UDC 544.1;544.41,544.47,544.65:544.4,541.138/.138.3

A. Velichenko [a], V. Kordan [b], O. Shmychkova [a], V. Knysh [a], P. Demchenko [b]

THE EFFECT OF Ti/TiO_2 TREATMENT ON MORPHOLOGY, PHASE COMPOSITION AND SEMICONDUCTOR PROPERTIES

[a] Ukrainian State University of Chemical Technology, Dnipro, Ukraine
[b] Ivan Franko National University of Lviv, Lviv, Ukraine

Naked Ti/TiO_2 contains a significant amount of X-ray amorphous compounds on the surface, which are most likely hydrated titanium oxides. The main crystalline phase is titanium dioxide in the allotropic anatase form. Metallic titanium is present on the surface in trace amounts. Thermal treatment of this material at a temperature of 500^{0}C for 3 hours in an air atmosphere leads to an increase in the proportion of the crystalline phase. The content of metallic titanium increases significantly, reaching about a third. A partial electrochemical reduction of nanotubes allows one to obtain more electrically conductive titanium suboxides. After cathodic reduction of nanotubes for one hour, a coating with metallic platinum is uniformly deposited on the surface of the material. Thermal treated Ti/TiO_2 nanotubes are an n-type semiconductor with a flat-band potential equal to −0.589 V and a carrier concentration of $6 \cdot 10^{20}$ cm^{-3}. Such a high concentration of carriers is obviously due to the small thickness of the oxide film and its nonstoichiometry, as a result of which the surface is not very depleted in electrons, since titanium metal acts as their donor.

Keywords: platinized Ti/TiO_2, nanotubes, thermal treatment, conductivity, phase composition.

DOI: 10.32434/0321-4095-2022-143-4-18-23

Introduction

Titanium dioxide is one of the main products of chemical industry. Due to its optical properties, it is most widely used in the paint and varnish industry and the production of pigments. Its sensory, adsorption, optical, electrical, and catalytic properties are widely recognized as the objects of close attention of researchers [1].

Due to its high chemical inertness, lack of toxicity and low cost, titanium dioxide is increasingly used as a photocatalyst, while it has a number of significant disadvantages: low quantum efficiency of the process due to weak separation of the electron-hole pair, limited absorption spectrum in the ultraviolet region, which makes it impossible to use the energy of sunlight [2,3]. Scientists in all leading countries of the world are engaged in solving these problems.

It is known that nanosized TiO_2 particles (<50 nm) have the highest photocatalytic activity; therefore, the preparation of TiO_2 nanoparticles is one of the ways to reduce the degree of charge recombination and increase the active surface area of the oxide [4].

It is important to note that the addition of dopants in TiO_2 structure can both positively and negatively affect the catalytic activity, so the study of the effect of various additives on the optical and photocatalytic properties of TiO_2 is one of the priorities in modern photochemistry. Modern titanium dioxide catalysts obtained in the form of powders have limited application in chemical technology. Therefore, the creation of photocatalitically active coatings with a highly developed surface based on TiO_2 is an urgent task, and the development of new methods for their production using nanosized TiO_2 particles, as well as ways to modify the resulting material to spatially separate charges in particles and shift the absorption spectrum to lower energies are promising direction

of creating a highly active photocatalyst.

TiO_2 nanoparticles are produced with different morphologies, mainly nanotubes, nanowires, nanorods and mesoporous structures [5]. In recent years, methods such as hydrothermal, solvothermal, sol-gel, direct oxidation methods, chemical vapor deposition, electrodeposition, sonochemical and microwave methods have been used to produce TiO_2 nanoparticles.

For the most part, the catalysts involved are used for cathodic processes, they are relatively stable during operation, but are rapidly destroyed and lose catalytic activity in reverse current or at high anodic polarization, especially in the presence of even small amounts of chloride ions. Under these conditions, there are also problems with current collectors. Carbon materials are rapidly destroyed, and metal and TiO_2 are passivated.

In this paper, we propose to use a combined electrochemical-pyrolytic method of nanotube synthesis. This method will allow one to create a porous developed surface of the matrix for electrodeposition of catalytic layers of platinum and palladium; and their subsequent heat treatment at different partial pressures of oxygen will allow one to design composites with different composition. The high number of cationic vacancies in the matrix and the deficiency of oxygen ions will significantly increase the mobility of platinum and palladium atoms during heat treatment, and the resulting composite will have practically metal conductivity, high catalytic activity, selectivity and extended service life.

