SYNTHESIS and INVESTIGATION OF ELECTRONIC STRUCTURE FEATURES OF ELECTROEXPLOSIVE TiO_2 and TiO_2:Ag

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ABSTRACT

Nanopowders of titanium oxide were synthesized by method of electrical explosion of wires with the purpose of creation of photocatalytic electrode materials on their base. To improve the photocatalytic properties of titanium oxide its surface was modified by silver. In the work the procedure of doping of TiO_2 matrice by Ag_2O directly during explosion was used.

Nanostructured fractal TiO_2 films were formed from synthesized nanopowders. After annealing of the films on air at 450°C a mesoporous surface is formed. Its feature is the presence of nanosized TiO_2 fibers.

The investigations of an electronic structure of nanopowders and films were carried out using XPS, optical and electron microscopy. The presence of Ti^{3+}-states on the surface is the characteristic feature of TiO_2 films. After annealing the ratio of Ti^{3+}-/Ti^{4+}-states and OH-groups connected with them is changing. The appearance of nanosized TiO_2 fibers on the surface after annealing and features of their electron structure may be interesting for photo- and electrocatalysis.

Key words: nanopowders, TiO_2, electrical explosion of wires.

INTRODUCTION

Electrical explosion of wires is a promising technology which allows to obtain nanopowders with high density of surface catalytically-active centers, that is a sequence of nonequilibrium of synthesis process [1-2]. Electroexplosive films and titanium dioxide nanopowders are promising for using in photo-electrochemical systems of solar energy conversion. The attention to TiO_2 nanopowders incorporated nanoparticles of noble metals is caused by the fact that the particles of silver on the surface of metal can be centers of charge distribution and accumulation. At that such parameter as photosensitivity greatly increases [3]. In the work the phase contents changes of the surface of doped TiO_2 nanopowders were examined at different annealing conditions.

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METHODS OF SAMPLES MANUFACTURING AND ANALYSIS

The features of the electron structure of the surface of nanodisperse TiO_2:Ag samples were explored by XPS method at electron spectrometer with PHOIBOS-100_SPECS energy analyzer and X-ray source with magnesium anode (E MgK_α = 1253.6 eV, P = 200 W).

The spectra of Ti2p- and Ag3d-levels were decomposed into related pairs of components $2p_{3/2}/2p_{1/2}$ and $3d_{5/2}/3d_{3/2}$ with parameters E = 5.76 eV, I_1/I_2 = 0.3 and ΔE = 6.0 eV, I_1/I_2 = 0.66 correspondingly for taking into account spin-orbit splitting. The decomposition was carried out by Gauss-Newton method in linked parameters mode. The intensity of components and binding energy was varied. The width of components and ratio of the contributions of Gauss-Lorentz distributions during process of spectra decomposition were constant. The area of the components was determined after background subtraction by Shirley method [4]. Obtained in such way integral intensities of components were proportional to the contents of nonequivalent ions of titanium and silver in the samples.

TiO_2, TiO_2:3%Ag, TiO_2:5%Ag nanopowders were synthesized in dry air atmosphere. The energy of explosion was $E = 3{,}1 \cdot E_c$, where E_c is sublimation energy of titanium.

RESULTS AND DISCUSSION

The main feature of Ti2p-spectra of electroexplosive titanium oxide nanopowders is the considerable contents of the states with $E_bTi2p_{3/2}$ = 457.5 eV, which correspond to Ti^{3+}-states. This points out on the high degree of imperfection of the nanopowders surface. Dominating are the Ti^{4+}-states with $E_bTi2p_{3/2}$ = 458.3 eV, which can be related with the anatase phase, and states with $E_bTi2p_{3/2}$ = 458.8 eV, which can correspond to the rutile phase [5-6]. A shift to the region of higher binding energy represents the decrease of Ti – O bond length. A signal in the region $E_bTi2p_{3/2}$ = 459.4 eV can be related to Ti^{4+}-states in the titanium peroxicomplexes.

According to the XPS data silver on the electrode surface is present as Ag^0-, Ag^+- and Ag^{2+}-states. It was determined that the final phase distribution of silver is determined by the character of the segregation processes during annealing, temperature and medium of the annealing, influence of reduction processes and initial total contents of silver.

It was determined that modifying of TiO_2 by silver particles leads to increase of Ti^{3+}-states contribution. The highest contents of Ti^{3+}-states were recorded for TiO_2:5%Ag samples.

