Chinese Journal of Catalysis 38 (2017) 2132–2140

available at www.sciencedirect.com

ScienceDirect

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

Article (Special Issue on Photocatalysis in China)

Nanotube array-like WO_3/W photoanode fabricated by electrochemical anodization for photoelectrocatalytic overall water splitting

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ARTICLE INFO

Article history:
Received 9 October 2017
Accepted 27 October 2017
Published 5 December 2017

Keywords:
WO_3
W foil
Electrochemical anodization
Nanotube arrays
Photoelectrocatalysis
Water splitting

ABSTRACT

Photoactive WO_3 is attractive as a photocatalyst for green energy evolution through water splitting. In the present work, an electrochemical anodic oxidation method was used to fabricate a photo-responsive nanotube array-like WO_3/W (NA-WO_3/W) photoanode from W foil as a precursor. Compared with a reference commercial WO_3/W electrode, the NA-WO_3/W photoanode exhibited enhanced and stable photoelectrocatalytic (PEC) activity for visible-light-driven water splitting with a typical H_2/O_2 stoichiometric ratio of 2:1 and quantum efficiency of approximately 5.23% under visible-light irradiation from a light-emitting diode (λ = 420 nm, 15 mW/cm^2). The greatly enhanced PEC performance of the NA-WO_3/Wphotoanode was attributed to its fast electron–hole separation rate, which resulted from the one-dimensional nanotube array-like structure, high crystallinity of monoclinic WO_3, and strong interaction between WO_3 and W foil. This work paves the way to a facile route to prepare highly active photoelectrodes for solar light transfer to chemical energy.

1. Introduction

In recent years, the depletion of fossil fuels has led to the impetus to develop new energy sources [1,2]. Solar water splitting represents a sustainable and environmentally friendly method to produce H_2, which is considered an alternative, clean, and sustainable energy source to fossil fuels [3,4]. Photocatalytic water splitting has attracted considerable attention as a potential route to produce renewable energy with no reliance on fossil fuels and no carbon dioxide emission [5–7]. In 1972, Fujishima etal. [8] first reported TiO_2 as a photocatalyst for solar water splitting. Since then, TiO_2 has been extensively studied as a promising photocatalyst. Although TiO_2 possesses remarkable advantages, it suffers from low solar light utilization efficiency because of its wide band gap [9]. Some non-TiO_2 photocatalysts, including ferric oxide [10–12], cuprous oxide [13,14], cadmium sulfide [15,16], and composite materials, have been used as visible-light photocatalysts to drive water splitting under visible-light irradiation [17–26]. However, these photocatalysts are susceptible to photocorrosion [21,22]. Thus, a stable visible-light-driven photocatalyst for use in water splitting is still urgently required.

Recently, WO_3 has been proved an attractive candidate for photocatalytic applications in environmental remediation [23–31] and O_2 evolution [32–34] because of its suitable band gap to absorb visible light and excellent stability [35–39]. Alt-

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This work was supported by the National Natural Science Foundation of China (21207090, 21477079, 21261140333), PCSIRT (IRT1269), and a scheme administrated by Shanghai Normal University (DXL122, and S30406).

DOI: 10.1016/S1872-2067(17)62948-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 12, December 2017

hough WO_3 possesses an indirect band gap energy of 2.7–2.8 eV, it still cannot directly reduce water to H_2 because of its high conduction band position (0.3 V vs. RHE) [40]. As a result, the photogenerated electrons do not reach the potential of water reduction (0 V vs. RHE) [41]. In addition, WO_3 still suffered from the rapid recombination of photogenerated electron–hole pairs in the photocatalytic process, like other powder photocatalysts [32,42,43].

Photoelectrocatalytic (PEC) water splitting has been proved an effective method to solve the problem of the rapid recombination of photogenerated electron–hole pairs [44–46]. In a typical PEC water splitting system, photogenerated holes (or electrons) migrate to the anode (or cathode) surface to participate in water oxidation (or reduction) reactions [47]. The external field induces the photogenerated electron–hole pairs to separate rapidly, thus slowing the recombination rate of charge carriers [48]. Meanwhile, the applied bias voltage allows the photogenerated electrons to reduce water to H_2 [41]. Recently, photoanode-driven PEC systems have been widely used in water splitting [47,45–51]. Considerable effort has been focused on the development of n-type semiconductor-based photoanodes for solar-light-driven water oxidation in PEC systems[41,52]. For example, highly crystalline WO_3 with small mesopores produced via a one-step procedure demonstrated high visible-light-driven PEC performance in water oxidation [53]. Pore-rich WO_3 ultrathin nanosheets were fabricated as an effective photoanode for PEC water oxidation, displaying more photogenerated holes, higher carrier migration rate, shorter migration path, and stronger oxidizing capability than normal nanostructured WO_3. More recently, a porous WO_3 photoanode was used for the photoelectrochemical mineralization of emerging contaminants [54].

