PAPER • OPEN ACCESS

Co$_{1-x}$Zn$_x$In$_2$S$_4$ Photocatalysts for Photocatalytic H$_2$ Production Activity

View the article online for updates and enhancements.

$Co_{1-x}Zn_xIn_2S_4$ Photocatalysts for Photocatalytic H_2 Production Activity

Renzhang Wang, Zhiyun Liang, Fuying Li, Qiyou Wu, Peijing Xu and Yu Niu[*]

Fujian Provincial Collaborative Innovation Center for Clean Coal Gasification, Sanming University, Sanming 365004, China.
E-mail: niuyu200704@163.com;

Abstract. In this work, $Co_{1-x}Zn_xIn_2S_4$ nanocomposites photocatalysts were synthesized by hydrothermal method, and characterized by UV-visible DRS. The prepared $Co_{0.5}Zn_{0.5}In_2S_4$ nanocomposites, which exhibits the highest H_2 production rate, the value is 36.08 umol·h^{-1}·g^{-1}, exceeding more than 8 times compared with the pure $ZnIn_2S_4$ and $CoIn_2S_4$. $Co_{0.5}Zn_{0.5}In_2S_4$ nanocomposites also has good reuse and stability. Two reasons lead to higher photocatalytic H_2 production activity are enough visible-light absorption capacity and suitable conduction band potential of the $Co_{0.5}Zn_{0.5}In_2S_4$. In this research, it is proven that $Co_{0.5}Zn_{0.5}In_2S_4$ nanocompositesphotocatalystscan enhance the photocatalytic H_2 production activity. The significant improvement in the performance of $Co_{0.5}Zn_{0.5}In_2S_4$ nanocomposites is mainly due to effective charge separation.

1. Introduction

Using semiconductor as photocatalyst to produce hydrogen by water cracking under sunlight is an ideal way to convert solar energy into chemical energy efficiently [1-3]. However, TiO_2 has a band gap width of 3.2 eV and cannot respond to visible light [4, 5]. Since visible light accounts for a larger proportion of solar energy than ultraviolet light, in order to make more efficient use of solar energy resources, many studies have focused on the development of visible light responsive photocatalysts[6, 7]. On the basis of previous studies, metallic sulfide compounds [8-10] with suitable band gap width and edge position can make use of visible light, which has attracted more attention in the production of photocatalytic H_2.

In this study, we reported for the first time the preparation of $Co_{1-x}Zn_xIn_2S_4$ composite nanoparticles by hydrothermal method, and tested its performance of photocatalytic water decomposition in visible light irradiation to produce hydrogen. This study provides a new perspective for the understanding of photocatalyst response to visible light and the mechanism of promoting catalytic activity and provides a new idea for the design of new ternary metal sulfide photocatalytic materials.

2. Experimental

2.1. Catalyst Preparation

All the chemicals were of reagent grade and used as received without any further purification.

$Co_{1-x}Zn_xIn_2S_4$ solid solutions were prepared by the hydrothermal method. In a typical procedure, given amounts of $In(NO_3)_3$, $Co(NO_3)_3 \cdot 6H_2O$ and $Zn(CH_3COO)_2$ in different Co/Zn molar ratios were dissolved in 5 mL deionized water and 20 mL ethyl alcohol were stirred at room temperature for 0.5 h. The total amount of Co $(NO_3)_3 \cdot 6H_2O$ and Zn $(CH_3COO)_2$ was 0.5 mmol, $In(NO_3)_3$ was 1 mmol. At the

same time, 2.5 mmol of thiourea ($(NH_4)_2S$) was added to the above solution as the S precursors, and in order to prepare a well-mixed solution, stirring was continued for 0.5 h and sonicated for 0.5 h. Subsequently, the mixture was transferred to a Teflon lining of an autoclave and heated at 180 ° C for 12 h. Finally, the obtained precipitate was collected by centrifugation and washed three times with distilled water and ethanol to remove unbound impurities, and then dried in air at 60 ° C for 12 h, and then ground for 1 h. The x of the prepared $Co_{1-x}Zn_xIn_2S_4$ solid solution is 0, 0.3, 0.5, 0.7 and 1.0, respectively.

2.2. Characterization of Catalysts
The UV-vis diffuse reflectance spectroscopy (DRS) of the samples were recorded using a Varian Cary 500 Scan UV-vis-NIR spectrometer with $BaSO_4$ as the reference. The reflectance spectra were transformed to absorption intensity by using KubelkaeMunk method.
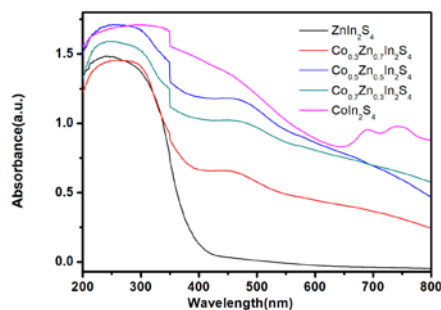
2.3. Catalytic Performance
The photocatalytic reactions were carried out in a sealed 25 mL quartz tube reactor using a 300 W Xe lamp with a UV-cutoff filter ($\geq$ 400 nm) as the light source. Under ultrasonic conditions, 25 mg of the solid catalyst powder was dispersed in 5.0 mL of a mixed solution containing 76 wt% CH_3OH and 24 wt% H_2O. The air in the reactor was evacuated and filled with high purity (99.999%)nitrogen, and then subjected to a photocatalytic reaction at room temperature for 12 h.The H_2 produced by the reaction were analyzed using an Agilent Micro GC3000 with a 5A molecular sieve column and a thermal conductivity detector.
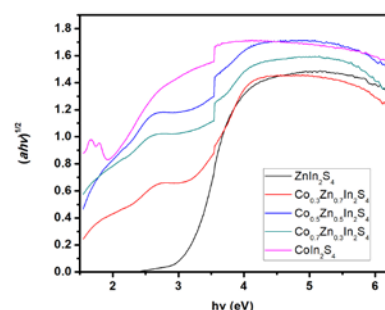
3. Results and Discussion

