



Nanotextured cupric oxide nanofibers coated with atomic layer deposited ZnO-TiO₂ as highly efficient photocathodes



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ARTICLE INFO

Article history:

Received 6 May 2016

Received in revised form 27 July 2016

Accepted 24 August 2016

Available online 24 August 2016

Keywords:

Cupric oxide nanofibers

Photocathode

Water splitting

Photocurrent density

Atomic layer deposition

ABSTRACT

We report the fabrication and performance of a CuO/ZnO/TiO₂ nanofiber photocathode that achieved a photocurrent density (PCD) of -4.1 mA/cm^2 , which is among the highest PCD values reported for a copper oxide based photocathode without a co-catalyst. To prepare this photocathode, we coated electrospun nanofibers with copper by electroplating, then dried them in air to produce cuprous oxide (Cu₂O) nanofibers. Further annealing in air converted them to cupric oxide (CuO). The CuO nanofibers exhibit nanotextured surfaces, resembling the skin of the “thorny-devil” lizard of Australia, providing high accessible surface area for photocatalysis. These CuO nanofibers were uniformly coated with thin ZnO and TiO₂ layers by atomic layer deposition (ALD) to promote electron migration from CuO to TiO₂ and protect the CuO from corrosion. The nanofibrous photocathode films were characterized by X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, scanning electron microscopy, and transmission electron microscopy, as well as by incident photon-to-electron conversion efficiency measurements.

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1. Introduction

Cu₂O (cuprous oxide) and CuO (cupric oxide) have attracted considerable attention as photocathode materials for solar water splitting [1–22]. They have also shown promise in other applications, such as photovoltaics [22–31], gas sensing [32], heterogeneous catalysis [8,18,33–35], and lithium-ion batteries [36–38]. Relative to other metal oxides, such as TiO₂, ZnO, Fe₂O₃, and WO₃, Cu₂O and CuO exhibit smaller bandgaps of 2.0–2.2 eV [21] and 0.7–1.6 eV [39], respectively, allowing them to absorb a larger fraction of the solar spectrum. However, this is accompanied by disadvantages, such as low redox potential [8]. The conduction bands of Cu₂O and CuO are at -0.7 V and -0.2 V , which are relatively more negative than those of other metal oxides, making

them more efficient cathodes for producing hydrogen. The theoretical maximum photocurrent densities of Cu₂O and CuO are 14.7 and 35 mA/cm², respectively, under AM 1.5 irradiation [17]. The Grätzel group [8] has reported a photocurrent density of 7 mA/cm² for their electrodeposited and atomic-layer-deposited (ALD) Cu₂O films. Multiple ZnO and TiO₂ layers together with a Pt co-catalyst were electrodeposited to produce stable Cu₂O films. Since that report, studies of copper oxides for water splitting have mainly focused on Cu₂O. Advantages of Cu₂O over CuO include the relatively large bandgap of Cu₂O (i.e., 2.0–2.2 eV), which facilitates efficient water oxidation. On the other hand, relatively few studies have been reported on CuO despite its higher chemical stability [14,21] and its higher theoretical maximum photocurrent density (PCD) associated with its narrower bandgap.

Jang et al. [19] and Masudy-Panah et al. [22] reported the best-performing CuO-based photocathodes to date, with PCD values of 4.4 and 2.5 mA/cm², respectively. Masudy-Panah et al. increased the surface area by manipulating deposition parameters during sputtering, while Jang et al. produced a complex tree-branch-

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shaped CuO film by electrodeposition and microwave annealing. These two studies demonstrate the importance of high surface area for increasing the PCD of CuO films.

Like those previous reports, here we produce increased surface area to achieve high PCD. However, the fabrication methodology employed here is completely different from that employed in previous studies. First, electrospun nanofibers were electroplated with copper, followed by air-drying for 24 h. This process results in the formation of sharp “thorns,” resembling the skin of the thorny devil lizard [40] (Fig. 1). This thorny morphology increases the surface area and number of reaction sites. Layers of ZnO and TiO₂ were coated onto the thorny devil copper oxide to improve charge extraction and prevent CuO corrosion (Fig. 1) [41]. The flow of electrons from CuO to ZnO and TiO₂, as well as that of holes in the opposite direction, is promoted by this layered structure. At pH 14, the conduction band minima of both ZnO and TiO₂ are above 0V, facilitating the production of hydrogen. That is, they can serve in this system as a photocathode, even though they are more commonly employed as photoanodes. Another advantage of the ZnO and TiO₂ layers is that they can protect the CuO layer from corrosion. Copper oxide is unstable as a photocathode because the redox potential for reduction of Cu₂O to Cu is 0.47 V, and the redox potential for reduction of CuO to Cu₂O is 0.60 V, both of which lie within the bandgap of CuO. This energy alignment allows photocorrosion during the reduction of water, which is undesirable. That is, photogenerated electrons, in the presence of water, can reduce copper oxide, producing Cu and OH⁻, rather than reducing water to produce OH⁻ and H₂. ZnO and TiO₂ can prevent or mitigate corrosion because their reduction potentials (to produce Zn and OH⁻, for example) do not fall within their own bandgaps and are more negative than the reduction potential of water [8]. This issue has been discussed in detail by Chan and Wang [42] who provide band-edge positions and potentials for oxidation and reduction of numerous metal oxides and other materials used as photoelectrodes.

