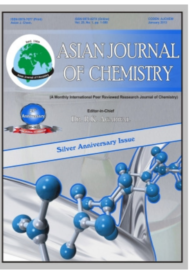
Asian Journal of Chemistry; Vol. 25, No. 6 (2013), 3285-3288

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13634



Influence of Surface Morphology and Titanium Oxide Film Thickness on Its Photo-Electrochemical Properties

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(*Received*: 21 February 2012; *Accepted*: 17 December 2012) AJC-12568

The goal of investigation is to determine the influence of porous structure of anodic titanium oxide on its photoelectrochemical properties. Results showed that within a certain thickness of tubular porous layer (from 300 nm and up) photocurrents can surge, mainly being dependent on electrophysical parameters of titanium oxide layer. After prolonged anodization of titanium (more than 3 h) in sulphuric acid electrolyte with added ammonium fluoride tubular structure of titanium oxide film changes into globular, which leads to a sharp change in photoelectrochemical characteristics-a more than twofold increase in photocurrent. It was concluded that ideally the electrode for photoelectrolysis of water must have minimum thickness with maximum possible porosity.

Key Words: Films, Morphology, Nanoporous anodic titanium dioxide, Nanostructure, Photoelectrolysis.

INTRODUCTION

Photoelectrochemical transformation of solar energy by water decomposition into hydrogen and oxygen on semiconductor electrodes under light is one of the possible ways of transformation of solar energy since the first publication of Fujishima and Honda[1]. We need to remember that such process is ecologically pure, renewable and as a result, environmentally pure fuel is obtained. This fuel is hydrogen, which can change the negative influence of greenhouse gases on the planet. Even though it's been almost 40 years since the pioneering work of Fujishima and Honda, the hydrogen they obtained using titanium dioxide as a photoanode is still far from being a commercially profitable project. With the development of nanotechnology there has been a steadfast interest not only in mesoporous titanium oxide, but also in nanotubes which, as a number of authors claim, are more effective in water decomposition reactions[2-8]. Although mesoporous structure obtained in different ways[2] can have significantly different photocatalytic properties. In any case, multiple investigations of photoelectrolysis on nanoporous (tubular) titanium oxide are held on the assumption that water in these pores can decompose easier than on a flat surface. Although Seitmagzimov and Pak[8] demonstrated that exactly in narrow nanoporoes the opposite phenomena can happen. Simultaneously, there have been attempts to give a definite answer-to what extent can geometry and form of pores influence photoelectrochemical properties of titanium dioxide[9]. In view of the above, we have attempted to answer these questions.

