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Research paper

Fabrication of CuO_x thin-film photocathodes by magnetron reactive sputtering for photoelectrochemical water reduction

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Abstract

The CuO_x thin film photocathodes were deposited on F-doped SnO_2 (FTO) transparent conducting glasses by alternating current (AC) magnetron reactive sputtering under different Ar:O_2 ratios. The advantage of this deposited method is that it can deposit a CuO_x thin film uniformly and rapidly with large scale. From the photoelectrochemical (PEC) properties of these CuO_x photocathodes, it can be found that the CuO_x photocathode with Ar/O_2 30:7 provide a photocurrent density of -3.2 mA cm^{-2} under a bias potential -0.5 V (vs. Ag/AgCl), which was found to be twice higher than that of Ar/O_2 with 30:5. A detailed characterization on the structure, morphology and electrochemical properties of these CuO_x thin film photocathodes was carried out, and it is found that the improved PEC performance of CuO_x semiconductor photocathode with Ar/O_2 30:7 attributed to the less defects in it, indicating that this Ar/O_2 30:7 is an optimized condition for excellent CuO_x semiconductor photocathode fabrication.

Keywords: CuO_x thin film; Magnetron sputtering; Photocathode; Defect controlling

1. Introduction

Photoelectrochemical (PEC) water splitting for hydrogen evolution is a potential technique to solve the crises of energy shortage and environment pollution [1]. In recent years, this research area has achieved great progress by the persistent efforts of the researchers. Related studies indicated that the methods to improve the overall solar-to-hydrogen efficiency in PEC devices mainly include: (1) obtaining better light absorption by engineering the absorber layer morphology of semiconductors [2,3]; (2) improving charge transfer efficiency of the semiconductors by establishing microstructure or nanostructure [4,5]; (3) improving the heterogeneous reaction kinetics by attaching catalysts to the photoelectrodes surfaces [6,7]; (4) protecting the semiconductors from corrosion by building surface passivation layers [8,9]; (5) reducing the rate of electrons–holes recombination by surface state passivation [10] or surface catalyst layers [11].

Cu_2O and CuO are considered as promising photocatalytic materials for water splitting owing to their cost-effective and abundant resources [12]. Yang et al. [13] prepared a Cu_2O/CuO bilayered composite photocathode by electrodeposition and thermal oxidation methods, this photocathode achieved a 3.15 mA cm^{-2} HER photocurrent at a bias potential of 0.4 V vs. RHE. Cu_2O is a kind of p-type semiconductors, its direct bandgap is approximately 2.0 eV [14], which has a high corresponding theoretical photocurrent and a high efficiency of light converts to hydrogen [15]. Compared with these hot research visible light responsive PEC materials, such as Ta_2N_3 [16],

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$BiVO_4$ [17,18], WO_3 [19,20], and Fe_2O_3 [21,22], etc., Cu_2O shows better cost-performance and higher theoretical maximum PEC water splitting conversion efficiency, it is highly deemed as a potential industry applications material for PEC water splitting. And the conduction band potential of Cu_2O is much negative than the water reduction potential (as shown in Fig. 1), the photogenerated electrons can reduce water to hydrogen smoothly. However, the valence band potential of Cu_2O is just near the water oxidation potential, so that the water oxidation process is difficult to drive by this small over potential. Simultaneously, its poor stability and fast carriers recombination rate [23] also limits the photoelectrochemical performance of Cu_2O. Consider compounding Cu_2O with other semiconductors, such as CuO [24,25], which can provide a much positive valence potential and then improve the water oxidation process. CuO is another semiconductor in cupper oxides group. It is a kind of p-type semiconductor with a direct bandgap of 1.4 eV [26], so that the light response range of CuO is much larger than Cu_2O, corresponding to a higher PEC performance than that of Cu_2O in theory. In addition, CuO has strong absorption under ultraviolet [27], which widens the absorption spectra of Cu_2O [28]. Copper oxide thin film can be prepared by several methods at present, such as magnetron sputtering [29], Sol–gel [12], metal organic chemical vapor deposition [30], electrochemical deposition [31]. Among these methods, magnetron sputtering is a simple and easy-to-control deposition method, which can be scaled up to mass-produced for industrial applications [32]. The thin film deposited by magnetron sputtering is uniform and the properties of the thin film can be reproducible.

