

Effects of Cu²⁺ Doping on Structure, Morphology and Photocatalytic Hydrogen Production Performance of Porous CdIn₂S₄ Microsphere

Xuefeng Bai^{1,2}, Wei Wu² and Hongfei Lv¹

1 Institute of Petrochemistry, Heilongjiang Academy of Sciences, Harbin 150040, China

2 School of Chemistry and Material Sciences, Heilongjiang University, Harbin 150080, China

Email: tommybai@126.com

Abstract. The Cu²⁺-doped porous CdIn₂S₄ microspheres (Cu@CdIn₂S₄) with better photocatalytic performance were prepared by sodium dodecyl sulphate (SDS)-assisted hydrothermal technology. The Cu@CdIn₂S₄ were characterized by SEM, XPS, XRD and DRS. The effects of Cu²⁺ doping amount on the morphology, structure and photocatalytic hydrogen production performance of CdIn₂S₄ were studied. The porous Cu@CdIn₂S₄ microspheres were flower shape of a average diameter of 3-5 μm and their maximum absorption edge was up to 700 nm. The Cu²⁺ doping was good for the improvement of photocatalytic performance. Cu@CdIn₂S₄ with 0.3wt% Cu²⁺ doping amount possessed the highest hydrogen production rate of 1248.1 μmol/ (h·g), much more than that of pure CdIn₂S₄.

1. Introduction

Since the photocatalytic splitting of water on TiO₂ electrodes was found by Fujishima and Honda in 1972 [1], a great many researchers have been carried out in theory and application of the photocatalytic reaction. At present, the environmental pollution has become an obstacle to sustainable development. Hydrogen as a clean fuel is the best way to solve environmental pollution [2].

Photocatalytic decomposition of water and hydrogen sulfide to produce hydrogen has attracted more and more attention from scientists in recent years, which provides the most suitable environmentally friendly process route of utilizing solar energy for valuable hydrogen production [3-4]. The development of efficient and cheap photocatalysts is the key to the research.

CdIn₂S₄, as a visible light response semiconductor material, had many unique optoelectronic and excellent photocatalytic properties and had been widely used in the field of solar cells, photocatalysts, and light-emitting diodes. CdIn₂S₄ with cubic spinel structure has stable chemical properties and narrow band gap suitable for absorbing less than 600 nm of light [5-6].

Metal ion doping into photoconductors not only acted as the trapping sites for benefiting to limit the recombination of e⁻-h⁺, but also formed impure energy levels in the forbidden band for red shifting the absorption side, which is regarded as the most effective way for improving the performance of photocatalytic hydrogen production [7-9].

In this paper, Cu²⁺ doped porous CdIn₂S₄ microspheres (Cu@CdIn₂S₄) with the better photocatalytic performance was prepared by sodium dodecyl sulfate (SDS)-assisted hydrothermal technology. The effect of Cu²⁺ doping on the structure, morphology and photocatalytic hydrogen performance of Cu@CdIn₂S₄ was discussed in detail.



2. Experimental

2.1. Preparation of Cu@CdIn₂S₄

All chemicals used are chemically pure. The Cu²⁺ doped porous CdIn₂S₄ microspheres were synthesized by sodium dodecyl sulfate (SDS)-assisted hydrothermal technology. 2 mmol Cd(NO₃)₂·6H₂O, 4 mmol In(NO₃)₃·4H₂O, 8 mmol thioacetamide (TAA) and a certain amounts of SDS were adding and mixing in 75 ml of distilled water. Then CuCl₂·2H₂O was added into as-above solution according to Cu²⁺ doping amount. The as-prepared solution was well mixed, and then transferred into Teflon-lined autoclave (100 ml). The hydrothermal synthesis of Cu@CdIn₂S₄ was completed at 160°C for 12 h. The final product was obtained after cooling, filtering, washing and drying at 80°C for 4 h, named as Cu@CdIn₂S₄.

2.2. Characterization of Cu@CdIn₂S₄

The X-ray diffraction spectrum (XRD) was obtained on a Bruker D8 Advance X-ray diffractometer using Cu K α ₁ irradiation. The patterns were recorded from 10° to 70° (2 θ). The UV-Vis diffuse reflectance spectra (DRS) were carried out on Shimadzu UV-2450 spectrophotometer in the scanning range from 250 to 700 nm. The experimental data were obtained by transferring from reflection to absorption by Kubelka-Munk method. The scanning electron microscopy (SEM) was characterized on a HITACHI S-4800 instrument operated at 230 kV. The X-ray photoelectron spectroscopy analysis (XPS) was completed on a Thermo Electron instrument at 10⁻⁷ Pa with Al K α radiation.

