KnE Materials Science

TECHNOGEN-2019
IV Congress "Fundamental research and applied developing of recycling and utilization processes of technogenic formations"
Volume 2020

Knowledge E
enriching | engaging | empowering

Conference Paper

Synthesis and Attestation of Titanium Dioxide Nanotubes Based Photocatalyst for Water and Air Purification out of Harmful Organic Impurities

A. A. Valeeva[1,2], I. B. Dorosheva[1,2,3], I. A. Weinstein[2,3], A. A. Rempel[1,2,3], and E. A. Kozlova[4]

[1]Institute of Solid State Chemistry, Ural Branch of the RAS, Ekaterinburg, Russia
[2]NANOTECH Centre, Ural Federal University, Ekaterinburg, Russia
[3]Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences 101, Amundsen street, Ekaterinburg, Russia
[4]Boreskov Institute of Catalysis, Siberian Branch of the RAS, Novosibirsk, Russia

Abstract

In the present work we have synthesized nanotubular TiO_2 film with a nonstoichiometric layer in the vicinity of titanium foil by anodization during 120 min. The catalytic activity of nanotubular titanium dioxide films formed during the oxidation of acetone to carbon dioxide under the action of visible light with a wavelength of 450 nm was found to be approximately 2 times higher compared to standard titanium dioxide (Degussa P25). Such a pronounced enhancement of activity may be attributed to a more efficient absorption of visible light by the films due to narrowing of the optical gap because of difference in the nonstoichiometry of titanium dioxide near the interface between nanotubular film and the titanium foil substrate.

Keywords: photocatalysis, nonstoichiometric titanium dioxide, purification of water.

Corresponding Author:
A. A. Valeeva
anibla_v@mail.ru

Published: 31 December 2020

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

1. Introduction

Recently, titanium dioxide TiO_2 has attracted great interest for green chemistry, as a photocatalyst for the removal of organic pollutants and renewable energy sources, such as solar panels and photoelectrochemical decomposition of water [1–9]. The main disadvantage of TiO_2 for green chemistry is it wide band gap. That is why its photoactivity takes place exclusively near ultraviolet (UV) irradiation, but UV intensity in the solar spectrum is only a few percent [10]. So, to eliminate this disadvantage one need to develop an approach based on the decrease of the band gap width. In present work we did it by creating structural vacancies on the oxygen sublattice in nanotubular TiO_2.

2. Experimental Part

Nanotubular titanium dioxide films were synthesized on a Digma setup consisting of electrochemical cell, thermostat and power supply [11, 12]. The anodic oxidation was carried out on a thin titanium foil. Anodization was carried out at the same voltage but different anodization time. A solution of ethylene glycol and ammonium fluoride was employed as an electrolyte. All the chemical reagents used in the study were of analytical grade. X-ray diffraction (XRD) of the films was performed with the Bragg-Brentano recording geometry. XRD patterns were measured using the step-scan mode at $\Delta(2\theta)$ = 0.02° in the wide angular range with a long exposure time at each step. The surface and morphology of the synthesized samples were studied by scanning electron microscope (SEM) under high vacuum using an InLens detector. Diffuse reflectance spectra (DRS) of the samples were recorded on a Lambda 35 (Perkin Elmer) UV-vis spectrophotometer with a RSA-PE-20 (Labsphere) diffuse reflectance attachment. Photocatalytic activity of the catalysts was measured in a flow reactor, and reactants were identified on a FTIR spectrometer. The study was performed using a light-emitting diode with a maximum wavelength of 450 nm and a 1.0 A / 30 V current. The other reaction condition were as follows: T = 40°C, relative humidity of 20%, acetone concentration of 800 ppm, and flow rate of 60 mL/min. Concentration of acetone was found from the area of absorption band at 1160-1265 cm^{-1}, and concentration of carbon dioxide, from the band at 2200-2450 cm^{-1}. The rate of photocatalytic oxidation was calculated from carbon dioxide accumulation, which is a sole gas product of the reaction

$$C_3H_6O + 4\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O$$

3. Results and Discussion

Analysis of TiO_2 films on a titanium foil showed that the morphology and properties of the synthesized nanotubular films depend on the anodization time, the titanium foil morphology, the composition and temperature of the electrolyte, and the current in the electrochemical cell. The morphological analysis of the resulting films made it possible to obtain the dependences of geometric parameters of the nanotubular titanium dioxide layer on anodization time (see Table 1). In addition, the roughness coefficient H, the solid fraction A and the effective surface area S_{eff} were estimated using a technique reported in [13].

