



Short communication

Novel Ag₂S/ZnS/carbon nanofiber ternary nanocomposite for highly efficient photocatalytic hydrogen production



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ARTICLE INFO

Article history:

Received 23 October 2015

Received in revised form 17 December 2015

Accepted 18 December 2015

Available online 23 December 2015

Keywords:

ZnS

Ag₂S

Carbon nanofiber

Ternary nanocomposite

Photocatalytic H₂ production

ABSTRACT

Novel Ag₂S/ZnS/carbon nanofiber (CNF) ternary nanocomposite with high photocatalytic H₂ production performance was synthesized by combination of an in-situ solid-state process and a cation-exchange reaction, using organic–inorganic layered zinc hydroxide nanofibers as precursor. Moreover, the loading amount of Ag₂S nanocrystals can be readily regulated by changing the AgNO₃ concentration, and the optimized H₂ production rate was 224.9 μmol h⁻¹, significantly higher than that of the reported ZnS-based composite photocatalysts. The synergistic effect of CNF and Ag₂S as water reduction and oxidation cocatalyst, respectively, can greatly suppress the charge recombination thus resulting in high photocatalytic H₂ production activity.

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1. Introduction

Photocatalytic water splitting into hydrogen using a semiconductor photocatalyst has attracted a lot of attention because it is a promising strategy to solve the increasing energy and environmental problems. Among various semiconductors, ZnS appears to be a suitable candidate for photocatalytic H₂ production because of its low price, nontoxicity, rapid generation of electron–hole pairs upon photoexcitation and highly negative reduction potentials of the excited electrons [1,2]. However, pure ZnS exhibits low photocatalytic activity due to the fast electron–hole recombination. The photocatalytic H₂ production activity on ZnS strongly depends on the type and amount of cocatalyst which can effectively capture the photogenerated electrons/holes to enhance the charge separation [3].

Carbon nanofiber (CNF), as a typical type of one-dimensional (1D) material in carbon family, has received a lot of attention due to its superior physicochemical, mechanical and electronic properties [4,5]. Large surface area, chemical stability and superior electronic conductivity of CNF not only make it as a high-performance support for semiconductor photocatalysts but also an efficient water reduction cocatalyst to induce electron transfer from the conduction band (CB) of semiconductors to CNF for H₂ production. For instance, several photocatalysts (such as ZnIn₂S₄, TiO₂, g-C₃N₄) have been combined with CNF to achieve enhanced photocatalytic water-splitting activity [6–8]. However, to our best knowledge, there is no report on H₂ production of ZnS/CNF nanocomposite with CNF as water reduction cocatalyst.

On the other hand, considering entire photocatalytic reaction, effective transport away of photogenerated holes from excitation site is also important. Several attempts have been made to combine water oxidation cocatalysts to improve the H₂ production activity [9–11]. Recently, Yang et al. reported the preparation of ZnS/Ag₂S porous nanosheets by a simple cation-exchange route [12]. It demonstrated that the application of Ag₂S as a water oxidation cocatalyst for assisting hole transfer is an effective way to enhance the H₂ production activity of ZnS. Herein, we report for the first time the construction of novel Ag₂S/ZnS/CNF ternary nanocomposite and its high photocatalytic performance. The H₂ production rate can reach up to 224.9 μmol h⁻¹ under optical conditions and the origin of high activity was also explored.

2. Experimental

Ag₂S/ZnS/CNF nanofibers were synthesized by simple combination of an in-situ solid-state process and a cation-exchange reaction, using benzoate (BA) anions intercalated layered zinc hydroxide (Zn(OH)BA) nanofibers as precursor (Fig. 1). First, well-dispersed ZnS nanoparticles embedded in CNF (denoted as ZnS/CNF) were prepared via in-situ sulfidation from Zn(OH)BA to ZnS/benzoic acid (HBA) and subsequent calcination of ZnS/HBA in N₂ atmosphere. Next, Ag₂S nanoparticles were directly deposited on the surface of ZnS by cation-exchange reaction between ZnS/CNF with a desired amount of AgNO₃ (0.2, 0.5, 1, 5 and 25 mM) to form ternary Ag₂S/ZnS/CNF nanofibers. The obtained samples were denoted as AZC-x, in which x stands for the additional amount of AgNO₃. Detailed experimental parts and characterization data of Zn(OH)BA and ZnS/HBA (Fig. S1–S3) are described in supporting information.

