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The Growth of TiO2 Nanostructures Prepared by Anodization in Combination with Hydrothermal Method on the Ti Foil

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Abstract. We have investigated TiO2 nanostructures prepared by anodization in conjunction with hydrothermal method using Ti metal plates. The TiO2 nanoporus were fabricated by electrochemical anodization in a NH4F/EG4/H2O electrolyte system. Ultrasonic wave was used to clean the surface of TiO2 nanoporus in the medium of water after completing the anodization. After drying in air, the nanoporusarrays were calcined at 450 °C for 2 h in air. The TiO2 nanostructures were converted by hydrothermal in air.The TiO2 nanostructures were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD patterns show the TiO2 anatase structure. SEM images indicate that the TiO2 structures depend on preparation temperatures. The density of TiO2 nanostructures increases as the time increases. The growth of TiO2 nanostructures was observed to be times dependence. The nanostructures are nanowires and nanospikes when the peraring time was 18 h, nanoflowers when the preparing time was 24h. This approach provides the capability of creating patterned 1D TiO2 nanowires at 18h. The diameter of TiO2 nanowires varies from 20 nm to 25 nm and length of several 250 nm.

1 Introduction

TiO_2 nanostructures have attracted great attention due to their unique ability to form a variety of nanostructures such as nanowires, nanoribbons, nanobelts, nanospheres and nanofibers and their properties. A special attention is focused on the TiO_2 in the forms of nanorods and nanorod arrays vertically arranged with respect to the substrate because of their unique properties. The ordered TiO_2 nanostructures are expected to enhance the performance of various technologically important devices such as electroluminescent devices [1], photocatalysis [2] gas sensors [3], and third generation of solar cells [4-5]. In this way, we prepared TiO_2 on the Zn plates with 1D material constructed surface by this novel simple method. Recently, a new approach for the preparation of TiO_2 nano tube on a patterned Ti foil has been developed by means of two step anodization process [6]. In the first step, potentiostatic anodization is applied and subsequently the developed TiO_2 nano tube are detached from the titanium foil leaving behind a pattern, where thenew tubes grow during the second anodization step [7]. Titania nanotubes prepared by the two step potentiostatic potentiostatic method, are organized in well ordered films and free of surface defects [8]. The potentiostatic potentiostatic preparation of TiO_2 nano tube has been further exploited for the guided anodization and fabrication of asymmetrical nanotubes onto patterned Ti foils treated by focused ionbeam lithography [9].The hydrothermal method is widely applied in titania nanotubes production because of its many advantages, such as high reactivity, lowenergy requirement, relatively non-polluting set-up and simple control of the aqueous solution [10]. The reaction pathway is very sensitive to the experimental conditions, such as pH, temperature and hydrothermal treatment time, but the technique achieves a high yield of titania nanotubes cheaply and in a relatively simpler manner under optimized conditions. There are three main reaction steps in hydrothermal method such as generation of the alkaline titanate nanotubes substitution of alkali ions with protons and heat dehydration reactions in air [11]. The hydrothermal method is amenable to the preparation of TiO_2 nanotubes with different crystallite phases such as the anatase, brookite, monoclinic and rutile phases [12].

2 Experimental

In the first step, preparation titanium foils (Jinsheng std.ASTMB265 Shaanxi company china, 0.3 mm) were used as substrate for the anodization. Prior to the anodization, pieces (radius 1.8 cm) of the Ti foils were ultrasonicated in acetone, 2-propanol and methanol for 10 min, then washed with water and dried under nitrogen. Anodization was performed in an appropriate

