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EFFECT OF ANODIZING VOLTAGE ON THE PHOTOCATALYTIC ACTIVITY OF FILMS FORMED BY TITANIUM DIOXIDE NANOTUBES

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The influence of the anodizing voltage during synthesis on the specific surface area and on the photocatalytic activity of the TiO_2 nanotube was studied. Films formed by titanium dioxide nanotubes were obtained on the surface of titanium foil by electrochemical anodizing. It has been found that an increase in the anodizing voltage from 20 V to 60 V leads to an increase in the inner and outer diameters of nanotubes, an increase in the growth rate and the interpore distance of nanotubes. The photocatalytic activity of the samples was evaluated by measuring the magnitude of the photoinduced current. The film produced at low voltage generated a current 3.5 times higher than the film produced at high voltage, and the degradation of the dye in the presence of the films was 75 and 38%, respectively, over the same period of time. An increase in the photocatalytic activity of the films is mainly associated with an increase in the specific surface area of the nanotubes. Thus, the values of the specific surface area of TiO_2 nanotubes were determined by the method of low-temperature nitrogen adsorption. It has been established that with an increase in the anodizing voltage, the specific surface area of the films decreases.

Keywords: nanotube, titanium dioxide, photocatalysis, specific surface area, splitting of water.

Introduction

Titanium dioxide ‒ TiO_2 nanostructures, due to their semiconductor properties, low toxicity, chemical stability and low cost, are one of the promising photocatalysts for water purification from various pollutants and photocatalytic splitting of water for hydrogen production [1, 2]. However, it has a number of disadvantages, this is mainly due to the rapid recombination of photogenerated electron-hole pairs, a fast reverse reaction occurs in the production of hydrogen, the limitation of the use of visible light (the band gap of TiO_2 is about 2.9–3.2 eV), respectively, only UV-light [3]. The use of one-dimensional TiO_2 nanostructures in the form of nanotubes (NTs) makes it possible to carry out one-dimensional electron transport, which leads to a decrease in the electron free path time from charge generation centers to the anode. In addition, the use of films in the form of an array of NTs will significantly reduce the number of surface defects, which are an obstacle to electron transport, thereby suppressing its recombination [4].

Among the variety of methods for synthesizing NT TiO_2, electrochemical anodizing of metallic titanium is the most promising, since it allows one to control the geometric characteristics of NT by changing the temperature, electrolyte composition, anodizing voltage, and synthesis time [5]. This means that by controlling the geometric characteristics of the NT, one can control the specific surface area of the photocatalyst, since it is proportional to the dispersity or, which is the same, inversely proportional to the size of the nanostructures. The high specific surface of the photocatalyst makes it possible to increase its activity by increasing the amount of adsorbed decomposable substance. For example, the most common and accessible photocatalyst in the form of nanoparticles is Degussa P25, whose specific surface area is about 50 m2/g, and its increase leads to a significant acceleration of the photocatalytic process [6]. A sufficient number of works have been published devoted to increasing the specific surface area of TiO2 NT by various surface modifications [7–13]. However, in the works, NTs were synthesized mainly at one voltage of electrochemical anodization, which were then subjected to modification of the NT surface, and there are practically no works on the study of the photocatalytic activity of NTs with a change in the anodizing voltage. Previously, we have demonstrated how anodizing voltage affects the specific surface area and efficiency of dye-sensitized solar cells based on NTs TiO_2. [14].

In this regard, the present work is devoted to the study of the effect of anodizing voltage during synthesis on the specific surface area and photocatalytic activity of NTs TiO_2.