According to experimental data, the nanotube length ranges from 550 to 2000 nm; the value of inner diameter D_{in} of nanotubes varies from 27 to 39 nm; and outer diameter D_{out}, from 42 to 53 nm. It was shown that the solid fraction A of nanotubes decreases

Table 1: Parameters of the synthesized nanotubular TiO_2 film samples.

Parameters of nanotubular TiO_2 samples	Anodization time, min					
	15	30	60	120	180	360
NT length (*L*, nm)	700	750	550	1000-2000	1300	1200
Inner diameter of NT (D_{in}, nm)	27	33	33	38	38	39
Outer diameter of NT (D_{out}, nm)	42	46.2	49.6	53.4	50.6	49.6
Thickness of NT walls (*w*, nm)	7.5	6.6	8.3	7.7	6.3	5.3
Distance between NT (*y*, nm)	7	9	9	8	8	9
Roughness coefficient (*H*)	73	71	48	132	122	112
Effective surface area (S_{eff}, cm^2)	229	223	151	415	383	352
Solid fraction (*A*)	0.39	0.31	0.36	0.34	0.29	0.25

from 0.39 to 0.25 with increasing the anodization time t_A. It should be noted that at a certain time point the growth of the oxide layer slows down considerably because the current density decreases and hence the dissolution of the oxide layer becomes more intense than the oxidation. Effective surface area S_{eff} = 415 cm^2 for the grown array reaches its maximum at t_A = 120 min; this anodization time is sufficient to achieve a maximum length of nanotube *L* = 2000 nm.

On the XRD pattern of the foil received by anodizing for 120 minutes, an increase in the signal in the form of a diffuse halo was observed in the region of small scattering angles. Intense diffuse halo, in the range from 20 to 32°, and the absence of diffraction peaks indicate that the nanotubular titanium dioxide film is amorphous [14].

Table 2 lists data on the catalytic activity of three different nanotubular TiO_2 films prepared by anodization under similar conditions during 120 min. The catalytic activity (see Table 2) varies over a wide range, from 2.9 to 5.2 μmol/(min·g), which testifies to a significant role of different nonstoichiometry in the resulting films.

Table 2: Catalytic activity of films with a nanotubular TiO_2 layer (anodization for 120 min) in comparison with Degussa P25 titanium dioxide.

Sample	Nanotube length, nm	Oxidation rate, μmol/(min·g)
1	2000	5.2
2	1500	2.9
3	1000	5.1
TiO_2 – Degussa P25	-	2.0

Nonstoichiometry of nanotubular films was studied by diffuse reflection. In the optical DRS of the nanotubular TiO_2 layer in the visible spectral region near 450 nm, a wide dip of diffuse reflection is observed. This indicates the presence of nonstoichiometry in the amorphous titanium dioxide film. Atomic defects represented by vacancies in the amorphous network lead to the formation of energy levels in the band gap of titanium

dioxide, which in its turn results in the absorption of visible light with a wavelength of about 450 nm. This exerts a pronounced effect on the catalytic activity of the film in the visible region.

A comparison of Kubelka-Munk functions for nanotubular amorphous film and Degussa P25 titanium dioxide nanopowder corroborates the model of indirect transition in semiconductor nanotubular film. The extrapolation with a linear function to zero absorption in the region of high photon energies shows that the maximum band gap width for a nanotubular TiO_2 layer anodized for 120 min is *Eg* = 3.3 eV, while *Eg* = 3.0 eV for the Degussa P25 TiO_2 nanopowder.

Thus, we have synthesized films with a nanotubular TiO_2 layer whose nonstoichiometry depends on synthesis conditions. This parameter exerts an essential effect on the activity of samples, which varies between 2.9 and 5.2 μmol/(min·g). According to the DRS, the optical gap width for nanotubular film changes along the film thickness from 3.3 eV to small values corresponding to the photon energy of visible light, due to nonstoichiometry of the film near the interface with the metal substrate. Thus, the structural amorphism in nanotubular titanium dioxide does not produce a switching from indirect transition (crystalline titanium dioxide) to direct one (amorphous titanium dioxide). With the modeling of harmful organic impurities by acetone it is shown that synthesized nonstoichiometric nanotubular titanium dioxide should be useful for purification of water and air.

