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Fabrication, characterization and photoelectrochemical activity of tungsten-copper co-sensitized TiO_2 nanotube composite photoanodes

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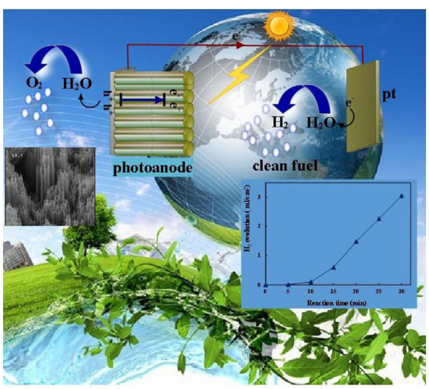
GRAPHICAL ABSTRACT



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ABSTRACT

Tungsten-copper co-sensitized TiO_2 nanotube films on titanium substrate, used as photoanodes in photoelectrochemical (PEC) water splitting to produce hydrogen, have been synthesized via anodization and chemical bath deposition (CBD) methods. Field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) were used to study the morphology and elemental composition of the synthetic samples. UV–Vis diffuse reflection spectroscopy (UV–Vis DRS) was sued to investigate the optical features of the samples. The impact of copper and tungsten ratio on the photocatalytic behavior of co-sensitized TiO_2 nanotube photoelectrodes in PEC water splitting has been investigated. High photocatalytic activity has been exhibited by the co-sensitized TiO_2 nanotube samples due to the synergistic effects of the copper and tungsten. Sample T4 had the highest photoelectrochemical activity compared with other samples. In addition, this sample exhibited outstanding photochemical stability even after four runs in the photocatalytic test. A simple method for the synthesis of high performance co-sensitized TiO_2 nanotube photocatalysts for application in solar energy conversion has thus been proposed in this work. The advantages of these new photoanodes for practical applications are low cost, ease of synthesis, high activity in visible light and excellent stability.

1. Introduction

It is essential to develop clean energy to overcome serious environmental issues and create a sustainable world. A promising, widely considered approach toward renewable resources is

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photoelectrochemical (PEC) water splitting with a semiconductor to produce hydrogen and oxygen using solar energy [1–3]. Currently, semiconductor materials are promising for applications in many fields, such as solar cells, transistors, microchips, LEDs, sensors, applications of semiconductor photocatalysis for reducing pollution in the environment and so on [4–10]. Given its high photocatalytic activity, non-toxicity, low cost, resistance to corrosion and stable characteristic, titanium dioxide (TiO_2) has been used as a well-known photocatalyst for hydrogen production since 1972 [11–13]. There are three different crystalline forms of titanium dioxide; anatase, rutile and brookite. The most active and commonly used form of TiO_2 is anatase. However, there are drawbacks for TiO_2 such as low quantum yield and poor photocatalytic efficiency, which are caused by relatively wide band gap (~3.2 eV) and the high recombination rate of photogenerated electrons and holes [13–18]. Therefore, to improve the photocatalytic efficiency of TiO_2, many attempts have been made including surface modification, structure optimizations and doping using metal or nonmetal elements, dye or quantum dot sensitization and narrow gap semiconductor coupling [13–18].

Special attention has been recently focused on titanium dioxide nanotube arrays prepared by anodization of titanium foils considering their high orientation, tunable pore size, large internal surface area and excellent recovery and reutilization [12,13,15,17]. Unlike TiO_2 films consisting of nanoparticles, direct electrical pathways for photogenerated electrons transfer are provided by TiO_2 nanotube arrays, which lead to high electron transport rates. This in turn prevents the recombination of photogenerated electron hole pairs.

The synthesis of TiO_2 nanotubes co-sensitized by tungsten and copper nanoparticles for application in photoelectrochemical water splitting has been carried out in this work. TiO_2 nanotube arrays have been prepared on titanium sheets by simple and facile anodization process. Copper, tungsten and copper-tungsten have then been deposited on the TiO_2 nanotube surfaces via chemical bath deposition process. Compared with bare TiO_2 photoanodes, co-sensitized TiO_2 photoanodes have shown considerable photocatalytic properties. TiO_2 nanotubes have been co-sensitized with both Cu and W for the first time. A new pattern for the development of efficient, long term recyclable photoanodes for PEC water splitting has been presented in this work.

2. Experimental

2.1. Experimental reagents and materials

Analytical reagent grades were used in this work. The aqueous solutions were all prepared using distilled water. Table 1 shows the chemicals used in this work.