1. Experimental technique

NTs TiO_2 were obtained by 2-stage electrochemical anodization of titanium foil (VT1–0, 99.7%, Russia) at a temperature of 5–70 C and anodizing voltage varied from 20 to 60 V. The thickness of the foil was 60 μm. The electrolyte used was $C_2H_6O_2$ containing 0.3 wt% NH_4F and 3 wt% H_2O. A Pt electrode served as the cathode. During the anodizing process, the solution was intensively mixed with a magnetic stirrer. The film of LT TiO_2 and by-products of hydrolysis, obtained after the first stage for 2 hours, was removed from the surface of the foil in an ultrasonic bath in HCl solution. The second stage of anodization was 24 hours. After the second anodizing, the obtained NTs TiO_2 was treated with ultrasound to remove by-products, washed with a large amount of distilled water and dried at room temperature. The crystallization of TiO_2 was carried out by heat treatment in a muffle furnace at a temperature of 5000C for 2 hours.

The determination of the phase composition of the samples was carried out using X-ray diffraction patterns obtained on an instrument using an automatic powder diffractometer STOE STADI-P (STOE & Cie GmbH), CuKα radiation, λ=1.54056Å. X-ray patterns were analyzed using the PDF-2 powder database and the standard WinXPow software package. The images of the surface and transverse cleavages of the samples were obtained on a MIRA 3LMU (Tescan) scanning electron microscope. Spectrophotometric measurements were carried out on a Solar SM 2203 spectrophotometer (Solar). The specific surface area of the samples was estimated from low temperature nitrogen adsorption on a Sorbi MS (Meta, Russian). Thermal training of the samples was carried out at a temperature of 100^0C for 180 minutes in the SorbiPrep pre-treatment block. The photocatalytic activity of the samples was evaluated by measuring the magnitude of the photoinduced current with an illuminated area of 1 cm^2 in a standard three-electrode cell using a CS350 potentiostat/galvanostat with an integrated EIS analyzer (Corrtest Instruments, China). The platinum foil served as the opposite electrode, and the AgCl electrode was used as the reference electrode. The measurements were carried out in an electrolyte of 0.1 M NaOH in a specially made photoelectrochemical cell with a quartz window. In addition, the photoactivity of the films was estimated from the photodegradation of the dye methylene blue (MB). Methylene blue dye is used as a model pollutant. Plates sized 1×2 cm were vertically lowered into a quartz reactor containing 50 ml of methylene blue solution with an initial concentration of 10^{-5} mol/l, and kept for 20 hours. Then the used solution was replaced with a similar solution of methylene blue with a concentration of 10^{-5} mol/l. This procedure makes it possible to exclude errors in measuring the optical density of the dye associated with the adsorption of molecules in its pores. The solution was continuously stirred with a magnetic stirrer. A xenon lamp with a power of 300 W/cm^2 (Newport, USA) was used as a radiation source in all experiments. Figure 3b shows a cell in which photocatalytic splitting of water occurs. The amount of released and identification of hydrogen was carried out using an Agilent gas chromatograph located at the Moscow State University named after M.V. Lomonosov. An electrochemical cell was used with solution separation using a Nafion filter and a quartz window to illuminate the surface of the photocatalyst (Minihua Store). The opposite electrode was a Pt plate. Both sides of the chamber are pre-purged with an argon flow. Then, the test gas was taken from the chamber using a syringe and injected into the chromatograph column.

2. Results and discussions

During electrochemical anodization of titanium foil, a film formed on its surface is formed from densely packed cylindrical NTs TiO_2. The images of the surface of the films separated from the titanium foil are shown in Figure 1. The upper part of the nanotubes is open (Fig. 1a). Closer to the bottom of the NT, the inner channel narrows up to complete closure (Fig. 1b). Each NT is fixed to each other by roots, which are clearly shown in Figure 1c, d. With an increase in the applied voltage during electrochemical anodizing between the titanium foil and the opposite electrode, the inner and outer diameters increased, while the wall thickness practically did not change and amounted to about 10–15 nm. According to the results of microscopic examination on the SEM, Table 1 was compiled, which shows the length, outer diameter, the number of NTs per unit surface and the specific surface area with the duration of the second stage of anodizing for 24 hours. It can be seen from the presented data that an increase in the anodizing voltage leads not only to a change in the outer diameter, but also to an increase in the growth rate of the NT. At an anodizing voltage of 20 V, the total length of the NT was 17.1 μm, and at a voltage of 60 V, 37 μm. On the basis of the SEM image, the number of NTs per 1 cm^2 was calculated.