2.3. Evaluation of Photocatalytic Hydrogen Production Performance

Photocatalytic experiments were carried out in an inner-irradiation quartz reactor. A 250 W high-pressure lamp was been used as light source. In order to get visible light, 1 M NaNO₂ solution was added into an inner circulating system to remove the UV part of the light with a wavelength less than 400 nm. 0.1 g Cu@CdIn₂S₄ was added into 300 ml aqueous solution of 0.25 M Na₂SO₃/0.35 M Na₂S. Before opening light source, N₂ was purged through as-above prepared solution to remove oxygen. The photocatalytic reaction temperature was controlled at 30 ± 5°C. Photocatalytic hydrogen production performance was evaluated by measuring the amount of hydrogen evolution by drainage extraction method. Hydrogen purity analysis was conducted on GC with thermal conductivity detector.

3. Results and Discussion

3.1. Structure

Figure 1(A&B) showed the typical XRD patterns of porous Cu@CdIn₂S₄ with different Cu²⁺ doping amount. It was shown in Figure 1(A) that all Cu@CdIn₂S₄ belongs to pure cubic spinel phase, the same as CdIn₂S₄. With the increasing of Cu²⁺ doping amount, the position of peak (511) shown in Figure 1(B) moves gradually towards a large diffraction angle. This is due to Cu²⁺ partly occupying the Cd²⁺ site, incorporating into the lattice or inserting the interspace of CdIn₂S₄. The XRD analysis indicated Cu²⁺ doping has an effect on crystal structure of CdIn₂S₄.

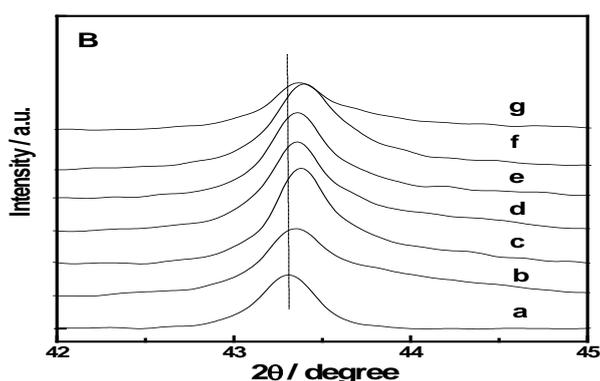


Figure 1. The XRD Patterns of Cu@CdIn₂S₄ with Different Doping Amount (A) and the Position of (115) Reflection (B)

3.2. Morphology

Figure 2(a-f) showed that SEM images of Cu@CdIn₂S₄ with different Cu²⁺ doping amount. It was seen from Figure 2 that the porous Cu@CdIn₂S₄ microspheres with unique flower shape of an average diameter of 3-5 μm could be obtained by hydrothermal synthesis technology. The Cu²⁺ doping had great effect on the morphology of Cu@CdIn₂S₄ microspheres. It was seen in Figure 2 (a) that the pure CdIn₂S₄ without Cu²⁺ doping showed loose flower-like microspheres with numerous sheets. The sheets were interconnected with each other to form many slit-like pores inside of petals and among the curved nanosheets. However, as seen in Figure 2 (b-f), with Cu²⁺ as dopant, abundant floss-like spheres with rough surface were mangled partly under this condition. As the concentration of Cu²⁺ dopant increased to 0.7%, mass rule less dollops without pore structure were produced, and obvious aggregation of particles could be seen in Figure 2 (e). When the doping is greater than 1.0 %, the spherical structure is destroyed. This phenomenon is due to that Cu²⁺ doping hindering the self-assembly growth of crystallites into porous microspheres during hydrothermal synthesis process.

