



Preparation and characterization of In and Cu co-doped ZnS photocatalysts for hydrogen production under visible light irradiation

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ABSTRACT

In this work, a new photocatalysts In(0.1),Cu(x)-ZnS ($x=0.01, 0.03, 0.05$) is successfully synthesized using simple hydrothermal method. The physical and chemical properties of the In and Cu co-doped ZnS photocatalyst were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), diffuse reflectance UV-visible spectroscopy (DR UV-visible) and photoluminescence spectroscopy (PL). The photocatalytic activity of the as-prepared In and Cu co-doped ZnS for hydrogen production from water with Na₂SO₃ and Na₂S as sacrificial agent under visible light irradiation ($\lambda \geq 425$ nm) was investigated. The presence of co-dopants facilitated the separation of electron-hole as well as increases the visible light absorption. The absorption edge of the co-doped ZnS photocatalyst shifted to longer wavelength as the amount of Cu increases. This indicates that the absorption properties depended on the amount of Cu doped. The photocatalytic activity of single doped In(0.1)-ZnS was significantly enhanced by co-doping with Cu under visible light irradiation. The highest photocatalytic activity was observed on In(0.1),Cu(0.03)-ZnS with the hydrogen production rate of 131.32 $\mu\text{mol/h}$ under visible light irradiation. This is almost 8 times higher than single doped In(0.1)-ZnS.

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1. Introduction

Hydrogen production under light irradiation with the assistance of semiconductor photocatalyst has been regarded as an attractive solution to resolve the global energy and environmental problems [1–4]. As large portion of solar light consist of visible light, the development of visible light active photocatalyst that are able to utilize most of the solar light are important.

CdS is one of the most extensively studied metal sulfide photocatalyst for visible light hydrogen production [5–13]. The band gap positions of CdS are ideal for hydrogen production. However, CdS is prone to photocorrosion since the holes in the valence band tend to oxidize CdS [14]. Moreover, Cd metal ions are toxic. Thus, the search for a new metal sulfide photocatalyst that are less toxic is greatly explored.

Recently, some multi component metal sulfides have been reported to be more stable and show higher photocatalytic activity under visible light [15–18]. The host for multi-component metal

sulfides are generally ZnS. This is because ZnS possess high conduction band that are essential for photocatalytic hydrogen production [19–21]. Since ZnS are not visible light active, the modifications of ZnS by doping with foreign elements [22–25] or forming solid solution with narrow band gap semiconductor [15–18] are often done. Studies on photocatalytic hydrogen production utilizing In₂S₃ photocatalyst with band gap of 2.0–2.2 eV [26] under visible light showed good efficiency [27]. The binary metal sulfides of Zn_mIn₂S_{m+3} was also studied and proven to have high photocatalytic activity for hydrogen production [15]. On the other hand, Cu metal dopant is often used in photocatalytic hydrogen production to improve the visible light absorption [22,23,28–30]. Thus, the addition of Cu to this binary metal sulfide is proposed to further improve the photocatalytic activity by enhancing the visible light absorption to longer wavelength.

In this work, it is proposed that In(0.1),Cu(x)-ZnS photocatalyst, will show an enhanced photocatalytic activity for hydrogen production as compared to single doped ZnS photocatalyst. Herein, the In(0.1),Cu(x)-ZnS was successfully prepared by hydrothermal method and the photocatalytic hydrogen production activity was investigated. The benefits of co-dopants in improving the photocatalytic performance for hydrogen production were also investigated.

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2. Experimental

2.1. Synthesis of photocatalyst

Simple hydrothermal method was used to synthesize the powder samples of In(0.1)-ZnS and In(0.1),Cu(x)-ZnS ($x=0.01, 0.03, 0.05$) in a similar way to the previous literatures [31,32]. The samples were labeled as In(0.1),Cu(x)-ZnS, with x showing the doping amount of Cu. In a typical synthesis, for In(0.1),Cu(0.01)-ZnS, 0.2 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Fluka, 98%), 2 mmol of $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Aldrich, 98%), 18 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (GCE chemicals, 98%) and 20 mmol of CH_3CSNH_2 (Merck, 99%) were dissolved in 50 mL of distilled water. The solution was added into a Teflon-lined autoclave that was sealed and heated in an oven at 433 K for 8 h. After natural cooling to room temperature, the precipitates were washed with distilled water for several times and dried in vacuum at room temperature.

2.2. Characterization of photocatalyst

Powder X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer, Bruker Advance D8 Siemens 5000 using Cu $K\alpha$ radiation ($\lambda=0.15418$ nm, 40 kV, 40 mA). The diffuse reflectance UV–visible (DR UV–visible) spectra were recorded on a Perkin Elmer Ultraviolet–visible Spectrometer Lambda 900. Barium sulfate (BaSO_4) was used as the reference. Photoluminescence (PL) spectra were measured at room temperature using a photoluminescence spectrophotometer (PTI QM-4) with an excitation wavelength of 250 nm. The morphologies and nanocrystal sizes of the samples were determined with field emission scanning electron microscopy (FESEM) using JEOL JSM 6701F with platinum coating (2 kV, 10 mA). The elemental ratio was measured using energy dispersive X-ray (EDX) spectroscopy utilizing an Oxford Instrument INCA X-sight analyzer equipped with a Sapphire super ultra-window detector attached to the Zeiss Supra 35VP FE-SEM. The accelerating voltage of the electron gun was set to 15 kV. The elemental analysis was completed on a Bruker S4 PIONEER X-ray fluorescence spectrum (XRF), using Ru target and 4 kW power.