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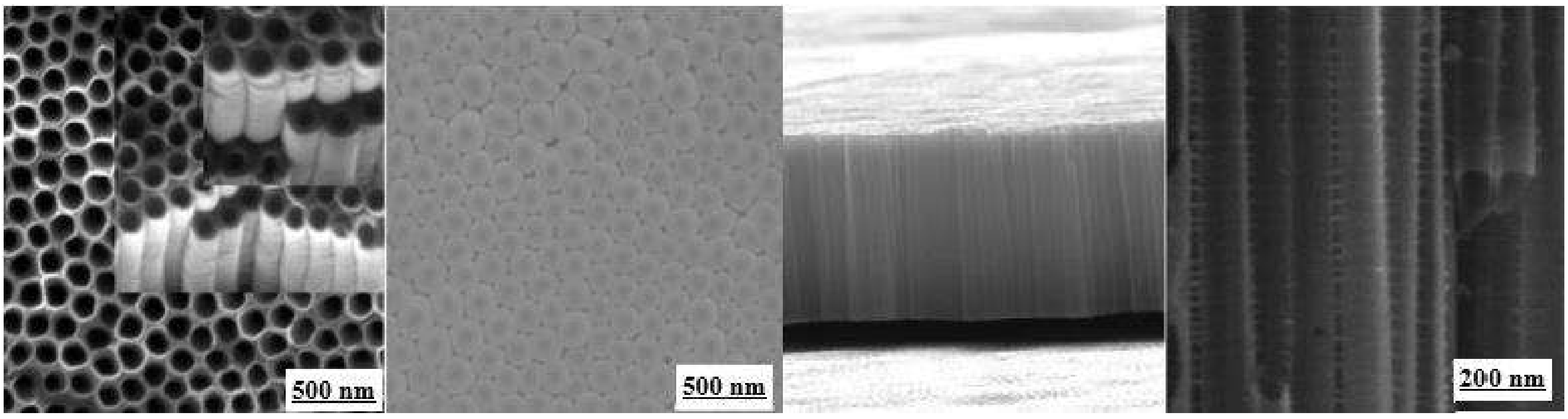


a) b) c) d)

Fig.1. SEM image of NTs TiO_2 separated from titanium foil

As can be seen from the tabular data, at a low voltage (20 V), the amount of NTs per unit area of the film was higher compared to the films obtained at high voltages. This circumstance leads to a change in the specific surface area of the films. Thus, for a film obtained at an anodizing voltage of 20 V, the value of the specific surface area is 72.4 ± 0.1 m^2/g, and for a film of 60 V it is 57.10 ± 0.4 m^2/g. The remaining samples are intermediate values.

Table 1. Characteristics of films formed by NTs TiO_2 obtained at different anodizing voltages

Anodizing voltage, B	L, µm	D_{cp}, nm	Number of nanotubes, $10^9 pcs/cm^2$	Specific surface area of nanotubes (BET), m^2/g
20	17.1	55	32.2	72.40±0.1
30	22.0	70	21.4	66.78±0.2
40	27.0	90	11.2	64.50±0.6
50	36.0	110	6.7	60.65±0.3
60	37.0	140	2.7	57.10±0.4

Figure 2 shows an X-ray diffraction pattern of a NTs TiO_2 film obtained at an anodizing voltage of 50 V. It was found that the anodizing voltage does not affect the phase. Diffraction peaks (101), (004), (200), (105), (211), (204), (116), (220), and (215) for NTs TiO_2 films correspond to the anatase tetragonal phase (JCPDS, no. 84–1286, a = b = 0.1949 nm and c = 0.1980 nm).

