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Modification of Titanium Oxide Films by Ferric Ions in Hydrothermal Conditions and their Photo-Electrochemical Properties

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Anodic titanium oxide films were doped using ferric ions in hydrothermal conditions. Doping is accompanied by a full change in the structure and morphology of the surface of titanium oxide while anatase is established radiographically. Deep redshift in optical spectrum of titanium oxide takes place. This is accompanied by anodic photo-current sharply increasing 2.5 times under visible lighting with simultaneous decrease of current characteristics under ultraviolet light. This is explained by the synergistic effect of Fe-Ti compound formed on the surface of the anodic oxide. Firstly, deep acceptor levels of Fe^{3+} in titanium oxide energy band gap are created while dopant conductivity becomes prevalent and titanium oxide's own conductivity partially leveled. Secondly, its proper layer of ferric oxide is formed.

Keywords: Titanium oxide, Conductivity, Spectrum, Anodic photo-current, Width of energy band gap, Doping.

INTRODUCTION

Photo-electrochemical splitting of water into hydrogen and oxygen using semiconducting photoelectrodes is most ecologically pure method of solar power conversion. For this process titanium dioxide is well-known and investigated one as a photoanode among semiconducting materials due to its high corrosion resistance in electrolyte water solutions and high quantum efficiency[1].

The main difficulty in realization of such a scheme is the width of the energy band gap of titanium oxide, which is 3 eV, hence the sensitivity only to UV light. Multiple attempts have been made to "sensitize" TiO_2 to visible light by doping it with transition metal ions. However, the results were often inconsistent and to date there isn't a single opinion about the mechanism of sensibilization of titanium oxide using ions of transition metals[2-21]. There are works where no improvements in photocatalytic properties of titanium oxide are noted[3,4] or they are insignificant when doping with ions of transition elements, whilst carbon and nitrogen doping gives significant improvement[7,9,10].

Although the most studied doping element is trivalent iron[22,23], the mechanism of sensibilization and the conditions of its implementation are still not fully known[4-23]. Literature analysis shows that the condition of effective doping of titanium oxide with trivalent ferric is effective replacement of Ti^{4+} ions with Fe^{3+} ions in crystalline lattice of titanium oxide, which however does not always show in X-ray diffraction patterns[11,23].

On the other hand, much research is dedicated to production of photoactive materials based on oxide structures in hydrothermal conditions[24,25]. However, their majority deals with implementation of material hydrothermal synthesis and its subsequent application to the base. Much less attention is given to the synthesis of films in hydrothermal conditions "*in situ*"[26,27]. In this regard we conducted an experiment to reveal the influence of doping using Fe^{3+} on photocatalytic properties of titanium oxide on the metal surface in hydrothermal conditions.

EXPERIMENTAL

The experiment was carried out on metallic titanium plates 2 cm × 2 cm in size with current collector made from the same titanium. Formation of titanium oxide films on pure titanium films was performed by anodizing in the electrolyte of the following composition: 0.1 M sulfuric acid and 0.05 M ammonium fluoride with voltage on the basin clamps of 20 V; time of anodizing was 40 min. Under such conditions we obtained porous films with an effective pore diameter of 60-80 nm (Fig. 1, a). Since anodic titanium oxide is X-ray amorphous and its photocatalytic properties in this case are very low, anodized and modified plates were annealed in the air under 500 °C, after which current-voltage characteristics were taken.

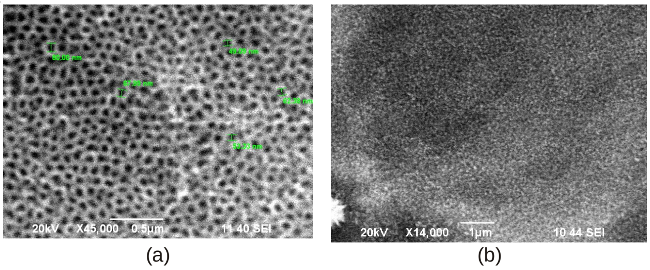

Fig. 1. Changes in morphology of the titanium oxide surface (a) after hydrothermal treatment (b)

During modification anodized plates were rinsed with distilled water, placed in a special fluoroplastic cup with modifying electrolyte solution and held in a steel autoclave under a certain temperature and pressure.

