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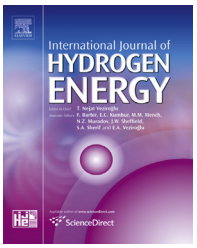

Application of CuS–ZnS PN junction for photoelectrochemical water splitting

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ABSTRACT

A CuS thin film was prepared by the sulfurization of the electrodeposited copper layer on the FTO substrate using sulfur powder at 400 °C. Surface morphology and structure of the CuS thin film were investigated by scanning electron microscopy and X-ray diffraction. The surface morphology of the CuS thin film was worm-like with the diameter of 70 nm and its crystal structure was hexagonal. Band gap energy of the CuS thin film was obtained as 1.5 eV using absorption spectra. Photoelectrochemical response of the CuS thin film was analyzed under chopped illumination at negative and positive potentials. It showed photoelectrochemical response at negative potentials (ca. 2.6 μA cm^{-2} at −0.4 V vs. Ag/AgCl), but not at positive potentials, which confirmed its p-type semiconductivity. A ZnS thin film was synthesized by spray pyrolysis method and characterized using field emission scanning electron microscopy, X-ray diffraction and UV–vis spectrometer. It was shown that the surface morphology was smooth with the grain size of about 50–150 nm. Also, its crystal structure and band gap energy were hexagonal and 3.72 eV, respectively. In order to obtain PN (positive–negative) junction and increase photoelectrochemical response, the ZnS (n-type semiconductor) thin film was deposited on CuS (p-type semiconductor). Linear scan of elemental composition confirmed the presence of FTO, CuS and ZnS layers. Photoelectrochemical characterization showed more photoresponse than the CuS thin film at negative potentials (13.6 μA cm^{-2} at −0.4 V vs. Ag/AgCl) and no photoresponse at positive potentials. The results confirmed the synthesizing of PN junction at the interface of CuS and ZnS.

Introduction

Production of hydrogen as an environmentally friendly and economical energy source by photoelectrochemical water splitting has attracted great attention [1]. Photoelectrochemical (PEC) water splitting is an economically viable technology, however there are still problems should be addressed to find its route to industry [2]. Finding materials which provide the requirements for photoelectrochemical water splitting is of great importance. Since Fujishima and Honda first reported the photoelectrochemical water splitting on a TiO_2 electrode, numerous active photocatalysts for water splitting have been synthesized and investigated [3,4]. Photoactive materials for water splitting should meet suitable chemical and optical properties, including good visible

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response [5], high stability in dark (corrosion) and under illumination (photocorrosion), suitable bands' edge positions to enable the reduction/oxidation of water by the photo generated electrons/holes, efficient charge transport in the semiconductor and low over-potentials for the reduction/oxidation reaction (high catalytic activity) [6]. Recently, metal sulfides have been intensively studied in photocatalysis and photoelectrochemical water splitting because of their suitable band gap and catalytic function [7,8].

CuS is a prominent I–VI semiconductor owing to its excellent optical, electronic, physical and chemical properties. It is found to be a p-type semiconductor with the direct band gap of (1.63–1.87 [9]) (2.433–2.526 [10]) 1.26 [11] (1.6–2.4 [12]) 2.8 [13] (2.52–2.58 [14]), which makes it interesting for energy conversion and photocatalysis under visible light [15–17]. Several techniques have been reported for the preparation of various shapes of CuS to make full use of its photocatalytical abilities under visible light, such as hydrothermal route [9,15], chemical solution method [18,19], RF reactive sputtering [20], multi-deposition process [14], spray pyrolysis [21], chemical bath deposition [10,12,13], electrochemical deposition [11,22] and exposing of Cu to Na_2S solution [23]. Electrochemical deposition is one of the promising methods for preparing thin films due to its simplicity and less energy consumption [24]. In this work, the Cu film was first electrodeposited on the FTO glass followed by sulfurization to form the CuS thin film.