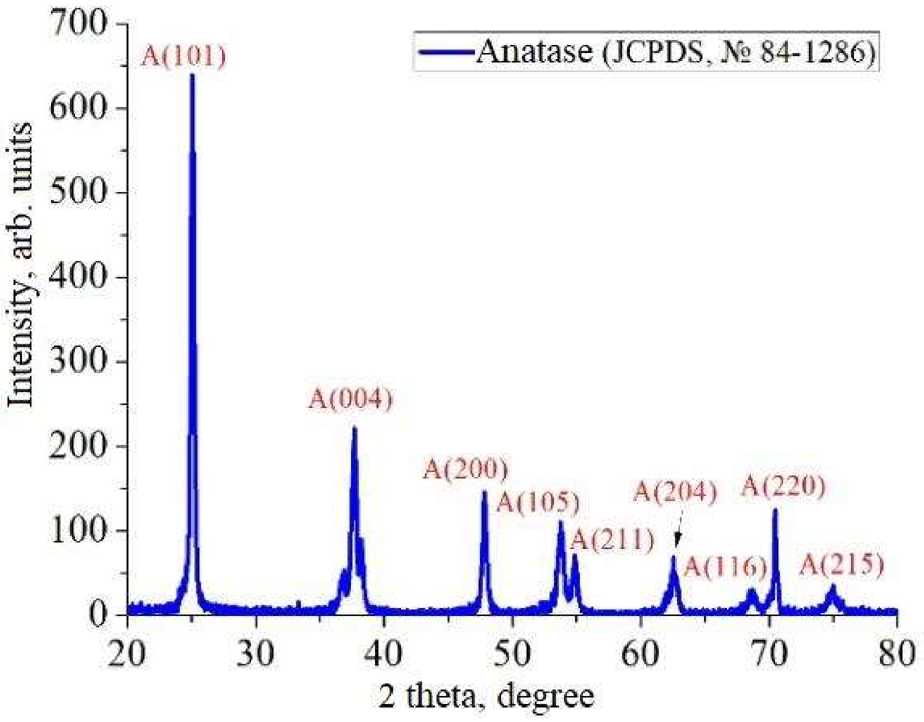
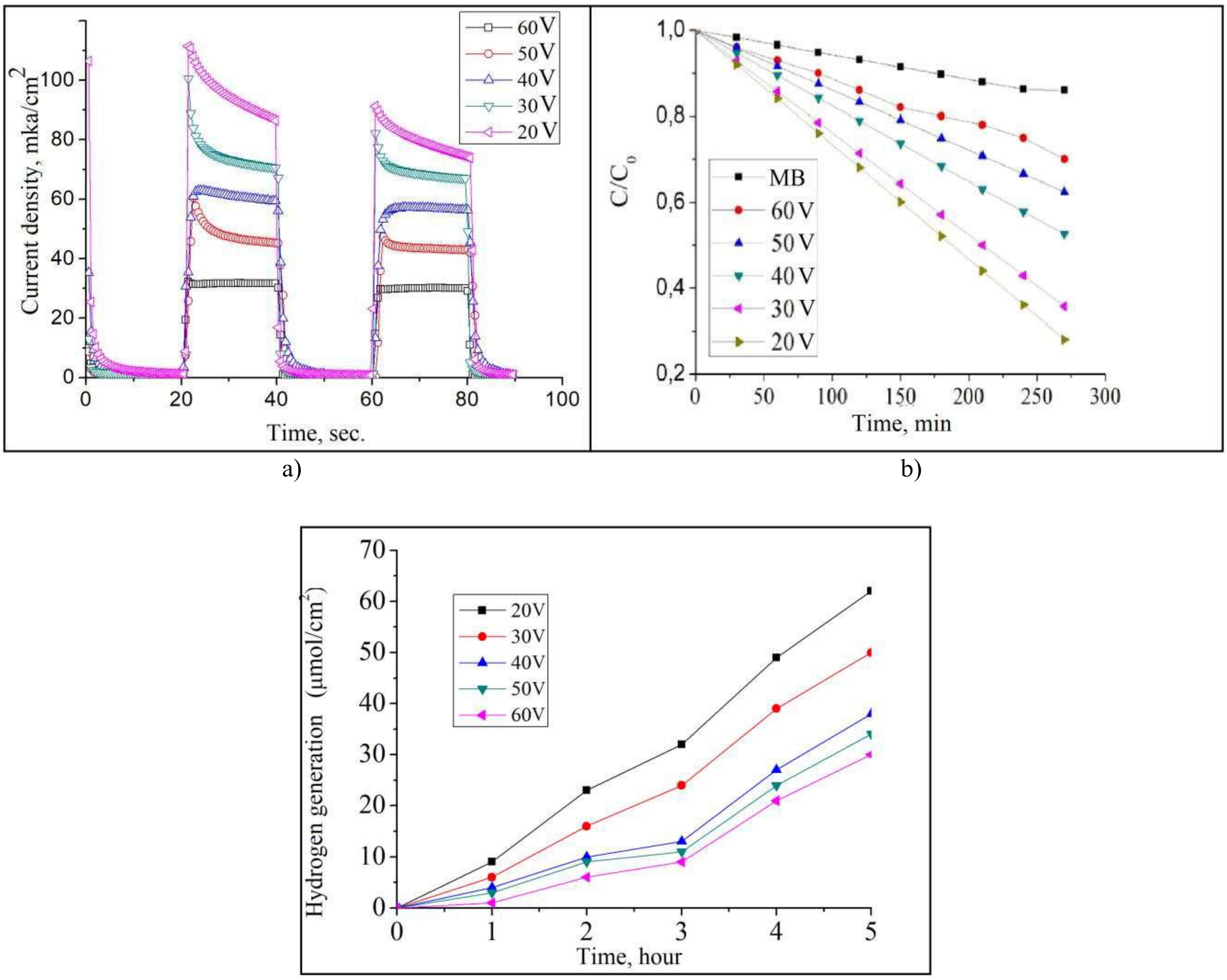