Modifying iron solution was prepared from a solution with content 20 mg of $FeCl_3$ per 1 mL of solution. We poured 15 mL of water and 2 mL of $FeCl_3$ solution into a fluoroplastic cup and placed the 2 cm × 2 cm anodized titanium plates in it. Indicator pH of the modifying solution was held in the interval 1-2 by adding 1 M HCl solution. Autoclaving of the samples was performed under 190 °C, during which pressure changed from 0.1 to 0.8 MPa for 6 h of heating and cooling of the steel cylinder of the autoclave. Then the autoclave was cooled, the plates were taken out of the fluoroplastic cup, thoroughly rinsed with distilled water, dried and annealed under 500 °C in the air during 1 h.

X-Ray diffraction patterns were taken on the stationary installation DRON-3 with CuK_α radiation directly from the metallic plates of anodized titanium. Anodic photocurrents of titanium oxide electrodes were captured using the three-electrode scheme. A platinum wire was used as a counter electrode and a silver-chloride electrode was used as a comparison electrode. We used a UV lamp DRT-230 and a visible light (xenon) lamp for lighting of the electrodes. Radiation was performed using the full spectrum of the mentioned lamps without colour filters. Illumination intensity of the samples was measured using a lux meter and was captured at (160-180) × 10^3 lx for the xenon lamp and 12 × 10^3 lx for the UV lamp. Sunlight level in Shymkent, South Kazakhstan measured at noon in June was 130 × 10^3 lx.

Microphotographs and semi-quantitative analysis of the surface of electrodes were performed on a raster electronic microscope JSM-6490LV (JEOL, Japan). Optical spectra of the reflection were captured directly from the plates using a special attachment with multiple light fiber to the spectrophotometer.

RESULTS AND DISCUSSION

Fig. 2 shows anodic photocurrents of titanium oxide films under different lighting. One can clearly see in the Fig. 2 that photocurrents under UV lighting are significantly higher than those under the visible lighting, which is in well agreement with the data on the energy band gap of titanium oxide and its optical characteristics presented in Fig. 3. It is observed that the absorption band edge of titanium oxide is in the near ultraviolet zone-380 nm.

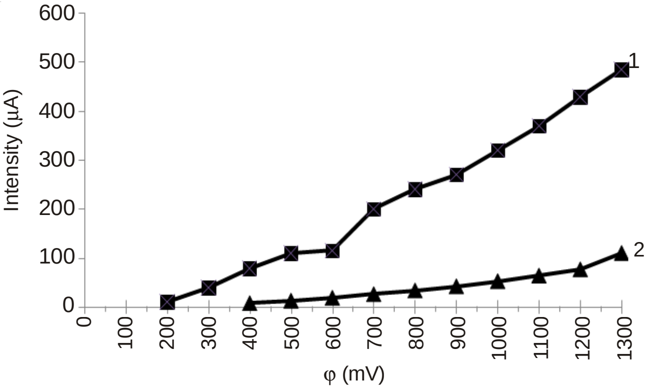

Fig. 2. Current-voltage characteristics of titanium oxide electrodes in 1M KOH solution under 60 second anodization time in UV (1) and xenon (2) illumination

