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Pulsed laser/ electrodeposited $CuBi_2O_4/BiVO_4$ p-n heterojunction for solar water splitting

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ABSTRACT

$CuBi_2O_4$ is regarded as p-type candidate for photoelectrochemical water splitting due to its attractive thermodynamic and band structure features. In this work, we present the optimization of $CuBi_2O_4$ thin films synthesized by electrodeposition method on FTO glass substrate. $CuBi_2O_4/BiVO_4$ heterojunction were further fabricated by depositing $BiVO_4$ on $CuBi_2O_4$ with pulsed laser deposition method. The influence of parameters such as the electrodeposition time and pulse count of PLD deposition on performance of the heterojunctions was studied. The films were characterized by X-ray diffraction, SEM, UV–Vis and electrochemical properties. The optimal deposition condition for $CuBi_2O_4$ sample was found to be electrodeposition for 20 min and annealing at 500 °C for 4 h. Pulse laser deposition (PLD) was used for the first time to deposit $BiVO_4$ on $CuBi_2O_4$ to form p-n heterojunction. The photoelectrochemical behavior study of sample with different $BiVO_4$ thin film thickness showed that the optimal photocurrent is $-0.25\ mA/cm^2$ in 0.1 M Na_2SO_4 (pH = 6), which is doubled comparing to that of the bare $CuBi_2O_4$ film.

1. Introduction

The increasing consumption of fossil fuels causes the global warming and the sea level rising with glacier melting. The air is also polluted which threatens people's health with toxin fog in winter [1]. Therefore, there is an urgent necessity to develop an alternative environmental-friendly and sustainable energy. Solar hydrogen is a promising solution that uses free solar energy as source and clean hydrogen as carrier.

In 1972, Japanese scientists Fujishima and Honda proved that TiO_2 can split water into hydrogen and oxygen under the illumination of ultraviolet light, which triggered a decades-long and ongoing research for photocatalytic/photoelectrochemical water splitting [2]. Until now, lots of researchers have conducted studies on various materials and structures for efficient water splitting for hydrogen.

These investigated semiconductor materials for photoelectrochemical (PEC) water splitting can be divided into two types: p-type semiconductors and n-type semiconductors [3]. Between them, the n-type semiconductors have been intensively investigated and some materials show excellent photoelectrochemical performance. For instance, TiO_2 [4], Fe_2O_3 [5], WO_3 and $BiVO_4$ [6,7] are typical n-type semiconductor materials which show good photoelectrochemical performance. However, these n-type photoanode is mainly used to achieve the water oxidation rather than water reduction for hydrogen. While the material for the cathodic hydrogen evolution have been much less investigated. Recently, p-type based semiconductor materials become an increasing hot research direction. Up to now, many photocathode materials have been fabricated for water reduction, such as Cu_2O [8], CuZnSnS [9] etc. These p-type materials-based photocathodes have high photocurrent but they have drawbacks such as instability and photocorrosion. Thus, more studies are needed on stable p-type materials with good photoelectrical performance.

$CuBi_2O_4$ as a p-type semiconductor has attracted intense research recently [10]. It has a band gap of ~ 1.5 eV [11], high absorption coefficient and proper band edge position with conductive band more negative than water reduction potential and valence band more positive than water oxidation potential [12]. There are many approaches to fabricate $CuBi_2O_4$ film as photocathode such as electrodeposition [13], spray pyrolysis [14] and flux-mediated one-pot solution [15]. For the reported $CuBi_2O_4$ film photocathode [13], the photocurrent is relatively low at about $0.1\ mA/cm^2$ compared to that of other p-type semiconductors like Cu_2O($7.6\ mA/cm^2$) [8]. Therefore, measures should be taken to improve the photocurrent of $CuBi_2O_4$ photocathode. As being widely recognized, heterojunction is a significant structure for improving the photoelectrochemical performance of single semiconductor materials. For example, Cu_2O/ZnO heterojunction was used to improve the stability of Cu_2O and its performance [16]. $WO_3/BiVO_4$ heterojunction core/shell structure facilitates the separation of charge carriers

