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Enhanced photocatalytic activity of CoO/TiO_2 nanotube composite

Guoge Zhang[a,*], Haitao Huang[b,**], Wenfang Li[a], Fei Yu[a], Huijun Wu[c], Limin Zhou[d]

[a] *School of Materials Science and Engineering, South China University of Technology, Guangzhou, PR China*
[b] *Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong*
[c] *School of Civil Engineering, Guangzhou University, Guangzhou, PR China*
[d] *Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hong Kong*

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ABSTRACT

Titania nanotube (TNT) array was fabricated by anodization of titanium in 0.2 wt.% HF aqueous solution. The as-anodized TNT was crystallized to anatase phase with a heat treatment at 450 °C. CoO/TNT nanocomposite was synthesized by cathodic deposition over the annealed TNT in 0.05 M $Co(NO_3)_2$. The surface morphology and crystalline structure of the resultant CoO/TNT nanocomposite were characterized by X-ray diffraction (XRD), Raman spectrum and field emission scanning electron microscopy (FESEM). The influences of deposition time and current density on the surface morphology of CoO/TNT were studied. The photoelectrochemical response of CoO/TNT nanocomposite was investigated. All CoO/TNT exhibited higher photocurrent than bare annealed TNT did, which was caused by the enhanced photogenerated electron–hole pairs separation. However, the photocatalytic activity cannot be straightforwardly related to photocurrent response because it also depends on some other factors such as catalyst acidic properties, specific surface area and the adsorption of organic dye. Transient photocurrent measurement should not be used alone for the screening of photocatalytic materials.

1. Introduction

Photocatalytic degradation of organic compound is of great importance to the elimination of hazardous wastes [1]. TiO_2 nanomaterials are very stable, nontoxic and cheap, and have been widely studied for water and air purification [2]. Although TiO_2 photocatalysis is regarded as one of the most potential environment treatment technologies, there are still some issues relating with its practical applications, such as the extension of photoresponse region of TiO_2 and the improvement of photoefficiency under UV and/or visible light irradiation. A lot of research has been carried out to enhance the photocatalytic activity of TiO_2, including doping with metal or non-metal elements to narrow the TiO_2 nanomaterials band gap [3,4], sensitizing with colorful compounds to improve the optical activity in the visible light region [5,6], and the preparation of metal/TiO_2 or semiconductor/TiO_2 nanocomposite for the enhanced charge transfer and electron–hole pairs separation [7–9].

Over the past few years, novel approach for the fabrication of self-organized TiO_2 nanotube (TNT) by anodization has been reported [10,11]. Such TNT array has gained enormous and growing interest due to the combination of functional properties with a well controllable nano-architecture [12]. Significant progress has been made in both synthesis [13–16] and applications of anodic TNT [17–24]. Compared with TiO_2 nanoparticles, TNT has some advantages such as large specific surface area, high mechanical stability, integrity and unique shape with fewer grain boundaries, which promote charge transport and electron–hole pairs separation [8,25]. Anodic TNT array was reported to possess better photocatalytic properties [26,27]. The functional application of TNT is usually more effective in its crystallized form [12]. Two TiO_2 polymorphs are typically being used – anatase and rutile, with the anatase phase exhibiting a significantly higher photocatalytic activity. Although the reasons are not yet fully understood, it is speculated that the higher charge carrier mobility in anatase ($80\,cm^2\,V^{-1}\,s^{-1}$, 89 times faster than that in rutile) is responsible for the superior photocatalytic properties [28]. Therefore, thermal treatment at a temperature between 300 and 500 °C is normally carried out to transform the as-anodized amorphous TNT into anatase for various applications [12]. Just like TiO_2 nanoparticles, there is also the need to narrow the band gap of TNT (around 3.2 eV) to improve the TNT performance. Some of the modification approaches that are already established for bulk or nano-particulate TiO_2 can also be applied to TNT [29]. Considering the *p*-type semiconducting nature of CoO, it is expected that the formation of CoO over *n*-type TNT would form a Schottky barrier at the hetero-junction and help enhance the charge transfer and electron–hole separation. The photocatalytic efficiency of TNT can thus be improved. In the present work, we investigate the fabrication of CoO/TNT nanocomposite through

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* Corresponding author. Tel.: +86 87113747.
** Corresponding author. Tel.: +852 27665694; fax: +852 23337629.
E-mail addresses: ggzhang@scut.edu.cn (G. Zhang), aphhuang@polyu.edu.hk (H. Huang).