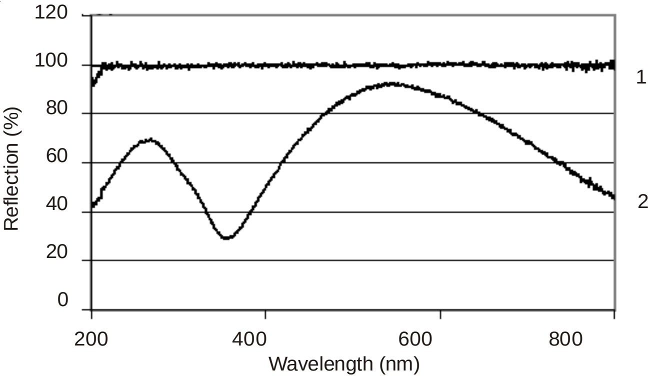

Fig. 3. Optical spectra of absorption of titanium oxide films taken directly from titanium films: 1-metallic titanium without the film, 2- spectrum of anodic titanium oxide

Semi-quantitative analysis of ferric content in modified films showed differences in its content depending on hydrothermal treatment conditions (Table-1). Table-1 shows that in general with pressure rise in the autoclave an improvement in ferric ions penetration into the film structure of titanium oxide is observed under equal time of samples incubation in the autoclave. Modifying with ferric ions gives 3-5 times increase

TABLE-1
IRON CONTENT IN MODIFIED TiO_2 FILMS UNDER DIFFERENT MODES OF HYDROTHERMAL TREATMENT, AND CORRESPONDING PHOTOCURRENT VALUES UNDER VISIBLE LIGHTING

Trial number	Maximum pressure in autoclave, MPa	Iron content according to the raster electronic microscope data, % mass	Maximum value of photocurrent under xenon lighting with electrode potential of 1200 mV, mkA
Original film	0	0	80
1	0.8	1,6	400
2	0,5	1,5	350
3	0,4	1,1	440
4	0,2	0,73	450
5	0,1	0	80

of photocurrents under visible lighting. It should be observed that Fe^{3+} content in the film should be above 0.7 %, while it's not optimal content.

X-Ray analysis (Fig. 4) of films modified with Fe^{3+} ions has shown the main reflection of anatase for samples 2,3,4,5, which was also observed by authors in the work[11], while sample 1 didn't show the main anatase reflection (Fig. 4). We suppose that with Fe^{3+} concentration increase in the film composition the partial amorphization of its structure takes place. Previous workers[14,22] reported that Fe^{3+} ions are built into the TiO_2 lattice, thus forming Ti-O-Fe bonds. Improvement of titanium oxide catalytic properties in visible lighting by modifying it with Fe^{3+} ions is seen in change of elementary lattice size and parameters of TiO_2 cell. In present case - under hydrothermal conditions the reprecipitation of titanium oxide film with simultaneous formation of Ti-O-Fe bonds took place. This led to a strong change in morphology of TiO_2 film surface (Fig. 1) - porous structure of anodic oxide was completely leveled, having freed up space for a microglobular structure.

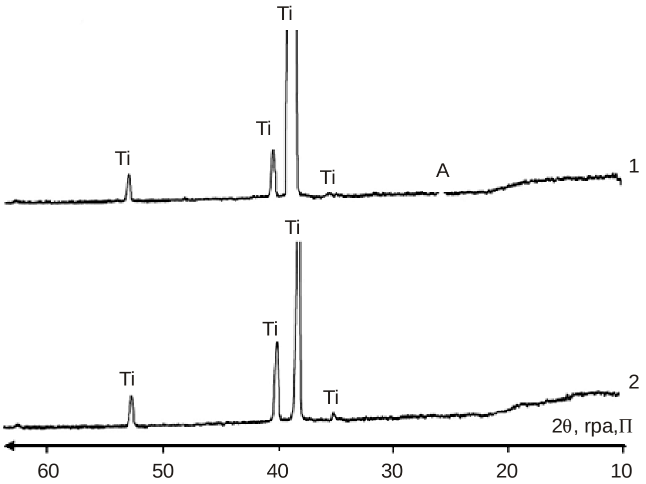

Fig. 4. X-Ray diffraction patterns of annealed titanium oxide film with ferric ions (curve 1) and modified with ferric ions under 0.8 MPa (curve 2): Ti are reflections of metallic titanium, A is the main reflection of anatase