Material and methods

All chemicals were analytical reagent grade. Composites were obtained by the original method, which includes the stages of preliminary preparation of the titanium substrate [6]. Next, the Ti substance grew enhanced TiO_2 nanotubes follows the twice anodization and cathodization process [7–9] and galvanic platinization. Platinum was electrodeposited at 80^0C at the cathodic current density of 10 mA cm^{-2} from a solution containing 0.05 M K_2PtCl_6+1.5 M $NaNO_2$+100 g/L NH_3 [10]. The coating thickness was about 1 μm (~2 mg Pt per cm^{-2}). Some samples were thermally treated in the air using tube furnace at 500^0C for 1–3 hrs.

Surface morphology was studied by scanning electron microscopy (SEM) with Tescan Vega 3 LMU with energy-dispersive X-ray microanalyzer Oxford Instruments Aztec ONE with X-Max^{N}20 detector. X-Ray powder diffraction (XRPD) data were collected in the transmission mode on a STOE STADI P diffractometer with CuKα_1-radiation, curved Ge(1 1 1) monochromator on primary beam, 2θ/ω-scan, angular range for data collection 20.000–110.225 2θ with increment 0.015, linear position sensitive detector with step of recording 0.480 ^{0}2θ and times per step 75–300 s, U=40 kV, I=35 mA, and T=298 K. A calibration procedure was performed utilizing SRM 640b (Si) and SRM 676 (Al_2O_3) NIST standards. Preliminary data processing and X-ray qualitative phase analysis were performed using STOE WinXPOW and PowderCell program packages. Crystal structures of the phases were refined by the Rietveld method with the program FullProf.2k, applying a pseudo-Voigt profile function and isotropic approximation for the atomic displacement parameters, together with quantitative phase analysis.

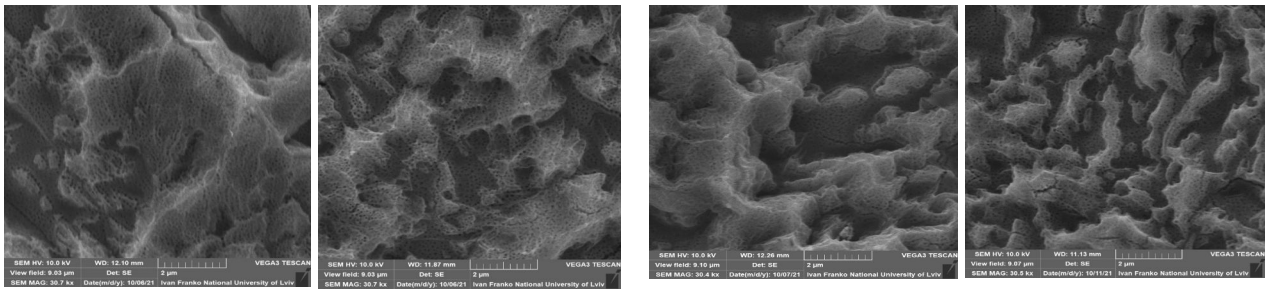
Oxygen evolution reaction was investigated by steady-state polarization on computer controlled MTech PGP-550M potentiostat-galvanostat in different electrolytes depending on the purposes of experiment.

Results and discussion

TiO_2 belongs to the class of transition metal oxides and has several modifications: anatase, rutile, brookite, TiO_2(B), TiO_2(II), TiO_2(H) [11]. The first three are widespread in nature. TiO_2(B), with a monoclinic structure, is also found in nature, but rarely. TiO_2(II) with a PbO_2 structure and TiO_2(H) with a hollandite structure were obtained artificially from rutile under high pressure conditions. The crystal structure of these polymorphic modifications is based on the TiO_6 octahedra. The octahedra are arranged in such a way that they can have common vertices or edges. In anatase, there are 4 common edges per octahedron; in rutile, there are 2 [11]. This is the reason for the difference in their characteristics. Titanium dioxide with a brookite structure belongs to the rhombic crystal system. In a brookite, each octahedron shares edges with two adjacent ones, and they are shorter than the others. The unit cell consists of 8 TiO_2 units and is formed from TiO_6 octahedra. Brookite has a more complex unit cell structure, a larger volume, and is also the least dense. During heat treatment, anatase and brookite transform into rutile at temperatures of 400–1000^0C and ~750^0C, respectively [12].