Fig.2. X-ray pattern of NTs TiO_2 obtained at a voltage of 50 V.

The photocatalytic activity of NTs TiO_2 was estimated from the response of the photocurrent when the surface was illuminated by a 1 cm^2 xenon lamp source with a 20-s intermittent on-off switch. Figure 3a shows the change in the photocurrent of all samples. The films exhibit sufficiently good stability. The photocurrent is zero in the absence of light and increases instantly when it is turned on. With an increase in the anodization voltage, the photocurrent density generated by the samples decreased. Thus, a film obtained at an anodization voltage of 20 V generates a high value of photocurrent in comparison with other samples and is about 112 μA/cm^2, while a film synthesized at an anodization voltage of 60 V generates 33 μA/cm^2.

The photocatalytic activity of NTs TiO_2 was also evaluated by the photodegradation of the methylene blue dye (MB). This dye is a model and serves as an example of any contaminant. The photodecomposition of the dye was determined at the wavelength of the maximum absorption of the dye, 662 nm. Irradiation with light leads to the generation of electron-hole (e^- – h^+) pairs in NTs TiO_2 due to photon absorption. 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. In this case, holes in the TiO_2 valence band react with water molecules and contribute to the formation of hydroxyl radicals (OH^-). Highly reactive hydroxyl radicals (OH^-) and superoxide radicals (O_2) react with the dye molecule adsorbed on TiO_2 nanostructures and lead to its degradation. In the presence of NTs TiO_2 films in an aqueous solution of the dye, a much stronger decrease in the optical density of the dye is observed, which indicates that the molecules in the solution gradually decompose under the action of the light rays of a xenon lamp (Fig. 3b).



a) b)

c)

Fig.3. Photocurrent (a), MB dye photodegradation curves (b) and hydrogen generation (c) for films formed by TiO_2 NTs obtained at different anodizing voltages