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electrochemical cell, made of teflon, at ambient temperature [13-14]. The working area was 10.18 cm^2 and the distance between the anode (Ti foil) and the cathode (Pt mesh) was set at 1.5 cm. The titanium foil were anodized at 50 V for 1 h in a fluorinated solution of ethylene glycol (0.25wt%NH_4F, 10wt% DI H_2O), followed by a brief cleaning with deionized (DI) water. The titanium nanostructures were further cleaned by dipping the anodes in a beaker of DI water under ultrasonication for 1-3 s. After drying in air, the nanotubes were calcined at 450 °C for 2 h in air. In the second step, the synthesis method of nanostructure was basically the same as in previous works [15]. A commercial, TiO_2 powder (commercial; a mixture of crystalline rutile and anatase phases) was used as a starting material. In a typical synthesis, 1 g of TiO_2 powder wascrushedwith 25 mL of 10 M NaOH aqueous solution were putt into a teflon- lined stainless autoclave and then heated at 180 ^{o}C for 6 h, 12 h, 18 h, 24 h and 46 h. The samples were cooled down to room temperature.. The treated samples were washed thoroughly with DI water and 0.1 mol/L HCl aqueous solutions until the pH value of the washing solution lower than 7 and dried at 60 ^{o}C. The structural and chemical natures of the obtained materials were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM).

3 Results and discussion

The samples were synthesized under different periods of time and were assinged as 6h, 12h, 18 h, 24 h, and 46h. Ti-anealed (substrates for the anodization) and TiO_2crystal structure were used for comparision purpose. XRD patterns are shown in Fig. 1.

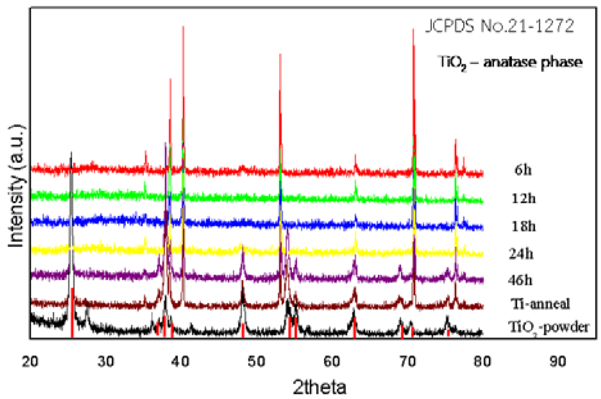
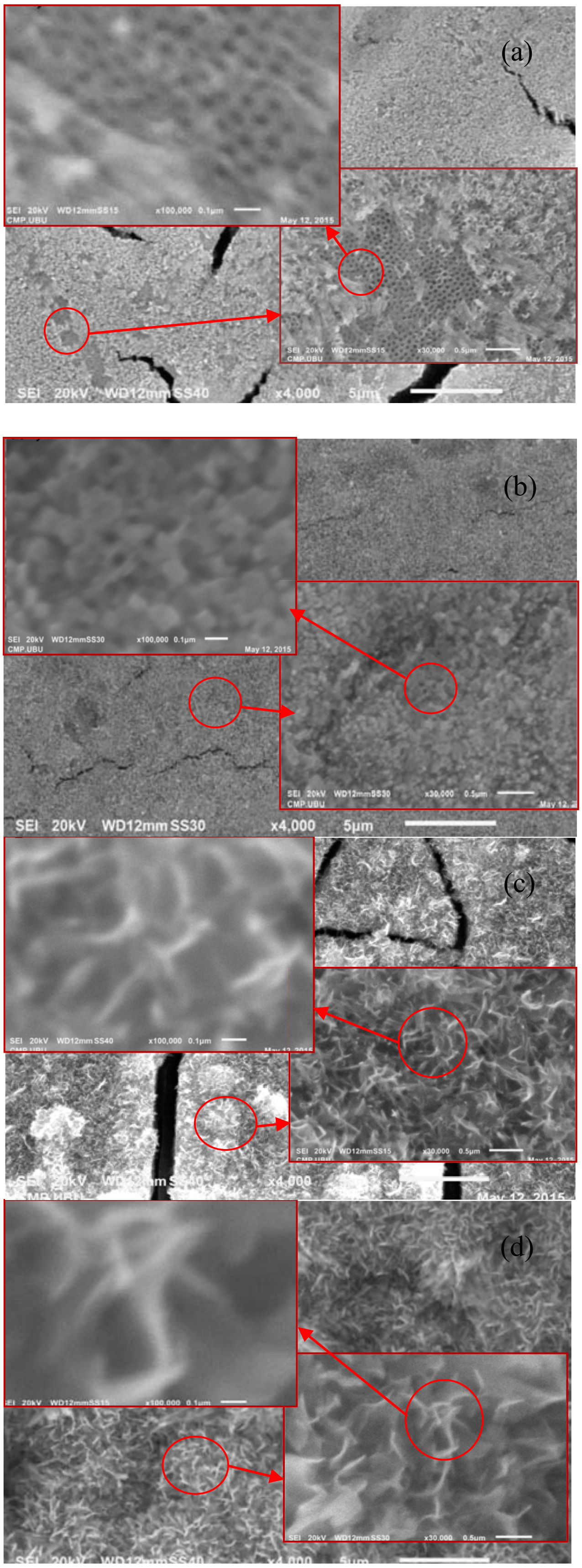