As one can see from Fig. 1, the resulting nanotubes, obtained by the method involved, contain a significant amount of X-ray amorphous compounds on the surface, which are most likely hydrated titanium oxides.

The main crystalline phase is titanium dioxide in the allotropic anatase form. Metallic titanium is present on the surface in trace amounts. Thermal treatment of this material at a temperature of 500^0C



a **b** **c** **d**

Fig. 1. SEM-images of following surfaces: a – Ti/TiO_2 nanotubes; b – thermal treated Ti/TiO_2 nanotubes; c – reduced Ti/TiO_2 nanotubes; and d – thermal treated reduced Ti/TiO_2 nanotubes

Table 1

Phase composition of TiO_2-nanotubes treated in various ways

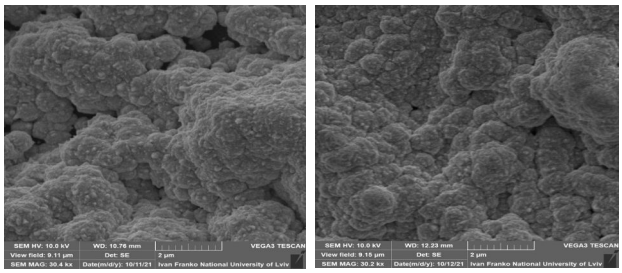
Material	Phase composition
Ti/TiO_2 nanotubes	TiO_2 anatase (space group $I4_1/amd$); traces Ti (structure type Mg, space group $P6_3/mmc$)
Ti/TiO_2 nanotubes after thermal treatment	TiO_2 anatase 62.7(9) wt.%; Ti 37.3(4) wt.%
Reduced Ti/TiO_2 nanotubes	Ti; traces of phase with a structure of the NaCl type. Having in mind SEM/EDAX results it can be $TiC_{1-x}(O,F)_x$
Thermal treated reduced Ti/TiO_2 nanotubes	TiO_2 anatase 57.6(9) wt.%; Ti 42.4(5) wt.%

for 3 hours in an air atmosphere leads to an increase in the proportion of the crystalline phase (Fig. 1, Table 1).

In this case, the content of metallic titanium increases significantly, reaching about a third. It should be noted that we failed to deposit metallic platinum on the surface of TiO_2 nanotubes obtained by electrolysis. Their heat treatment also did not allow significant progress. In the best case, local deposition of the coating was observed in certain areas. In this regard, we carried out a partial electrochemical reduction of nanotubes to obtain more electrically conductive titanium suboxides.

As follows from the results, a significant amorphization of the material surface occurred. Thermal treatment of this material leads to an increase in its crystallinity and an increase in the proportion of metallic titanium in the coating. Thus, as expected, there was a decrease in the proportion of oxygen in the composite material, which should contribute to an increase in its electrical conductivity and an increase in the possibility of applying a metal coating to the surface.

Indeed, after cathodic reduction of nanotubes



a **b**

Fig. 2. SEM-images of following surfaces:
a – reduced Ti/TiO_2-Pt nanotubes; and
b – thermal treated reduced Ti/TiO_2-Pt nanotubes

for one hour, a coating with metallic platinum is uniformly deposited on the surface of the material (Fig. 2).

Thermal treatment leads to an increase in the grain size of the phases and a decrease in microstresses, as well as, as in the case of nanotubes or reduced nanotubes, to the formation of anatase and an increase in the proportion of metallic titanium in the composite (Table 2).

The semiconducting properties of the obtained

Table 2

Phase composition of platinated TiO_2-nanotubes treated in various ways

Material	Phase composition
Reduced Ti/TiO_2-Pt nanotubes	Pt 76.9(5) wt.%; Ti 23.1(5) wt.%
Thermal treated reduced Ti/TiO_2-Pt nanotubes	Pt 50.6(3) wt.%; Ti 24.4(4) wt.%; TiO_2 anatase 25.0(4) wt.%

materials are of great importance, since they affect the value of the electrode potential under galvanostatic conditions. TiO_2 belongs to semiconductors with a wide band gap. According to the literature data, the band gap is 3.2 eV, 3.3 eV, and 3.0 eV for the anatase, brookite, and rutile structures, respectively [13].

