Composites: Part B 52 (2013) 292–302

Contents lists available at SciVerse ScienceDirect

Composites: Part B

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

Photoelectrochemical responses of doped and coated titanium dioxide composite nanotube anodes

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ARTICLE INFO

Article history:
Received 14 January 2013
Received in revised form 25 March 2013
Accepted 2 April 2013
Available online 13 April 2013

Keywords:
A. Nano-structures
B. Electrical properties
B. Optical properties/techniques
D. Electron microscopy

ABSTRACT

Nanostructured photoelectrochemical anodes were made from titanium dioxide nanotubes doped with various metals including Fe, Cu, Ni, Ag, and added with polyaniline to enhance the photosensitivity. The TiO_2 nanotubes were obtained through electrochemical oxidation of Ti foil in a glycerol aqueous solution. Electroplating followed by high temperature treatment induced element substitution approach was used to achieve doping effect. Transmission electron microscopy and energy dispersive X-ray diffraction analysis were performed to reveal the structure and obtain the composition information. To examine the photoelectrochemical response, the anode was polarized at the constant bias voltages of 0.5, 1.0, 1.5, 2.0 V and under the exposure of both ultraviolet and visible light. Linear scan was also performed in the potential range of 0–2 V. It is found that Fe, Ni, and Cu doped and polyaniline covered nanotubes show obvious photoelectrochemical activities. Polyaniline covered nanotube anode has better performance than others. Cu-doped anode shows the highest current density in the linear scan voltage range.

1. Introduction

A photoelectrochemical fuel cell is an energy conversion device which converts photo and chemical energy into electrical energy and produces hydrogen [1]. Meanwhile, pollutants or organic materials can be decomposed. Nanostructured titanium dioxide (TiO_2) has been widely studied because it has photo catalysis function [2–4]. TiO_2 nanotubes (NTs) have been used for water splitting, organics decomposition, etc. Electrochemical oxidation synthesis of TiO_2 NTs is a popular method as introduced by Zwilling et al. [5]. Due to its wide band gap, TiO_2 only absorbs ultraviolet (UV) light. Besides, pure TiO_2 has high electrical resistivity at ambient temperature, which limits its application as photosensitive anode for pollutant decomposition and water splitting. Improving the photosensitivity of TiO_2 has recently been studied [6–8]. Doping with metal and non-metal to enhance the photocatalytic activity and reduce the electrical resistivity of TiO_2 nanotube and film was studied [9–14].

Typically, the dopants that have higher valance state than Ti^{4+} are chosen to increase the conductivity of TiO_2 nanostructures. As an example, Nb was found as an effective dopant for such a purpose [15–17]. Elements that have lower valance state than Ti^{4+}, for example hydrogen, are also found to be effective on increasing the conductivity of the TiO_2. This is because the electrons donated by lower valance elements allow the formation of Ti^{3+}, which helps the charge transfer within TiO_2 [18,19]. Fe and Cu are easily oxidized at room temperature. Multiform oxides include FeO, Cu_2O, Fe_2O_3 and CuO form. Obviously, the interactions of the multiform oxides, i.e. $Fe^{3+} - e = Fe^{2+}$, and $Cu^{2+} - e = Cu^{+}$ provide extra electrons. Therefore, Fe and Cu as dopants in titanium dioxide are favorable to supply extra electrons to generate Ti^{3+}. The conducting polymer, polyaniline, has a conjugated structure. It could serve as either an electron donor or an acceptor. Once polyaniline is deposited onto the TiO_2 nanotubes through electrochemical oxidation [20], it causes change in the band structure of TiO_2. The red-shift of light absorption is expected. These motivate us to study the effect of incorporating lower valance elements and conducting polymers into titanium oxide on its photo electrochemical behavior.

Plasmonics is a promising approach to promoting the light trapping property in nanostructured materials [21]. The resonance of noble metals is mostly in the visible light region. Metal doped oxides may also show plasmonics in infrared wavelength range. In order to make Ag nanoparticle loaded TiO_2 NT arrays, ultrasound aided photochemical synthesis was used [22]. Doping Pt to TiO_2 nanotubes was achieved by electrochemical reduction [23]. The photosensitivity of TiO_2 nanotubes is size-dependent. Longer nanotubes show stronger photo responses because more photons

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http://dx.doi.org/10.1016/j.compositesb.2013.04.001

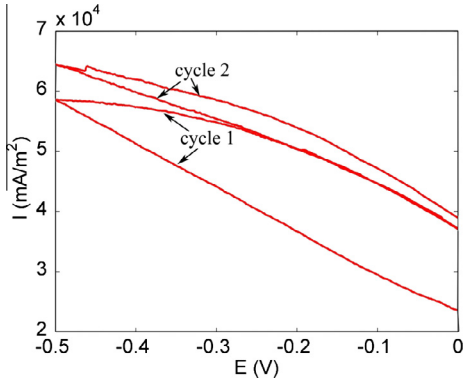

Fig. 1. *I–V* curve for electroplating Cu onto TiO_2 nanotubes.