It is suggested that a very thin film (within several nanometers) of ferric oxide itself could have formed simultaneously on the titanium oxide surface. The ferric oxide could have significantly affected the electro-physical properties of the obtained hetero-structure. In the work[15] an increase in catalytic activity of Rhodamine-B oxidation was observed and in[23] catalytic activity increased 2.5 times under *p*-xylene oxidation, which is directly linked by the authors to infusion of Fe^{3+} ions into the titanium oxide structure. Alternatively, we attribute the significant increase in photocurrents in the spectrum visible area to the additional layer of ferric oxide catalyst, which renders a synergetic effect on the photoelectric properties of the newly formed film on the metal surface in the autoclave along with the mechanism described earlier in works[7-23]. The disappearance of the main anatase reflection on X-ray diffraction patterns of modified films with increased ferric content (over 1.5 %) indicates reconstruction of the crystalline lattice of titanium oxide towards amorphisation as well as change in surface complexes, which leads to formation of improved electro-physical properties of modified titanium oxide.

It is a matter of discussion about formation of new phases with reserve because the sensitivity of X-ray investigation in our case leaves much to be desired. Secondly, the semi-quantitative analysis on JSM-6490LV electronic microscope allows to analyze the signal of secondary electrons from the depth of the film (sample). Conducting layer analysis of the film for the strictly assigned value of thickness of the film was not feasible. Nevertheless, positive influence of modification by ferric ions can be clearly observed as a sharp increase (more than double) of anodic photocurrents of modified films under visible lighting (Fig. 5). Such a sharp increase in anodic photocurrents corresponds to redshift of the absorption band edge of titanium oxide modified film (Fig. 6). Displacement can be observed up to 500 nm.

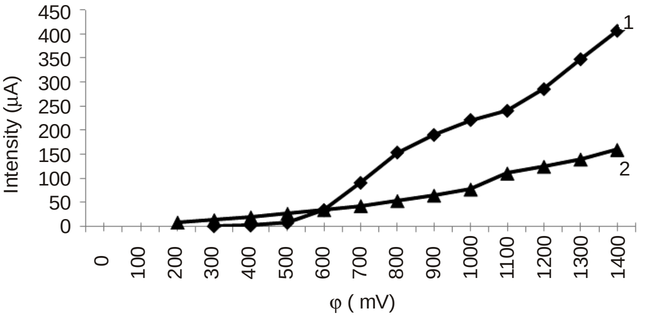

Fig. 5. Anodic photocurrents under visible lighting of titanium oxide films modified with ferric ions (1) and original titanium oxide (2)

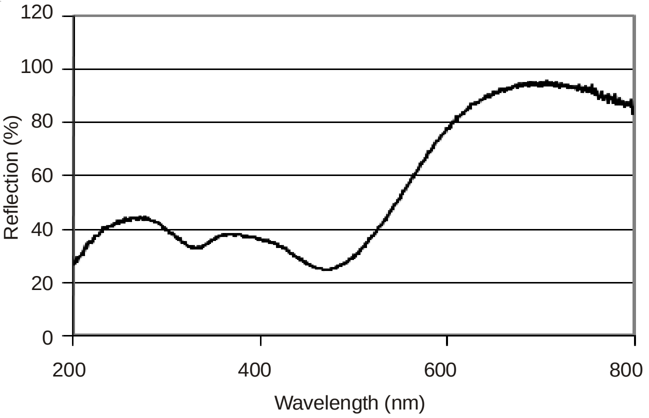

Fig. 6. Optical spectra of absorption of titanium oxide films on a metallic base modified with trivalent ferric ions

It is supposed that the suggested model of formation of dopant ferric levels in the energy band gap of titanium oxide works in present case only partly. If we look at the measurement data of current characteristics under UV lighting (Fig. 7) from these positions, then the observed more than twofold decrease in current characteristics of modified electrodes can be explained by a change in surface structure and its electro-physical parameters.