2.3. Photocatalytic hydrogen production reaction

Photocatalytic hydrogen production was performed in a closed-side irradiated-Pyrex cell equipped with an outer water cooling system to keep the temperature throughout the reaction at 25 ± 0.2 °C. In all experiments, the powder sample (0.2 g) was dispersed by magnetic stirring in an aqueous solution (190 mL) containing 0.25 M Na_2SO_3 and 0.35 M Na_2S [15,29] as sacrificial agents. Nitrogen gas was purged through the reaction cell for 30 min before reaction to remove air. A 300 W Xe lamp was focused on the side window of the cell through a cut-off filter ($\lambda \geq 425$ nm, TrusTech PLS-SXE 300).

3. Results and discussion

3.1. Crystal structure and morphology

Fig. 1 shows the XRD data of ZnS, In(0.1)-ZnS and In(0.1),Cu(x)-ZnS ($x=0.01, 0.03, 0.05$). The XRD pattern shows three major diffraction peaks at 2θ of 28.6°, 47.6° and 56.3°, which can be indexed to the formation of predominantly the cubic zinc blende phase at (111), (200) and (311) planes [31,32]. As for the pure ZnS sample, it was observed that there are some traces of the wurtzite hexagonal phase at 2θ of 27.5°, 31.0° and 52.0° which corresponds to the (100), (101) and (103) planes, respectively [33,34]. In(0.1)-ZnS and In(0.1),Cu(x)-ZnS samples showed no other measurable phases produced. The presence of doped ions into the ZnS samples

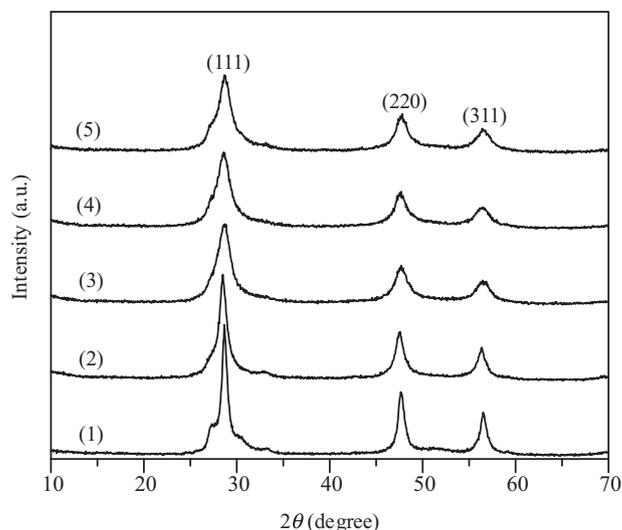


Fig. 1. XRD patterns of different samples. (1) ZnS, (2) In(0.1)-ZnS, (3) In(0.1),Cu(0.01)-ZnS, (4) In(0.1),Cu(0.03)-ZnS, (5) In(0.1),Cu(0.05)-ZnS.

prevented the growth of hexagonal phase. There was no obvious peak shifting when In or In and Cu was doped into ZnS. There were also no shifts as the amount of Cu added increased. This indicates that Cu was successfully doped inside the lattice without causing crystal distortion since the ionic radius of Cu^{2+} (0.72 Å) are similar to Zn^{2+} (0.74 Å).

When Cu was co-doped into In(0.1)-ZnS, the intensity decreased and the peaks became broader. However, the decreased in peak intensity was not dependent on the amount of Cu added. The relatively small crystallite size of the Cu co-doped ZnS makes the diffraction peaks broad. The average crystallite size was estimated by using the Debye–Scherrer formula on the basis of the broadening of the (111) diffraction peak and is listed in Table 1. The crystallite size decreased as Cu was added into In(0.1)-ZnS might be due to the substitution of smaller ionic radius Cu compared to In and Zn. The d-spacing and lattice parameter also decreased as the amount of Cu increased. This was due to the slight peak shifting to higher angle due to smaller ionic radius Cu substituting In or Zn. This confirms that some substitution by doping had taken place.

The FESEM images of the samples are shown in Fig. 2. ZnS composed of small nanospheres in the range of 20 to 150 nm, which agglomerated into undefined shape. For In(0.1)-ZnS and In(0.1),Cu(x)-ZnS, the large nanospheres in the range of 200 to 400 nm are composed of smaller agglomerated spheres in the range of 20 to 50 nm. The sizes of the large nanospheres are not uniform and more compact compared to ZnS. The doping of Cu does not change the morphology of the samples. Fig. 2(f) of In(0.1),Cu(0.03)-ZnS (as representative) shows only the presence of In, Cu, Zn and S with O, C and Pt impurities (not labeled). The chemical composition of In(0.1),Cu(0.03)-ZnS was analyzed by XRF and compared with EDS composition in Table 2. Both show small amount of Cu present in the bulk and surface.

3.2. Optical properties

Fig. 3 shows the DR UV–visible absorption spectra of In(0.1)-ZnS and In(0.1),Cu(x)-ZnS ($x=0.01, 0.03, 0.05$). The absorption edge of In(0.1),Cu(x)-ZnS exhibited a gradual red shift toward longer wavelength in the visible light region with increasing Cu concentration. For 0.03 and 0.05 Cu content, the absorption shifted but with tail towards the longer wavelength, which is a characteristic of doped photocatalysts [23–25,28–31]. This could be due to the doping of Cu forming discrete level from Cu 3d above the valence band

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