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INVESTIGATION OF THE STRUCTURAL, OPTICAL AND PHOTOCATALYTIC PROPERTIES OF TiO₂ NANOTUBES

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A method for the synthesis of transparent films based on TiO₂ nanotubes has been developed that possesses sufficient strength for use in photocatalysis. The obtained materials have an ordered structure of cylindrical pores of controlled diameter with a narrow size distribution. The TiO₂ nanotubes spectra were investigated. It is shown that the peaks of Raman spectra are characteristic for a structure with anatase form. The calculation is based on the photocatalytic efficiency of nanostructured TiO₂ films.

Keywords: anodizing, electrochemical polishing, porous alumina, two-electrode electrochemical cell

Introduction

In recent years, there has been a growing interest in nanomaterials based on titanium dioxide in connection with their unique physicochemical properties. This is due to the extensive use of TiO₂ for various practical applications. Thus, nanomaterials based on titanium dioxide are used in photocatalysis, solar energy, for cleaning water and air from organic contaminants, as well as for the destruction of bacteria [1, 2].

Titanium dioxide has a wide forbidden band and its photocatalytic properties begin to appear when it is irradiated in the ultraviolet region of the spectrum. It is known that the powdery particles TiO₂ (P25, Hombikat UV-100) have the greatest catalytic activity. It is believed that its high activity is due to the effective separation of charge carriers at the interface between two semiconductors [3]. Despite the fact that powder particles are highly efficient and inexpensive photocatalysts, the work to produce TiO₂ with improved photocatalytic properties continues [4]. Therefore, at present, to expand the scope of these catalysts, the main emphasis is on the creation of thin films based on TiO₂, since in this form TiO₂ is more convenient to use for photocatalysis in a variety of conditions [5].

In the present work the results of the developed technology for the production of thin-film material based on titanium dioxide are presented, the structural, photophysical and photocatalytic properties of the obtained films are studied.

1. Experimental procedure

Synthesis of TiO₂ nanotubes was carried out under conditions involving three anodizing stages at a voltage $U = 80$ V in a solution of NH₄F. Titanium plates (99.99% purity) with a thickness of 250 μm and dimensions of 3.5 × 3.5 cm were used as the starting material. The process of self-separation of TiO₂ films in the third anodizing step is shown in Fig. 1.

The specific surface area of the alumina films was determined by the BET method (Brunauer, Emmet, Teller). The pore volume and pore size distribution were determined from the isotherm of adsorption and desorption of nitrogen in the «Sorbi MS» measuring complex (Russia). Before the measurements, the samples were placed in a special calibrated flask made from a temperature resistant glass of a special sample «Sintex» for continuous drying and release of samples from moisture by heating and purging with an inert gas in the additional pre-preparation complex of «SorbiPrep» samples. The microstructure of the samples was studied by SEM with field emission of

MIRA 3LMU (Tescan, Czech Republic). A carbon layer was applied to the surface of nonconducting samples by thermal spraying on a Q150R ES unit (Quorum Technologies, England) prior to their examination.

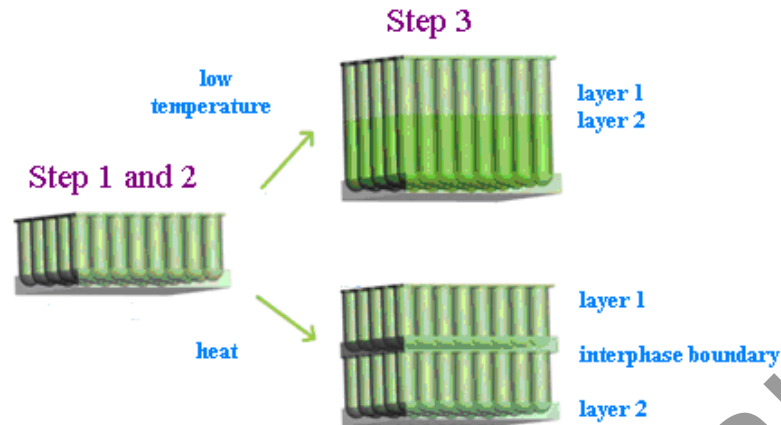


Fig.1. Self-separation process TiO₂ films

The photocatalytic properties of TiO₂ films were studied by photo degradation of dye molecules of methylene blue (MG) adsorbed on the semiconductor surface.