When the films formed by NTs TiO_2 were lowered into the solution, the optical density of the MB dye decreased, and over the same time interval, the changes were different for the films obtained at different voltages. The largest decrease is observed for the 20 V film, the smallest for the film obtained at 60 V. It can be assumed that the contribution to the photodegradation rate of the MB dye is mainly made by the value of the active surface area, since it is the highest for the film obtained at the anodizing voltage. The larger the area of the semiconductor/dye interface, the faster degradation will occur. Figure 3b shows the photodegradation curves of the MB dye. Before determining the degree of dye degradation, all samples of NTs TiO_2 films were kept in an aqueous solution of the dye for about 2 hours to eliminate the error associated with the adsorption of the dye on its surface. With the duration of irradiation of the dye solution without a photocatalyst, the degradation of the dye is insignificant and amounts to only 9% for 4.5 hours of irradiation. When the films formed by NTs TiO_2 were immersed in the dye solution, the rate of dye degradation increased significantly. Thus, in the presence of a film obtained at an anodizing voltage of 60 V for 4.5 hours of irradiation, the degradation of the dye was 30%, and for a film of 20 V for a similar time interval 91%. In the work of H. Li, et al. “Preparation of TiO2 nanotube arrays with efficient photocatalytic performance and super-hydrophilic properties utilizing anodized voltage method”, a similar research method was used, and it was found that at an oxidation voltage of 30 V, the photodegradation efficiency reaches 65% in six hours , and at 50 V for a similar time period it reaches 98%. At an oxidation voltage of 60 V, the photodegradation efficiency tends to decrease. The reason is that the efficiency of photodegradation is closely related to the wall thickness and diameter of TiO_2 nanotubes [15]. The data obtained indicate that the photocatalytic activity of the film obtained at a voltage of 20 V is higher compared to other samples.

The photocatalytic process of splitting water into hydrogen and oxygen with the participation of a photocatalyst and illuminating its surface with an electromagnetic wave resembles the method of artificial photosynthesis. First, the photocatalyst, absorbing a quantum of light, generates electron-hole pairs, that is, electrons pass from the valence band to the conduction band, while holes remain in the valence band. Further, charge separation and migration of photogenerated electron-hole pairs occur if there is no recombination. Further, the electrons participate in the reduction reaction and generate hydrogen, and the holes participate in the oxidation reaction with the formation of oxygen. Figure 3c shows the kinetics of hydrogen generation as a function of time. Almost all curves have a linear dependence, which indicates a sufficiently high stability of photocatalysts. From the presented data it can be seen that in 5 hours the film produced at 20V is capable of generating up to 62 $\mu mol/cm^2$ of hydrogen gas, while the film produced at 60 V generates 30 $\mu mol/cm^2$.

Conclusion

NTs TiO_2 were synthesized by electrochemical anodizing at various voltages on the surface of titanium foil. A change in the anodization voltage leads to a change in the geometric characteristics of NTs, which together affected the value of their specific surface area. Since with an increase in the area of the contact boundary of the semiconductor/dye or water, the faster the photocatalytic processes will get through. In photocurrent generation, dye degradation, and hydrogen generation, the film obtained at an anodizing voltage of 20 V demonstrates the best results. For the film obtained at an anodizing voltage of 20 V, the specific surface area is 71 m^2/g, and for the film obtained at 60 V, it is 61 m^2/g. These results can be useful in creating effective photocatalysts with a high specific surface area. For example, instead of the accepted voltages, when obtaining NTs TiO_2 (40–50 V), use a voltage of 20 V and then modify its surface in various ways.

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REFERENCES

1 Wang J., Guo R.T., Bi Z.X., Chen X., et al A review on TiO_2-x-based materials for photocatalytic CO_2 reduction. *Nanoscale,* 2022, Vol. 32, pp. 11512–11528. doi: 10.1039/d2nr02527b

2 Kazuhiko M., Kazunari D. Photocatalytic water splitting: recent progress and future challenges. *Journal of physical chemistry letters,* 2010, Vol. 1, No. 18, pp. 2655–2661. doi: 10.1021/jz1007966

