Applied Catalysis B: Environmental 179 (2015) 61–68

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

$AgSbS_2$ modified ZnO nanotube arrays for photoelectrochemical water splitting

Jianhua Han, Zhifeng Liu*, Keying Guo, Xueqi Zhang, Tiantian Hong, Bo Wang

School of Materials Science and Engineering, Tianjin Chengjian University, 300384 Tianjin, China

ARTICLE INFO

Article history:
Received 1 March 2015
Received in revised form 5 May 2015
Accepted 5 May 2015
Available online 6 May 2015

Keywords:
$AgSbS_2$
ZnO
Nanotube
Photoelectrochemical
Water splitting

ABSTRACT

Large-scale, vertically aligned $AgSbS_2$ modified ZnO nanotube arrays have been fabricated directly on conducting glass substrates (ITO) via a facile, versatile and low-cost hydrothermal chemical process by using ZnO nanorods as reactive templates. This method is easy to be controlled to develop uniform morphology, and it can be generalized to fabricate other ternary sensitizer nanomaterial for PEC water splitting. In this work, we present a novel ternary sensitizer miargyrite $AgSbS_2$ for optimized ZnO, and the $ZnO/AgSbS_2$ nanoarrays film was applied on photoelectrochemical (PEC) photoelectrodes. Strikingly, the photocurrent density of this electrode was up to 5.08 mA cm^{-2} at 0.096 V versus Ag/AgCl. The excellent PEC properties stems from the enhanced absorption spectrum, high speed of photo-induced charges transmission velocity and appropriate energy gap of coupled nanostructures. Furthermore, this work demonstrates a promising low-cost method for preparing ternary sensitizer modified ZnO nanoarrays as PEC electodes for hydrogen production by water splitting.

1. Introduction

As a sustainable, renewable and clean energy, hydrogen energy is considered for an ideal candidate for instead of the traditional fossil energy in view of the growing crisis from energy and environment issues [1–3]. In the past decades, the development and application of hydrogen technologies have received considerable attention due to its intrinsic properties such as carbon-free and high gravimetric energy [4–5]. Among all the methods to manufacture hydrogen, PEC water splitting into hydrogen by semiconductor photoelectrodes is one of the most promising and eco-friendly methods [6–9]. Since the first report on water splitting using TiO_2 photoelectrode by Fujishima and Honda, metal oxides (such as ZnO, TiO_2 and Fe_2O_3) have been intensively investigated as photoelectrodes in PEC system because of their low cost and easy availability [10–13]. The PEC performance of metallic oxide-based photoelectrodes was significantly related to its morphology and structure [14]. Zinc oxide, ZnO, is an important photoelectric semiconductor material due to its simply synthesized to multifarious nanostructures and its extremely fast electron transmission rate [15–16]. Of particular interest are one-dimensional (1D) ZnO nanostructures (such as nanowires [17], nanotubes [18] and nanorods [19]), which provide a direct electrical pathway for electron transmission that can promote photo-induced electrons transport and reduce the recombination of carriers [20–21]. Nevertheless, one of the major drawbacks that ZnO-based photoelectrodes suffer from is only the UV fraction can be absorbed on account of the wide band-gap of ZnO, which restricts its practical applications [22].

In order to solve the aforementioned problem, many efforts have been put to broaden the adsorption spectrum of ZnO, including elemental doping and coupling with narrow band-gap semiconductors etc. [23–24]. Among these techniques, an efficient way is to deposit a sensitizer with appropriate band gap on ZnO. Silver antimony sulfide ($AgSbS_2$, Miargyrite), which has a suitable band gap (1.72 eV) according with the visible light region and a high absorption coefficient ($\alpha \sim 10^5$ cm^{-1}), has attracted great interest [25–26]. However, to our best knowledge, there has been no report on PEC electrodes of one-dimensional ZnO nanoarrays modified with ternary $AgSbS_2$ so far, this study extends the work to a new coupled semiconductor of ternary sensitizer $AgSbS_2$ decorated ZnO nanoarrays.