2. Discussion of the results

The morphology of the surface and transverse cleavage of separated TiO₂ films is shown in Fig. 2. As can be seen from Fig. 2a, the resulting structure of the anodization surface layer is characterized by a slender system of tightly fitting nanotubes with an internal diameter within 100 nm. On the lower side, the nanotubes are closed and have a hemispherical bottom (Fig. 2b). On the transverse cleavage of the sample (Fig. 2c), parallel direct nanotubes are located perpendicular to the surface with an external diameter of the order of 155-200 nm. The thickness of the separated TiO₂ film is 9.56 μm (Figure 2 d).

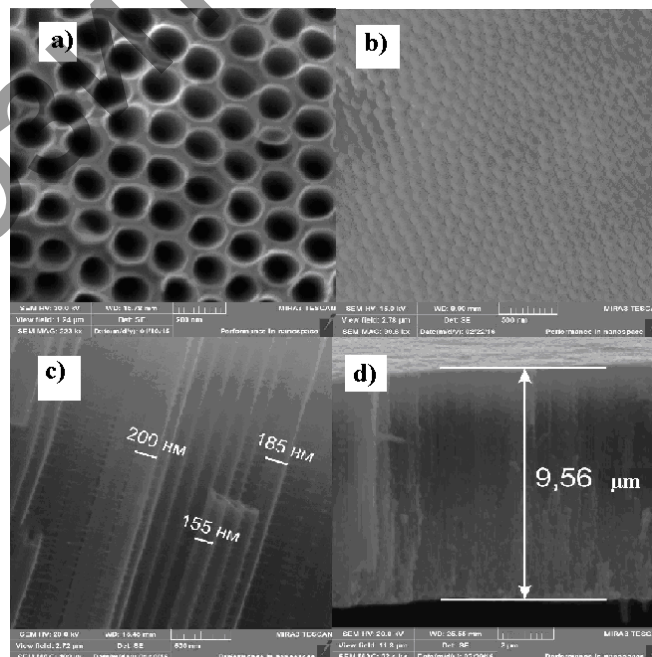


Fig.2. SEM image of TiO₂ film.

According to the SEM data, the surface of the titanium oxide film is flat and does not contain characteristic fragments of the endings of titanium dioxide nanotubes. A large area of the film is shown on the micrograph (Figure 2a), it should be noted that there are no cracks and voids between the channels. However, the microphotography of the cleavage reveals voids between individual nanotubes (Figure 2c), such voids are found throughout the thickness of the layer of the porous layer. The presence of voids can be explained by dissolving a layer of non-stoichiometric titanium dioxide between the tubes in NH_4F , as a result of the penetration of the electrolyte through cracks or defects in the protective layer of TiO_2 . An estimate of the specific surface area of TiO_2 nanotubes was carried out using the BET method at the Sorbi MS measuring complex (Meta, Russia). The results obtained showed that the specific surface area of the TiO_2 nanotubes obtained was $55.3 \pm 2.0 \text{ m}^2 / \text{g}$.

Figure 3 shows micrographs of nanotubes synthesized at voltages of 50 V in electrolyte based on ethylene glycol. The accelerating voltage was 200 kV, the maximum magnification of microphotographs $\times 400,000$. As can be seen from the figure, the outer and inner diameter of nanotubes is the same over the entire length of the tubes, which indicates the constancy of the potential in the anodizing process. The transmission electron microscopy data is in good agreement with SEM data.