3 Yucheng L, Yalin L, Zhifeng R. Mini review on photocatalysis of titanium dioxide nanoparticles and their solar applications. *Nano energy*, 2013, Vol. 2, pp. 1031–1045. doi: 10.1016/J.NANOEN.2013.04.002

4 Serikov T.M. The effect of electric transport properties of titanium dioxide nanostructures on their photocatalytic activity. *Bulletin of Karaganda University. Physics,* 2020, Vol.99, No.3, pp.13–21. doi: 10.31489/2020Ph3/13-21

5 Ibrayev N.Kh., Serikov T.M., Gladkova V.K. Synthesis and investigation of the geometric characteristics of titanium dioxide nanotubes. *IOP Conf. Series: Materials science and engineering*, 2015, Vol. 81, pp. 1–6. doi: 10.1088/1757-899X/81/1/012121

6 Morozov R.S. *Properties and modification of the surface of microporous spherical TiO_2 and SiO_2-TiO_2 particles obtained by the peroxide method*. Diss. for the Candidate of chem. sciences degree, Chelyabinsk, 2018, 154 p. [in Russian]

7 Ge M.Z., Li Q.S., Cao C.Y., et al. One-dimensional TiO_2 Nanotube photocatalysts for solar water splitting. *Advanced science*, 2017, Vol. 4, No. 1, pp. 1600152. doi: 10.1002/advs.201600152

8 Sofiane S., Bilel M. Effect of specific surface area on photoelectrochemical properties of TiO_2 nanotubes, nanosheets and nanowires coated with TiC thin films. *Journal of photocmemistry and photobiology A-chemisrty*, 2016. Vol. 324, pp. 126–133. doi: 10.1016/j.jphotochem.2016.03.030

9 Valeeva A.A., Dorosheva I.B., Kozlova E.A., et al. Solar photocatalysts based on titanium dioxide nanotubes for hydrogen evolution from aqueous solutions of ethanol. *International Journal of hydrogen energy*, 2021, Vol. 46, No. 32, pp. 16917–16924. doi: 10.1016/j.ijhydene.2020.12.190

10 Yang W.T., Li M.X., Pan K., et al. Surface engineering of mesoporous anatase titanium dioxide nanotubes for rapid spatial charge separation on horizontal-vertical dimensions and efficient solar-driven photocatalytic hydrogen evolution. *Journal of colloid and interface science,* 2021, Vol. 586, pp. 75–83. doi: 10.1016/j.jcis.2020.10.071

11 Li Z., Liu H.M., Yao Z.X., et al. Preparation and characterization of titanium dioxide nanotube array/titanium pH electrode. *Chinese journal of analytical chemistry*, 2018.,Vol. 46, pp. 1961–1967. doi: 10.1016/j.ijleo.2019.163432

12 Rempel A.A., Valeeva A.A., Vokhmintsev A.S., Weinstein I.A. Titanium dioxide nanotubes: synthesis, structure, properties and applications. *Russian chemical reviews,* 2021, Vol. 90, pp. 1397. doi: 10.1070/RCR4991

13 Liang H.C., Li X.Z. Effects of structure of anodic TiO_2 nanotube arrays on photocatalytic activity for the degradation of 2,3-dichlorophenol in aqueous solution. *Journal of hazardous materials*, 2009, Vol. 162, pp. 1415–1422. doi: 10.1016/j.jhazmat.2008.06.033

14 Serikov T.M., Ibrayev N.K., Nuraje N., Savilov S.V., Lunin V.V. Influence of surface properties of the titanium dioxide porous films on the characteristics of solar cells. *Russian Chemical Bulletin*, 2017, Vol. 66, No. 4, pp. 614–621. doi: 10.1007/s11172-017-1781-0

15 Lia H., Wanga G., Niua J., Wanga E., Niub G., Xiea Ch. Preparation of TiO_2 nanotube arrays with efficient photocatalytic performance and super-hydrophilic properties utilizing anodized voltage method. *Results in Physics,* 2019, Vol. 14, No. 102499. doi: 10.1016/j.rinp.2019.102499

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