Motivated by the above concerns, we have successfully fabricated a coupled semiconductor based on $AgSbS_2$ modified ZnO nanoarrays through a simple hydrothermal chemical process. The hydrothermal chemical method is inexpensive, facile and eco-friendly. In addition, the $ZnO/AgSbS_2$ nanotube arrays were demonstrated to exhibit enhanced PEC activity in hydrogen evolution from water splitting. In this study, ternary $AgSbS_2$ sensitizer

---

* Corresponding author. Tel.: +86 22 23085236; fax: +86 22 23085110.
E-mail address: tjulzf@163.com (Z. Liu).

http://dx.doi.org/10.1016/j.apcatb.2015.05.008

modified ZnO nanotube arrays was fabricated on ITO substrate and apply as PEC electrodes, the photocurrent density and the calculated theoretical efficiency for hydrogen production of the samples were evaluated to be up to 5.08 mA cm^{-2} and 5.76%, respectively. It is founded that the excellent performance is ascribed to the enhanced absorption efficiency, high speed of photo-induced charges transmission velocity and appropriate energy gap of coupled nanostructures. This study provides a promising low-cost method in the development of ternary absorber modified ZnO-based PEC electodes for water splitting system.

2. Experimental

2.1. Preparation of ZnO nanorod arrays

The preparation of ZnO nanorod arrays involves substrate pre-treatment and hydrothermal deposition. The ITO substrates ultrasonically rinsed for 30 min in acetone, isopropyl alcohol and ethanol absolution, respectively. A seed layer was firstly deposited on ITO by a dip-coating method, after heat treatment in muffle furnace at 400 °C for 1 h, followed by the incubation in the mixed solution of 0.05 M zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and 0.05 M hexamethylenetetramine (HMTA) at 90 °C for 4 h. The obtained samples were subsequently washed with distilled water and finally dried in air.

2.2. Preparation of ZnO/ZnS nanotube arrays

The ZnO/ZnS nanotube arrays were prepared by a chemical etching and ion-exchange process by using ZnO nanorods as reactive templates. The ZnO nanorods were immersed in 0.1 M thiacetamide (TAA) solution at 90 °C for 7 h to form ZnO/ZnS nanotube arrays. The as-prepared products were washed using distilled water and then dried in air.

2.3. Preparation of ZnO/$AgSbS_2$ nanotube arrays

The ZnO/$AgSbS_2$ nanotube arrays were prepared by means of a two-stage ion-exchange process. First, Ag_2S shell was grown around the ZnO core. Second, Sb_2S_3 shell was grown on the Ag_2S. The double layer Ag_2S/Sb_2S_3 was transformed into the $AgSbS_2$ by heating the sample to 300 °C in air for 30 min.

For the growth of ZnO/Ag_2S naonotube arrays process, 4 mg of siliver nitrate ($AgNO_3$) was dissolved in 25 mL deionized water, and the ZnO/ZnS naonotube arrays was immersed in the $AgNO_3$ solution and kept for 20 min at 28 °C. For the coating of Sb_2S_3 shell, 6 mg antimony trichloride ($SbCl_3$) was dissolved in 25 mL absolute ethanol, and the ZnO/Ag_2S nanotube arrays were immersed in the $SbCl_3$ solution kept at 35 °C for 2 h. The large difference in solubility product constant of ZnS, Ag_2S and Sb_2S_3 leading to the ZnO/Ag_2S/Sb_2S_3 can be formed adopt ion-exchange process. Finally, the samples of ZnO/$AgSbS_2$ were washed with deionized water and dried in air.