The thickness of the TiO₂ layer was fixed at 10 nm, while that of the ZnO layer was varied from 10 to 80 nm. The optimal thickness of the ZnO layer was determined, and its overall effect on the PEC performance of the thorny devil copper nanofibers was investigated. These nanofibers were characterized by X-ray diffraction (XRD), Raman spectroscopy (Raman), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and photoelectrochemical (PEC) measurements including incident photon-to-electron conversion efficiency (IPCE) spectra.

2. Experimental

2.1. Preparation of CuO nanofibers

First, thin films of CuO with varying thickness were deposited on indium-doped tin oxide (ITO) substrates by electroplating. The electroplating solution was prepared by mixing sulfuric acid (10 g, Matsuno Chemicals), hydrochloric acid (1 g, Sigma-Aldrich), copper sulfate (32 g, Sigma-Aldrich), formaldehyde (20 g, Sigma-Aldrich), and deionized (DI) water (200 mL). The solution was stirred for a few hours at room temperature. A bare Cu foil and the ITO substrate were used as the anode and cathode, respectively, and were entirely immersed in the electroplating solution. Table 1 summarizes the details of the electroplating process.

For deposition of the polymer nanofibers on the above CuO thin film, 6 wt% polyacrylonitrile (PAN, $M_w = 150$ kDa) powder was dissolved in *N,N*-dimethylformamide (DMF, 99.8%) by stirring for 24 h at room temperature, and the completely dissolved 6 wt% PAN solution was electrospun at a fixed flow rate of $Q = 130$ μ L/h (Legato 100, KDS) and a DC voltage of $V = 5.5$ – 6.5 kV (EL20P2, Glassman High

Table 1

Operating conditions for the electroplating process.

Items	Conditions
Applied voltage [V]	1
Electrode size [cm]	2.5 × 2.5 (ITO glass) 4 × 3 (copper foil)
Distance between electrodes [cm]	3
Electroplating time [s]	10

Voltage Inc.), as depicted in Fig. 1. The nozzle-to-substrate distance was 4.5 cm. The ambient temperature during electrospinning was 27 °C and the relative humidity level was 45%.

Next, the nanofiber film was seeded with a few nm of platinum to provide sufficient conductivity for electroplating. The sputtered nanofiber film was electroplated a second time using the same electroplating conditions (Table 1), except that the electroplating time was changed to 15 s (cf. Fig. 1). The plated thorny devil nanofiber film was rinsed with DI water and air-dried, reinforcing the adhesion between layers and the thorny devil structure. Finally, films were heated to 500 °C at a rate of 5 °C/min in air, and held at 500 °C for 1 h.

2.2. Atomic-layer-deposition of ZnO and TiO₂ layers

To improve PEC performance, ZnO and TiO₂ layers were deposited on the CuO thorny devil films. The ZnO and TiO₂ films were fabricated by atomic layer deposition (ALD, Lucida™ D series ALD, NCDtech, Korea). The ZnO layer was prepared using diethyl zinc (DEZ, EGChem) and H₂O, and the TiO₂ film was deposited from titanium(IV) isopropoxide (TTIP, EGChem) and H₂O. The temperature used in both ALD steps was 200 °C, and the overall pressure in the reactor was approximately 3×10^{-1} Torr. The ZnO deposition rate was ~0.2 nm per cycle. To study the effect of ZnO thickness, we prepared samples with 0, 10, 20, 40, and 80 nm ZnO layers. A 10 nm thick TiO₂ layer was deposited on the CuO/ZnO film at ~0.1 nm per cycle. After ALD, the CuO/ZnO/TiO₂ films were heated to 500 °C for 30 min.

2.3. Characterization

Crystal structure and crystallinity were investigated by XRD (Rigaku, Japan, D/max-2500) using Cu K α radiation over a 2θ range of 20°–80°. The surface chemical composition of the films was investigated by XPS (Theta probe base system, Thermo Fisher Scientific Co.). The morphology of the CuO nanofibers was studied by high-resolution scanning electron microscopy (HR-SEM, XL30 SFEG, Phillips Co., Holland) at 15 kV. The thickness of films was determined by averaging values obtained from five measurements. TEM images were recorded on a JOEL-2010F system at an accelerating voltage of 200 kV. The CuO nanofibers were investigated by Raman scattering using the 532 nm (diode) line of a combined Raman and FTIR spectrometer (LabRam ARAMIS IR2, Horiba Jobin Yvon). The surface morphology of the films was characterized by atomic force microscopy (AFM, XE-100, Park System, Suwon, South Korea).

2.4. Photoelectrochemical measurements

A single cell with three electrodes was used for all PEC measurements. The CuO films were used as the working electrode, while a Ag/AgCl rod and platinum wire were used as the reference and counter electrodes, respectively. These three electrodes were placed as close as possible to one another, and their positions were fixed for acquiring consistent data and minimizing any transport limitation in the electrolyte. A 1 M KOH (pH = 14) solution was used as the electrolyte. Nitrogen gas was purged through

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