The electronic structure of titanium dioxide has been well studied using various approaches [14]. The valence band of TiO_2 is formed by the outer *p*-electrons of oxygen, and the bottom of the conduction band is predominantly formed by excited titanium ions [13]. The presence of partially reduced titanium (Ti^{3+}) is of particular importance for the electronic properties of titanium dioxide, the level of which is located ~0.2–0.8 eV below the conduction band [15] and acts as a donor. The presence of Ti^{3+} determines in many cases the conductivity of TiO_2.

If in the investigated potential range, the near-surface region of the semiconductor electrode is depleted in basic carriers, then the experimental data obtained by measuring the electrode capacitance should be linear in the coordinates C^{-2} vs. E and obey the Mott-Schottky equation:

$$C^{-2} = \frac{2}{e\varepsilon\varepsilon_0 N}\left(E - E_{fb} - \frac{kT}{e}\right), \quad (1)$$

where C is the electrode capacitance; e is the electron charge; N is the concentration of carriers; E_{fb} is the potential of flat band; k is the Boltzmann constant; T is the absolute temperature; ε and ε_0 are the dielectric constant of the semiconductor and vacuum, respectively.

As preliminary studies have shown, the materials involved are highly doped semiconductors ($N>10^{18}$ cm^{-3}), and therefore, in the Mott-Schottky equation, it is necessary to take into account the capacity of the Helmholtz layer C_H:

$$C^{-2} = C_H^{-2} + \frac{2}{e\varepsilon\varepsilon_0 N}\left(E - E_{fb} - \frac{kT}{e}\right). \quad (2)$$

The slopes of the straight lines in equations (1) and (2) are the same, but in contrast to the value of E_{fb} obtained from (1):

$$E_{fb} = E_{C^{-2}=0} - \frac{kT}{e}, \quad (3)$$

in the second case we have

$$E_{fb} = E_{C^{-2}=0} + \frac{e\varepsilon\varepsilon_0 N}{2C_H^{-2}} - \frac{kT}{e}. \quad (4)$$

At an alternating current frequency of 5 Hz, the C^{-2} vs. E dependences for the materials involved are linear in a wide potential range. The carrier concentrations were found from the slopes of the straight lines, and the flat-band potentials were found from the intercepts using Eq. (4). The results are presented in Table 3.

In all cases, the straight lines are characterized by positive slopes, therefore the materials involved are n-type semiconductors. With the anodic polarization of such electrodes above the potential of the flat bands, the depletion of the semiconductor in carriers will occur. This, in turn, will lead to a decrease in the capacitance of the semiconductor component and, as a result, an increase in the slope of the polarization curve plotted in semilogarithmic coordinates. Thus, an increase in the potential of flat bands leads to a decrease in the total potential, and an increase in the number of carriers leads to a decrease in the slope of the polarization curve.

For comparison with materials obtained on titanium dioxide nanotubes, we investigated the semiconducting properties of an oxide film obtained on titanium during its thermal treatment in a tubular furnace in air at 500^0C for three hours. This material is an n-type semiconductor with a flat-band potential equal to −0.589 V and a carrier concentration of $6\cdot10^{20}$ cm^{-3}. Such a high concentration of carriers is obviously due to the small thickness of the oxide film and its nonstoichiometry, as a result of which the surface is not very depleted in electrons, since titanium metal acts as their donor.

Table 3

Semiconductor properties of TiO_2-nanotubes treated in various ways

Material	Flat band potential E_{fb}, V	Carriers amount N, cm^{-3}
Thermal treated Ti/TiO_2 nanotubes	–0.589	$6\cdot10^{20}$
Ti/TiO_2 nanotubes	0.122	$8\cdot10^{22}$
Reduced Ti/TiO_2 nanotubes	0.254	$1\cdot10^{23}$
Thermal treated reduced Ti/TiO_2 nanotubes	0.351	$3\cdot10^{23}$
Reduced Ti/TiO_2-Pt nanotubes	0.487	$6\cdot10^{23}$
Thermal treated reduced Ti/TiO_2-Pt nanotubes	0.788	$9\cdot10^{23}$