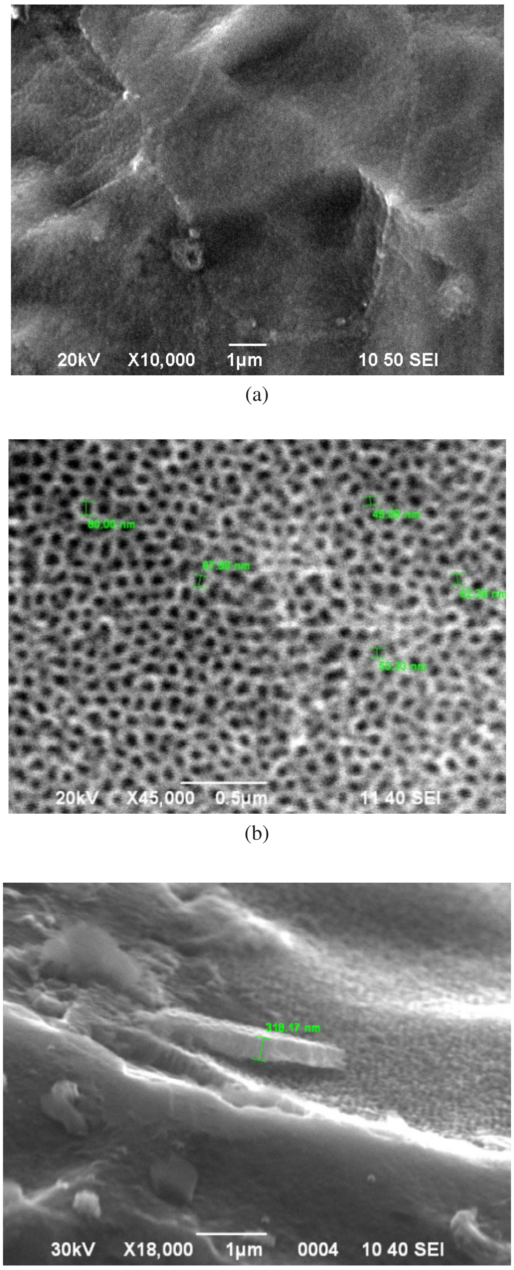
EXPERIMENTAL

The most rational way of obtaining titanium oxide nanotubes is electrochemical oxidation of metallic titanium in different electrolytes. This gave a number of advantages in formation of a set of properties of nanotubes *i.e.*, the possibility of regulation of nanotube thickness (length) in a wide diapason, constancy of chemical composition of the environment and substrate, the possibility of regulation of titanium oxide pores by shape and size. For investigation we used 2 cm × 2 cm titanium plates that were 2 mm thick with a conductor made from the same titanium. Formation of titanium oxide films was performed by the anodizing method in electrolyte of the following composition: (a) for nonporous films: 0.2 M solution of sulphuric acid and 0.05 M solution of ammonium fluoride, voltage on the tank clamps-20 V, (b) for porous films: 0.1 M solution of sulphuric acid and 0.05 M solution of ammonium fluoride, voltage on the tank clamps- 20 V; the time of anodization varied from 5 s to 300 min. Since anodic titanium oxide is X-ray amorphous and its photocatalytic properties in this case are very low, anodized plates were annealed in air at 50 ºC, after which current-voltage characteristics were taken.

RESULTS AND DISCUSSION

Anodic photocurrents of titanium oxide electrodes were measured on the three-electrode scheme with a platinum wire for counter electrode and silver-chloride control electrode. For illumination of electrodes we used a ultra-violet lamp DRT-230 and a visible light lamp-xenon with a N3 cap.

Photomicrographs were taken using electron-scan microscope JSM-6490LV (JEOL, Japan). Differences in morphology of both types of films can be seen in Fig. 1.



(a)

(b)

(c)

Fig. 1. Images of nonporous (a) and porous (b) titanium oxide, chip (c) of titanium oxide film with 318 nm thickness at 40 min anodization

As can be seen in the picture, porous film has cylindric pores with average pore diameter of 60-80 nm. The thickness of porous film equal approximately to 300-320 nm at 40 min anodization can also be observed on the chip of such film.

Fig. 2 shows the thickness values of porous films at different anodization times taken from film chips. One thing is clear-there is no direct dependency of the film thickness on the time of anodization. Firstly this is due to the electrolyte solution undergoing changes over time because anodization was conducted in limited volume of electrolyte, so the speed of film growth varied significantly. Nevertheless, films with oxide layer thickness from 320 nm (40 min anodization) to 1200-1300 nm (300 min anodization) were grown.

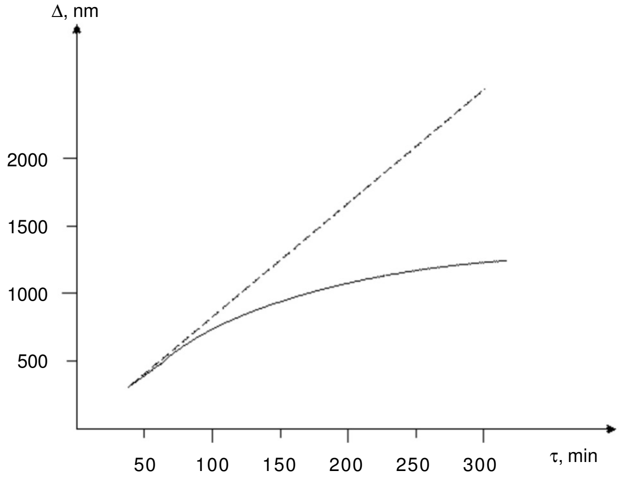


Fig. 2. Dependence of the thickness of anodized titanium oxide films on the time of anodization

Fig. 3 shows the values of photocurrent of porous films under UV illumination in 1 M solution KOH. We can see that with increase in thickness of titanium oxide (the anodization time) the values of photocurrents in general increase almost 3 times. From these results one could claim that the length of titanium oxide nanotubes definitely affects the photocatalytic properties of titanium oxide. However, as it appeared, not everything is so simple according to the data of raster electronic microscopy.

