

Research Article

Preparation of High Activity Ga and Cu Doped ZnS by Hydrothermal Method for Hydrogen Production under Visible Light Irradiation

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Received 6 May 2015; Accepted 14 July 2015

Academic Editor: Balachandran Jeyadevan

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Ga(0.1),Cu(x)-ZnS ($x = 0.01, 0.03, 0.05$) photocatalysts were successfully synthesized by hydrothermal method. The synthesized Ga and Cu codoped ZnS photocatalysts showed photocatalytic property effective for hydrogen production from aqueous solution containing Na_2SO_3 and Na_2S as sacrificial reagent under visible light irradiation. The rate of hydrogen production was found to be strongly dependent on Cu doping content. The highest photocatalytic activity is observed for Ga(0.1),Cu(0.01)-ZnS with hydrogen production rate of $114 \mu\text{mol/h}$. The addition of Ga as codoped increased the photocatalytic activity to 58 times as compared to single doped Cu-ZnS. The Ga and Cu codoped ZnS photocatalysts are also stable under long irradiation. The enhancement in the photocatalytic activity of Ga and Cu codoped photocatalyst can be attributed to the synergistic effect between Ga and Cu. The photocatalytic activity was greatly enhanced with the addition of 0.5 wt% Ru as cocatalyst with a hydrogen production rate of $744 \mu\text{mol/h}$.

1. Introduction

Hydrogen, an attractive clean energy source with high energy capacity, is a very promising candidate as a primary energy source in the future [1, 2]. Photocatalytic water splitting is considered as an alternative method to produce hydrogen utilizing solar energy. Up to now, considerable efforts have been devoted to developing highly active photocatalysts for the water splitting reaction and remarkable progress has been made [3–6].

ZnS is known to be a highly active photocatalyst for hydrogen evolution from aqueous solutions containing sacrificial reagents such as SO_3^{2-} and S^{2-} , even without the addition of Pt cocatalyst. This is due to the high conduction band level of ZnS to reduce water to hydrogen [7–9]. However, the large band gap of ZnS restricts its photocatalytic applications within the UV light range. To effectively utilize solar light energy, visible light response photocatalysts with high photocatalytic activity are desired.

Doping of ZnS is considered as one of the many ways to enhance the light absorption ability of ZnS to the visible light region while still maintaining the high conduction band. Cu doped ZnS [10, 11], Ni doped ZnS [12], and Bi doped ZnS [13] have been reported to show considerable high photocatalytic activities for hydrogen evolution under visible light from aqueous solution containing S^{2-} and/or SO_3^{2-} as electron donors. The visible light response is obtained by the formation of donor levels by the doped metal cations in the wide band gap of the ZnS host material.

Although Cu doped ZnS [10] showed high photocatalytic activity for hydrogen evolution, it suffers from photocorrosion. One of the possible methods to maintain the high photocatalytic activity of Cu doped ZnS without suffering from photocorrosion is to carry out doping with another metal. It is known that codoping is effective to suppress the recombination rate of electron-hole pairs [14, 15]. This is due to the synergic effects produced when two metals are doped together. The negative effects caused by doping

can be partially improved by codoping with another dopant. Dopants like Sn^{4+} and Eu^{3+} were incorporated in TiO_2 to improve the visible light absorption and photocatalytic activity. The purpose of using Sn and Eu was that the former is known to help in the charge separation of photogenerated electrons and holes and the latter being a lower valent cation than Ti^{4+} can generate anion vacancies in TiO_2 thereby leading to visible light absorption [14].

Ga doped ZnS has been reported to be photocatalytically active under UV light irradiation [16]. In addition to the absorption spectrum, the mobility of photogenerated charges is critical for photocatalytic activity. Metal compounds associated with d^{10} electronic configurations such as Ga^{3+} are attractive because their conduction and valence bands are formed by hybridized sp orbitals with large band dispersion that would lead to high charge mobility and, hence, high photocatalytic performance [17, 18]. Ga was selected as the dopant in this study as it is regarded as the most efficient donor for ZnS to generate more charge carriers [19].

