Journal of Colloid and Interface Science 534 (2019) 338–342

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

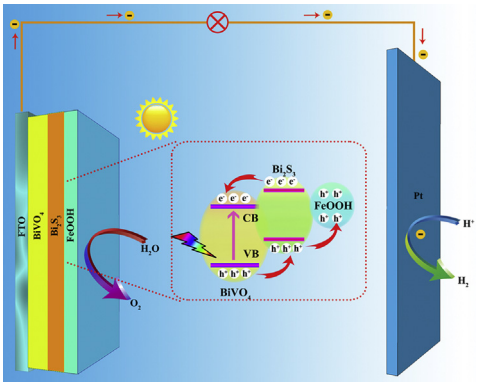
Regular Article

In situ fabrication of nanoporous $BiVO_4/Bi_2S_3$ nanosheets for enhanced photoelectrochemical water splitting

Min Wang, Qiming Wang, Peizhi Guo *, Zhengbo Jiao *

Institute of Materials for Energy and Environment, and College of Material Science and Engineering, Qingdao University, Qingdao 266071, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 August 2018
Revised 6 September 2018
Accepted 17 September 2018
Available online 18 September 2018

Keywords:
Photoelectrochemical
Nanocomposites
Water splitting
Co-catalysts
$BiVO_4$

ABSTRACT

Nanoporous $BiVO_4/Bi_2S_3$ nanosheets have been firstly fabricated through a two-step annealing followed by hydrothermal method using BiOI two-dimensional nanosheets as precursors, which could greatly improve the photoelectrochemical performances of $BiVO_4$ due to the enhanced charge separation efficiency and the enlarged absorption range. The optimal content of Bi_2S_3 in the $BiVO_4/Bi_2S_3$ nanocomposites has been explored by tuning the reaction time. In addition, it is found that loading co-catalysts FeOOH could further optimize the hole transfer pathway and thus enhance the photoelectrochemical water splitting ability.

1. Introduction

Solar driven photoelectrochemical (PEC) water splitting offers a potential strategy to harvest and store solar energy in the hydrogen form, which could alleviate the energy and environmental crisis [1]. Ever since the first demonstration of PEC water splitting using a TiO_2 photoelectrode, great efforts have been paid on the exploration of various semiconductors, such as ZnO, TiO_2 and WO_3 [2,3]. Nevertheless, most of the metal oxides are merely responsive to UV light due to their wide band gaps (>3 eV), and thus severely restrict their practical applications [4]. Thereby, research interests are stimulated to explore and study the visible light active photocatalysts.

Recently, Bi-based semiconductors ($BiVO_4$, Bi_5O_7I, Bi_2O_3, Bi_2WO_6, Bi_2MoO_6, $BiFeO_3$) have aroused great interests owing to

* Corresponding author.
E-mail addresses: pzguo@qdu.edu.cn (P. Guo), jiaozhb@qdu.edu.cn (Z. Jiao).

https://doi.org/10.1016/j.jcis.2018.09.056
0021-9797/

their appropriate band gap, nontoxicity, and chemical stability [5–8]. Among them, monoclinic bismuth vanadate (m-$BiVO_4$) was considered as a superior visible light responsive photoanode for PEC water splitting because of its moderate band gap. The valence band position of $BiVO_4$ located below the water oxidation potential enables it to produce oxygen. Moreover, it has an early photoconversion onset because its conduction band is near to hydrogen evolution potential. Nevertheless, pristine $BiVO_4$ usually exhibits low PEC performances because of the high recombination of photogenerated electron-hole pairs and the insufficient absorption ability [9]. Hence, numerous means have been adopted, such as hetero-coupling and co-catalysts loading [10–14].

Hetero-junction coupling with narrower bandgap semiconductors is an effective strategy to improve the light absorption range and facilitate the charge separation efficiency. Bi_2S_3 is a promising semiconductor for the construction of PEC devices due to its large absorption coefficient and narrow bandgap. Previous studies have demonstrated that $BiVO_4/Bi_2S_3$ heterostructures exhibit improved charge separation efficiency and enhanced photocatalytic performances [15–17]. However, there are rarely investigations about the PEC performances of $BiVO_4/Bi_2S_3$ nanoporous sheets. Furthermore, the influence of co-catalyst such as FeOOH on their PEC activities have not been disclosed until now.

In this work, we have firstly fabricated the $BiVO_4/Bi_2S_3$ nanoporous sheets with a simple two-step annealing followed by hydrothermal method using BiOI two-dimensional nanosheets as precursors. The uniform hybrid nanosheets are well aligned on FTO substrate and there are no obvious morphology changes with different reaction times from 20 min to 80 min. Nevertheless, it is found that the $BiVO_4/Bi_2S_3$ nanocomposites with 40 min demonstrated the best PEC activities, and the photocurrent would decrease if extending the reaction time. Moreover, the photocurrent could be further increased by loading co-catalyst FeOOH owing to the improved hole transfer pathway [18–20].