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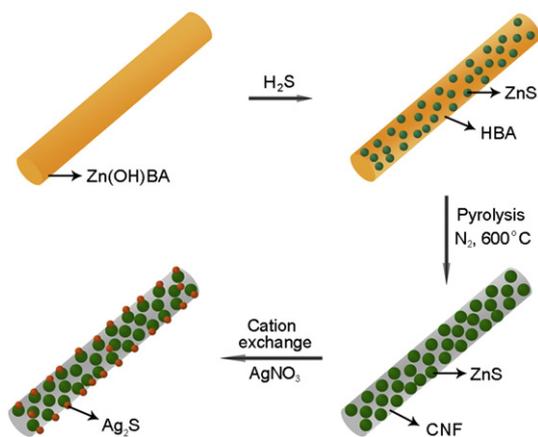


Fig. 1. Schematic illustration of the fabrication process of $\text{Ag}_2\text{S}/\text{ZnS}/\text{CNF}$ nanofibers.

3. Results and discussion

XRD patterns of ZnS/CNF and $\text{Ag}_2\text{S}/\text{ZnS}/\text{CNF}$ samples are shown in Fig. 2. For ZnS/CNF , all diffraction peaks matched well with the standard pattern of cubic ZnS without other impurity. Estimated size of ZnS using the Scherrer equation was about 13 nm. No typical peaks corresponding to CNF are detected, which was probably caused by its low crystallinity [6]. XRD detection in AZC-0.2 sample does not find obvious Ag_2S phases because of its low amount and relatively low diffraction intensity. As for the AZC-0.5 and AZC-1 samples, it could be found that there was a main cubic phase of ZnS with a small amount of monoclinic Ag_2S (JCPDS No. 14-0072) present in the composite, indicating the successful formation of Ag_2S . This is due to the fact that Ag_2S has a smaller solubility product (K_{sp}) (6.7×10^{-50}) than ZnS (2.9×10^{-25}), and such large difference in solubility provides the driving force for cation exchange to achieve the formation of $\text{Ag}_2\text{S}/\text{ZnS}/\text{CNF}$ nanocomposite [12]. The intensities of Ag_2S diffraction peaks strengthened along with the increase of Ag_2S amounts for AZC-5 sample, while ZnS peaks weakened simultaneously as its amount was decreased. For AZC-25 sample, no obvious peaks of ZnS can be found and the sample is mostly Ag_2S . The composition of different samples was carried out by EDX measurement (Fig. S4).

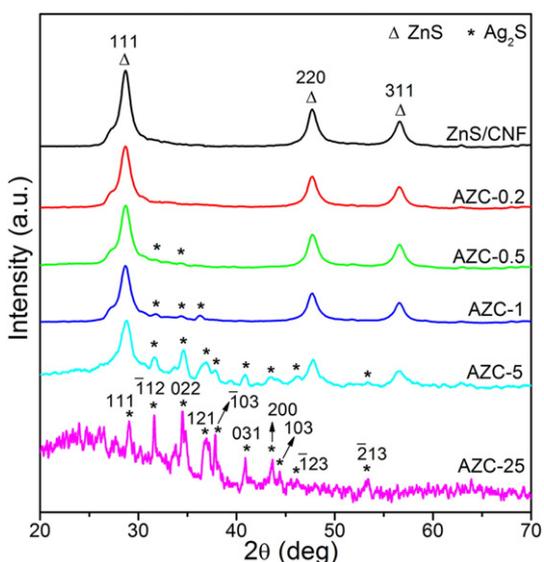


Fig. 2. XRD patterns of ZnS/CNF , AZC-0.2, AZC-0.5, AZC-1, AZC-5 and AZC-25 samples.

