Original Article

Construction of microsphere-shaped ZnSe-AgZnInS and its charge transport property

Fen Qiao\textsuperscript{a,*}, Zhenya Chen\textsuperscript{a}, Yi Xie\textsuperscript{b}, Baodong Mao\textsuperscript{c}, Dongqi Zhang\textsuperscript{c}, Huaqiang Chu\textsuperscript{d,*}, Qinglin Zhang\textsuperscript{e,*}

\textsuperscript{a} School of Energy & Power Engineering, Jiangsu University, Zhenjiang, 212013, China
\textsuperscript{b} State Key Laboratory of Silicate Materials for Architecture, Wuhan University of Technology, Wuhan, 430070, China
\textsuperscript{c} School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, China
\textsuperscript{d} School of Energy and Environment, Anhui University of Technology, Ma’an shan, 243002, China
\textsuperscript{e} Key Laboratory for Micro/Nano Optoelectronic Devices of Ministry of Education, Hunan Provincial Key Laboratory of Low-Dimensional Structural Physics and Devices, School of Physics and Electronics, Hunan University, Changsha, 410082, China

\begin{abstract}
The composite structure of ZnSe-AgZnInS microspheres was synthesized by two-step hydrothermal reaction, in which AgZnInS quantum dots (QDs) attached to the surface of ZnSe microspheres. Compared with pure ZnSe and AgZnInS QDs, the ZnSe-AgZnInS exhibited excellent photocatalytic activity for \text{H}_2\text{ generation} under the illumination of a simulated sunlight. The results also showed that different mass ratios of AgZnInS QDs had a great influence on the photocatalytic performance of ZnSe-AgZnInS microspheres. When the AgZnInS QDs was 0.05 g/mol with the photocatalytic reduction time of 5 h, the \text{H}_2\text{ formation rate of ZnSe-AgZnInS reached the optimal value (343.108 \mu molg^{-1} h^{-1})}, which was \text{~}20\text{ times} and more than 2 times higher than bare ZnSe and AgZnInS QDs, respectively. The related mechanism of photocatalytic hydrogen generation was investigated by surface photovoltage spectroscopy and transient fluorescence. It was found that the efficient transport of photogenerated carriers at the interface between ZnSe and AgZnInS QDs contributed to the improvement of the photocatalytic performance of ZnSe-AgZnInS. This work provides further insights for the design and preparation of composite photocatalysts.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
\end{abstract}

1. Introduction

As one of the II–VI semiconductor materials, ZnSe is a direct bandgap semiconductor (band gap: 2.7 eV). Due to its unique optical, electrical and chemical properties, ZnSe has potential applications in optoelectronic devices such as lasers, diodes and solar cells [1–3]. Although ZnSe can absorb a wide range of visible light, most reports on ZnSe as a pho-

* Corresponding authors.
E-mails: fqiao@ujs.edu.cn (F. Qiao), hqchust163.com (H. Chu), qinglin.zhang@hnu.edu.cn (Q. Zhang).
https://doi.org/10.1016/j.jmrt.2019.12.054
2238-7854/© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
tocatalyst are about photocatalytic degradation of dyes [4–8]. Compared with Cd analogues (e.g., CdS, CdSe), ZnSe has many theoretical advantages [9], but its practical application in the field of photocatalytic hydrogen production is very limited. H. Kaneko et al. used the ZnSe/CulnGaSe photocathodes for hydrogen production, and the photocurrent was up to 12 mA cm−2 (0 V vs. RHE) [10]. (Cd2Zn1−xSe/CdP composite materials as a photocatalyst for H2 production were prepared by B. Qiu et al., a efficiency of 45.1 mmol h−1 g−1 were obtained [11]. However, these complexes usually requires CdS as charge separation layer or Pt as reduction catalyst, and only few of them can be photocatalyzed to produce Cd-free hydrogen. Therefore, a great effort have been devoted to constructing heterojunctions to modify ZnSe and promote the separation and transport of photocarriers. A. F. Shaikh et al. reported one-dimensional ZnSe/ZnO nanoheterostructure prepared by solvent/hydrothermal reaction, and ZnSe/ZnO (10:90 by weight) showed 491 mmol of H2 production after irradiation for 4 h. With the content of ZnSe increases to 10 mol%, the precipitation of H2 was enhanced due to the adjusted band gap and the suppression of charge carrier recombination rate [12]. M. F. et al. demonstrated a photocatalyst system free of precious metals and Cd, which can effectively precipitate H2 from water, which was comparable to that of Cd-based quantum dots (QDs). Ni-(BF4)2 was used as a co-catalyst dispersed in ascorbic acid aqueous solution, the hydrogen production efficiency of ZnSe nanorods can be as high as 54 ± 2 mmolg−1 h−1, quantum yield 50 ± 4% (λ = 400 nm) [13]. However, when ZnSe nanoparticles were used for photohydrogen production, the intercrystalline boundary barrier between nanoparticles can easily hinder the transfer of photogenerated charges, and therefore reduce their separation efficiency. In addition, because of drawbacks such as easy agglomeration and difficult separation, the research and development of micro-scale photocatalytic materials will be more conducive to the practical and industrialization of photocatalytic technology [14,15]. Numerous studies have shown that the morphology and bandgap of photocatalytic materials have a great impact on their catalytic activity [16–18]. The band gap of AgZnInS QDs can be adjusted from blue-green to near-infrared range through controlling its size and doping composition, thereby changing its optical characteristics and making it suitable for applications in solar cells, light-emitting diodes, medical imaging and catalysis areas [19–21]. By combining the AgZnInS QDs on the surface of ZnSe can not only broaden the absorption range of ZnSe, but also improve the lifetime of the photocarrier by adjusting the unique structure between the interfaces with the help of high catalytic activity and stability of AgZnInS QDs. Thus, rapid separation of carriers around the interface can be achieved and their photocatalytic ability can be improved.