In order to explain this effect we suggest that: (a) for each quant of absorbed light energy an electron-hole pair is formed; (b) the whole photocurrent is conditioned with electron injection from dopant ferric level into the conduction band of titanium oxide; (c) the mechanism of injection of own electrons

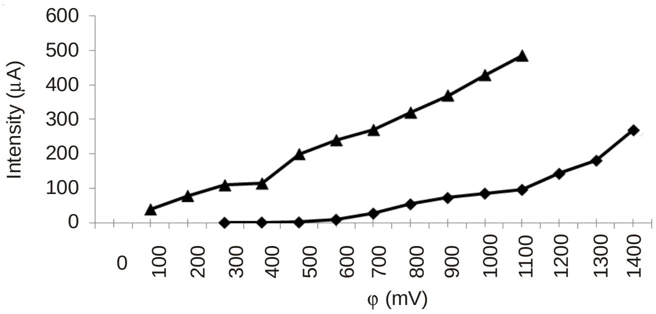

Fig. 7. Anodic photocurrents under ultraviolet lighting of titanium oxide films modified with ferric ions (1) and original titanium oxide (2)

from valence band into conduction band in titanium dioxide as if "switches off" leaving space for the dopant photocurrent. Therefore the decreased own conductivity of modified titanium oxide, having manifested in the decrease of photocurrent under UV lighting, is compensated by the dopant photocurrent under more long-wave lighting.

We can definitely say that, having only changed significantly the type of chemical bonds in titanium oxide, it is possible to attain a sharp change in its photocatalytic properties. In present case isomorphic titanium substitution with trivalent ferric ions leads to such significant changes in photocatalytic properties of titanium oxide. Simultaneously a very thin film of the new compound forms itself over the modified film in hydrothermal conditions. This film has properties closer to ferric oxide.

The formation of the best electro-physical properties of the synthesized material because it is obvious that mobility of carriers, presence of defects, concentration of carriers are connected with the doping agent concentration and its position in the energy band gap of titanium oxide.

It is suggested that in order to get a more precise mechanism of photoactive film formation in hydrothermal conditions it is required to continue investigations to determine the influence of electrolyte composition, its concentration and doping agents on photo-electrochemical properties of formed electrodes on the conductive glass surface, as well as to determine phase composition of films.

Conclusions

Based on the obtained results it is noted that the main characteristics of doping of titanium oxide anodic film with trivalent ferric ions in hydrothermal conditions:

- In hydrothermal conditions a partial "reprecipitation" of titanium oxide films takes place along with a significant reorganization of surface morphology.
- The obtained displacement of the optical absorption edge of titanium oxide into the long-wave area when doping is explained by creation of additional levels of the doping element in the energy band gap of TiO_2.
- The doping of anodic oxide films of titanium oxide with ferric ions (Fe^{3+}) in hydrothermal conditions allows us to achieve a multiple increase in photocurrent of the photolyzable cell under visible lighting.

This is explained by the presence of two factors responsible for formation of photocatalytic properties of the formed film. Firstly, it is creation of deep acceptor levels of ferric in titanium oxide energy band gap while dopant conductivity becomes prevalent and titanium oxide's own conductivity becomes leveled. Secondly, it is formation of a new composite compound with properties close to the ferric oxide layer.

