Estimation of Local and Long-range Ordering of the Structure of TiO_2 Nanotubes

N.B. Kondrikov, P.L. Titov, S.A. Shchegoleva, V.V. Korochentcev, I.V. Stepanov
Far Eastern Federal University, Vladivostok, Russia, e-mail: sveta170@bk.ru

Introduction

Nanostructured and microstructured materials, whose principally new physical properties result from the developed surface and quantum-size effects, constitute the group of promising objects of the advanced materials science. Porous titanium oxides are well-known representatives of this type of materials. Recently, adsorption, optical, electrical, catalytic, and photocatalytic properties of TiO_2 have attracted a special interest of researchers.

Up to present, a number of efficient methods of creating nanostructures, including those based on the self-organization principle, have been developed. Self-organization of titanium oxide can be attained by its anodization in acids (for instance, sulfuric or phosphoric), most often, in fluorine-containing electrolytes, since dissolution proceeds there through formation of fluoride complexes. Anodic oxidation of titanium in a fluorine-containing electrolyte enables one to obtain nanostructured coatings consisting of TiO_2 nanotubes, whose parameters can be controlled varying the oxidation conditions.

Experiment

Anodic oxidation of titanium was performed in a two-electrode electrochemical cell using a B5-49 direct current source. Pt served as an auxiliary electrode, the Ti plate was a working electrode.

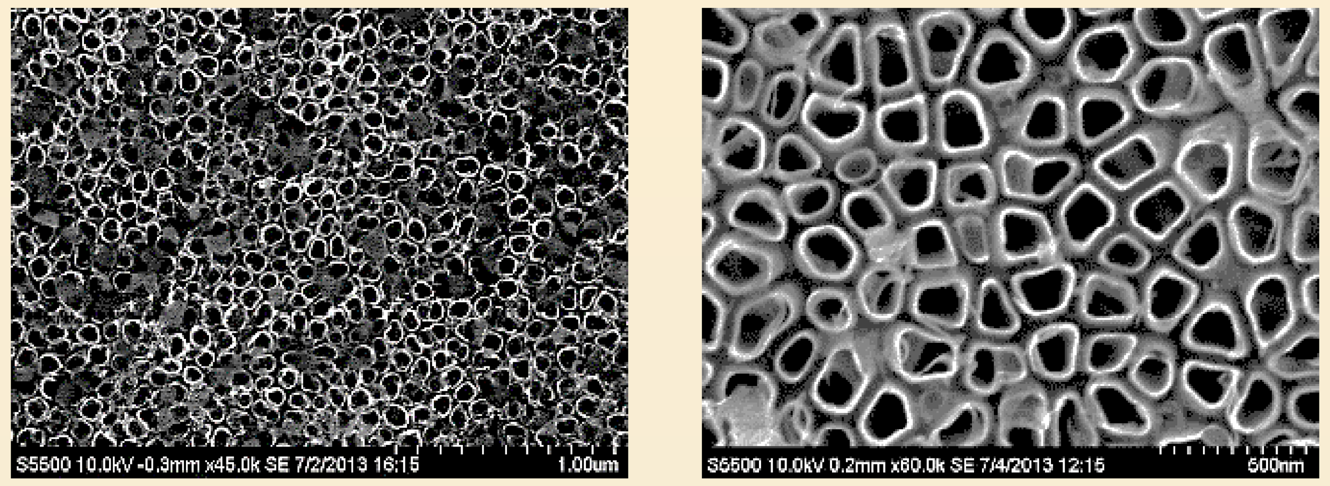
The electrolyte temperature during anodization was maintained constant and equal to 20 °C using a thermostat. To obtain the nanotubular structure of titanium anodes, an aqueous solution of $NH_4F{\cdot}HF$ with addition of Na_2SO_4 and complexing agents was used. Thereafter, for the sake of properties modification, the obtained Ti/TiO_2(nano) systems were held in an aqueous solution of H_2PtCl_6 of the concentration $3{\cdot}10^{-2}$ $mol{\cdot}l^{-1}$ (Ti/TiO_2(nano),Pt) for 1 h, dried, and annealed in a muffle furnace at 500 °C for 4 h (Table).

The surface structure was investigated on a Hitachi S-5500 scanning electron microscope (SEM) (Hitachi, Japan).