The morphology and microstructure of ZnS/CNF and AZC-0.5 samples were investigated by TEM and HRTEM. ZnS/CNF well preserved nanofiber morphology after calcination with many spots highly dispersed in nanofiber (Fig. 3a). SAED pattern (inset in Fig. 3a) shows a set of concentric rings corresponding to the (111), (220) and (311) planes of cubic ZnS , which is in agreement with the XRD result. HRTEM image in Fig. 3b shows that ZnS nanoparticles about 15 nm in diameter are highly crystallized as evidenced by the well-resolved lattice fringes, and the d spacing of 0.31 nm can be assigned to the (111) lattice plane. Transparent and 1D continuous CNF deriving from the carbonation of HBA can be clearly observed after the removal of ZnS nanoparticles by HNO_3 (Fig. 3c). Raman result (Fig. 3d) was additionally used to confirm the graphitic nature of the CNF, which was demonstrated by the observation of G and D bands centered at 1580 and 1360 cm^{-1} , respectively. These results confirm that highly dispersed ZnS nanoparticles on CNF matrix were successfully generated via direct calcination of ZnS/HBA nanofibers under N_2 atmosphere.

When ZnS/CNF nanofibers were added into AgNO_3 solution, cation exchange began at the interfaces between ZnS and Ag^+ . The morphology and structure of the AZC-0.5 sample remain intact (Fig. 3e) compared to ZnS/CNF . HRTEM image taken from the edge of the nanofiber in Fig. 3f shows that tiny Ag_2S particles, about 4 nm in diameter, are deposited on surface of ZnS . The d spacing of 0.18, 0.31 and 0.26 nm can be assigned to the (220) and (111) lattice planes of ZnS and the (022) lattice plane of Ag_2S , respectively. The co-existence of ZnS and Ag_2S in AZC-0.5 was further proved by SAED pattern (inset in Fig. 3e). Moreover, the intimate lattice contact between ZnS and Ag_2S would be in favor of efficient photo-generated carriers transfer across the $\text{ZnS}-\text{Ag}_2\text{S}$ interface and consequently enhance the charge separation [13].

The chemical status of different elements in ZnS/CNF and AZC-0.5 was further analyzed by XPS. Compared with ZnS/CNF , a slight shift in binding energy (BE) for AZC-0.5 of Zn 2p peaks was observed due to the electronic exchange at the interfaces from Zn to Ag caused by the difference of the electronegativity of Zn (1.6) and Ag (2.0) (Fig. 4a) [14,15]. The BE of S 2p centers at 162 eV, which is a typical value for metal sulfides (Fig. 4b). The absence of sulfate-related peak of S 2p at 168.4 eV suggests that ZnS and Ag_2S nanoparticles are chemically stable without oxidation. Moreover, slight broadening of S 2p peak for sample AZC-0.5 further indicates the presence of composite sulfides [15]. In Fig. 4c, the BEs of Ag 3d at around 368.0 eV and 375.5 eV are assigned to Ag 3d_{5/2} and Ag 3d_{3/2} states of Ag^+ [16], respectively. The intense peak at 284.8 eV in C 1s spectra (Fig. 4d) is attributed to the sp^2 -hybridized graphitic carbon, and two weak peaks at 286.3 eV and 288.4 eV are attributed to C–OH and C–O–Zn [17], respectively. These oxygen-containing carbon groups were also confirmed by FT-IR spectrum in range of 1000–1630 cm^{-1} (Fig. S5). The –OH groups facilitate easy dispersion of photocatalysts in water, providing the prerequisite for photocatalytic splitting of water, while, the presence of C–O–Zn suggests that CNF is chemically bonded with ZnS which favors the structural stability and electron transfer upon light excitation.

UV–Vis DRS were used to investigate the optical absorption of different samples (Fig. 5a). ZnS/HBA nanofibers show significant absorption at wavelength smaller than 360 nm, which can be assigned to the intrinsic bandgap absorption of ZnS . After calcination, ZnS/CNF nanofibers exhibit a continuous absorption in the visible light region ascribed to CNF itself absorbing visible light, which is in accordance with the color change of the samples during calcination from white to black (Fig. S6). The absorption edge of ZnS/CNF shows an obvious red shift of about 40 nm in comparison with ZnS/HBA due to the formation Zn–O–C bonds as confirmed by XPS [18], and the bandgap of ZnS/CNF is calculated to be 3.10 eV. With addition of a small amount of Ag_2S , a slight red-shift was observed. The absorption edges of AZC-0.2, AZC-0.5 and AZC-1 are shifted to 408, 410 and 420 nm with the corresponding bandgaps of 3.03, 3.02 and 2.95 eV, respectively. In addition, with increasing Ag_2S content, all $\text{Ag}_2\text{S}/\text{ZnS}/\text{CNF}$ samples exhibit an increasing absorption in visible light range due to the light absorption of Ag_2S .

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