Applied Surface Science 280 (2013) 523–529

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Nitrogen doped TiO_2 nanotube arrays with high photoelectrochemical activity for photocatalytic applications

Bao Yuan[a,b], Yan Wang[a,b,*], Haidong Bian[a,b], Tiankuo Shen[a,b],
Yucheng Wu[a,c,*], Zhong Chen[a,c]

[a] *Laboratory of Functional Nanomaterials and Devices, School of Materials Science and Engineering, Hefei University of Technology, Hefei, 230009, China*
[b] *Key Laboratory of Advanced Functional Materials and Devices, Hefei University of Technology, Hefei, 230009, China*
[c] *School of Materials Science & Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore*

ARTICLE INFO

Article history:
Received 21 December 2012
Received in revised form 7 April 2013
Accepted 6 May 2013
Available online 20 May 2013

Keywords:
Anodization
Nitrogen doped TiO_2 nanotube arrays
Methyl orange
Photocurrent
Photocatalytic property

ABSTRACT

Nitrogen doped TiO_2 nanotube arrays (N-TNAs) were prepared by immersing TNAs in 1 M $NH_3{\cdot}H_2O$ solution and then annealing in different temperatures. The morphology, structure and composition of the N-TNAs were characterized by field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and UV–vis spectroscopy, respectively. Effects of annealing temperatures on structure, photocatalytic properties, and the crystal structure transformation process of the N-TNAs were discussed. Photocatalytic properties of the N-TNAs were evaluated in term of the degradation of methyl orange (MO) under UV light and visible light, and the photocurrent of N-TNAs were tested by electrochemical workstation. The XPS results showed that the N-TNAs were achieved by interstitial doping and substitutional doping, and the FESEM results showed the morphology was not changed after doping process. Compared with the pure TNAs, the N-TNAs annealed at 500 °C for 2 h with a mixed phase of anatase and rutile exhibited higher photocatalytic degradation activity to MO. Furthermore, the photocatalytic mechanism of organic pollutants degradation (MO) was discussed based on our experiments.

1. Introduction

Nanostructured materials, especially the highly ordered nanotube materials, have attracted a great deal of attention in various fields. In recent decades, the preparation of nanomaterials has diversified with the development of science and technology. Advances in the nanoscale technology [1] facilitated the fabrication of highly ordered and multidimensional structured materials. Many efforts have focused on new synthesis methods and photoelectrochemical properties of the tubular structure, large specific surface area, oriented charge transfer channel and the other distinct properties. TiO_2 nanotube arrays as nanostructure semiconductor compound have attracted increasing research interests in photocatalysis [2–5], dye sensitized solar cells [6,7], gas sensors [8,9], biomedical applications [10] and so on. Particularly, TNAs are expected to exhibit better photocatalytic properties compared with nanoparticles or other forms of titanium dioxide [11], due to their high specific surface area, short diffusion path and high activity in the band-edge positions, which make it more suitable to be used as catalyst [12].

Consequently, the synthesis or modification of TiO_2 nanotube arrays have been widely studied [13,14], and considerable efforts of fabrication TiO_2 nanotubes such as hydrothermal treatment [15], template-deposition [16], sonoelectrochemical method [17] and anodic oxidation [18,19] have been developed. Gong and co-workers [20] pioneered the synthesis of vertically ordered TiO_2 nanotube arrays up to 500 nm in length by a potentiostatic electrochemical anodization of titanium in hydrofluoric acid aqueous electrolyte. The experimental process is very convenient without any complex apparatus. Subsequently, various organic electrolytes including dimethyl sulfoxide [21], formamide [22] and ethylene glycol [23] have been adopted to fabricate TiO_2 nanotube arrays with greatly extended length.

Though TNAs as photocatalysts were firstly used in environmental applications [24], many challenges still remain such as the TNAs could not absorb visible light ($\lambda > 387$ nm) of the solar spectrum efficiently because of their large band gap (3.2 eV) as well as the recombination of photogenerated electrons and holes. In order to overcome these disadvantages, considerable efforts have been made to modify TNAs in order to reduce the band gap. In the present case, many transition metal ions [25,26] and nonmetal ions [27–30] have been studied to increase the visible light absorption or suppress the recombination of

---

[*] Corresponding author. Tel.: +86 551 62901012; fax: +86 551 62904517.
E-mail address: ycwu@hfut.edu.cn (Y. Wu).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.05.021