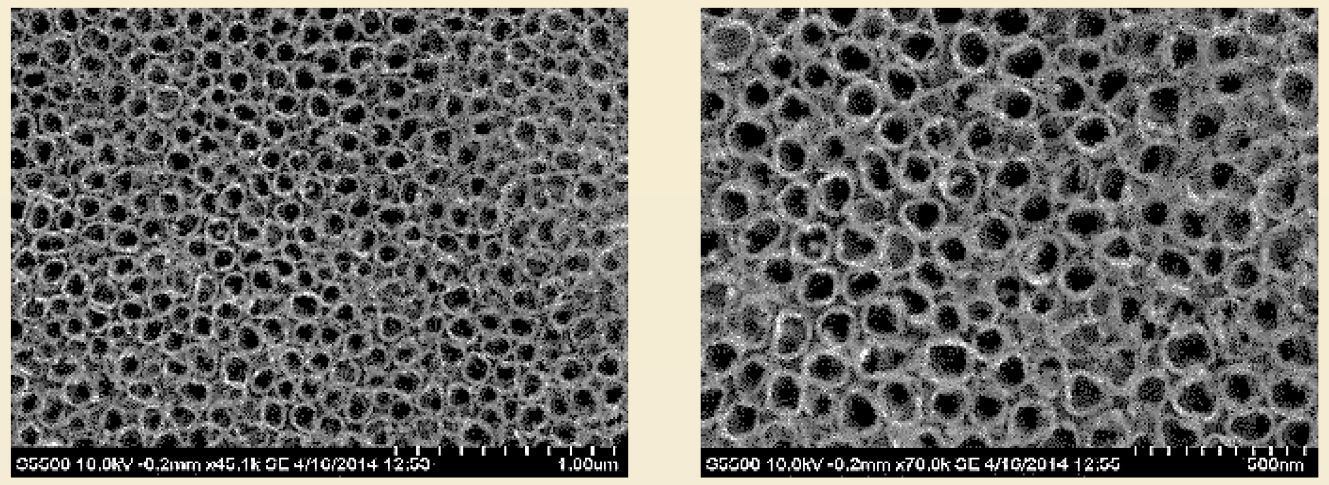
Modification conditions

Sample	Concentration H_2PtCl_6, M	Anneal time, h
No. 1	-	-
No. 2	-	4
No. 3	$3{\cdot}10^{-2}$	-
No. 4	$3{\cdot}10^{-2}$	4

