Fabrication and photoelectrochemical study of selenide and oxide heterostructures for solar hydrogen evolution

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Abstract. We report the synthesis and photoelectrochemical (PEC) studies of a novel CdSe/BiVO₄ planar heterojunction photoelectrodes for photoelectrochemical water splitting fabricated by chemical bath deposition of CdSe on the spin-coated BiVO₄ layers. Temperature and time of chemical bath deposition were investigated to obtain the optimal deposition condition. The optimized CdSe/BiVO₄ with enhanced photo absorption yielded a maximum photocurrent density of 2.48 mA under the irradiation of AM 1.5 G (100 mW/cm²) simulated solar light illumination, which is enhanced by 3.87 times compared to bare BiVO₄.

1 Introduction

Photoelectrochemical water splitting for hydrogen production has attracted intensive efforts as a feasible solution for solar energy conversion since the 1970s in the situation of energy crisis and environmental issues^[1-3]. Although much progress has been achieved, the energy conversion efficiency and stability of the materials remain the two main challenges. Metal oxides and metal (oxy)nitrides usually have satisfactory stability under experimental condition while the efficiencies of those are not high enough^[4]. Metal sulphides show excellent efficiencies while they are not quite stable^[5, 6]. TiO₂ is one of the first and most studied semiconductor materials. However, the poor ability of visible light utilization blocks its further development.

Since then, numerous metal oxides such as WO₃^[7-9], BiVO₄, and Fe₂O₃^[10-12] with visible light response have been investigated. BiVO₄ shows the potential as one of the most promising candidate materials for photocatalytic water splitting because of its high activity and advantageous visible light absorption. However, the severe charge recombination and poor electron/hole conductivity hinder the further application^[13]. Nevertheless, the visible light absorption range of BiVO₄ is not wide, which can only utilize irradiation wavelength less than 520 nm from sunlight. Therefore, many strategies have been developed to promote the efficiency of metal oxides^[14].

Constructing the suitable heterojunction structure is an effective solution among the modification strategies^[15, 16]. Metal selenides such as CdSe have been widely used as sensitizers for their narrow band gaps and wide range absorption spectra. TiO₂ and many other wide band gap metal oxides have been investigated to form heterojunction structures for enhanced light absorption and improved charge separation.

However, BiVO₄ has been rarely sensitized with narrow band gap materials such as CdSe. In the present study, a facile method for the fabrication of planar heterostructure of CdSe/BiVO₄ films has been adopted and the structure resulted in enhanced photoelectrochemical performance. The physical and photoelectrochemical properties were investigated and the mechanism was also discussed in detail.

2 Experimental Section

2.1 Preparation procedure

Preparation of BiVO₄ films. BiVO₄ films on transparent conductive fluorine-doped tin oxide (FTO) substrates were synthesized by a polymer-assisted sol-gel method^[17]. FTO coated glasses (TEC-15 15 Ω/sp) were cleaned by ultrasonic cleaning in acetone, ethanol and deionized water for 30 min, respectively, and then dried under nitrogen stream. The precursors were prepared by adding EDTA (Ethylene Diamine Tetraacetic Acid) into Bi(NO₃)₃·5H₂O in nitric acid and NH₄VO₃ in ammonia water, respectively, and then mixed the two solutions to obtain the BiVO₄ precursor (0.1 M, 100 mL). 10 g of polyvinyl alcohol (PVA) was dissolved into 100 mL deionized water. The BiVO₄ precursor and PVA solution were mixed (V/V=1:1) to obtain a colloidal solution. The colloidal solution was then spin-coated on FTO substrates (3000 rpm, 30 s), dried at 120 °C and then calcined at 450 °C for 2 h.

Chemical bath deposition of CdSe. Deposition of CdSe on BiVO₄ films to form heterostructures was conducted by chemical bath deposition (CBD) method. 0.02 mol of Se powder was solved into 100 mL of 0.5 M Na₂SO₃ aqueous solution. Then the Se solution was maintained at 70 °C and refluxed for 5 h with nitrogen as

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protection atmosphere to obtain solution. The solution was stored for further use under 60 °C. 0.253 g KOH was added into 50 mL of deionized water and stirred. 0.285 g of aminotriacetic acid was added after KOH completely dissolved into the solution. After 0.5 h reaction, 0.309 g of chromic nitrate was added. Then the solution was kept at reaction temperature for 0.5 h and 5 mL of Na₂SeSO₃ solution was added slowly. The as-prepared BiVO₄ films glass was then put into the flask at a certain angle. Then the flasks were transfer to oven for chemical bath deposition. After reaction, the electrodes were taken out and rinsed with clean water and then dried under nitrogen stream. The prepared photoelectrodes are named as CdSe/BiVO₄-70-6h.

2.2 Photoelectrochemical measurements

Photoelectrochemical and electrochemical measurements were carried out in a conventional three electrodes cell, with illumination from the backside and a saturated Ag/AgCl as the reference electrode, with a CHI760D electrochemical workstation. Photocurrents were recorded under 100 mW/cm² AM 1.5 G irradiation with a 300 W xenon lamp as the white-light source in a 0.5 M Na₂SO₃ aqueous electrolyte. Incident photon to current conversion efficiencies (IPCEs) were measured at 0.76 V vs. RHE in 0.5 M Na₂SO₃ solution with a monochromator. The potentials vs. Ag/AgCl were converted to potentials vs. the reversible hydrogen electrode (RHE) by the following Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.059\text{pH} + E^{\circ}_{Ag/AgCl}$, where $E^{\circ}_{Ag/AgCl} = 0.1976$ V at 25 °C.