The contact of the nanopowders surface with H_2O_2 with further annealing on air leads to the decrease of contents of the phase with $E_bTi2p_{3/2}$ = 458.3 eV and increase of the contribution of the phase with $E_bTi2p_{3/2}$ = 458.8 eV, that depicts rutilization process of TiO_2. Simultaneously a part of oxide forms of silver reduces to metal.

The replacement of air medium by argon during anneal practically doesn't change the phase contents for silver and greatly changes the phase contents for titanium.

From the initial TiO_2 nanopowders the nanostructured fractal films which have highly developed surface were formed (*fig.1*) with agglomerates size 20-60 nm (*fig. 2*).

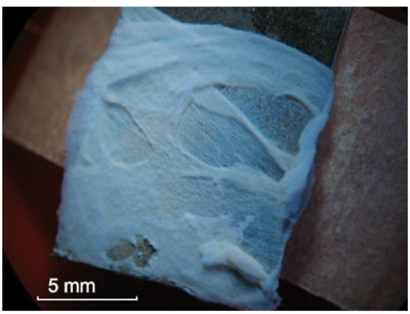

Fig. 1 – Nanostructured TiO_2 film

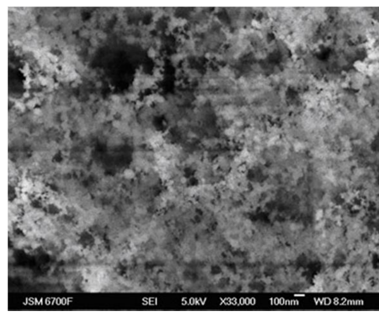

Fig. 2 – SEM image of nanostructured TiO_2 film

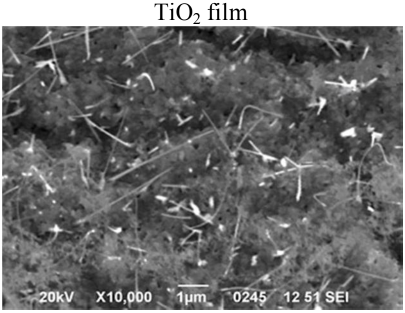

Fig. 3 – SEM image of nanostructured TiO_2 film after annealing

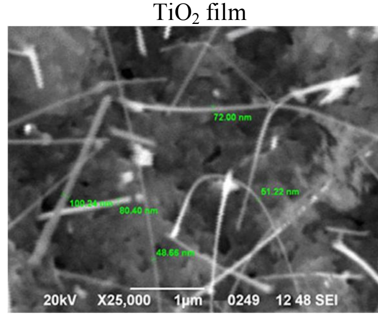

Fig. 4 – SEM image of nanostructured TiO_2 film after annealing

After anneal on air at 450°C the mesoporous surface of the films is formed. Its main feature is the presence of nanosized TiO_2 fibers with diameter 50 – 100 nm and length 1 - 5 µm (fig. 3-4). Applied approach allows to create on the base of nanopowders miscellaneous nanodisperce films and materias with high specific surface without connectives and loading.

CONCLUSIONS

The possibility of synthesis of TiO_2:Ag nanopowders by EEW method was shown.

Doping of the electroexplosive titanium oxide powders by silver leads to the increase of the contribution of Ti^{3+}-states.

A contact of TiO_2 and TiO_2:Ag nanopowders with hydrogen peroxide and further annealing switches on the rutilization process of TiO_2-matrice.

REFERENCES

[1] A.P. Shpak, A.M. Korduban, T.V. Kryshchuk, V.A. Kandyba, Metal Physics and Newest Technologies, 2008, 30(11), P. 1432-1437 (in Russian).

[2] A.P.Shpak, A.M.Korduban, T.V.Kryshchuk, M.M.Medvedskij, Metal Physics and Newest Technologies 2007, 29(4), P. 507-513 (in Russian).

[3] J. He, I. Ichinose, T. Kunitake, A. Nakao, Langmuir, 2003, Vol. 18.P. 1005-1010.

[4] D. Briggs, M.P. Seach, Practical surface analysis by Auger and X-ray photoelectron spectroscopy, John Wiley & Sons, Chichester, New York, 1983.

[5] S. Agarwala, G.W. Ho, Materials Letters 63, 2009, P. 1624–1627

[6] M. Browne, P.J. Gregson, West RH. J Mater Sci Mater Med, 1996, No7, P. 323–329.