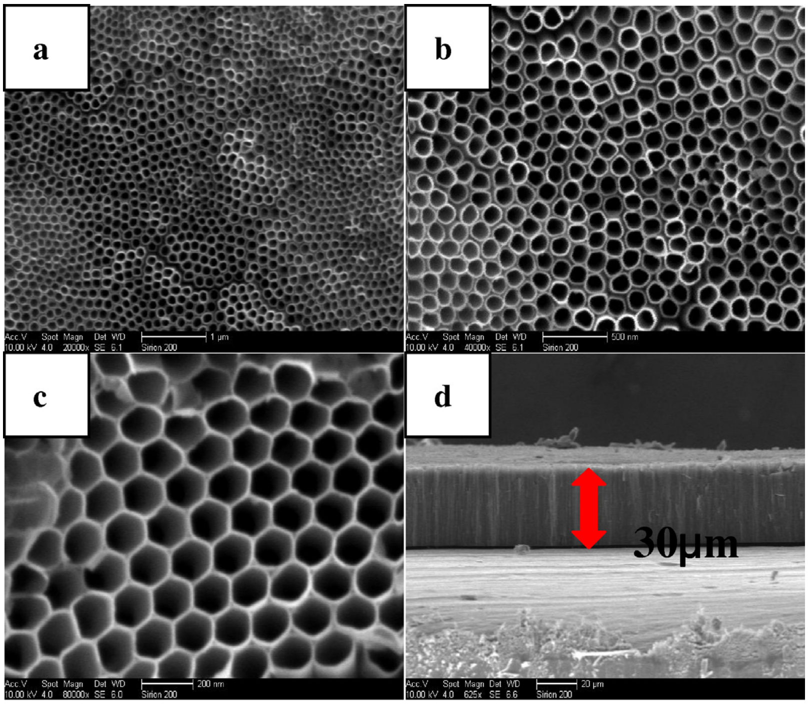

Fig. 1. SEM images of the highly ordered TNAs with different magnifications. (a), (b), (c) top views, and (d) cross-sectional views.

photogenerated electron–holes. Asahi et al. [31] investigated a visible-light photocatalysis in nitrogen-doped titanium oxides by sputtering the TiO_2 target in a N_2/Ar gas mixture. Tokudome and co-workers [32] reported nitrogen-doped TiO_2 nanotubes by a wet process. In this paper, nitrogen doped TiO_2 nanotube arrays (N-TNAs) were fabricated by immersing TNAs in ammonia aqueous solution following with annealing in air atmosphere. Effects of annealing temperature on the photocatalytic performance of N-TNAs were investigated.

2. Experiments

2.1. Preparation of nitrogen doped TiO_2 nanotube arrays

Highly ordered TiO_2 nanotube arrays were fabricated by anodization method. Titanium foil was anodized in ethylene glycol electrolytes containing 0.3 M ammonium fluoride and 2 vol% water with potential of 60 V for 6 h. The as-prepared TNAs samples were immersed in 1 M $NH_3{\cdot}H_2O$ solution for 10 h and then annealed in a tube furnace for 2 h at different temperatures with heating and cooling rates of 2 °C/min.

2.2. Characterization of N-TNAs

The surface morphologies of samples were observed using the field-emission scanning electron microscopy (FESEM, FEI Sirion-200). Crystal structures of N-TNAs were characterized by X-ray diffraction spectrometer (XRD, D/Max-rB, Japan). Average crystallite sizes of N-TNAs were determined according to the Scherrer equation using the full-width half-maximum data of each diffraction peak after correcting the instrumental broadening. Surface chemical states of samples were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB-250). All the binding energies were referenced to the C1s peak at 285.0 eV of the surface adventitious carbon.

2.3. Photoelectrochemical and photocatalytic activity measurements

The photocatalytic activities of TNAs and N-TNAs were evaluated by the photocurrent and degradation of MO. Photoelectrochemical measurements were carried out in 0.05 M phospate buffer solution with pH value of 7 by adjusting the ratio of Na_2HPO_4 and NaH_2PO_4. LED lamp with a quartz window was used as UV source. Photocurrent was measured by an electrochemical workstation with the N-TNAs as working electrode. All the samples were measured twice to get the average photocurrent value.

In the photocatalytic experiments, the prepared samples were used as photocatalysts and the MO was chosen as target pollutant. The experiment was performed in a UV-light reactor with a 300 W high-pressure mercury lamp (390 nm) and a 250 W metal–halogen lamp (420 nm). The initial concentration of MO aqueous solution was 20 mg/L. The change of concentration was monitored for analyzing the photocatalytic activity at different irradiation time intervals by measuring the absorption at 464 nm using a UV1800 spectrometer.

3. Results and discussion

3.1. The morphology of TNAs and N-TNAs

SEM morphologies of typical TNAs are shown in Fig. 1. The TNAs are well-aligned with average diameter of 140 nm, wall thickness of 10 nm, and length of 30 μm. The morphologies of N-TNAs are shown in Fig. 2. N-TNAs annealed at 500 °C are shown in Fig. 3. Both undoped and the N-doped TiO_2 nanotube arrays annealed at 500 °C show similar morphologies with the as-fabricated TNAs. These results indicate no significant effect of annealing on surface morphology and microstructure of the TNAs. However, the nanotube collapsed when the annealing temperature increase to 700 °C. This is ascribed to the rapid grain growth during the phase transition from anatase to rutile at high temperature [33], which is in good agreement with what reported in literature [34].