3 Results and discussion

Fig. 1 shows the SEM images of CdSe/BiVO₄ films in different deposition conditions and bare BiVO₄ for comparison. From the images, all the samples fabricated under various temperatures and time conditions show flat and smooth surfaces, which indicates that the combination of spin-coating and CBD methods works well. The CdSe particles are deposited onto BiVO₄ films and the latter are covered as underlayer, which resulted into a planar heterojunction. When the reaction time is not sufficient (2h), the size of CdSe particles are relatively small. With the increase of deposition time, the particle sizes grow from 30 nm to more than 100nm. From the inset image (Fig. 1d), the thickness of CdSe of 8 h deposition can be estimated to be 500 nm.

Figure 1. SEM images of the CdSe/BiVO₄ heterostructure photoelectrodes. (a)70 °C, 2h, (b)70 °C, 4h, (c)70 °C, 6h, (d)70 °C, 8h.

The photocurrent densities of the various samples are shown in Fig. 2. The optimal temperature for high photocurrent densities are between 70 and 80 °C. When the temperature is too much higher or lower, the activities decreases due to the aggregation of particles. The reaction time is more important than temperature. When the reaction time is short, the activities are all very low, while the reaction time increase to ~6 h, the activities show the best performances. Obviously, when reaction time are too long, the activities of the samples also decrease due to the larger sizes.

Figure 2. Photocurrent activities of the CdSe/BiVO₄ planar heterostructure photoelectrodes under various conditions.

In order to confirm the crystal structure of the hybrid films, XRD patterns are tested and shown in Figure 3. The patterns of monoclinic BiVO₄ are also shown for comparison, which indicate that the film has good crystallinity and the patterns match well with JCPDS card NO.14-0688. After chemical bath deposition of CdSe, the XRD signals show apparent changes. The new peaks at 25.4° and 42.5° are attributed to CdSe characteristic patterns. With the increasing deposition time, the signals intensities become much stronger, indicating the successful deposition of CdSe.

Figure 3. XRD patterns of CdSe/ BiVO₄ heterostructure photoelectrodes prepared with different deposition time and the patterns of bare BiVO₄ film as a reference.

As is well known, BiVO₄ has a relatively narrow band gap of 2.0-2.1 eV. As a result, the photo absorbance has a great potential to be enhanced. The absorbance onset of BiVO₄ is around 500 nm (Fig. 4), which indicates that only a small part of visible can be absorb and utilized by bare BiVO₄ film. After deposition with CdSe, the photoelectrodes shows remarkable improvement of absorbance. The absorbance onset was around 680 nm. It is noteworthy that when the deposition time increases after 6 h, the absorbance of the films remains unchanged, indicating that the amount of CdSe do not increase with the deposition time but only influence the particle size. As a result, the deposition time should be no more than 6 h for cost-effective consideration.

Figure 4. UV-Vis absorbance spectra of bare BiVO₄ and CdSe/ BiVO₄ heterostructure photoelectrodes at different deposition time.

Fig. 5 shows the photocurrent-potential plots of the CdSe sensitized heterostructures and the plot of bare BiVO₄ is also shown for comparison. All the samples show good irradiation response and the dark current can be neglected. The photocurrent density of bare BiVO₄ is relatively low and the current onset locates at around 0.3 V vs. RHE. After CdSe deposition, the photocurrent

densities show a remarkable increase. With the deposition time grow, the thicknesses of the hybrid films also increase, which lead to the increase of the light absorption and thus the photocurrent density increases consequently. And the best performance shows at the sample of 70 °C and 6 h, which is about 2.48 mA/cm² and 3.87 times higher than that of bare BiVO₄. However, the sample prepared at 70 °C and 8h shows a decrease of photocurrent, which is ascribed to the aggregation of the larger particles. The significant enhancement of CdSe sensitization verifies the strategy of selenide and oxide heterostructure. On one hand, CdSe acts as the solar absorber, which can absorb much more light than bare BiVO₄. On the other hand, the heterojunction structure is beneficial for the charge transfer, which promotes the PEC performance.

Figure 5. Photocurrent-potential plots of bare BiVO₄ and CdSe/ BiVO₄ heterostructure photoelectrodes.

Incident photon to current conversion efficiency (IPCE) data were also tested to evaluate the PEC performances of the samples under specific solar illumination wavelengths. The IPCE values were calculated by the equation:

$$IPCE = (1240I)/(\lambda P),$$

where I is the photocurrent density measured at a specific wavelength, λ is the wavelength of incident light and P is the power intensity of the light. Both the samples before and after sensitization show substantial visible light responses from Fig. 6. Bare BiVO₄ shows a narrow visible light response till to 500 nm. After 6 h CdSe deposition at 70 °C, the visible light response red shift to ~680 nm and the values are much higher.

Figure 6. Incident photon to current conversion efficiency (IPCE) plots of the samples measured at 0.76 V vs. RHE in 0.5 M Na₂SO₃ solution.

4 Conclusions

Via the effective spin-coating of oxides layers and chemical bath deposition of selenides, the visible light material BiVO₄ can be further sensitized to utilize broader range of solar irradiation. The successful fabrication of CdSe/BiVO₄ heterojunction photoanodes results in the enhanced PEC performance, which is ascribed to both the enhanced solar absorbance and the improved charge transport and transfer properties. The maximum photocurrent density of 2.48 mA is 3.87 times higher compared to bare BiVO₄. From the physical and PEC measurements, the heterostructure proves to be an effective strategy for efficient PEC hydrogen production. The present work can provide beneficial guides and deep insights for the sensitization of visible light photoelectrochemical materials for PEC water splitting.

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