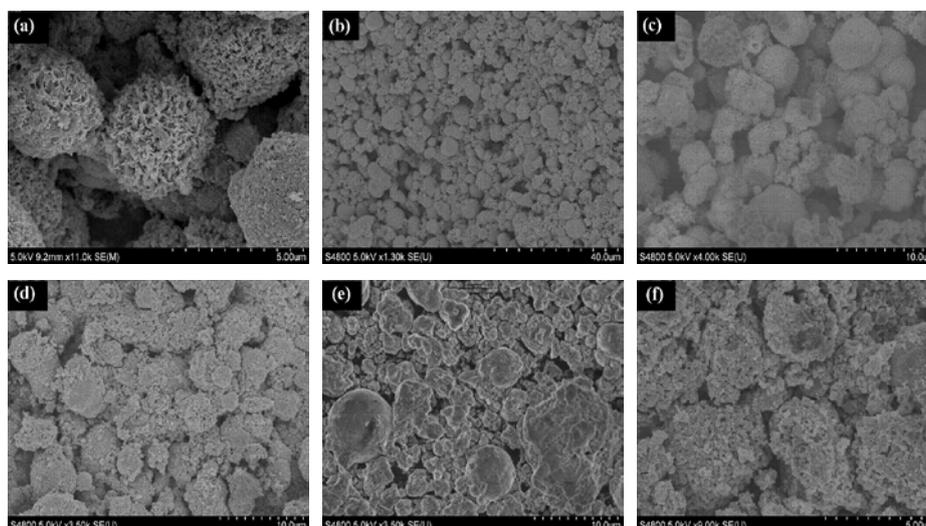


Figure 2. SEM Images of Cu@CdIn₂S₄ with Different Doping Amount: (a) 0.0%, (b) 0.1%, (c) 0.3%, (d) 0.5%, (e) 0.7%, (f) 1.0%

3.3. Surface State Analysis

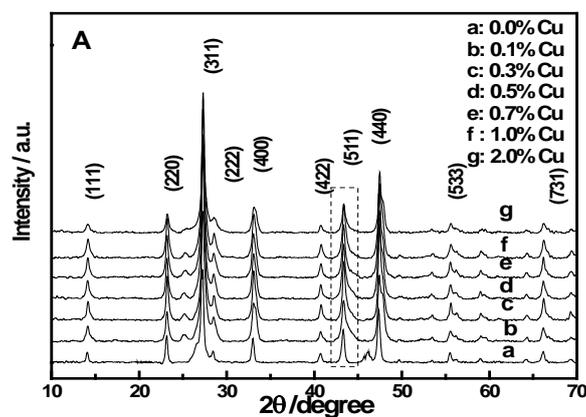


Figure 3. XPS Spectra of Cu@CdIn₂S₄ with 0.3wt% Doping Amount: (a) Cu@CdIn₂S₄; (b) Cd3d; (c) In3d; (d) S2p; (e) Cu 2p

3.4. Optical Properties

Figure 4 showed the DRS spectra of Cu@CdIn₂S₄ with different Cu²⁺ doping amount. With the increasing of Cu²⁺ doping amount from 0 to 2 wt%, the maximum absorption edge of Cu@CdIn₂S₄ gradually shifted red from 600 nm (band gap of 2.08 eV) without doping to 625 nm~700 nm (band gap of 1.98 eV~1.77 eV). The reason for this phenomenon is due to the formation of impure energy levels by the Cu²⁺ doping in the forbidden band, reducing band gaps to enhance utilization of visible-light. In addition, the impure energy levels of Cu@CdIn₂S₄ could improve the diffusion and transfer of the photo excited charge carriers, and limit the recombination of e⁻-h⁺.

3.5. Photocatalytic Hydrogen Production Performance

Figure 5 showed the photocatalytic hydrogen production rate of Cu@CdIn₂S₄ with different Cu²⁺ doping amount. It was seen from Figure 5 that Cu@CdIn₂S₄ exhibited the higher hydrogen production performance in visible spectra than pure CdIn₂S₄. With the increasing of Cu²⁺ doping amount, H₂ production rate showed a trend of increasing first and then decreasing. Cu@CdIn₂S₄ with 0.3wt% Cu²⁺ doping amount exhibited the highest rate of 1248.1 μmol / (h·g), much more than that of pure CdIn₂S₄.

Cu²⁺ doping into CdIn₂S₄ acted as the trapping sites for benefiting to limit the recombination of e⁻-h⁺. The number of trapping sites was increased with the Cu²⁺ doping amount at low-level. However, when Cu²⁺ doping amount increase at a high addition, a mass of trapping sites acting as recombination centers could make photo excited charge carriers inactive. It has been reported that suitable metal ion doping amount greatly improved the photocatalytic performance [10].