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a facile electrochemical process. The as-prepared CoO/TNT showed higher photocatalytic activity toward the degradation of methyl orange (MO). Moreover, it was found that the CoO/TNT composite showed the highest photocurrent was not the one which demonstrated the best photocatalytic activity. Such result suggests that transient photocurrent response should not be used alone for the screening of photocatalytic materials.

2. Experimental

Titanium foils (0.25 mm thickness, 10 mm × 30 mm, 99.6% purity, Strem chemicals, USA) were degreased ultrasonically in acetone and ethanol for 10 min, respectively, followed by rinsing with deionized water and drying in hot air. Anodization of Ti was then carried out following the procedure published elsewhere [11,20], using a DC power supply (Agilent N5751A) in 0.2 wt.% HF at 20 V for 30 min, with platinum plate (0.3 mm thickness, 20 mm × 50 mm) as the cathode. The resulting TNT was amorphous with the thickness around 300 nm. Crystallization of as-anodized TNT to anatase phase was induced by the heat treatment at 450 °C for 3 h, with a ramp rate of 4 °C min^{-1}. The annealed TNT was then subjected to a cathodic deposition for the synthesis of CoO/TNT composite. CoO/TNT was named by the deposition current density (e.g., 1 mA CoO/TNT referring to the sample fabricated under 1 mA cm^{-2}). The deposition was carried out using an electrochemical workstation (CHI 660B) in 0.05 M $Co(NO_3)_2$, with platinum plate as both the counter electrode and reference electrode.

The surface morphology and crystalline structure of the resultant CoO/TNT nanocomposite were characterized by X-ray diffraction (XRD), Raman spectrum (Horiba HR800) and field emission scanning electron microscopy (FESEM, JEOL JSM-6335F). The cross section image was taken on mechanically bent sample. Raman spectra were recorded using an excitation wavelength of 488 nm. Chemical composition was determined by energy dispersive X-ray spectroscopy (EDX). The electrochemical measurements were performed in a standard three-electrode configuration, with platinum as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The transient photocurrent was measured using CHI 660B in 0.1 M Na_2SO_4, with a UV lamp (central wavelength: 369 nm, irradiation intensity: 6 W m^{-2}) as the light source. The photocatalytic activity of CoO/TNT composite (10 mm × 20 mm) was evaluated by the decomposition of MO solution (12 mg L^{-1}) under the illumination of the same UV lamp as used in the photocurrent measurement. Prior to the irradiation, the catalyst was soaked in the MO solution in dark for 2 h. Afterwards, the CoO/TNT was exposed to the UV irradiation under normal incidence with a distance of 4 cm. The change of MO concentration with the irradiation time was monitored by measuring the absorbance of MO solution at 466 nm using a UV–vis spectrophotometer (Shimadzu, UV-2550).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of CoO/TNT composite fabricated with the deposition current density of 1 mA cm^{-2} for 10 min. As shown before, TNT could be transformed to anatase without discernible changes in surface morphology after annealing at 450 °C for 3 h [30]. The corresponding peaks relating with anatase phase (PDF# 21-1272) and titanium substrate (PDF# 44-1294) were well observed. The peak appeared at 34.3° was ascribed to that of cubic CoO (PDF# 42-1300), indicating the formation of CoO/TNT composite. CoO was proposed to be obtained from the cathodic deposition process expressed as [31]