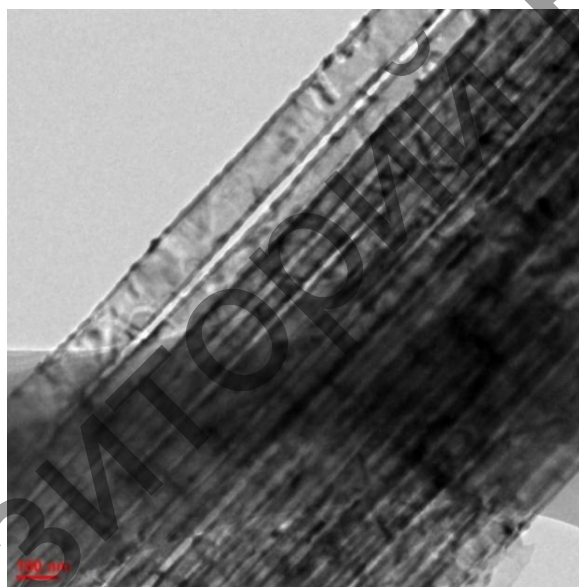


Fig.3. TEM image of TiO_2 nanotubes

To determine the composition of TiO_2 nanotubes, the elemental composition was studied by the method of energy-dispersive spectral analysis (Figures 4a). The study of the elemental composition of the films showed the presence of titanium and oxygen atoms. The insignificant presence of carbon in the image indicates the presence of an admixture of organic compounds on the surface of the film.

The insignificant presence of magnesium, fluorine, nickel and copper is associated with the residues of the impurity from the electrolyte. Using the method of energy-dispersive X-ray spectroscopy, micro-images of the distribution of chemical elements of TiO_2 nanotubes were obtained and maps of distributions of the main elements were constructed (Fig. 4b). Raman scattering spectra (Raman scattering) of nanotubes are shown in Fig. 5. It can be seen from the figure that 3 E_g -peaks can be observed in the Raman spectrum, which are located at 145, 197 and 639 cm^{-1} , 2 B_{1g} -peaks (398 and 518 cm^{-1}). According to the published data [6], the observed peaks are characteristic for Raman spectra of anatase at room temperature.

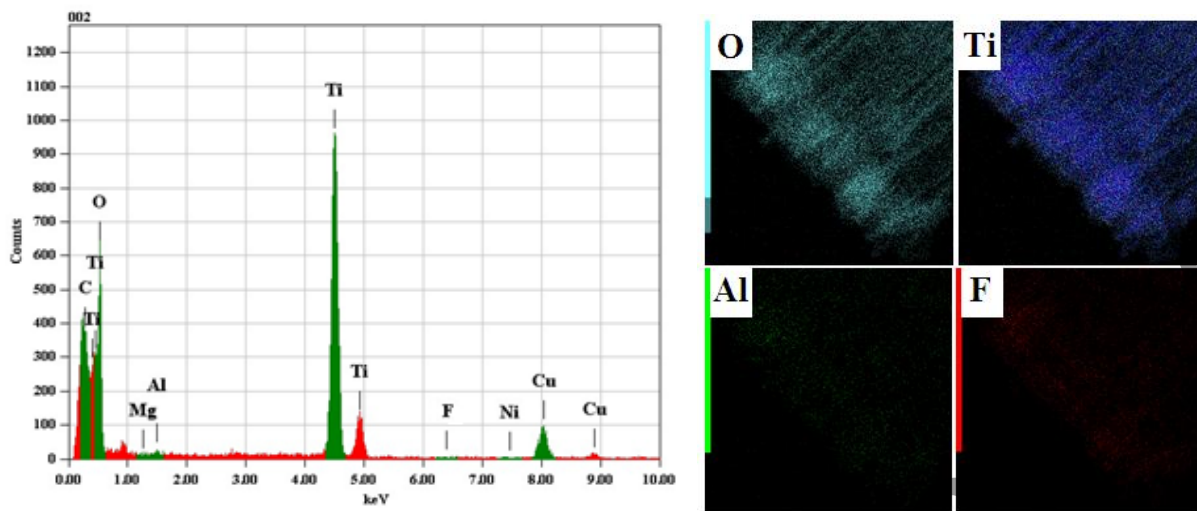


Fig.4. Energy dispersive analysis and distribution maps surface elements of TiO₂ nanotubes