Table 1
The experimental reagents and their specifications.

Material and reagent	Purity grade
Titanium sheet	Purity > 99.9%
Ammonium fluoride	Analytically pure
Ethylene glycol	Analytically pure
Nitric acid	Mass fraction = 65–68%
Hydrogen fluoride	Mass fraction = 40%
Sulfuric acid	Mass fraction = 98%
Potassium hydroxide	Analytically pure
Sodium tungstate, $Na_2WO_4{\cdot}2H_2O$	Analytically pure
Copper(II) nitrate, $Cu(NO_3)_2$	Analytically pure
Disodium ethylenediaminetetraacetate dihydrate, $Na_2EDTA{\cdot}2H_2O$	Analytically pure

2.2. Preparation of co-sensitized TiO_2 photoanodes

Electrochemical anodization method previously reported has been used to synthesize TiO_2 nanotubes [17]. Samples were rinsed thoroughly with distilled water and dried in air following anodization. Tungsten and copper were then loaded on the TiO_2 nanotubes by facile chemical bath deposition method. TiO_2 nanotubes were soaked in a 0.1 M H_2SO_4 solution for 90 min, after which they were soaked in an aqueous solution composed of appropriate quantities of $Na_2WO_4{\cdot}2H_2O$ and $Cu(NO_3)_2$ for 30 min at 70 °C. The samples were rinsed with distilled water, air dried and annealed by heating at 400 °C for 2 h at a rate of 2 °C/min to form metal oxides and obtain crystalline samples. The photoelectrochemical performance of bare TiO_2 and TiO_2 sensitized using different compositions of tungsten and copper referred to as T1, T2, T3, T4, T5 and T6 have been compared in this work. The experimental conditions for different samples are shown in Table 2. Also cyclic voltammetry method was applied in the estimation of the electroactive surface areas of different sensitized TiO_2 nanotubes using $K_3[Fe(CN)_6]$ as a probe and results are shown in Table 2 (Also see Fig. S1). Fig. 1 shows the schematic presentation of titanium pretreatment and preparation of copper-tungsten-sensitized TiO_2 nanotube films on titanium foils.

2.3. Characterization

The surface morphology of the prepared samples was studied using field emission scanning electron microscopy (Hitachi S-4160, Japan). UV–Vis spectrophotometry (JASCO V-570) was used to characterize the optical absorption properties of annealed samples in the 250–600 nm range. Photoluminescence (PL) spectra were measured at room temperature using aAvant's spectrophotometer (Avaspec 2048 TEC, Holland). X-ray diffraction analysis (XRD, Philips X'Pert PRO) was used to analyze the crystal structure of the samples using a Cu K radiation. Origaflex electrochemical working station (OGF500 potentiostat/galvanostat, France) was used to carry out the photoelectrochemical measurements in a 1 M KOH aqueous solution containing 5 vol% ethylene glycol at ambient temperature using a three electrode configuration. Tungsten-copper co-sensitized TiO_2 nanotubes were used as the anode and Pt foil and Ag/AgCl (KCl saturated) were used as counter and reference electrodes, respectively. The measurements were performed under a 55 W xenon lamp illumination (200 mW/cm^2). The linear sweep voltammograms (LSVs) were conducted at 10 mV/s in the potential range of −1.0 to +1.5 V vs. Ag/AgCl both in the dark and under illumination. The hydrogen generations from samples were recorded under a 55 W xenon lamp illumination and H_2 gas was collected by water displacement technique. Hydrogen gas was formed at the counter electrode in the PEC cell. The platinum cathode was inserted into a burette, in which hydrogen was collected by electrolyte displacement. The measurement of hydrogen volume was directly carried out by reading the electrolyte level variation in the burette at various time intervals. Mott-Schottky plots were generated from capacitance obtained from the electrochemical impedance spectroscopy (EIS) spectra at each potential with a frequency of 3 KHz in 1 M KOH aqueous solution containing 5 vol% ethylene glycol.

3. Results and discussion

FESEM images of different sensitized TiO_2 nanotubes are shown in Fig. 2. Nanotubular structure of TiO_2 is observed to maintain its integrity with no significant morphological change after co-sensitizing. Sensitized nanotubular structures are uniform and clear according to low magnification FESEM images of the samples. Nanotubular structures and nanoparticles deposited on both the