In this study, we report on the PEC performance of CuO_x photoelectrodes prepared by AC magnetron reactive sputtering. The electrochemical properties of the CuO_x photoelectrodes were characterized by electrochemical impedance spectroscopy (EIS), Mott–Schottky and PEC performance measurement. Scanning electron microscope (SEM), X-ray diffraction (XRD), Raman spectrum, X-ray photoelectron spectroscope (XPS) and UV–Vis diffuse reflectance spectrum were utilized to characterize the structures and morphologies of the CuO_x thin films.

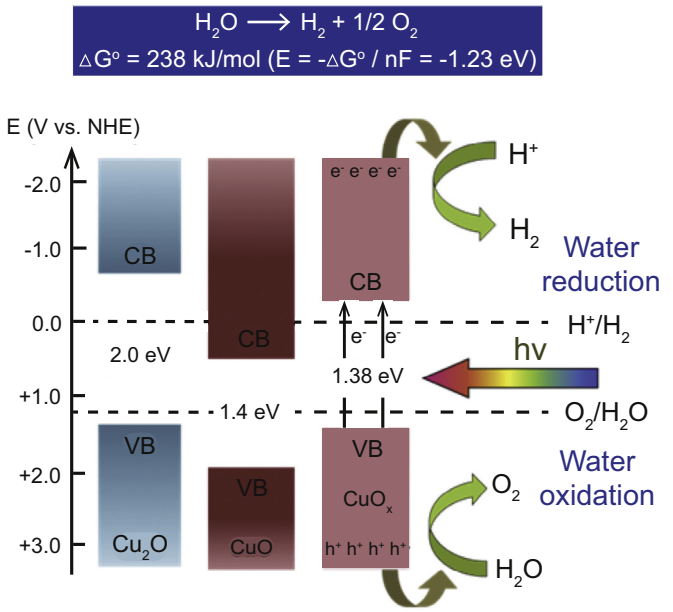

Fig. 1. Band diagram of mixed valence copper oxide system.

2. Experimental

2.1. Preparation of CuO_x thin films and photoelectrodes

FTO glasses (1.2 cm × 1.0 cm) were ultrasonically cleaned with ethanol and acetone (1:1) mixed solutions for 5 min firstly, then ultrasonically cleaned with ultrapure water for 5 min, and blow-dried with N_2. The CuO_x thin films were prepared by AC magnetron reactive sputtering at room temperature in Ar and O_2 ambient, using a target metal of copper. During the process of sputtering, the deposition chamber was pumped down to a pressure of 2×10^{-5} Pa. The target was cleaned by a pre-sputtering in Ar gas atmosphere for 5 min, then followed by a second pre-sputtering with Ar and O_2 mixture ambient for 3 min. In this experiment, the sputtering power was fixed at 30 W, and the Ar gas flow was fixed at 30 sccm. The O_2 gas flow was adjusted from 5 sccm to 9 sccm to analyze the effects of Ar/O_2 gas ratio on PEC performance of the products. The thickness of the CuO_x thin films is approximately 220 nm. After deposition, use a conductive sliver tape to connect copper wires with the conductive parts of FTO glasses. And after the conductive tape dried, isolated the exposed conductive parts of FTO glasses with parafilm.

2.2. Characterization

The microstructures of the products were characterized by X-ray diffraction (X'Pert Powder, PANalytical B.V., Almelo, The Netherlands), scanning electron microscope (JSM-6700F, JEOL, Tokyo, Japan), and Raman spectrum (STR-500, Cornes Technologies LTD., Tokyo, Japan). X-ray photoelectron spectroscopy (PHI 5000 Versa Probe, 2ULVAC-PHI, Chigasaki, Japan) was utilized to investigate the element composition, the element chemical and electronic state of the products. Whereas their light absorption capabilities were analyzed by UV–Vis diffuse reflectance spectrophotometer (U-2600, SHIMADZU Co., Kyoto, Japan).

2.3. Photoelectrochemical measurements

The Photoelectrochemical test was performed on CHI660D Electrochemical Workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). In which, using a three-electrode system, the prepared CuO_x thin film (1 cm^2), Pt sheet and Ag/AgCl (saturated KCl) electrode were acted as the working electrode, counter electrode and reference electrode, respectively. The three-electrode was immersed into 0.1 mol/L Na_2SO_4 electrolyte solutions. The incident light is from 300 W Xe lamp light source (PLS-SXE300, Beijing bofeilai Technology Co., Ltd., Beijing, China) with a light intensity adjusted to 200 mW/cm^2. The photoinduced current with potential was tested from 0.5 V to −0.5 V (vs. Ag/AgCl) with a

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