Journal of Alloys and Compounds 597 (2014) 101–109

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Characterization and photocatalytic activity of large-area single crystalline anatase TiO_2 nanotube films hydrothermal synthesized on Plasma electrolytic oxidation seed layers

Qiang Luo [a], Qizhou Cai [a,*], Xinwei Li [a], Xidi Chen [a,b]

[a] State Key Lab of Material Processing and Dies & Mould Technology, Huazhong University of Science and Technology, Wuhan 430074, China
[b] Institute of Functional Materials, Wuyi University, Jiangmen 529020, China

ARTICLE INFO

Article history:
Received 14 November 2013
Received in revised form 26 January 2014
Accepted 28 January 2014
Available online 5 February 2014

Keywords:
TiO_2 nanotube film
Large-area
Hydrothermal
Plasma electrolytic oxidation
Photocatalytic

ABSTRACT

The layer produced by Plasma electrolytic oxidation technique was used as seed layer for hydrothermal synthesis of large-area TiO_2 nanotube film in this paper. The effects of hydrothermal parameters on the surface morphologies of films were investigated by field emission scanning electron microscopy (FSEM). The results showed that the surface morphologies of films can be easily changed by varying the NaOH concentration, reaction temperature and reaction time. In addition, the effect of calcination temperature on the morphologies, crystal structure, photophysical properties and photocatalytic activity of the nanotube films were also studied using field emission scanning electron microscopy (FSEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), UV–Vis spectrophotometry and Fluorescence spectrophotometry. Calcination resulted in crystallization of the nanotubes from amorphous state to single-crystalline anatase phase. Furthermore, the increase of calcination temperature was beneficial to the improvement of crystallization degree. However, the nanotubes completely collapsed to form short nanorods when the calcination temperature increased to 700 °C. The TiO_2 nanotube film calcined at 600 °C exhibited the narrowest band gap energy, the strongest UV light absorption, the weakest band–band PL intensity and the best photocatalytic activity.

1. Introduction

Titanium oxide (TiO_2) nanostructured materials have attracted tremendous attention in a lot of fields, such as in photocatalysis [1,2], dye-sensitized solar cell [3], water splitting catalysts for hydrogen generation [4], and electrochemical sensing [5]. TiO_2 nanotubes possess remarkably superior properties in these applications compared with other forms of nanocrystalline TiO_2 because of their high surface area and charge transport property [6]. Furthermore, the tube-like structure can supply sufficiently reactive points for the reaction [7]. Therefore, synthesis, properties and applications of TiO_2 nanotubes has been intensively investigated by scientists in recent years [8]. A number of methods have been developed for preparing TiO_2 nanotubes, including anodic oxidation [9–12], template-based approaches [13,14] and hydrothermal technique [15].

Since Kasuga et al. [16] firstly reported the preparation of TiO_2 nanotubes through hydrothermal method, the preparation of TiO_2 nanotubes by hydrothermal method has caught the attention of the scientific community due to its simplicity and easy operation. Wang et al. [17] investigated the formation mechanism of nanotubes, which can be explained as a process of three-dimensional crystal transforming to lamellar structure and then rolling to form nanotubes. Sreekantan and Wei [18] studied the effect of NaOH to TiO_2 ratio, reaction temperature, time and annealing temperature on the structural characteristic of the nanotubes. The general principle of this method is the reaction between the seeds and highly concentrated NaOH aqueous solution under hydrothermal environment, followed by acid treatment and calcination. However, most of TiO_2 nanotubes prepared by hydrothermal treatment are obtained in powder form, which is difficult for practical application due to that powder is hard to separate, recycle and reuse. Therefore, the development of TiO_2 nanotube film from the large-area seed is very useful for practical application. Some scientists have successfully synthesized the TiO_2 nanotube film by hydrothermal method in recent years. For example, Yang et al. [19] prepared the nanotube-like TiO_2 by oxidizing the surface of a titanium sheet through calcining under an atmosphere of air to form rutile TiO_2 and then treating it to form the tubular structure in NaOH aqueous solution. Losilla et al. [20] prepared TiO_2 nanotube films by pulsed

* Corresponding author.
E-mail address: caiqizhou@hust.edu.cn (Q. Cai).

http://dx.doi.org/10.1016/j.jallcom.2014.01.216
0925-8388/

Table 1
Parameters of hydrothermal treatment and calcination.

No.	NaOH concentration (mol dm^{-3})	Reaction temperature (°C)	Reaction time (h)	Calcination temperature (°C)
1	1	180	10	–
2	4	180	10	–
3	7	180	10	–
4	10	180	10	–
5	7	120	10	–
6	7	150	10	–
7	7	210	10	–
8	7	180	1	–
9	7	180	4	–
10	7	180	7	–
11	7	180	13	–
12	7	180	10	400
13	7	180	10	500
14	7	180	10	600
15	7	180	10	700

laser deposition of P25 and P90 TiO_2 nanoparticles onto stainless steel foils followed by a hydrothermal treatment. Finally, Bavykin et al. [21] prepared the films of random titanate nanotubes obtained from anodized TiO_2 nanotubes array via hydrothermal route in order to control over titanate nanotube agglomerates.

Plasma electrolytic oxidation (PEO) technique has been widely used to prepare the oxide films on the valve metals such as Al, Mg and Ti [22–25]. The distinct properties of oxide films formed through PEO include porous structure, remarkable thickness and well adhesion to the substrates [26], which allow the TiO_2 film produced through PEO to become a potential seed layer for the synthesis of TiO_2 nanotube film. Therefore, a novel and useful method to prepare TiO_2 nanotube films with well adhesion and large-area through hydrothermal method on the seed layers prepared by PEO technique was reported in this study. This method is a hybrid technique which includes the initial nucleation of seed layer controlled by PEO and subsequent growth of nanostructures produced by the hydrothermal method. The effects of different experimental conditions, such as NaOH concentration, reaction temperature, reaction time and calcination temperature on the morphology and crystal structure of the nanotube films were also investigated. In addition, the effect of calcination temperation on the photophysical properties and photocatalytic activity of TiO_2 nanotube films was studied.