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and improvement of the efficiency of PEC water splitting [17]. As for $CuBi_2O_4$ film, few papers about its heterojunction for photoelectrochemical application were reported. Therefore, fabricating $CuBi_2O_4$ based heterojunction structure remains as a potential approach to improve the separation of charge carriers. Herewith, $CuBi_2O_4/BiVO_4$ film heterojunction was fabricated to achieve this goal. In the experiment, $CuBi_2O_4$ film photocathode was fabricated by electrodeposition with its deposition parameters optimized. Besides, Pulse laser deposition (PLD) was used for the first time to deposit $BiVO_4$ on $CuBi_2O_4$ to form p-n heterojunction. The thickness of $BiVO_4$ was optimized by varying the PLD laser shooting times. The $CuBi_2O_4/BiVO_4$ heterojunction enhanced the photoelectrochemical performance of $CuBi_2O_4$ with a doubled photocurrent.

2. Experimental

2.1. Chemical reagents

Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), copper (II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), tartaric acid, sodium sulfate (Na_2SO_4), acetone(CH_3COCH_3), ethanol (C_2H_5OH) and sodium hydroxide (NaOH) were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. $BiVO_4$ target (99.99%) was purchased from Hefei Kejing Materials Technology Co., Ltd and used without further purification.

2.2. Fabrication of $CuBi_2O_4$ film photocathode

The $CuBi_2O_4$ film photocathode was fabricated by electrodeposition (ED) method described elsewhere [13]. Briefly, a three-electrode system was used in the experiment to electrodeposit $CuBi_2O_4$ film electrode. The FTO (Fluorine doped Tin oxide) coated glass with the size of 2 cm × 4 cm was used as the working electrode and Pt coil was used as the counter electrode. The reference electrode was Ag/AgCl (KCl, saturated) electrode.

Before the ED was carried out, the FTO glass substrate was cleaned in acetone, ethanol and deionized water (18.25 MΩ cm) separately for 20 min. Then the FTO glass was dried by N_2 stream. The plate solution consisted of 0.03 M $CuSO_4{\cdot}5H_2O$, 0.02 M $Bi(NO_3)_3{\cdot}5H_2O$ and 0.05 M tartaric acid. The pH of plate solution was adjusted to 13.0 by 2 M NaOH solution.

During the electrodeposition process, the plate solution was maintained at 65 °C and under slow stirring. The ED was carried out at a constant potential of 2.2 V (vs. Ag/AgCl), which was provided by an electrochemical station CHI 760D from Chenhua Instruments of Shanghai. After electrodeposition, the film was rinsed with deionized water and dried in N_2 flow. Finally, the film was annealed at certain temperature for 4 h at a heating rate of 10 °C/min in muffle furnace.

2.3. Fabrication of $CuBi_2O_4/BiVO_4$ heterojunction electrode

Pulsed Laser Deposition (PLD) system consisting of an excimer laser (COMPex Pro 102F, Coherent, USA) and a deposition chamber (Pioneer 180, Neocera, USA) was used to deposit $BiVO_4$ film on $CuBi_2O_4$ prepared by electrodeposition to form $CuBi_2O_4/BiVO_4$ heterojunction. The $BiVO_4$ target material with the purity of 99.99% was purchased from Hefei Kejing Materials Technology Co., Ltd. The $CuBi_2O_4$ film electrode was used as the substrate, which was inserted into the PLD vacuum chamber and maintained at room temperature (25 °C) under O_2 pressure of 10 mTorr. The substrate was preablation with laser pulses at 10 Hz for 1000 shots with the total energy of 300 mJ. The deposition of $BiVO_4$ was carried out at 5 Hz with the same total energy. Laser shooting counts were varied to optimize the $CuBi_2O_4/BiVO_4$ heterojunction electrode. After PLD process, the $CuBi_2O_4/BiVO_4$ heterojunction was annealed at 500 °C for 4 h at the heating rate of 5 °C/min in muffle furnace.