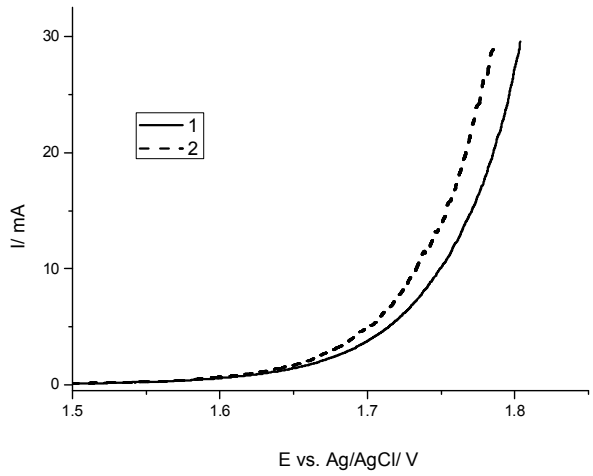


Fig. 3. Quasi steady-state polarisation curvev for reduced Ti/TiO_2-Pt nanotubes (1); thermal treated reduced Ti/TiO_2-Pt nanotubes (2)

During thermal treatment, the value of the potential of flat bands and the concentration of carriers increases, which may be due to the more crystalline structure of the material, which is accompanied by an increase in the proportion of metallic titanium, which acts as an electron donor. A similar phenomenon is observed when a non-continuous platinum coating is applied to the surface of reduced nanotubes. In this case, heat treatment leads to migration of platinum into the bulk of the composite, which, due to its dispersion in the oxide, additionally increases the number of carriers.

The data on the electrocatalytic activity of the obtained materials correlate satisfactorily with the semiconducting properties of the obtained materials (Fig. 3).

Conclusions

An original technique was developed for the deposition of platinized Ti/TiO_2 nanotubes, including the stage of thermal treatment of the coating in an air atmosphere. It has been shown that the deposition of platinum on the previously reduced surface of nanotubes allows obtaining composite coatings with a higher electrical conductivity, and the heat treatment of such a coating is characterized by the content of a larger fraction of TiO_2, increased adhesion to the current collector, and an increase in the crystallinity of the coating. At the same time, the internal stresses of the coating are reduced by several times.

Acknowledgements

The authors are indebted to the Ministry of Education and Science of Ukraine and the National Research Foundation of Ukraine who supported this work.

REFERENCES

1. *Latest* developments on TiO_2-based photocatalysis: a special focus on selectivity and hollowness for enhanced photonic efficiency / Ferreira V.R.A., Santos P.R.M., Silva C.I.Q., Azenha M.A. // Appl. Catal. A. – 2021. – Vol.623. – Art. No. 118243.

2. *Trend* in using TiO_2 nanotubes as photoelectrodes in PEC processes for wastewater treatment / Palmas S., Mais L., Mascia M., Vacca A. // Curr. Opin. Electrochem. – 2021. – Vol.28. – Art. No. 100699.

3. *Brillas E.* A critical review on ibuprofen removal from synthetic waters, natural waters, and real wastewaters by advanced oxidation processes // Chemosphere. – 2022. – Vol.286. – Art. No. 131849.

4. *Preparation* and photoactivity of samarium loaded anatase, brookite and rutile catalysts / Bellardita M., Di Paola A., Palmisano L., Parrino F., Buscarino G., Amadelli R. // Appl. Catal. B. – 2011. – Vol.104. – P.291-299.

5. *Chen X., Mao S.S.* Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications // Chem. Rev. – 2007. – Vol.107. – P.2891-2959.

6. *Electrodeposition* of Ni^{2+}-doped PbO_2 and physicochemical properties of the coating / Shmychkova O., Luk'yanenko T., Amadelli R., Velichenko A. // J. Electroanal. Chem. – 2016. – Vol.774. – P.88-94.

7. *Electrochemical* oxidation of reverse osmosis concentrates using enhanced TiO_2-NTA/SnO_2-Sb anodes with/without PbO_2 layer / Chen M., Pan S., Zhang C., Wang C., Zhang W., Chen Z., et al. // Chem. Eng. J. – 2020. – Vol.399. – Art. No. 125756.

8. *Yang Y. Hoffmann M.R.* Synthesis and stabilization of blue-black TiO_2 nanotube arrays for electrochemical oxidant generation and wastewater treatment // Environ. Sci. Technol. – 2016. – Vol.50. – P.11888-11894.

9. *Kinetic*, mechanism and mass transfer impact on electrochemical oxidation of MIT using Ti-enhanced nanotube arrays/SnO_2-Sb anode / Chen M., Wang C., Wang Y., Meng X., Chen Z., Zhang W., et al. // Electrochim. Acta. – 2019. – Vol.323. – Art. No. 134779.