2. Experimental

2.1. Preparation of seed layers

The pure Ti sheet with thickness of 2 mm was selected as anode and the reaction area was fixed as 20 × 20 mm. Prior to PEO, the Ti sheets were polished with emery papers (#180 ~ #800 grit), degreased using acetone and then rinsed with distilled water. The stainless steel plate was used as cathode. The equipment used in the PEO process consisted of an AC power supply, an electrolyte cell, a stirring system, a cooling system and an exhaust system. The positive voltage, negative voltage, frequency and duty cycle were 400 V, −50 V, 700 Hz and 0.3, respectively. Na_3PO_4 aqueous solution with the concentration of 0.05 mol dm^{-3} was selected as electrolyte. The treatment period was 10 min and the temperature of electrolyte was kept under 40 °C. The prepared seed layers were rinsed with distilled water and dried with hot air.

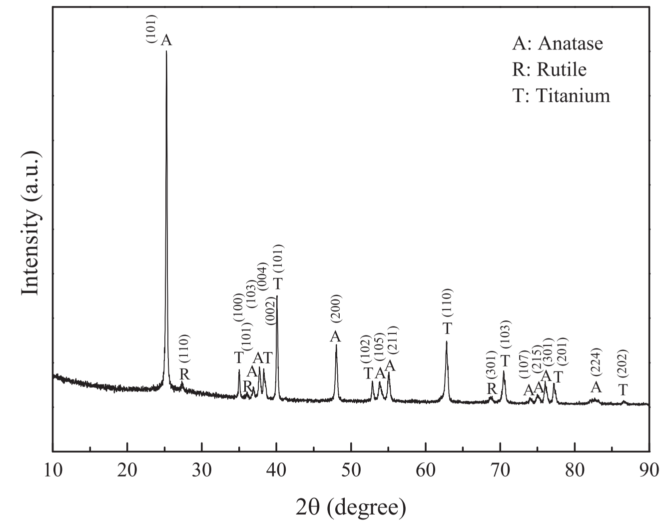

Fig. 2. XRD pattern of the seed layer.

2.2. Preparation of nanotube films

The seed layers were placed against the wall of a 210 mL Teflon-lined stainless steel autoclave filled with 100 mL of aqueous NaOH solution and then the sealed autoclave was heated in an electric oven. After the hydrothermal treatment, the as-synthesized films were washed with distilled water, immersed in 100 mL of 0.1 mol dm^{-3} HCl aqueous solution for 10 min and then washed with distilled water again. Finally, the as-synthesized films were calcined at 400, 500, 600, 700 °C in air for 1 h. The parameters of hydrothermal treatment and calcination are listed in Table 1.

2.3. Analysis of nanotube films

The morphologies of films were characterized by field emission scanning electron microscopy (FSEM, FEI Sirion 200, FEI Company, Eindhoven, Netherlands) and transmission electron microscopy (TEM, JEM 2100, JEOL, Tokyo, Japan). The composition of the nanotube films were analyzed with energy dispersive X-ray (EDX) detector incorporated into the FSEM. The crystal structure of nanotube films were determined by using X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V., Almelo, Netherlands). The UV–Vis absorption spectra of TiO_2 nanotube films were recorded on UV–Vis spectrophotometer (UV-2550, Shimadzu, Kyoto, Japan) with an integrating sphere attachment. Photoluminescence spectra of TiO_2 nanotube films were measured with Fluorescence spectrophotometer (FP-6500, Jasco, Tokyo, Japan).

2.4. Evaluation of photocatalytic activity

Photocatalytic activities of the TiO_2 nanotube films were measured by monitoring photodegradation of methylene blue (MB) in aqueous solution. Films were immersed into 10 mL of the aqueous MB solution (10 mg dm^{-3}) for 30 min prior to

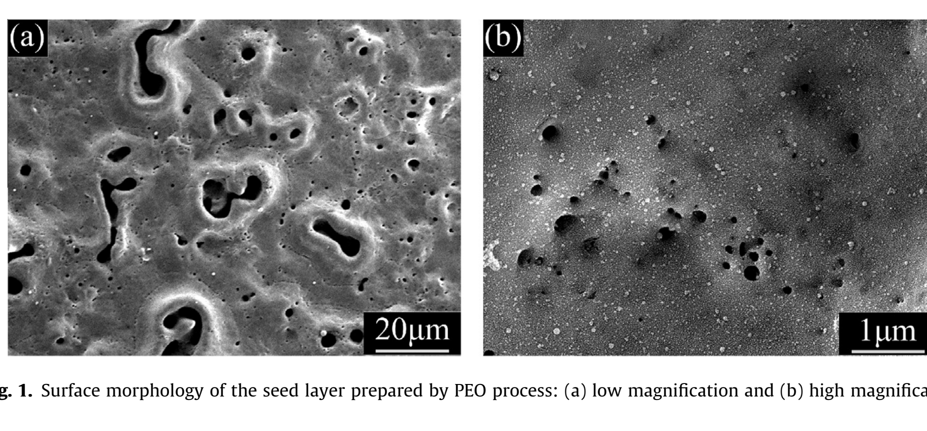

Fig. 1. Surface morphology of the seed layer prepared by PEO process: (a) low magnification and (b) high magnification.