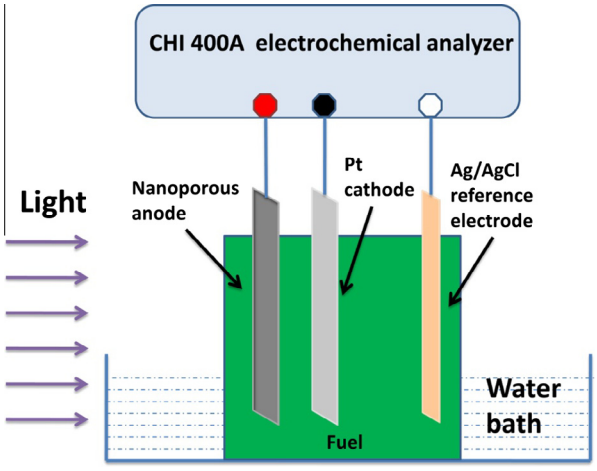

Fig. 2. Schematic of the experimental set-up.

are absorbed. However, Chang et al. [24] considered if the length is larger than the effective depth of light penetration, the lower part of the TiO_2 NTs is ineffective on absorbing light. Kim et al. [25] demonstrated the good photo response ability of Pt, Pd doped TiO_2 nanotube photo anodes. Pt doped TiO_2 can be made by the simple sputtering method [26].

A photoelectrochemical cell for waste decomposition may work without externally imposed bias, but the efficiency is relatively low [27]. Typically, an externally applied bias could be electrical or chemical in nature and can increase the reaction rate of electron-hole separation. Peng et al. [28] studied the N-doped TiO_2 thin film photo anode with electrical bias. The highest current reached 0.65 mA at the bias voltage of 2 V. The reaction rate at the cathode increased under the bias. But in some cases, a bias voltage may decrease the reaction rate of a photochemical cell. For example, Wheatley et al. [29] showed that a reversed bias caused the degradation of performance of a dye sensitized photoelectrochemical cell.

There are only a few of papers dealing with the effect of bias on photochemical fuel cells. Since transition metals are inexpensive besides the advantage as effective electron donors as mentioned before, this paper focuses on Fe, Ni, and Cu as the dopants. Considering the plasmonic effect of noble metal nanoparticles on enhancement of photosensitivity, Ag@Cu and Ag@Ni doped TiO_2 nanotubes are used in the work. The photosensitivity of polyaniline coated TiO_2 nanotubes is also studied. The performances of the photo anodes under external bias potentials were compared.

2. Materials and experimental methods

2.1. Materials and instruments

Titanium foil (99.9% purity) was purchased from McMaster.com. Other chemicals including acetone, NH_4F, urea, $NiCl_2$, $Fe(NO_3)_3$, $CuSO_4$ and glycerol in ACS purity were purchased from Alfa Aesar. An ultraviolet lamp with the model of UVL-21 (365 nm UV, 4 W, 0.16 A) and the power density of 40 mW/cm^2 was used as the UV source. A 250 W light bulb was used as the visible (Vis-) light source. The illumination intensity of the visible light was also kept at 40 mW/cm^2. A CHI 400A electrochemical workstation was purchased from CH Instrument, Austin, Texas. The power supply for the electrochemical oxidation of the titanium is a regulated DC power source, model HY5003 (0–50 V, 0–3 A). A JEOL 2100F transmission electron microscope (TEM) was used to observe the nanotubes and to generate elemental composition information.

2.2. Preparation of pure and composite TiO_2 nanotubes on Ti

Highly ordered TiO_2 nanotubes (NTs) were obtained via electrochemical oxidization of Ti foil. All chemicals were used as received. The Ti foil was cut into 3 × 40 mm and degreased in acetone before anodization. An organic based electrolyte containing glycerol as the main composition with 10 wt.% water and 0.4 wt.% NH_4F was made. Anodic oxidization was performed in a two-electrode cell at 20 V for 2 h at 25 °C. After oxidization, TiO_2 nanotubes on the

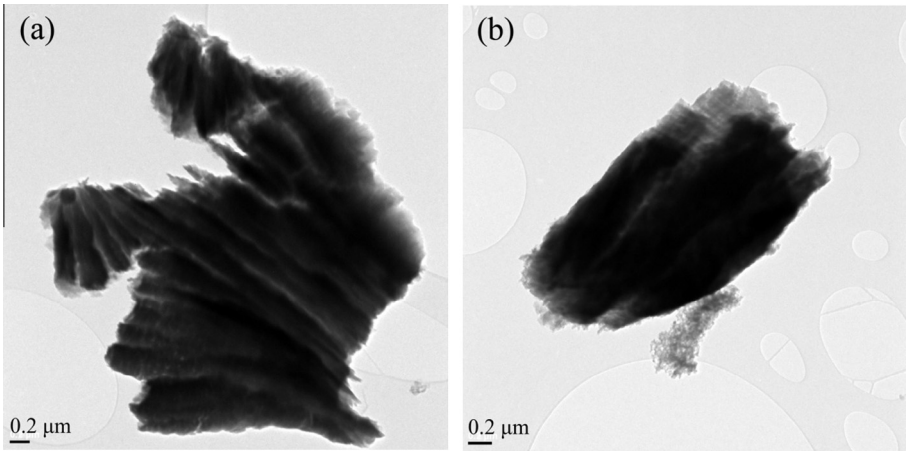

Fig. 3. TEM images of Fe-doped TiO_2 nanotubes in clusters.