10. *Electrochemical* behavior of platinized Ebonex® electrodes / Kasian O., Luk'yanenko T., Velichenko A., Amadelli R. // Int. J. Electrochem. Sci. – 2012. – Vol.7. – P.7915-7926.

11. *Simons P.Y., Dachille F.* The structure of TiO_2II, a high-pressure phase of TiO_2 // Acta Cryst. – 1967. – Vol.23. – P.334-336.

12. *Brookite* versus anatase TiO_2 photocatalysts: phase transformations and photocatalytic activitiese / Kandiel T.A., Robben L., Alkaim A., Bahnemann D. // Photochem. Photobiol. Sci. – 2013. – Vol.12. – P.602-609.

13. *Landmann M., Rauls E., Schmidt W.G.* The electronic structure and optical response of rutile, anatase and brookite TiO_2 // J. Phys. Condens. Matter. – 2012. – Vol.24. – Art. No. 195503.

14. *Electronic* and optical properties of anatase TiO_2 / Asahi R., Taga Y., Mannstadt W., Freeman A.J. // Phys. Rev. – 2000. – Vol.61. – P.7459-7465.

15. *Thompson T.L., Yates J.T.* Surface science studies of the photoactivation of TiO_2 new photochemical processes // Chem. Rev. – 2006. – Vol.106. – P.4428-4453.

Received 17.03.2022

ВПЛИВ ОБРОБЛЕННЯ Ti/TiO_2 НА МОРФОЛОГІЮ, ФАЗОВИЙ СКЛАД І ВЛАСТИВОСТІ НАПІВПРОВІДНИКІВ

О. Веліченко, В. Кордан, О. Шмичкова, В. Книш, П. Демченко

Немодифікований Ti/TiO_2 містить значну кількість рентгеноаморфних сполук на поверхні, які, швидше за все, є гідратованими оксидами титану. Основною кристалічною фазою є діоксид титану в формі алотропного анатазу. Металічний титан присутній на поверхні в незначних кількостях. Термічне оброблення цього матеріалу за температури 500°C впродовж 3 годин у атмосфері повітря приводить до збільшення частки кристалічної фази. Вміст металічного титану значно зростає, досягаючи приблизно третини. Часткове електрохімічне відновлення нанотрубок дозволяє одержати більш електропровідні субоксиди титану. Після катодного відновлення нанотрубок впродовж однієї години на поверхню матеріалу рівномірно осідає гальванічне покриття з металічною платиною. Термічно оброблені нанотрубки Ti/TiO_2 є напівпровідником n-типу з потенціалом пласкої зони, рівним −0,589 В, і концентрацією носіїв $6 \cdot 10^{20}$ $см^{-3}$. Така висока концентрація носіїв, очевидно, пояснюється малою товщиною оксидної плівки та її нестехіометричністю, внаслідок чого поверхня не дуже збіднена електронами, оскільки їх донором виступає металічний титан.

Ключові слова: платинований Ti/TiO_2, нанотрубки, термічне оброблення, провідність, фазовий склад.

THE EFFECT OF Ti/TiO_2 TREATMENT ON MORPHOLOGY, PHASE COMPOSITION AND SEMICONDUCTOR PROPERTIES

A. Velichenko [a], V. Kordan [b], O. Shmychkova [a, *], V. Knysh [a], P. Demchenko [b]

[a] Ukrainian State University of Chemical Technology, Dnipro, Ukraine

[b] Ivan Franko National University of Lviv, Lviv, Ukraine

[*] e-mail: lesiandra08@gmail.com

Naked Ti/TiO_2 contains a significant amount of X-ray amorphous compounds on the surface, which are most likely hydrated titanium oxides. The main crystalline phase is titanium dioxide in the allotropic anatase form. Metallic titanium is present on the surface in trace amounts. Thermal treatment of this material at a temperature of 500°C for 3 hours in an air atmosphere leads to an increase in the proportion of the crystalline phase. The content of metallic titanium increases significantly, reaching about a third. A partial electrochemical reduction of nanotubes allows one to obtain more electrically conductive titanium suboxides. After cathodic reduction of nanotubes for one hour, a coating with metallic platinum is uniformly deposited on the surface of the material. Thermal treated Ti/TiO_2 nanotubes are an n-type semiconductor with a flat-band potential equal to −0.589 V and a carrier concentration of $6 \cdot 10^{20}$ cm^{-3}. Such a high concentration of carriers is obviously due to the small thickness of the oxide film and its nonstoichiometry, as a result of which the surface is not very depleted in electrons, since titanium metal acts as their donor.