$$NO_3{}^- + H_2O + 2e^- \Rightarrow NO_2{}^- + 2OH^- \qquad (1)$$

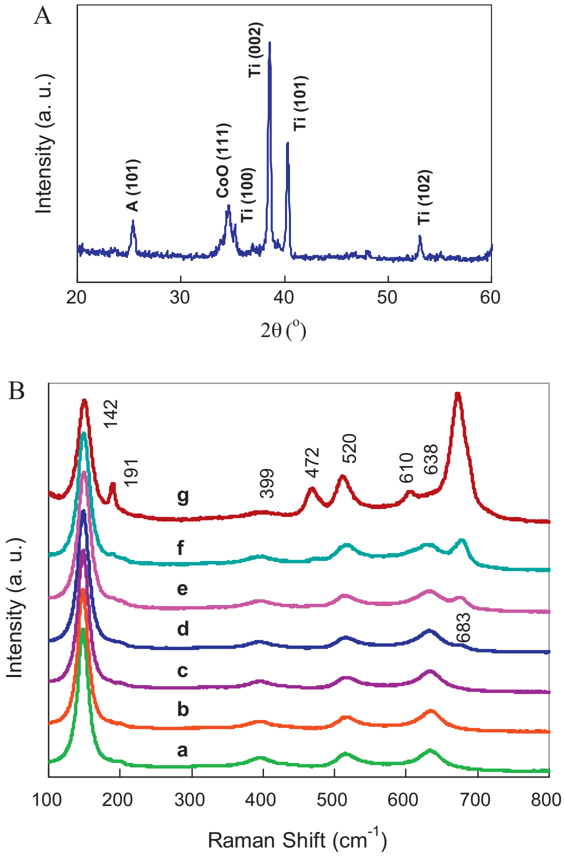

Fig. 1. (A) XRD patterns of CoO/TNT synthesized by cathodic depostion, "A" refers to anatase phase and (B) Raman spectra of (a) annealed TNT and the TNTs after deposition at different current densities for 10 min: (b) 0.01 mA cm^{-2}, (c) 0.02 mA cm^{-2}, (d) 0.03 mA cm^{-2}, (e) 0.04 mA cm^{-2}, (f) 0.05 mA cm^{-2} and (g) 1 mA cm^{-2}.

$$Co^{2+} + 2OH^- \Rightarrow CoO \downarrow + H_2O \qquad (2)$$

Fig. 1(b) shows the Raman spectroscopy of annealed TNT and the TNTs subjected to deposition under different current densities for 10 min. The annealed TNT showed typical anatase Raman bands around 142, 399, 520 and 638 cm^{-1}. No new Raman peaks were observed for the TNTs subjected to deposition at 0.01 and 0.02 mA cm^{-2}, indicating little material was formed over TNT under such conditions. New Raman peak was found at 683 cm^{-1} when current density was increased to 0.03 mA cm^{-2}, corresponding to the A_{1g} phonon mode resulted from CoO in TiO_2 lattice [32]. For the CoO/TNT fabricated under a current density of 1 mA cm^{-2}, the peaks appeared at 191, 472 and 610 cm^{-1} were also attributed to CoO. Such result agreed well with that of XRD and confirmed the formation of CoO/TNT composite when the deposition current density was higher than 0.03 mA cm^{-2}.

Fig. 2 shows the SEM images and EDX result of CoO/TNT fabricated by different current densities for 10 min. No deposited material was found for the sample synthesized with a current density smaller than 0.02 mA cm^{-2}, as indicated by both the SEM image and corresponding EDX spectra (Fig. 2a). Such result was in line with the Raman spectra as shown above (Fig. 1b). When current density was increased over 0.03 mA cm^{-2}, TNT was partially covered by a thin layer of interlaced vertically grown nanosheets. These nanosheets' thickness, size and coverage were increased with the increase of current density. At the same time, diffraction peaks at 0.79, 6.9 and 7.6 keV were detected by the EDX and attributed to cobalt element. The atomic percentage of cobalt was increased quickly on the increase of deposition current density. Coupled with the XRD result, it is inferred that these nanosheets were made of