2.4. Characterization

Morphology and structure of the samples was observed by HITACHI S-4800I field emission scanning electron microscope (FE-SEM) and HITACHI H-7650 transmission electron microscopy (TEM) operated at an accelerating voltage of 100 kV. X-ray diffraction (XRD) patterns of the films were performed using a Rigaku D/max-2500 using Cu Kα radiation (λ = 0.154059 nm). Optical absorption spectrums of the samples were examined by DU-8B UV/vis double-beam spectrophotometer. The calculated efficiencies of hydrogen generation (η) of the ZnO/$AgSbS_2$ nanotube arrays were estimated using the following equation [27]:

$$\eta = \left[\frac{I(1.23 - E_{\mathrm{bias}})}{J_{\mathrm{light}}}\right] \times 100\% \qquad (1)$$

where I is the photocurrent density (mA cm^{-2}), 1.23 is the standard reduction potential of water formation from hydrogen and oxygen, E_{bias} is the applied external potential and J_{light} is the intensity of the solar simulated incident light (100 mW cm^{-2}).

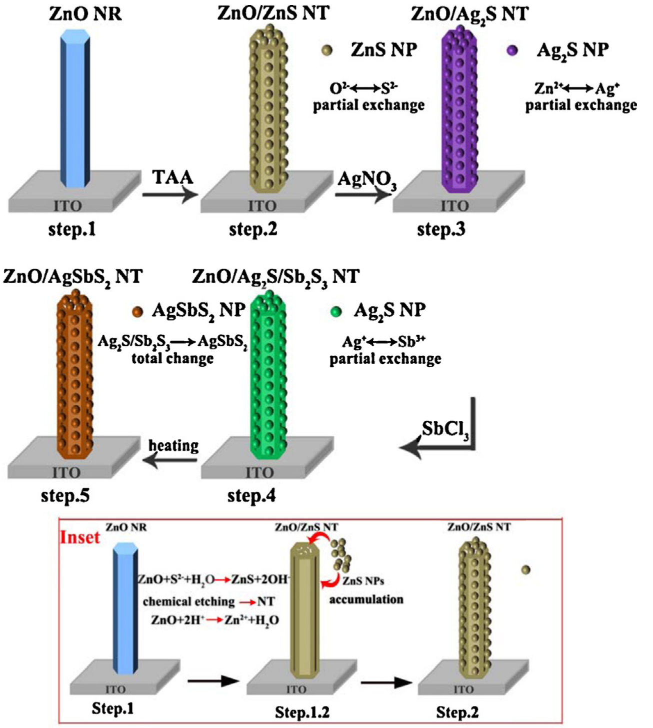

Fig. 1. Schematic illustration for the synthesis ZnO/$AgSbS_2$ nanotube arrays step by step; Inset shows: synthesis process of ZnO/ZnS NT arrays (Step.1–Step.2).

3. Results and discussion

In this work, miargyrite $AgSbS_2$ modified ZnO nanotube arrays were successfully fabricated on ITO substrates through a facile hydrothermal chemical method, and the preparation process is schematically illustrated in Fig. 1. First of all, large-scale orderly hexagonal ZnO NR arrays were fabricated on ITO by a simple hydrothermal process (Step.1). In this step, a seed layer of ZnO was coated on ITO substrate after heat treating, on which seed layer would develop into ZnO NR arrays in the growth solution. It should be noted that the chemical conversion method based on ion-exchange would take place spontaneously when there are sufficient differences in the solubility products constants (K_{sp}) between the reactants and the products [28–31]. Therefore, when the ITO coated with ZnO NR arrays is immersed into 0.1 M TAA solution, the sulfidation based on ion-change will occur due to large difference between the solubility product constants (K_{sp}) of ZnO (6.8×10^{-17}) and ZnS (2.93×10^{-25}) (Eqs. (2)–(4)).

$$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S \qquad (2)$$

$$H_2S \rightarrow 2H^{+} + S^{2-} \qquad (3)$$

$$ZnO + S^{2-} + H_2O \rightarrow ZnS + 2OH^{-} \qquad (4)$$

The further reaction of ZnO with H_2S around the surface leads to the ZnO/ZnS core/shell nanostructures (Step.2). Meanwhile, when the ZnO NR arrays were immersed in 0.1 M TAA solution, the NR