3.1. UV–visDiffuse Reflection Spectra (DRS)
A comparison of UV−visible diffuse absorption spectra of the $Co_{1-x}Zn_xIn_2S_4$ (x = 0, 0.3, 0.5, 0.7 and 1.0) samples is displayed in Fig. 1. In the spectra of, with the increase of cobalt content in $Co_{1-x}Zn_xIn_2S_4$ nanoparticles, there is a significant and continuous red shift of absorption edge of the samples. By controlling the molar ratio of cobalt and zinc in the composite nanoparticles, the band gapof $Co_{1-x}Zn_xIn_2S_4$photocatalysts absorption edge redshift can be achieved. The spectra have been converted from corresponding diffuse reflectance spectra by means of the Kubelka-Munk function. Fig. 2 shows the curves of $(ahv)^{1/2}$vs (hn) for the samples, by extrapolating the linear portion of the curves to $(ahv)^{1/2} = 0$, the E_g values of $Co_{1-x}Zn_xIn_2S_4$ were evaluated to be less than 3.0 eV. As a result, the narrow band gap enables the photocatalysts to have visible light hydrogen production activity. This result is consistent with the increasing wavelength range absorption edge in semiconductor is related to the optical absorption edge energy decreases.

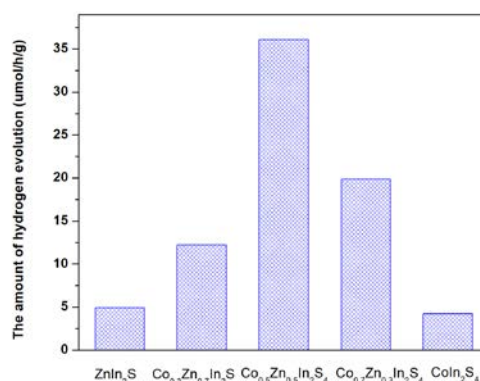**Figure 1.** UV–vis DRS of the samples.

Figure 2. Plots of $(ahv)^{1/2}$vs (hv) for estimating optical band gaps of the samples.

3.2. PhotocatalyticPerformance of Samples
The photocatalytic activities of $Co_{1-x}Zn_xIn_2S_4$samples were evaluated by using the photocatalytichydrogen generation under methanol aqueous solution. The results are shown in Fig. 3.

As it can be seen from the figure, the comparison of the H_2 production rate ofphotocatalysts.

Compared with the samples of $Co_{1-x}Zn_xIn_2S_4$ (x = 0, 0.3, 0.5, 0.7, and 1.0), the visible-light photocatalytic H_2 activity of pure $ZnIn_2S_4$ and $CoIn_2S_4$ are almost negligible, and the H_2 production rate are 4.23 $umol·h^{-1}·g^{-1}$ and 4.91 $umol·h^{-1}·g^{-1}$ respectively. When the value of x is less than 0.5, the H_2 production rate of $Co_{1-x}Zn_xIn_2S_4$ increases with the increase of cobalt content; When the value of x is equal to 0.5, it reaches the highest 36.08 $umol·h^{-1}·g^{-1}$; However, when the value of x continues to increase, as the cobalt content is further increased, the photocatalytic H_2 production performance is rapidly deteriorated.

Figure 3. Photocatalytic H_2 production activity of the samples

4. Conclusion
In summary, $Co_{1-x}Zn_xIn_2S_4$ catalysts were synthesized using the hydrothermal methods. The results show that $Co_{1-x}Zn_xIn_2S_4$ had the photocatalytic activity in the H_2 production reactions under 300 W Xe lamp irradiation. When the cobalt and zinc molar ratio is 1:1, the $Co_{0.5}Zn_{0.5}In_2S_4$ sample exhibits theoptimal H_2 production rate of 36.08 $umol·h^{-1}·g^{-1}$. This study not only used a simple and novel method to prepare $Co_{1-x}Zn_xIn_2S_4$ composite nanoparticles with high photocatalytic water decomposition activity for hydrogen production, but also provided a new perspective for understanding visible light absorption and photocatalytic enhancement mechanism.

5. Conflict of Interests
All authors of this article declare that there is no conflict of interests in this publication.

6. Acknowledgments

7. References
[1] KUDO A. Catalysis Surveys from Asia, 2003, 7(1): 31-8.
[2] CARLSSON J M. Nature Materials, 2009, 8(1): 76-80.
[3] MAEDA K, TERAMURA K, LU D, et al. Nature, 2006, 440(7082): 295.
[4] OHNO T. Applied Catalysis A General, 2004, 265(1): 115-21.
[5] S I, A O, R B, et al. Journal of the American Chemical Society, 2007, 129(45): 13790-1.
[6] ASAHI R, MORIKAWA T, OHWAKI T, et al. Science, 2001, 293(5528): 269-71.
[7] ANPO M, TAKEUCHI M. Journal of Catalysis, 2003, 216(1): 505-16.
[8] CHENG F, XIANG Q. Rsc Advances, 2016, 6(80)

[9] JING D, LIU M, CHEN Q, et al. International Journal of Hydrogen Energy, 2010, 35(16): 8521-7.
[10] ZONG X, YAN H, WU G, et al. Journal of the American Chemical Society, 2008, 130(23): 7176-7.