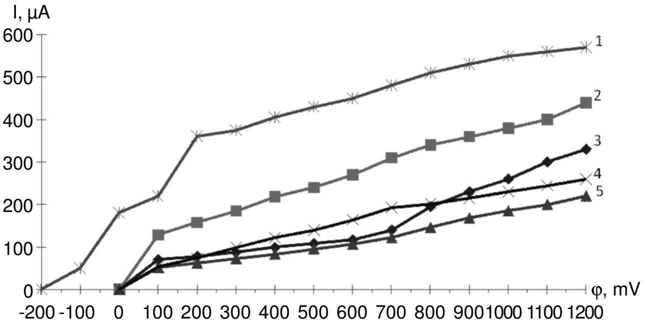
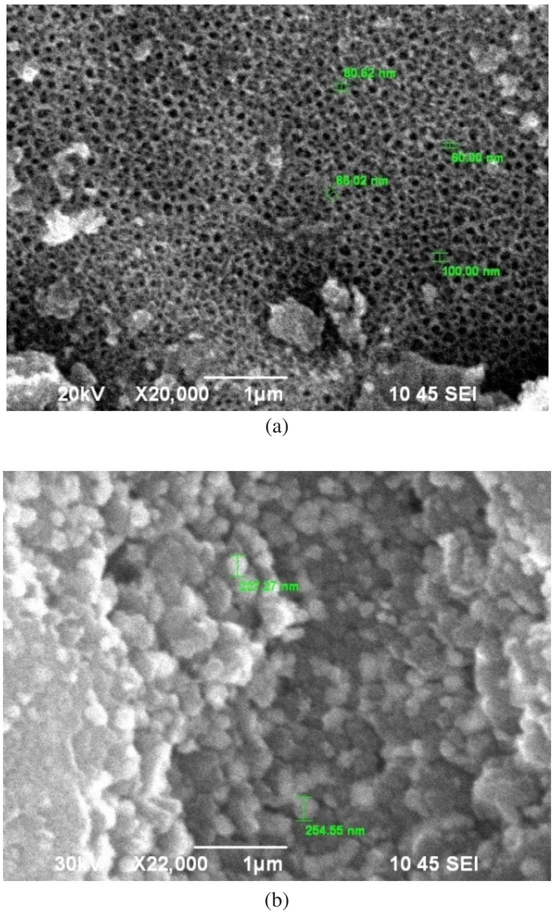


Fig. 3. Influence of anodization time [(1)-300, (2)-90, (3)-40, (4)-180, (5)-120 min] on photocurrents of titanium oxide in 1 M solution of KOH

It is noted that after prolonged anodization along with growth in film thickness a change in morphology of the porous layer takes place [Fig. 4(a)]. After 3 h of anodization under unchanged conditions, not only the size of nanopores changes, but also a sort of aeration of anodic oxide nanostructure takes place. Also the shape of the curve of anodic photocurrent changes-maximum values of photocurrent are observed during more prolonged changes in photoelectrode potential. Further anodization-up to 5 h-leads to complete regeneration of the layer of nanotubes into porous globular structure [Fig. 4(b)]. It is presumed that regeneration of films takes places after electrolyte pH changes significantly (increases) as a result of continuous anodization. In the state of acid "shortage" the



(a)

(b)

Fig. 4. Change in morphology of anodic titanium oxide film structure after 3(a) and 5(b) hours of anodization

titanium dioxide film changes its structure under the influence of ions of dissociated salt NH_4F. Analogous changes were noted by Alivov and Fan[10], where regeneration of tubular titanium dioxide into globular takes place in a gaseous phase under the influence of NH_4F.

It follows from Figs. 3-5 that change in anodic oxide structure from nanotubular to nanoglobular structure results in a sharp increase of photo-electric current. Also the area of beginning of anodic photo-electric current shifts to the side of negative potentials of photoelectrodes in general by 200 mV.