In addition, ZnS is a well-known semiconductor, owing to its bands' edge positions, showing a high activity for H_2 evolution. ZnS is an n-type semiconductor with a wide band gap energy (3.5–3.7 eV), which makes it solely absorb UV light. Absorbing only 4% of the total sunlight restricts its practical application [25]. Thus, it is highly desirable to combine ZnS semiconductor with a semiconductor with narrow band gap energy like CuS. Besides, CuS is highly susceptible to photocorrosion and it is suggested to be protected by a large band gap semiconductor [26]. Formation of PN junction using CuS (p-type) and ZnS (n-type) semiconductors increases electron–hole lifetime before recombination. CuS/ZnS has been used for photocatalytic application [26–28] and photoelectrochemical hydrogen production [3,29]. ZnS has been deposited by various techniques, including chemical bath deposition [30], electrodeposition [31] and spray pyrolysis [32]. Spray pyrolysis is a simple and inexpensive method with the capability to fabricate large-area films and has been used to deposit ZnS thin films. In spray pyrolysis method, the precursor solution is sprayed by a stream of a gas onto the pre-heated substrate, where upon the thermal decomposition of the precursor an adherent film forms. The most important parameters including the initial solution, the substrate surface temperature and the spray rate of solution determine the quality of the thin film [33,34]. In this study, ZnS thin film was deposited on the CuS semiconductor by spray pyrolysis method and its photoelectrochemical properties were investigated. The prime novelty of this work was the fabrication of CuS–ZnS PN junction by two simple methods: electrodeposition and spray pyrolysis, and evaluating their photoelectrochemical water splitting.

Material and methods

Synthesizing CuS by electrodeposition and sulfurization

Analytical reagent grade chemicals (supplied by MERCK) were used for bath preparation. Copper precursor layer was electrodeposited in an aqueous electrolytic solution containing copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), 0.02 M, trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), 0.02 M, and sodium sulfate (Na_2SO_4), 0.6 M. The electrodeposition was performed at the potential of −0.4 V vs. Ag/AgCl and 25 °C without stirring for 1000 s in order to maintain the process diffusion control. The electrochemical cell contained an Ag/AgCl reference electrode, a platinum electrode as an inert counter electrode and FTO as the substrate with the deposition area of 1×1 cm^2 as working electrode. Before electroplating, the FTO substrate was cleaned ultrasonically in a detergent, acetone and distilled water. The electrodeposited copper layer was sulfurized using sulfur powder at 400 °C. The sample was introduced with 10 mg sulfur powder (99.99% purity) into a pyrex ampoule. Then, the pyrex ampoule was sealed. Subsequently, the ampoules were placed in a box furnace. The temperature was increased from room temperature to 400 °C with the heating rate of 15 °C/min and, subsequently, held at that temperature for 60 min. After sulfurization, the pyrex ampoule was allowed to cool down to room temperature naturally.

Synthesizing ZnS thin film by spray pyrolysis method

Thin film of ZnS was prepared on the glass substrate using spray pyrolysis method. The precursor solution was prepared by dissolving high purity $ZnSO_4 \cdot 7H_2O$ (0.03 M) and $SC(NH_2)_2$ (0.12 M) in 200 cc deionized water. This aqueous solution was magnetically stirred for 60 min. The precursor solution thus obtained was sprayed intermittently on the pre-heated glass substrate with the dimensions of $75 \times 25 \times 2$ mm^3. The substrate was pre-cleaned ultrasonically with a detergent, acetone and distilled water, to remove contaminations. The intermittent spray deposition followed in this study was a two-step procedure: 25 cc spray and a 300 s interval. Regarding the preparation conditions, the distance between the spray nozzle and the substrate was 34 cm and the spray rate was 3 mL min^{-1}. The temperature of the glass substrate was maintained at 500 °C during the whole spraying process. This temperature value was selected based on our past investigations. The temperature of the substrate was monitored using a temperature controller with a chromel–alumel thermocouple.

Synthesizing ZnS by spray pyrolysis method on CuS

The CuS thin film was prepared on the FTO substrate as described in Section Synthesizing CuS by electrodeposition and sulfurization. Then, the ZnS thin film was fabricated on the CuS layer by spray pyrolysis method according to Section Synthesizing ZnS thin film by spray pyrolysis method.

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