Regarding overall water splitting, few reports on WO_3-based photoanodes have appeared to date. In the present work, a nanotube array-like monoclinic WO_3/W(NA-WO_3/W) electrode fabricated by an electrochemical anodization method is used as an effective photoanode to realize overall water splitting (stoichiometric H_2/O_2 ratio of 2:1) under visible-light irradiation (λ = 420 nm). We fabricated the first WO_3 nanotube-based electrodes by an anodization route [55,56]. Various morphologies, including nanopores, grains, and even formless WO_3 thin films and crystals can be produced by adjusting the anodization voltage, time, and electrolyte composition of the anodization process and the annealing temperature. Both the photoelectrochemical properties and PEC activity of the NA-WO_3/W photoanode are investigated using a commercial WO_3/W film as a standard photoanode. The NA-WO_3/W photoanode exhibits stronger visible-light absorption, lower charge recombination rate, and higher stability than the reference photoanode, leading to higher PEC activity in visible-light-driven overall water splitting; the quantum efficiency (QE) of the NA-WO_3/W photoanode in water splitting is approximately 5.23%. Such greatly enhanced PEC water-splitting performance is attributed to the highly crystalline WO_3 nanotube arrays, fast carrier separation and migration rates, and high visible-light absorption capability of the NA-WO_3/W photoanode.

2. Experimental

2.1. Preparation of NA-WO_3/W and commercial WO_3/W electrodes

W foil (20.0 × 30.0 × 0.1 mm, 99.95% purity, Chuang Qi, Baoji, China) was degreased by ultrasonication in acetone, deionized water, and ethanol in sequence for 15 min each and then dried in a nitrogen (N_2) stream. The WO_3/W nanostructures were fabricated through constant-voltage anodization in a two-electrode electrochemical cell at room temperature using the cleaned W foil as the anode and Pt foil (20.0 × 20.0 × 0.1 mm) as the cathode. The W foil was anodized in ammonium fluoride (NH_4F; 0.15 mol/L) aqueous electrolyte solution containing glycerol (glycerol/water = 50:50 vol %) under a DC oxidation voltage of 40 V for 1 h. The as-obtained WO_3/W film was annealed at 400 °C for 3 h in an air atmosphere after heating at a rate of 2 °C/min to form NA-WO_3/W. The effect of the electrochemical parameters, including the concentration of NH_4F (0.10–0.20 mol/L), oxidation voltage (30–70 V), and oxidation time (0.5–2.0 h), and the annealing temperature (300–500 °C) on the PEC activities of NA-WO_3/W photoanodes during visible-light-driven water splitting were investigated.

To aid comparison, a reference WO_3/W photoanode was also prepared by coating commercial WO_3 powder on W foil. In a typical process, polyethylene glycol (PEG; average MW 20000, 20 mg) was dissolved in ethanol (100 μL). Commercial WO_3nanoparticles (<200 nm, 99.9% metals basis, Aladdin, 100 mg) were dispersed in the PEG solution by grinding for 15 min. The as-obtained mixture was coated on W foil (20.0×30.0×0.1 mm, 99.95% purity, Chuang Qi) by the doctor-blade method to give an active area of 15.0×25.0 mm. Film thickness was controlled using plastic tape with a thickness of 20 μm. The WO_3 electrode was annealed at 400 °C for 3.0 h in an air atmosphere following heating at a rate of 5 °C/min [57]. The as-prepared reference WO_3 electrode is called standard WO_3.

2.2. Characterization

Wide-angle X-ray diffraction (XRD) measurements were carried out in a parallel mode (ω = 0.5°, 2θ from 10° to 80°) using a Rigaku D/max-3C Advance X-ray diffractometer with Cu K_α radiation (λ = 1.5406 Å). The morphologies of the products were observed by field-emission scanning electron microscopy (FESEM; S-4800, Hitachi, Japan). Surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS; PHI 5000, Perkin-Elmer, USA). All binding energy values were calibrated using the C 1*s* peak at 284.6 eV as a reference. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the samples over a range of 200–800 nm were collected on Dilor Super Lab Ram II and MC-2530 spectrometers using barium sulfate as a reference. Transmission electron microscopy (TEM; JEM-2010, JEOL, Japan, 200 kV) and high-resolution transmission electron microscopy (HRTEM; JEOL-2010F, JEOL, 200 kV) were used to analyze the structure of the photoelectrodes.