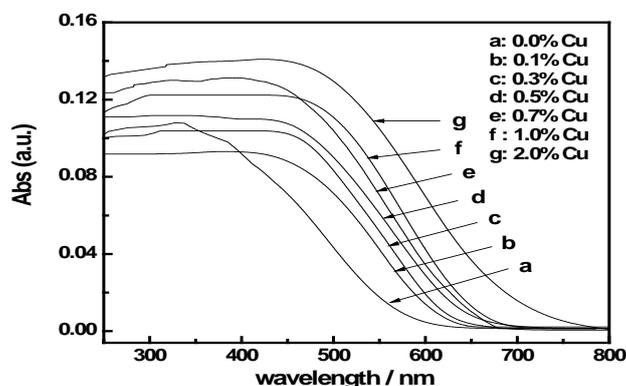


Figure 4. DRS Spectra of Cu@CdIn₂S₄ with Different Doping Amount Photocatalysts

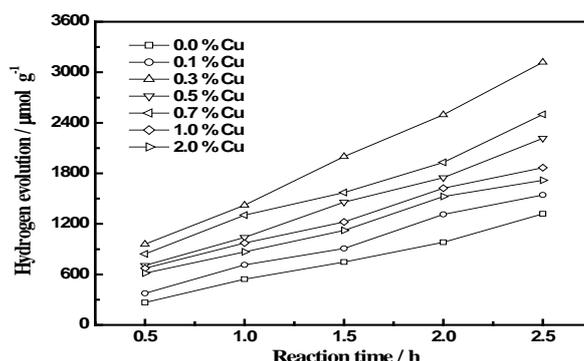


Figure 5. The H₂ Production over Cu@CdIn₂S₄ with Different Doping Amount Photocatalysts

4. Conclusions

The Cu²⁺ doped porous CdIn₂S₄ microspheres (Cu@CdIn₂S₄) with the better photocatalytic performance was prepared by sodium dodecyl sulfate (SDS)-assisted hydrothermal technology. It was indicated from characterization results that the porous Cu@CdIn₂S₄ microspheres was unique flower shape of a average diameter of 3-5 μm, and Cu²⁺ partly occupied the Cd²⁺ site and incorporated into the lattice or inserted the interspace of CdIn₂S₄. The maximum absorption edge of Cu@CdIn₂S₄ gradually shifted red, up to 700 nm. The photocatalytic hydrogen production performance over Cu@CdIn₂S₄ was greatly enhanced by Cu²⁺ doping. With the increasing of Cu²⁺ doping amount, hydrogen production rate showed a trend of increasing first and then decreasing. Cu@CdIn₂S₄ with 0.3wt% Cu²⁺ doping amount exhibited the highest rate of 1248.1 μmol/ (h·g), much more than that of pure CdIn₂S₄.

5. Acknowledgements

This work was funded by Project of Heilongjiang Science and technology (ZY17A06).

6. References

- [1] A Fujishima, K Honda 1972 *Nature*, **238** 37-38
- [2] P M Modisha, N M Ouma, R Garidzirai, P Wasserscheid 2019 *Energy & Fuels*, doi:10.1021/acs.energyfuels.9b00296
- [3] V Preethi, S Kanmani, 2017 *Int J Hydrogen Energ*, **42** 8997-9002.
- [4] S Jeong, K H Chung, H Lee, et al, 2017 *Int J Hydrogen Energ*, **42** 17386-17393
- [5] W Jiang, X Yin, F Xin, et al, 2014 *Appl Surf Sci*, **288** 138-142
- [6] Q Zhou, Z Zheng, Y Zhang, et al, 2014 *Mater Lett*, **124** 61-63
- [7] H R Rajabi, M Farsi 2015, *J Mol Cat A: Chem*, **399** 53-61
- [8] Z Peng, D Wu, W Wang, et al. 2017 *Powder Technology*, **315** 73-80
- [9] K S Siddhapara, D V Shah, 2014 *J Nanosci & Nanotech*, **14** 6337-6341
- [10] W Li, J F Li, W Sun, et al. 2008 *J. Chem Phys.* **21** 487-492.