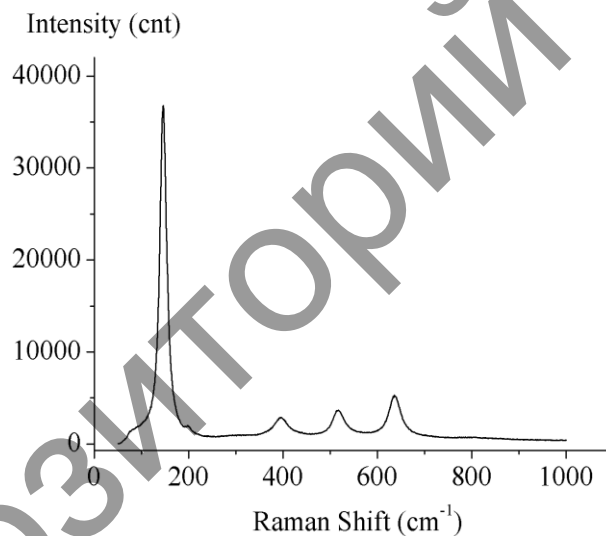


Fig.5. Raman spectra of TiO₂ nanotube samples.

Figure 6 shows the absorption and luminescence spectra of separated TiO₂ films. Figure 6a shows that the absorption band of TiO₂ films has a maximum at a wavelength of $\lambda = 250$ nm. In the spectra of low-temperature (90 K) luminescence of TiO₂ films, an intense band is observed in the visible region with a maximum at a wavelength $\lambda = 545$ nm. The obtained luminescence spectra of TiO₂ are associated with the presence of oxygen vacancies in anatase TiO₂ [6].

The kinetics of attenuation of the luminescence of TiO₂ nanotubes is shown in Fig. 7. The kinetics of the luminescence decay were measured with a pulsed spectro-fluorimeter with a picosecond resolution and recording in a time-correlated photon count (Becker & Hickl, Germany). The excitation of TiO₂ nanotubes was carried out using a semiconductor laser with a $\lambda_{\text{gen}} = 375$ nm generation wavelength with a pulse duration $\tau = 40$ ps. It can be seen from the figure that the kinetic curve as a whole is a non-exponential function, but at the initial stage of decay the kinetic curve has an exponential form of damping. The lifetimes of the excited states, calculated from the exponential part of the TiO₂ nanotube decay curves, were 2.4 ns.