Acknowledgements

The research was funded by RFBR according ti the project N 20-03-00299.

References

[1] Higashimoto, S., *et al*. (2010). Efficient and Selective Oxidation of Benzylic Alcohol by O_2 into Corresponding Aldehydes on a Tio_2 Photocatalyst under Visible Light Irradiation: Effect of Phenyl-Ring Substitution on the Photocatalytic Activity. *Journal of Catalysis*, vol. 276, pp. 76-83.

[2] Popkov VI, Bachina AK, Valeeva AA, Lobinsky AA, Gerasimov EY, Rempel AA. (2020) Synthesis, morphology and electrochemical properties of spherulite titania nanocrystals. Ceramics International, vol. 46, pp. 24483-24487.

[3] Rempel AA, Valeeva AA. (2019) Nanostructural titanium dioxide for medical chemistry. Russian chemical bulletin, Int. Ed. vol.68, pp. 2163-2171.

[4] Chen, X. and Mao, S. S. (2007). Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chem. Rev.,* vol. 107, pp. 2891-2959.

[5] Vasilevskaia AK, Popkov VI, Valeeva AA, Rempel AA. (2016). Formation of nonstoichiometric titanium oxides nanoparticles Ti_n O_{2n-1} upon heat-treatments of titanium hydroxide and anatase nanoparticles in a hydrogen flow. Russ. J. Appl. Chem., vol. 89, pp.1211–1220. .

[6] Dorosheva I.B, Valeeva A.A, Rempel A.A. (2017). Sol-gel synthesis of nanosized titanium dioxide at various pH of the initial solution. AIP Conf. Proc., vol.1886, p.020006.

[7] Li, C-J., *et al*. (2012). High Selectivity in Visible-Light-Driven Partial Photocatalytic Oxidation of Benzyl Alcohol into Benzaldehyde over Single-Crystalline Rutile Tio_2 Nanorods. Applied Catalysis B: Environmental, vols. 115-116, pp. 201-208.

[8] Rempel A.A, Kozlova E.A, Gorbunova T.I, Cherepanova S.V, Gerasimov E.Y, Kozhevnikova N.S, Valeeva A.A, Korovin E.Y, Kaichev V.V, Shchipunov Y.A. (2015) Synthesis and solar light catalytic properties of titania-cadmium sulfide hybrid nanostructures. Catalysis Communications, vol. 68, pp. 61-66.

[9] Rempel A.A, Kuznetsova Y.V, Dorosheva I.B, Valeeva A.A, Weinstein I.A, Kozlova E.A, Saraev A.A, Selishchev D.S. (2020). High photocatalytic activity under visible light of sandwich structures based on anodic TiO_2/CdS nanoparticles/sol-gel /CdS nanoparticles/sol-gel. Topics in Catalysis, vol. 63, pp. 130-138.

[10] Carp, O., Huisman, C. L. and Reller A. (2004). Photoinduced Reactivity of Titanium Dioxide. *Progress in Solid State Chemistry*, vol. 32, pp. 33-177.

[11] Valeeva, A. A., *et al*. (2018). Nonstoichiometric Titanium Dioxide Nanotubes with Enhanced Catalytical Activity under Visible Light. *Scientific Reports – Nature*, vol. 8, pp. 9607-9617.

[12] Vokhmintsev, A. S., *et al*. (2014). Memristive Effect in a Nanotubular Layer of Anodized Titanium Dioxide. *Bulletin of the Russian Academy of Sciences: Physics,* issue 78, pp. 1176-1179.

[13] Alivov, Y. and Fan Z. (2009). A TiO_2 Nanostructure Transformation: From Ordered Nanotubes to Nanoparticles. *Nanotechnology,* vol. 20, pp.1-6.

[14] Valeeva, A. A., *et al*. (2019). Influence of Calcination on Photocatalytic Properties of Nonstoichiometric Titanium Dioxide Nanotubes. *Alloys and Compounds*, vol. 796, pp. 293-299.