In this work, AgZnInS QDs were attached on the surface of ZnSe microspheres through two-step hydrothermal reaction. It was found that the appropriate loading amount of AgZnInS QDs significantly enhanced the photocatalytic activity of ZnSe microspheres. The photogenerated electron-hole pair transport behavior of ZnSe-AgZnInS composites were investigated by transient fluorescence spectroscopy, surface photovoltage (SPV) technology and impedance spectroscopy. The effective transfer of photocarriers at the interface between ZnSe microspheres and AgZnInS QDs enhanced the photocatalytic performance of the ZnSe-AgZnInS composite.

2. Experimental section

2.1. Synthesis of ZnSe-AgZnInS

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd and used directly. The synthesis protocol of AgZnInS QDs was modified according to reference [22]. The obtained AgZnInS QDs were dispersed in aqueous solution for subsequent composite preparation. The synthesis scheme of ZnSe refers to the hydrothermal method previously reported [23,24]. Typically, 0.3 g Zn(NO3)2·6H2O, 0.17 g Na2SeO3 and 0.8 g NaOH were added to the beaker and stirred in 30 ml of deionized water to dissolve completely. Then, 10 ml of N2H4·H2O (85%) was added during the stirring. The above mixed solution was transferred to the reaction vessel and reacted at 180 °C for 4 h, the precipitate was purified successively with DI water and ethanol. The obtained sample was heated at 60 °C for 6 h. The synthesis of ZnSe-AgZnInS composites was similar to that of ZnSe microspheres, the difference lied in the addition of AgZnInS QDs (0.05 g/ml) solution with different mass (0.05 g, 0.1 g, 0.15 g, 0.2 g) to the precursor. The samples were sequentially labeled as ZnSe-AgZnInS-1, ZnSe-AgZnInS-2, ZnSe-AgZnInS-3, and ZnSe-AgZnInS-4 according to the different mass addition amounts mentioned above.

2.2. Measurement

The structure and morphology of the samples were tested by XRD (XRD-6100), X-ray photoelectron spectroscopy (XPS, Escalab 250Xi), scanning electron microscopy (FE-SEM, 7800 F) and transmission electron microscopy (TEM). The optical properties were analyzed by UV–vis spectrophotometer and fluorescence spectrometer. The transport behavior of photocatalytic electron-hole pair was determined by transient fluorescence spectrometer, SPV and electrochemical impedance spectroscopy. Among them, transient fluorescence spectroscopy was measured by controlled gas discharge hydrogen light as an excitation source (Edinburgh FLS920); while SPV used a light source-monochromator-lock detection technology to test the sample, which was placed in a sandwich battery [25,26]. Gas chromatography was used to detect the hydrogen yield of samples.