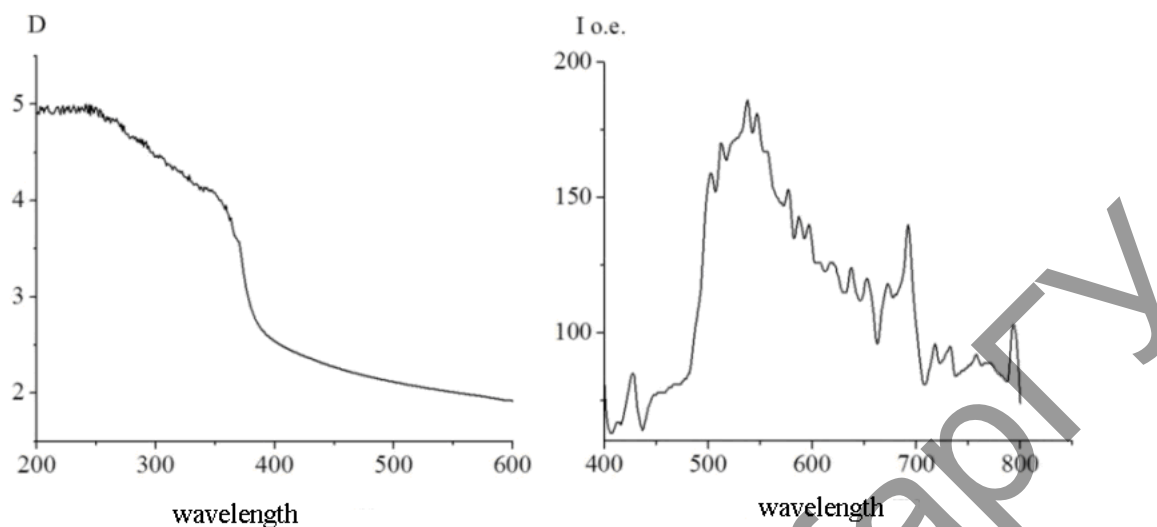


Fig.6. Absorption and luminescence spectra nanotubes TiO_2

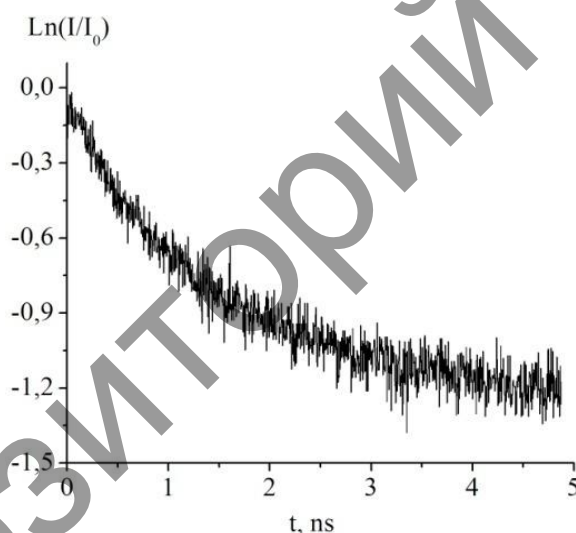


Fig.7. Luminescence decay kinetics nanotubes TiO_2

To evaluate the photocatalytic activity of nanotubes of TiO_2 films, the photocatalytic decomposition of the MG dye in TiO_2 nanotubes was used. The sorption of methylene blue dye molecules in nanotubes was carried out by keeping TiO_2 films in an ethanol solution of phosphor with an initial concentration $C' = 10^{-5}$ mol / L for 5 hours, followed by drying the films in a drying cabinet for 1 hour. Figure 8 shows the absorption spectra of MG in TiO_2 nanotubes as a function of the time of irradiation. It can be seen from the figure that when the MH lamp is irradiated with a mercury lamp PRK-2 for 30 minutes, the optical density of the dye decreases by a factor of 2.

The process of degradation of the methylene blue dye can be represented as follows. Irradiation with UV light leads to the generation of electron-hole ($e^- - h^+$) pairs in the TiO_2 nanostructure due to the absorption of a photon (process 1). Photogenerated electrons in the conduction band of TiO_2 interact with oxygen molecules adsorbed on TiO_2 , during which superoxide radicals (O_2^-) are formed (process 2). In this case, holes in the valence band of TiO_2 react with water molecules and contribute to the formation of hydroxyl radicals ($\text{OH} \cdot$) (process 3).