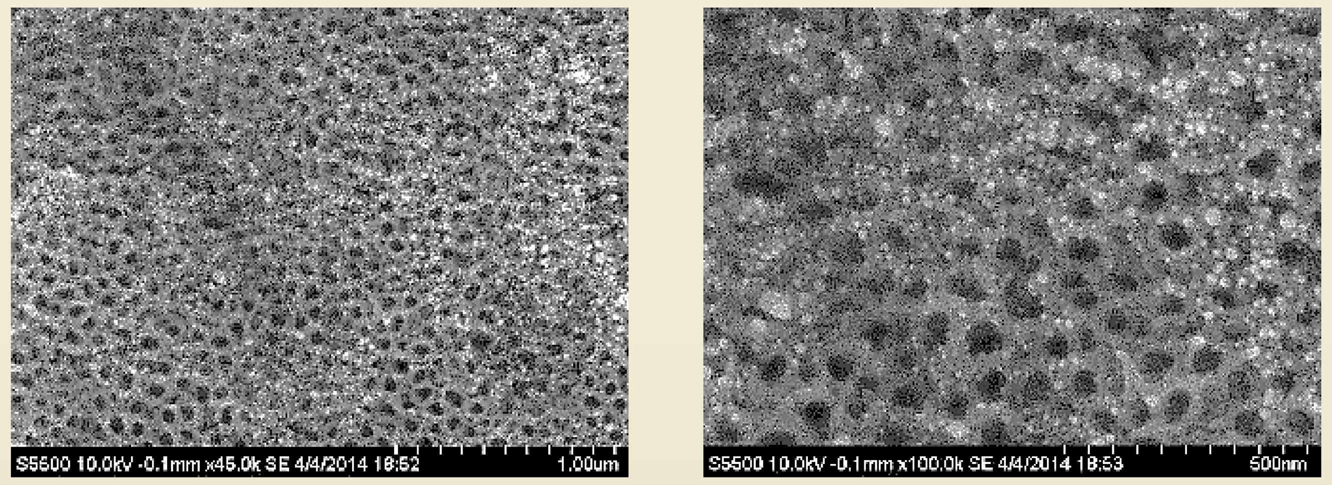
SEM images of electrodes surface



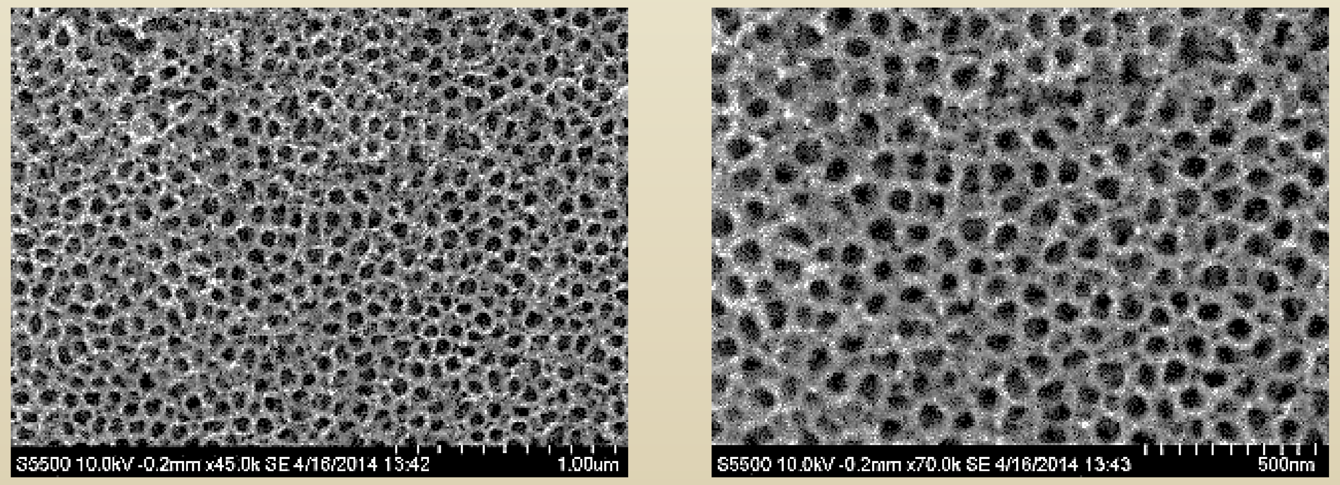
Sample No.1



Sample No.2 (annealing)



Sample No.3 (modification)



Sample No.4 (modification + annealing)

Sample No.1

The nanotubes with well-defined boundaries of a regular form are observed. The sufficiently great number of boundaries approximates in the form to convex polygons with well defined directions of sides. One can observe the near correct configurations in the form of square, rectangle and, less frequently, hexagon.

Sample No.2

After annealing, the boundaries of nanotubes become blurred and widen. However, one can still identify the boundaries associated with isolated nanotubes. Although the structure gets worse and becomes in whole more uneven, but the short-range local order in the relative positioning of nanotubes is preserved.

Sample No.3

The presence of the additional component changes materially the surface structure. Pt nanoparticles are observed over the whole sample surface, basically, at the boundaries of nanotubes. The nanotubes, in contrast to the sample No.1, have no individual boundaries. The neighbor nanotubes are separated by common and, at the same time, sufficiently wide boundaries (walls). It can be said that the structure of the nanotube array is in completely stochastically uniform.

Sample No.4

After annealing, the common structure of the nanotube array acquires a sharpness. The boundaries of nanotubes become essentially thinner. The image, as compared to the sample No. 3, is more contrast. The observed quantity of the platinum nanoparticles decreases essentially as compared to the sample No.3. In such case, the walls, as before annealing, are common for the neighbor nanotubes.

Results

- The titanium oxide nanotubes obtained when using the aqueous solution of $NH_4F{\cdot}HF$ with addition of Na_2SO_4 and complexing agents (sample No.1) have sufficiently well-defined structure
- The modification with Pt (sample No.3) results in changing the character of the nanotube structure and “coarseness”, “adhesion” of the boundaries of nanotubes with disturbance of geometry as well as appearance of large number of the Pt nanoparticles
- The annealing of these samples leads to different results. For unmodified sample (No.2), the form of the nanotube sections became less delineated. The SEM-image “became blurred” and local ordering was less pronounced. On the contrary, the annealing of the modified sample has resulted in the thinning of nanotubes boundaries and manifestation of this structure