3. Results and discussion

3.1. Morphology and structure of ZnSe-AgZnInS

Fig. 1 shows SEM images of the synthesized ZnSe, AgZnInS and ZnSe-AgZnInS composites. The morphology of ZnSe prepared is spherical (Fig. 1a). AgZnInS sample is of quantum size and has a uniform particle distribution with an average diameter of ~3.25 nm (Fig. 1b). Fig. 1c shows that AgZnInS QDs are successfully attached to the surface of ZnSe microspheres. Through the high-resolution transmission electron microscopy, it is obvious that the measured spacing between
adjacent crystal faces is 0.29 nm and 0.32 nm, respectively, which matches the (111) crystal plane of ZnSe and the (102) crystal plane of ZnIn$_2$S$_4$ (inset of Fig. 1c) [22], and the elements of Zn, Se, Ag, In and S were detected through the EDS measurement (Fig. 1d).

As can be seen from Fig. 2, the prepared ZnSe sample has three main crystal phase peaks at 27.5°, 46.2°, and 57.4°, corresponding to (111), (220) and (311) crystal faces of standard ZnSe sphalerite structure (JCPDS No.37–1643). Four ZnSe-AgZnInS samples not only preserve the diffraction peaks of ZnSe, but also retain the diffraction peaks of ZnIn$_2$S$_4$ (JCPDS No.72-0773), but there are no peaks and oxidation peaks associated with Ag$^+$ in the ZnSe-AgZnInS, which is because the amount of AgZnInS in this experiment is very small and no obvious lattice change. Further, the presence of Zn, Se, Ag, In and S elements in ZnSe-AgZnInS were detected via EDS mapping (Fig. S1a–S1g in Supporting Information), indicating that ZnSe-AgZnInS samples were successfully prepared by hydrothermal method.

3.2. UV–vis absorption and PL Spectrum

With the increase of AgZnInS content, the light absorption edge of ZnSe-AgZnInS composites presents red-shifting trend, and ZnSe-AgZnInS-4 sample has the best visible light absorption and widest absorption range for visible light compared with pure ZnSe and AgZnInS QDs (Fig. 3a). Therefore, it can be seen that the construction of heterostructure can improve the absorption capacity and utilization rate of light energy of materials, and has positive significance to boost its photocatalytic activity. According to the Tauc’s equation, the bandgap of ZnSe microspheres and AgZnInS QDs was calculated to be 2.5 eV and 2.28 eV, respectively (Fig. 3b), which was consistent with the literature results [22,23].

Compared with the fluorescence spectra of AgZnInS QDs, the fluorescence intensity of the four ZnSe-AgZnInS samples decreased significantly, among which the fluorescence intensity of ZnSe-AgZnInS-1 sample decreased the most, up to two orders of magnitude (Fig. S2). The decrease in fluorescence intensity implied that charge separation was
enhanced and the recombination of photogenerated carriers were effectively inhibited [27], indicating that AgZnInS QDs played a role in charge separation and photocatalytic activity of ZnSe-AgZnInS composite. In addition, compare with that of AgZnInS QDs, the positions of fluorescence peaks of the four ZnSe-AgZnInS composites showed blue shift, which was caused by the Zn ions diffusion to the AgZnInS QDs during the second hydrothermal reaction process [28].

3.3. XPS characteristics

XPS spectra used to detect the elemental composition of ZnSe, AgZnInS QDs and ZnSe-AgZnInS samples (Fig. 4). In addition to Zn, In, S, Se and Ag, the presence of C and O elements was also found, possibly caused by CO2 adsorption on the sample surface and introduced by the XPS instrument itself (Fig. 4a). Fig. 4b shows a narrow scan of Zn with a peak of Zn 2p1/2 at the binding energy of 1044.6 eV and Zn 2p3/2 at 1021.6 eV, respectively; In 3d5/2 and 3d3/2 at 452.2 eV and 444.6 eV correspond to In3+ (Fig. 4c). In Fig. 4d, two adapted peaks with combined energies of 161.7 eV and 160.2 eV, match to S 2p3/2 and S 2p1/2, respectively. Two fitted peaks with binding energies of 54 eV and 54.9 eV, corresponding to Se 3d5/2 and Se 3d3/2 (Fig. 4e). The peaks at 373.9 eV and 367.6 eV are attributed to Ag 3d3/2 and Ag 3d5/2, respectively (Fig. 4f).