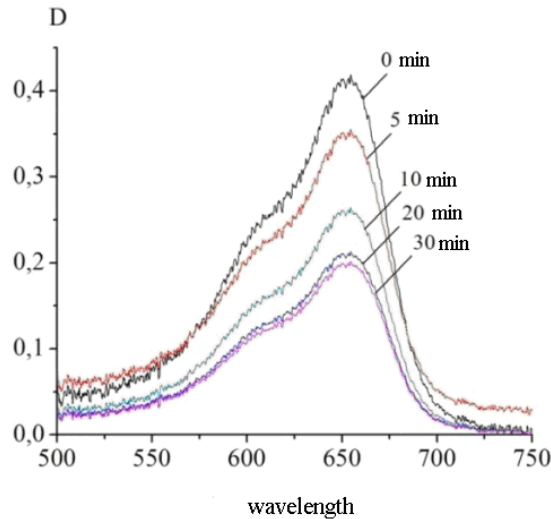


Fig.8. Absorption spectra of methylene blue in the TiO₂ film

Highly reactive hydroxyl radicals (OH •) and superoxide radicals (O₂⁻) react with a dye molecule adsorbed on TiO₂ nanostructures and lead to its degradation. During this reaction discoloration of the dye solution is observed (processes 4 and 5).



The processes occurring during the photocatalytic oxidation of organic compounds are schematically represented in Figure 9.

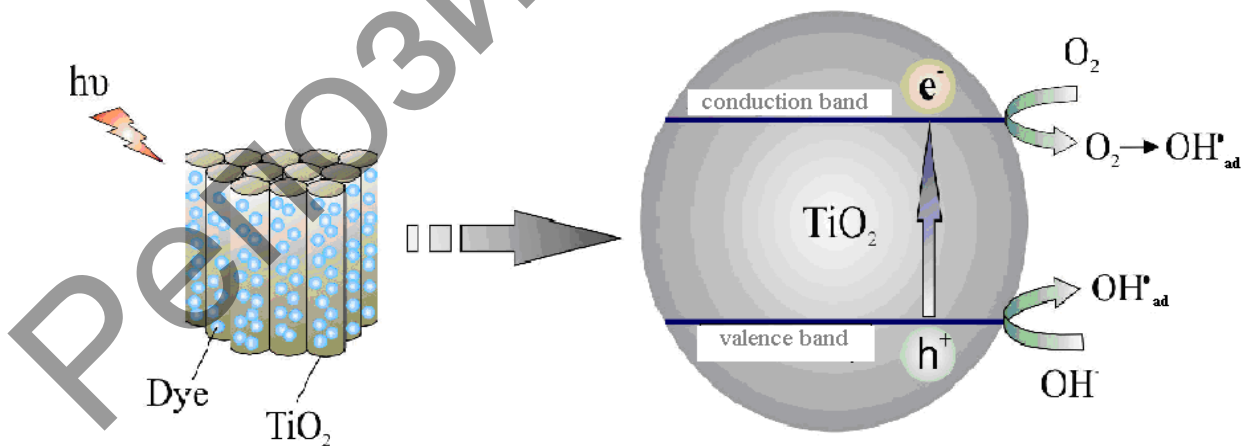


Fig.9. Photocatalytic oxidation scheme organic substances on the surface of TiO₂

The photocatalytic efficiency of nanostructured TiO₂ films in the model photodegradation reaction of the methylene blue dye was determined by the equation:

$$\eta = \frac{A_0 - A}{A_0}, \quad (6)$$

where A_0 is the optical density of the dye without the photocatalyst, A is the optical density of the dye with the photocatalyst.

The calculations carried out showed that when the dye is photodegraded without a catalyst, $\eta = 6.25\%$. In the case of TiO_2 nanotubes, the photocatalytic efficiency was 51.8%.

Conclusion

Thus, the developed method allows to obtain TiO_2 nanotube matrices with a highly ordered structure and with prescribed geometric pore sizes. With scanning electron microscopy, it has been found that the internal pore diameter is about 100 nm, and the distance between adjacent channels is about 50 nm. The thickness of the films is 9.56 μm , and the specific surface area of the porous alumina films, measured by capillary nitrogen condensation, is 55.3 m^2 / g . The Raman spectra obtained show that the TiO_2 nanotubes obtained have an anatase structure. It was found that TiO_2 nanotubes possess high photocatalytic activity.

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