REFERENCES

1. A. Seitmagzimov, G. Seitmagzimova and V. Bishimbayev, *Asian J. Chem.*, **25**, 3285 (2013).
2. K.T. Ranjit and B. Viswanathan, *J. Photochem. Photobiol. Chem.*, **108**, 79 (1997).
3. T. Lopez, J. Hernandez-Ventura, R. Gomez, F. Tzompantzi, E. Sanchez, X. Bokhimi and A. Garcia, *J. Mol. Catal. Chem.*, **167**, 101 (2001).
4. J.W.J. Hamilton, J.A. Byrne, C. McCullagh and P.S.M. Dunlop, *Int. J. Photoen.*, Article ID 631597 (2008).
5. A. Di Paola, G. Marci, L. Palmisano, M. Schiavello, K. Uosaki, S. Ikeda and B. Ohtani, *J. Phys. Chem. B*, **106**, 637 (2002).
6. S.I. Shah, W. Li, C.P. Huang, O. Jung and C. Ni, *Proc. Natl. Acad. Sci. USA*, **99 (suppl. 2)**, 6482 (20012).
7. M. Janczarek, H. Kisch and J. Hupka, *Physicochem. Prob. Miner. Process.*, **41**, 159 (2007).
8. V. Shymanovska, L. Kernazhitsky, G. Puchkovska, V. Naumov, Ò. Khalyavka, V. Kshnyakin, S. Kshnyakina and V. Chernyak, *J. Nano-Electron Phys.*, **3**, 79 (2011).
9. V.M. Zainullina, V.P. Zhukov, V.N. Krasilnikov, M.U. Yanchenko, L.U. Buldakova and E.V. Polyakov, *Solid State Phys.*, **52**, 271 (2010).
10. II.V. Kolesnik, G.S. Chebotaeva, A.A. Eliseev, A.V. Lukashin, Yu.D. Tretyakov, E-MRS Spring Meeting, Book of Abstracts, Strasbourg, France, June (2009).
11. M. Hirano, T. Joji, M. Inagaki and H. Iwata, *J. Am. Ceram. Soc.*, **87**, 35 (2004).
12. K.S. Raja, M. Misra, V.K. Mahajan, T. Gandhi, P. Pillai and S.K. Mohapatra, *J. Power Sources*, **161**, 1450 (2006).
13. H. Chen and L. Wang, *Beilstein J. Nanotechnol.*, **5**, 696 (2014).
14. M.D.S. Villalpando, A. Cugini and A.C. Miller, *Int. J. Oil, Gas Coal Technol.*, **3**, 75 (2010).
15. X. Wu, Q. Wei and J. Zhaohua, *Thin Solid Films*, **496**, 288 (2006).
16. K.-S. Hwang, Y.-S. Jeon, K.-O. Jeon and B.-H. Kim, *Optica Applicata*, **35**, 191 (2005).
17. Z.-D. Meng, K. Zhang and W.-C. Oh, *J. Korean Ceramic Soc.*, **46**, 621 (2009).
18. V.N. Nguyen, N.K.T. Nguyen and P.H. Nguyen, *Adv. Nat. Sci.: Nanosci. Nanotechnol.*, **2**, 035014 (2011).
19. P.H.C. Camargo, G.G. Nunes, G.R. Friedermann, D.J. Evans, G.J. Leigh, G. Tremiliosi-Filho, E.L. de Sá, A.J.G. Zarbin and J.F. Soares, *Mater. Res. Bull.*, **38**, 1915 (2003).
20. Y. Li, J. Chen, J. Liu, M. Ma, W. Chen and L. Li, *J. Environ. Sci. (China)*, **22**, 1290 (2010).
21. R.S. Sonawane, B.B. Kale and M.K. Dongare, *Mater. Chem. Phys.*, **85**, 52 (2004).
22. O. Carp, C.L. Huisman and A. Reller, *Prog. Solid State Chem.*, **32**, 33 (2004).
23. C.L. Luu, Q.T. Nguyen and S.T. Ho, *Adv. Nat. Sci.: Nanosci. Nanotechnol.*, **1**, 015008 (2010).
24. M. Milanovic, I. Stijepovic and L.M. Nikolic, *Proc. Appl. Ceramics*, **4**, 69 (2010).
25. M.A. Alpuche-Aviles and Y.Y. Wu, *J. Am. Chem. Soc.*, **161**, 1450 (2009).
26. A.T. Chien, J.S. Speck, F.F. Lange, A.C. Daykin and C.G. Levi, Mater. Res. Laboratory and Mater. Department, University of California (1995).
27. C.Y. Cui, J.D. Hu, Y.H. Liu and Z.X. Guo, *J. Mater. Sci. Technol.*, **24**, 964 (2008).