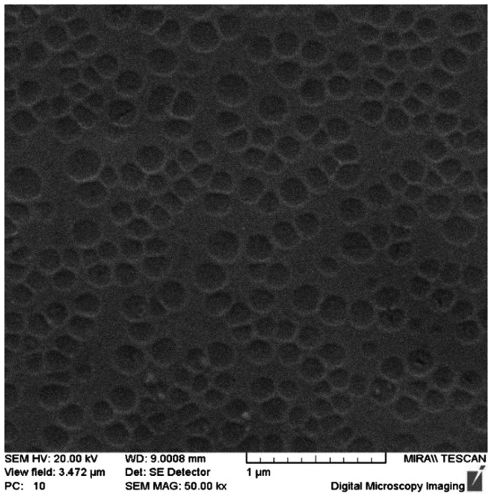

Fig. 2. SEM surface image of TiO2 coatings with a treatment temperature of 400 °C.

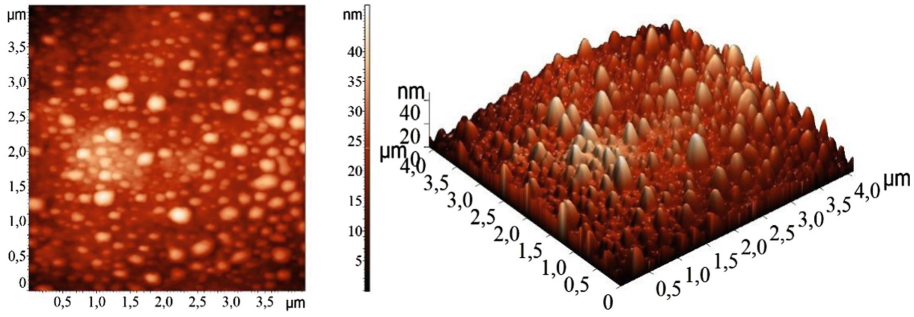

Fig. 3. 2D and 3D AFM surface image of TiO2 coatings with a treatment temperature of 400 °C.

a higher photocatalytic activity (Fig. 4), compared to the coatings (Fig. 5). This is due to the fact that volume samples have a larger superficial area in comparison with film samples on a mesh structure.

Having analyzed the research results of the photocatalytic properties of the resulting materials, it is possible to show that the samples, heat-treated at temperatures of 700 °C and 800 °C, have less pronounced photocatalytic properties in comparison with the samples manufactured at temperatures of 400–600 °C.

Such a result largely depends on the content of titanium dioxide in the anatase phase, which has more pronounced photocatalytic properties. At higher temperatures (about 700 °C), more rutile phase is formed and photocatalytic properties become worse.

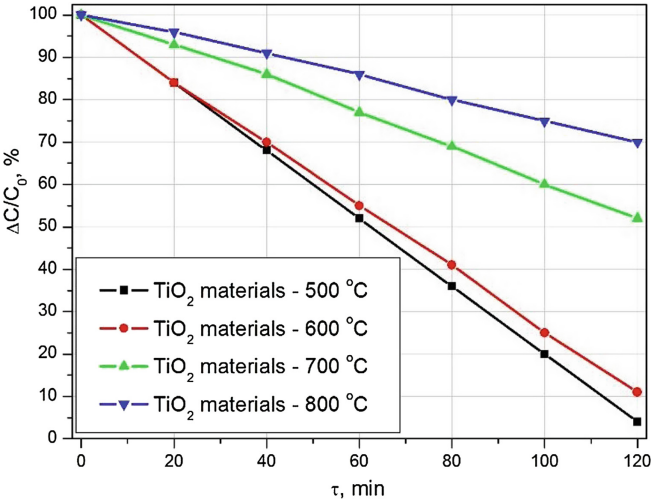

Fig. 4. Change in dye concentration - methylene blue with photo catalytic degradation on TiO2 volume materials.

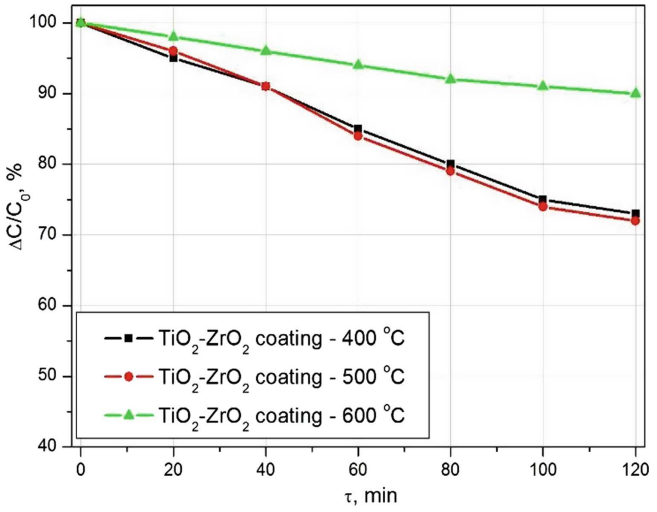

Fig. 5. Change in dye concentration - methylene blue with photo catalytic degradation on TiO2 coatings.

4 Conclusion

The paper presents a sol-gel method for producing the coatings and bulk materials based on titanium oxide. The surface morphology study indicates the formation of the ordered chains of spherical particles, based on hydrated titanium dioxide, on the

coating surface. During heating, the crystallization of amorphous films occurs with the formation of anatase (at a temperature of 400–600 °C), followed by transformation to rutile (at a temperature above 650 °C).

The photocatalytic properties of the obtained samples have been studied, and it has been established that volume materials with a processing temperature of 500–600 °C have the optimal photocatalytic properties. The developed coatings can be used in small cyclic water purification systems as oxidative photocatalytic materials.

Also, the coatings possess good self-cleaning properties due to their photocatalytic ones.

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References

1. Fujishima, A., Zhang, X., Tryk, D.A.: TiO photocatalysis and related surface phenomena. Surf. Sci. Rep. **63**(12), 515–582 (2018)
2. Kočí, K., Matějová, L., Reli, M., Čapek, L., Matějka, V., Lacný, Z., Kustrowski, P., Obalová, L.: Sol–gel derived Pd supported TiO_2–ZrO_2 and TiO_2 photocatalysts; their examination in photocatalytic reduction of carbon dioxide. Catal. Today **230**, 20–26 (2014)
3. Vaskevich, V.V., Kovalenko, D.L., Semchenko, A.V., Sidsky, V.V., Kovalevich, M.A.: Nanostructured photocatalytic sol-gel coating based on titanium. PFMT **4**(25), 7–10 (2015)
4. Ivicheva, S.N., Kargin, Y.F, Kutsev, S.V., Volkov, V.V.: Ordered TiO2 nH2O-based films and coatings. Inorg. Mater. **7**(51), 668–672 (2015)