Keywords: platinized Ti/TiO_2; nanotubes; thermal treatment; conductivity; phase composition.

REFERENCES

1. Ferreira VRA, Santos PRM, Silva CIQ, Azenha MA. Latest developments on TiO_2-based photocatalysis: a special focus on selectivity and hollowness for enhanced photonic efficiency. *Appl Catal A.* 2021; 623: 118243. doi: 10.1016/j.apcata.2021.118243.

2. Palmas S, Mais L, Mascia M, Vacca A. Trend in using TiO_2 nanotubes as photoelectrodes in PEC processes for wastewater treatment. *Curr Opin Electrochem.* 2021; 28: 100699. doi: 10.1016/j.coelec.2021.100699.

3. Brillas E. A critical review on ibuprofen removal from synthetic waters, natural waters, and real wastewaters by advanced oxidation processes. *Chemosphere.* 2022; 286: 131849. doi: 10.1016/j.chemosphere.2021.131849.

4. Bellardita M, Di Paola A, Palmisano L, Parrino F, Buscarino G, Amadelli R. Preparation and photoactivity of samarium loaded anatase, brookite and rutile catalysts. *Appl Catal B.* 2011; 104: 291-299. doi: 10.1016/j.apcatb.2011.03.016.

5. Chen X, Mao SS. Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. *Chem Rev.* 2007; 107: 2891-2959. doi: 10.1021/cr0500535.

6. Shmychkova O, Luk'yanenko T, Amadelli R, Velichenko A. Electrodeposition of Ni^{2+}-doped PbO_2 and physicochemical properties of the coating. *J Electroanal Chem.* 2016; 774: 88-94. doi: 10.1016/j.jelechem.2016.05.017.

7. Chen M, Pan S, Zhang C, Wang C, Zhang W, Chen Z, et al. Electrochemical oxidation of reverse osmosis concentrates using enhanced TiO_2-NTA/SnO_2-Sb anodes with/without PbO_2 layer. *Chem Eng J.* 2020; 399: 125756. doi: 10.1016/j.cej.2020.125756.

8. Yang Y, Hoffmann MR. Synthesis and stabilization of blue-black TiO_2 nanotube arrays for electrochemical oxidant generation and wastewater treatment. *Environ Sci Technol.* 2016; 50: 11888-11894. doi: 10.1021/acs.est.6b03540.

9. Chen M, Wang C, Wang Y, Meng X, Chen Z, Zhang W, et al. Kinetic, mechanism and mass transfer impact on electrochemical oxidation of MIT using Ti-enhanced nanotube arrays/SnO_2-Sb anode. *Electrochim Acta.* 2019; 323: 134779. doi: 10.1016/j.electacta.2019.134779.

10. Kasian O, Luk'yanenko T, Velichenko A, Amadelli R. Electrochemical behavior of platinized Ebonex® electrodes. *Int J Electrochem Sci.* 2012; 7: 7915-7926.

11. Simons PY, Dachille F. The structure of TiO_2II, a high-pressure phase of TiO_2. *Acta Cryst.* 1967; 23: 334-336. doi: 10.1107/S0365110X67002713.

12. Kandiel TA, Robben L, Alkaim A, Bahnemann D. Brookite versus anatase TiO_2 photocatalysts: phase transformations and photocatalytic activities. *Photochem Photobiol Sci.* 2013; 12: 602-609. doi: 10.1039/C2PP25217A.

13. Landmann M, Rauls E, Schmidt WG. The electronic structure and optical response of rutile, anatase and brookite TiO_2. *J Phys Condens Matter.* 2012; 24: 195503. doi: 10.1088/0953-8984/24/19/195503.

14. Asahi R, Taga Y, Mannstadt W, Freeman AJ. Electronic and optical properties of anatase TiO_2. *Phys Rev B.* 2000; 61: 7459-7465. doi: 10.1103/PhysRevB.61.7459.

15. Thompson TL, Yates JT. Surface science studies of the photoactivation of TiO_2 new photochemical processes. *Chem Rev.* 2006; 106(10): 4428-4453. doi: 10.1021/cr050172k.