Effects of Cu$^{2+}$ Doping on Structure, Morphology and Photocatalytic Hydrogen Production Performance of Porous CdIn$_2$S$_4$ Microsphere

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Abstract. The Cu$^{2+}$ doped porous CdIn$_2$S$_4$ microspheres (Cu@CdIn$_2$S$_4$) with better photocatalytic performance were prepared by sodium dodecyl sulphate (SDS)-assisted hydrothermal technology. The Cu@CdIn$_2$S$_4$ were characterized by SEM, XPS, XRD and DRS. The effects of Cu$^{2+}$ doping amount on the morphology, structure and photocatalytic hydrogen production performance of CdIn$_2$S$_4$ were studied. The porous Cu@CdIn$_2$S$_4$ microspheres were flower shape of a average diameter of 3-5 μm and their maximum absorption edge was up to 700 nm. The Cu$^{2+}$ doping was good for the improvement of photocatalytic performance. Cu@CdIn$_2$S$_4$ with 0.3wt% Cu$^{2+}$ doping amount possessed the highest hydrogen production rate of 1248.1 μmol/(h g), much more than that of pure CdIn$_2$S$_4$.

1. Introduction

Since the photocatalytic splitting of water on TiO$_2$ 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.

CdIn$_2$S$_4$, 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. CdIn$_2$S$_4$ 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, Cu$^{2+}$ doped porous CdIn$_2$S$_4$ microspheres (Cu@CdIn$_2$S$_4$) with the better photocatalytic performance was prepared by sodium dodecyl sulfate (SDS)-assisted hydrothermal technology. The effect of Cu$^{2+}$ doping on the structure, morphology and photocatalytic hydrogen performance of Cu@CdIn$_2$S$_4$ 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 CuKα irradiation. The patterns were recorded from 10˚ to 70˚ (2θ). 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 AlKα 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.
3.2. Morphology

Figure 2(a–f) showed that SEM images of Cu@CdIn$_2$S$_4$ with different Cu$^{2+}$ doping amount. It was seen from Figure 2 that the porous Cu@CdIn$_2$S$_4$ microspheres with unique flower shape of an average diameter of 3-5 μm could be obtained by hydrothermal synthesis technology. The Cu$^{2+}$ doping had great effect on the morphology of Cu@CdIn$_2$S$_4$ microspheres. It was seen in Figure 2 (a) that the pure CdIn$_2$S$_4$ without Cu$^{2+}$ 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 Cu$^{2+}$ as dopant, abundant floss-like spheres with rough surface were mangled partly under this condition. As the concentration of Cu$^{2+}$ 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 Cu$^{2+}$ doping hindering the self-assembly growth of crystallites into porous microspheres during hydrothermal synthesis process.
3.3. Surface State Analysis

![XPS Spectra of Cu@CdIn2S4 with 0.3wt% Doping Amount](image)

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].

![DSR Spectra of Cu@CdIn2S4 with Different Doping Amount Photocatalysts](image)

Figure 4. DSR 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.

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6. References
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