This present study aims to investigate the exact role of synergistic effect of codoping Ga and Cu into ZnS lattice in the physical-chemical properties and photocatalytic activity for hydrogen production. The new photocatalyst Ga, Cu codoped ZnS was prepared by using hydrothermal method. The role of Ga in promoting the photocatalytic activity was also examined.

2. Experimental

2.1. Synthesis of Samples. Simple hydrothermal method was used to synthesize the powder samples of ZnS, Cu(0.1)-ZnS, Ga(0.1)-ZnS, and Ga(0.1),Cu(x)-ZnS ($x = 0.01, 0.03, 0.05$) in a similar way to the previous literatures [20, 21]. The samples were labelled as Ga(0.1),Cu(x)-ZnS, with x showing the doping amount of Cu in mol ratio. In a typical synthesis for Ga(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 $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Aldrich, 99.9%), 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 to an 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. 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-vis) 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 crystal sizes of the samples were determined with field emission scanning electron microscopy (FESEM) using JEOL JSM 6701F with platinum coating (2 kV, 10 mA). Specific surface area was measured using the

Brunauer-Emmett-Teller (BET) method, Beckman Coulter SA3100 by nitrogen absorption at 77 K. The samples were previously outgassed at 393 K for 180 min. The elemental analysis was completed on a Bruker S4 PIONEER X-ray fluorescence (XRF) spectrum, using Ru target and 4 kW power.

The chemical forms of the products were studied using X-ray photoelectron spectroscopy (XPS), AXIS Ultra DLD, Shimadzu, with monochromatic Al $K\alpha$ radiation (1486.6 eV).

2.3. Photocatalytic Activities. Photocatalytic hydrogen evolution was performed in a closed-side irradiated-Pyrex cell equipped with an outer water cooling system to keep the temperature throughout the reaction at $25 \pm 0.2^\circ\text{C}$. 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 [20] 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). The apparent quantum yields (AQY) defined by (1) were measured using a 425 nm band pass filter and Avantes fibre optic spectrometer (Ava Spec USB 2000) connected to AveSoft 7.2. The amount of hydrogen evolved was determined with a thermal conductivity detector (TCD) gas chromatography (SP 2100) using NaX zeolite column and nitrogen as carrier gas. Cocatalyst ruthenium (0.1–1 wt%) was loaded on the photocatalyst surface by an *in situ* photodeposition method from the precursor of RuCl_3 . Consider

$$\begin{aligned} \text{AQY (\%)} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved H}_2 \text{ molecules}}{\text{number of incident photons}} \times 2. \end{aligned} \quad (1)$$

3. Results and Discussion

3.1. Crystal Structure. Figure 1 shows XRD patterns of ZnS, Cu(0.1)-ZnS, Ga(0.1)-ZnS, and Ga(0.1),Cu(x)-ZnS powder samples. The distinctive peaks are found at 2θ of 28.6, 32.5, 47.6, and 56.3, corresponding to the (111), (200), (220), and (311) planes, respectively, which is a typical pattern of cubic zinc blende phase [22, 23]. For ZnS, there is shoulder peak at $2\theta = 27$. This is due to (100) and (002) plane hexagonal phase of ZnS, which is in agreement with the reported values with similar synthesis temperature [24]. As for the Cu(0.1)-ZnS sample, there is a broad shoulder peak at $2\theta = 27$ which might be due to the (101) plane of CuS [25]. This peak has a different shape compared to the shoulder peak of ZnS at the same place. Furthermore, the peak at $2\theta = 30.5$ also disappeared for Cu(0.1)-ZnS. It is also observed that there is a shoulder peak at $2\theta = 33.5$ and $2\theta = 59$ corresponding to (006) and (116) plane of CuS, respectively [26, 27]. This confirms that, for Cu(0.1)-ZnS, both CuS and ZnS phases existed in the sample.

The peak became broad with the addition of Ga to the samples; thus the weak diffraction peak at (200) was not