2.4. Evaluation of $CuBi_2O_4$ film and $CuBi_2O_4/BiVO_4$ heterojunction

To measure the phase and composition of samples, X-Ray Diffraction (XRD) was used in the experiment (PANalytical, using Cu Kα as irradiation source, λ = 15.1484 nm). Field emission scanning electron microscopy (SEM) was performed to examine the morphology and cross-sectional view of samples (JEOL, JSM-7800FE). UV–vis–NIR absorption spectra were measured by a Cary 5000 UV–vis–NIR spectrophotometer (Agilent). The sample was placed in front of the integrating sphere for the transmission mode measurement. Reflection mode measurement was carried out by putting the sample at the backside of the integrating sphere. The standard three electrode system was used to measure the photoelectrochemical performance of films. The sample electrodes were used as working electrode and a Pt coil was used as counter electrode. The reference electrode was Ag/AgCl (KCl, saturated). The photocurrents and impedances of film electrodes were measured in a homemade reactor under the illumination of calibrated 100 mW/cm^2 simulated solar light using 350 W xenon lamp set with an AM1.5 filter. The electrolyte used for photoelectrochemical property measurement is 0.1 M Na_2SO_4 (pH = 6) and electrochemical station CHI 760D (Chenhua Instruments Company of Shanghai) was used to provide bias and record data. The dissolved oxygen in the Na_2SO_4 solution used in the measurement of photoelectrochemical performance had been diminished by a 30 min N_2 bubbling.

3. Results and discussion

3.1. Optimization of $CuBi_2O_4$ film

In the experiment, $CuBi_2O_4$ film was fabricated by electrodepositon [13]. To get a better $CuBi_2O_4$ film with even surface, electrodepositon time and annealing temperature were varied in our experiment. At the same time, the impact of electrodeposition time and annealing temperature on $CuBi_2O_4$ film were studied.

3.1.1. Influence of various annealing temperature

As we adopt a two-step method to fabricate $CuBi_2O_4$ film, the annealing temperature will be crucial for the growth of $CuBi_2O_4$. First, CuO and Bi_2O_3 were co-electrodeposited on FTO and the obtained film was then annealed to produce $CuBi_2O_4$. Meanwhile, annealing also improved the crystallization of $CuBi_2O_4$ film. To search for optimal annealing temperature, annealing at three different temperatures 200 °C, 400 °C and 500 °C were conducted.

X-Ray Diffraction (XRD) was carried out to study the crystal structure of film. Fig. 1 shows the XRD patterns of the films annealed at different temperatures. From the XRD result, it was clearly shown that

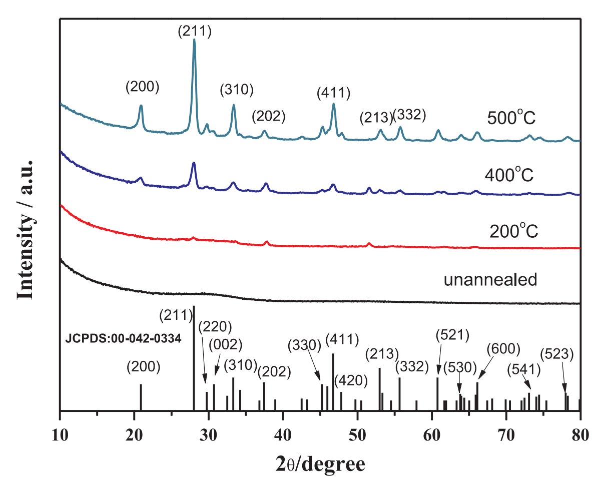

Fig. 1. XRD pattern of $CuBi_2O_4$ film at different annealing temperature.