2. Experimental section

2.1. Materials

Vanadyl acetylacetonate DMSO, NaOH, $Bi(NO_3)_3{\cdot}5H_2O$, *p*-benzoquinone, polyvinylpyrrolidone (PVP, MW K-30), Na_2S and nitric acid were obtained from Sinopharm Chemical Reagent Co., Ltd. ITO glasses were purchased from Baisite Co., Ltd. Deionized water (18 MW, Molecular) was used for preparing all solutions.

2.2. Electrodeposition of BiOI electrodes

Our experiment has performed according to the previous literature [21], in which BiOI two-dimensional nanosheets were prepared through an electrodeposition procedure. 0.04 M $Bi(NO_3)_3$ solution was prepared by dissolving $Bi(NO_3)_3{\cdot}5H_2O$ in 50 mL 0.4 M KI solution after its pH was adjusted to 1.7 by adding HNO_3. Then 20 mL of absolute ethanol containing 0.23 M *p*-benzoquinone was added into this solution, and vigorously stirred for a few minutes. A typical three-electrode cell was used for electrodeposition. The ITO is used as the working electrode (WE), and the potential and time of deposition are also different. In our work, cathodic deposition was performed potentiostatically at −0.1 V vs. SCE 5 min after initial potentiostatically at −0.3 V vs. SCE 5 s. This is conducive to acquire more uniform electrodeposition film.

2.3. Synthesis of $BiVO_4$ electrodes

According to the literature, the BiOI electrode plunge into a 0.4 M vanadyl acetylacetonate DMSO for 1 min. Excessive vanadium source solution was removed by absorb the bottom edge of electrode with filter paper. The calcination process is similar to that documented and the difference is heat preservation of two hours under the condition of 450 °C. $BiVO_4$ electrodes were soaked in 1 M NaOH solution for 1 h to remove excess V_2O_5 that present in the surface of $BiVO_4$. Then the electrodes rinsed with DI water and dried at RT to get pure $BiVO_4$ electrodes.

2.4. Preparation of a series of $BiVO_4/Bi_2S_3$ nanocomposites electrodes

1 g of polyvinylpyrrolidone (PVP, MW K-30) was dissolved in 25 mL of 0.0323 M Na_2S solution with the assistance of ultrasonication for 20 min, which was transferred into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was heated to 150 °C for 30 min, 40 min, 50 min, 60 min, 80 min and cooled to room temperature. The product washed by DI water for several times, and dried at 60 °C for 4 h.

2.5. Characterization

Rigaku Ultima IV X-ray diffractometer (XRD, Cu-Kα radiation λ = 0.15418 nm) was be used for testing phase composition and crystal structure of electrodes. SEM image was obtained by a JEOL JSM-7800F scanning electron microscope and TEM picture was acquired through a JEOL JEM-2100 plus transmission electron microscope, which used to characterize the morphology and structure of the samples. UV/Vis diffuse reflectance spectra were taken on an UV-2550 (Shimadzu) spectrometer using $BaSO_4$ as the reference. XPS analysis was performed on a PHI 5000 VersaProbe III. Light source be obtained by a 300 W Xe lamp and AM 1.5 was used to simulate sunlight. Chi 660e electrochemical workstation was used to perform a series of photochemical tests.

3. Results and discussion

UV–vis diffuse reflectance spectra used to demonstrate the optical properties of the prepared photoelectrodes were shown in Fig. 1a. It can be seen that the absorption edge of pure $BiVO_4$ electrode was located in 610 nm and the corresponding bandgap energy was about 2.03 eV, which coincide with previous reports. It is noteworthy that $BiVO_4/Bi_2S_3$ composites possessed a wider range of visible light absorption than $BiVO_4$ electrodes and its absorption edge red shift to visible region. This testifies that the $BiVO_4/Bi_2S_3$ composites can absorb more visible light for the production of electron-hole pairs and thus improve the photochemical properties. X-ray diffraction (XRD) patterns of the synthesized products consist of $BiVO_4$, Bi_2S_3 and $BiVO_4/Bi_2S_3$ composites are shown in Fig. 1b. The main diffraction peaks are detected over the sample $BiVO_4$ and Bi_2S_3, which can be assigned to monoclinic $BiVO_4$ (JCPDS No. 14-0688) and Bi_2S_3 (JCPDS No. 17-0320) respectively.[16] Apparently, in contrast to nanoporous $BiVO_4$, no obvious diffraction peaks of Bi_2S_3 were observed in the $BiVO_4/Bi_2S_3$ composites with 40 min hydrothermal reaction. The possible reason of this result is that only a small part of $BiVO_4$ converted to Bi_2S_3 and the amount of Bi_2S_3 is too small to reach the detection scope of the XRD instrument. Moreover, further experiments suggest that increase of the reaction time (50 min, 60 min) of hydrothermal process, the intensities in accordance with Bi_2S_3 diffraction peaks become larger, a powerful display of the faultless preparation a series of $BiVO_4/Bi_2S_3$ composites. But no other phases and redundant impurity diffraction peaks were observed in the $BiVO_4/Bi_2S_3$ composites, manifesting that the as-prepared composite only include $BiVO_4$ and Bi_2S_3.

In order to further prove the existence of sulfur element and clarify the photochemical reactions occur mainly on the near