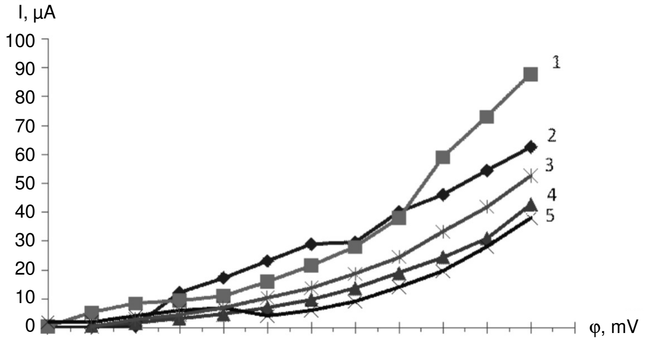


Fig. 5. Current-voltage characteristics of titanium oxide films in 1 M KOH obtained from nonporous anodization under different anodization time [(1)-60, (2)-600, (3)-5, (4)-20, (5)-10 seconds] with xenon illumination

The following question arises-are nanotubes really that necessary and what should be their optimal length? The data we obtained, along with the data in research[2], implies that in formation of photocatalytic properties of titanium oxide the smallest role is played by its porous structure. Such parameters as conductivity of the oxide layer, mobility of carriers, flat band potential and defect concentration should be at the forefront. These parameters are formed in the process of titanium anodization when the oxide layer in some conditions or others obtains the necessary qualities. Everything else held constant, when the above noted electrophysical parameters of the film are optimized, then the porous structure of oxide can be optimized while keeping electrophysical parameters. But, as a rule, when porous structure of semiconductor oxide is optimized, the researchers often make drastic changes in electrophysical properties of this film[2] and it can be difficult to interpret such results definitively. A direct example of these discussions is optimization of thickness of nonporous film of titanium oxide and values of photocurrents obtained on it (Fig. 5 and 6).

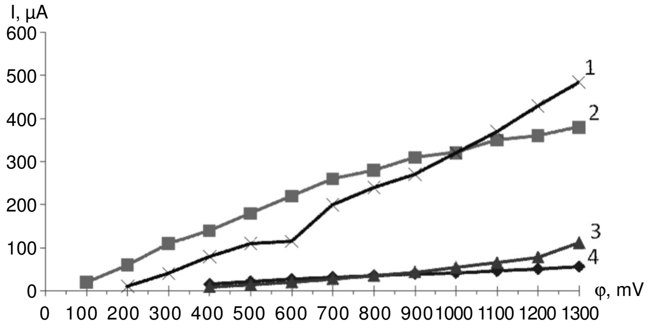


Fig. 6. Current-voltage characteristics of titanium oxide electrodes in 1 M solution of KOH under UV ((1)-1 min, nonporous film and (2)-40 min, porous film) and xenon ((3)-1 min, nonporous film and (4)-40 min, porous film) illumination

The differences in morphology of films are noted earlier [Fig. 1(a-b)]. We were not able to obtain chips of ultrathin nonporous films after 1 min anodization, which had reached maximum photocurrents.

Optimized in such a way, the thickness of anodic oxide (1 min anodization) of nonporous type showed photoelectrochemical characteristics practically identical to the porous type film (Fig. 6), in UV as well as visible light.

Thus, we can claim that porous structure is not one of the determining factors in formation of photocatalytic properties of titanium oxide electrodes. The major factors in this case are the bulk charge area in semiconductor (depleted layer) and conductivity of the whole volume of semiconductor. If we were to evaluate the layer of such bulk charge according to Gurevich and Pleskov[11] then, overlooking the fall in potential in Helmholz layer and the diffusion part of double electric layer, the border of bulk charge can be determined from proportion:

$$L_{sc} = \left[\frac{(\varepsilon_{sc} V_{sc})}{(2\pi N_d)}\right]^{1/2}$$

where ε_{sc}: Dielectric permeability, V_{sc}: fall in potential in bulk charge layer, N_d: concentration of carriers.

The evaluation conducted by us earlier in[12] for the bulk charge layer of semiconductor using experimentally obtained data for ultrathin film TiO_2 comprised 15 nm, which is close to the value of anodic oxide layer thickness of 8-15 nm with anodizing time of 1 min. Further increase in thickness of anodic oxide layer leads to the growth of ohmic losses in the semiconductor layer (TiO_2) and fall in photocurrent values (Fig. 6). While lesser thickness does not allow for the depleted layer to form in semiconductor, which also leads to the fall in photocurrent values.

Conclusion

Thus, based on the results of present investigations it is concluded the following: It is not essential to use films with tubular structure to obtain high values of photocurrents. All processes of electrochemical decomposition of water are determined by the area of semiconductor volume charge and sorption processes in double electric layer at the border of semiconductor and electrolyte. Therefore, in our opinion, the thickness of oxide layer should be minimal and herewith the surface should be maximal. This is possible with globular structure of the oxide layer.

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