Figure 1. XRD patterns of the samples were synthesized under at time and were as singed as 6h 12h, 18 h, 24 h, 46 h, Ti-anneal (substrate for the anodization) and TiO_2 powder.

All the peaks are sharp and strong in intensity indicating the highly crystalline in nature of the reaction products. TiO_2anatase phase was observed in the XRD patterns and diffraction data in agreement with JCPDS card of TiO_2 (JCPDS No. 21-1272), which indicated that the samples on the substrates were TiO2 and partially the crystalline of Ti-annealed substrates. The peaks located at 25.4, 37.8, 48.0, 54.5^{o}correspond to the (101), (004), (200), (105 and 211) planes of the anatase phase (JCPDS 21-1272), and the peaks located at 27.5, 36.1, 54.4^{o} correspond to the (110), (101), (211) planes of the rutile phase (JCPDS 21-1276), respectively.



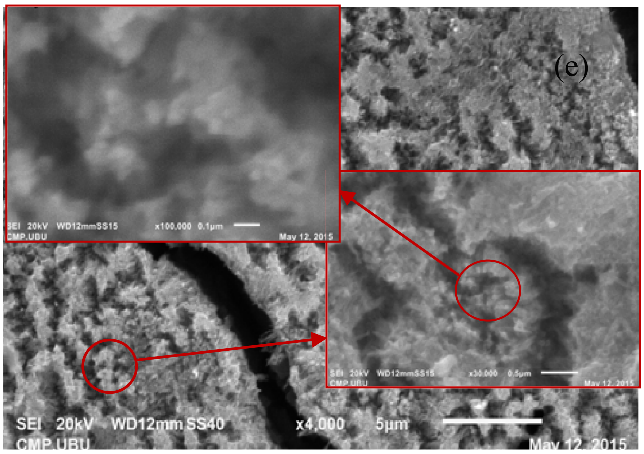


Figure 2. The side view SEM images of the samples,prepared using the heated at 180 ^{o}C for (a) 6h (b) 12h (c) 18 h (d) 24 h and (e) 46 h.

The top-view SEM images clearly show that anodized titania nanotubes with hydrothermal method are nanostructures.Their crystals form porosity and nanotube samples prepared by anodization.The pictures also show that when longer period of time of hydrothermal process was used toanneal, the nanocrystal structures increase. We found that the crystal structures become nanowires and nanospike.The nanowires and nanospikesare denser and vertically more scattered whenannealing temperatures of the hydrothermal process of180 ^{o}C for 18 hand 24 h.

4 Conclusion

TiO_2nanowires and nanospikeswere successfully fabricated by anodization in combination with hydrothermal method of Ti foil at 180 ^{o}C for 18 h and 24 h. The structures depend on time and the temperature of hydrothermal process. The diameter of TiO_2 nanowires varies from 20 nm to 50 nm and length of several 100 micrometers.

Acknowledgements

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