3.4. Hydrogen production activity

With the increase of the mass ratio of AgZnInS QDs compound with ZnSe, the photocatalytic hydrogen production of ZnSe-AgZnInS composites increased gradually (Fig. 5). When the amount of AgZnInS was 0.1 g, the hydrogen evolution rate of ZnSe-AgZnInS-2 reached a maximum of 343.108 μmolg−1 h−1. However, when the addition of AgZnInS QDs was further enhanced, the hydrogen generation of ZnSe-AgZnInS began to decline gradually, and the rate of hydrogen generation also showed the same tendency. This indicates that an appropriate amount of QDs can improve the absorption range of visible light, reduce surface defects, and enhance the photocatalytic activity, while electron-hole recombination centers may be provided to reduce photocarrier migration rate and hydrogen production when the addition of QDs is large.
3.5. Photocatalytic mechanism of ZnSe-AgZnInS

3.5.1. Time-resolved fluorescence Spectrum

In order to further explore the influence of the construction of ZnSe-AgZnInS on the transport properties of photogenerated electron-hole pairs, the transient fluorescence spectra of ZnSe microspheres, AgZnInS QDs and ZnSe-AgZnInS composite were characterized (Fig. 6). Compared with that of ZnSe microspheres and AgZnInS QDs, the fast decay component $\tau_1$ and slow decay component $\tau_2$ of ZnSe-AgZnInS-2 composite increase to 21.80 ns and 1.18 ns, respectively. The average lifetime $\tau$ of ZnSe-AgZnInS-2 increased from ZnSe microspheres (0.75 ns) and AgZnInS QDs (1.11 ns) to 1.18 ns (Table S1). Due to the effective separation of electron-holes together with the inhibited carrier recombination, the fluorescence lifetime of the ZnSe-AgZnInS is extended [29,30].

3.5.2. SPV characteristics

The surface photovoltage is generated from the spatially separation of the photo-induced electron-hole pairs. Consequently, the study of the surface photovoltage can give not only the fundamental light absorption information, but also the electric properties related to the surface or interface in the semiconductor materials or devices [31,32]. To further explore the photocarrier generation mechanism of ZnSe-AgZnInS samples, the electric field modulated surface photovoltage spectroscopy of ZnSe microspheres (Fig. 7a), AgZnInS QDs (Fig. 7b) and ZnSe-AgZnInS composite (Fig. 8a) was studied, respectively. As shown in Fig. 7, the surface photovoltage responses of both ZnSe microspheres (Fig. 7a) and AgZnInS QDs (Fig. 7b) increase (decrease) when the positive (negative) external electric field was applied. This is ascribed to the n-type conduction type of AgZnInS QDs and ZnSe microspheres [33]. For n-type semiconductors, the positive external electric field induces electrons to accumulate at the surface, increasing the built-in electric field, which will enhance the surface photovoltage response. Oppositely, the negative exter-
Fig. 8 – (a) SPV spectrum of ZnSe-AgZnInS QDs composites under different voltage, and (b) schematic illustration of band structure of ZnSe and AgZnInS.

4. Conclusions

A series of ZnSe-AgZnInS composites with different mass ratios of AgZnInS quantum QDs were prepared by two-step hydrothermal method. It showed that the absorption range of ZnSe was extended by attaching AgZnInS QDs on the surface of ZnSe. Moreover, the hydrogen production performance of ZnSe-AgZnInS composites were far superior to that of pure ZnSe and AgZnInS QDs, the correlation performance of the ZnSe-AgZnInS in the photocatalytic hydrogen production test was ~20 times and 2 times higher, respectively, which was mainly due to the matched band structure of ZnSe and AgZnInS QDs as well as the effective transport of interfacial photocarriers. Measurement by SPV indicated that the interface electronic structure played a key role in the separation of photogenerated charge carriers in the composites. This work provides an effective reference for the construction of functional photocatalytic composites in the future, and has certain guiding significance for the effective development of hydrogen energy conversion system. Future work will focus on how to further improve the hydrogen production performance by precisely regulating the composition and interface defects of composites.

Conflicts of interest

The authors declare no competing financial interest.

Author agreement

All authors have seen and approved the final version of the manuscript being submitted. We warrant that the article was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. All authors declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by National Natural Science Foundation of China (No.51976081).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmr2.2019.12.054.

REFERENCES


[10] Kaneko H, Minegishi T, Nakabayashi M, Shibata N, Domen K. Enhanced hydrogen evolution under simulated sunlight from neutral electrolytes on (ZnSe)0.85(Culn0.7Ga0.3Se)0.15 photocathodes prepared by a bilayer method. Angew Chem Int Ed 2016;55:15293–32.


