Journal of Chemical Reactivity and Synthesis 2019: 9(4) 25-31

Hydrogen solar fuel generation from photocatalytic decomposition of H_2S-containing media via nanostructured solid-solution semiconductor

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ARTICLE INFO:

Received:
2 August 2019

Accepted:
14 November 2019

Available online:
17 November 2019

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ABSTRACT

Hydrogen sulfide is a flammable, malodorous, highly toxic and corrosive compound which is produced in large quantities as a by-product in many industrial processes. However, it will be economically and environmentally advantageous if it is photodecomposed to generate hydrogen, which is a clean and renewable energy carrier. In this paper, a nanostructured solid-solution semiconductor material from the family of cadmium-zinc-sulfide was synthesized through a facile hydrothermal method and was applied as alloy photocatalyst to generate hydrogen fuel via a H2S photodecomposition process. Morphological and optical properties of the sample have been characterized by XRD, FE-SEM, EDS and UV-vis DRS techniques. Solid-solution semiconductor exhibited a good photocatalytic performance.

Keywords: Solar hydrogen generation, photocatalyst, H_2S photodecomposition, solid-solution semiconductor

1. Introduction

Hydrogen sulfide is a colourless, corrosive, flammable and greatly perilous gas with a “rotten egg” smell. Every year, millions of tons of H_2S are produced as a by-product in petroleum refineries and natural-gas extraction. Hence, decomposition of H_2S to H_2 over semiconductor photocatalysts has attracted attention because that could satisfy both energy and environment requirements [1-3]. In a photocatalytic H_2S decomposition reaction, photocatalysts play a crucial role. The photocatalytic decomposition of H_2S in alkaline solution can be summarized as [3]:

$$\text{Semiconductor} + h\nu \rightarrow h^{+}_{VB} + e^{-}_{CB} \quad (1)$$

$$H_2S + 2OH^{-} \rightarrow S_2^{-} + 2H_2O \quad (2)$$

$$H_2S + OH^{-} \rightarrow HS^{-} + H_2O \quad (3)$$

$$2S^{2-} + 2h^{+}_{VB} \rightarrow S_2^{2-} \quad (4)$$

$$2HS^{-} + 2h^{+}_{VB} \rightarrow S_2^{2-} + 2H^{+} \quad (5)$$

$$2H^{+} + 2e^{-}_{CB} \rightarrow H_2 \quad (6)$$

There, the photo-excited electrons can reduce the protons and the sulfide ion behaves as a hole scavenger.

Among diverse photocatalysts, just the sulfide type semiconductor materials can act stably in the hydrogen sulfide aqueous solution, while metallic or oxide type photocatalysts are sulfurized. Among the various metal sulfides, CdS and ZnS are the two finest semiconductors that have attracted extensive attention for H_2 production from photocatalytic decomposition of hydrogen sulfide [4]. However, their stability and photoactivity was observed to be very poor. To resolve these problems, forming solid solutions out of them is the most promising method [5]. Although the photocatalytic performance of Cd1-xZnxS solid solution was higher than those of CdS and ZnS but its band gap was wider than that of CdS. For efficient photocatalytic H_2 generation, we need materials with narrow band gap for the full utilization of the solar spectrum. Hence, metal ion doping is one of the solutions for reducing the band gap and enhancing the photocatalytic activities of solid solutions under visible light [6]. Several metal ion dopants in CdZnS have been reported to enhance the photocatalytic activity of CdZnS solid solution [7]. In our previous work, a novel photocatalyst Cd0.1Zn0.87Sn0.01Ag0.02S was synthesized and was used as alloy photocatalyst to generate hydrogen from water splitting [8].

Since photocatalytic hydrogen production with simultaneous photodecomposition of H_2S containing media is very more noteworthy, the Cd0.1Zn0.87Sn0.01Ag0.02S solid solution photocatalyst was synthesized according to our previous reports [8] and was used as alloy photocatalyst to generate hydrogen fuel from decomposition of hydrogen sulfide aqueous solution under visible light irradiation.

2. Experimental

A solid solution sample was synthesized in a similar way to the previous literature [8]. In a typical synthesis for Cd0.1Zn0.87Sn0.01Ag0.02S, we prepared a 50-mL aqueous solution containing 0.04M $Cd(NO_3)_2$ (Merck;98%, Darmstadt, Germany), 0.36M $Zn(CH_3COO)_2$ (Fluka; 98%, Gillingham, United Kingdom), 0.004M $SnCl_4$ (Merck; 98%), 0.008M $AgNO_3$ (Fluka; 9 8%), and 0.4M CH_3CSNH_2 (Merck; 99%), and agitated for 20 min at room temperature. The solution was heated in an oven at 433 K for 8 h and then cooled to room temperature naturally. The precipitates were washed with distilled water for several times and dried in vacuum at room temperature. Powder X-ray diffraction pattern of the sample was recorded using a Philips X ’Pert Pro X-ray powder diffractometer (λ = 1.54Å; Cu K α beam). Field emission scanning electron microscopy (FE-SEM) images were taken by a ZEISS SIGMA VP. UV-vis absorption spectra were recorded on a Varian Cary 5 UV-visible-NIR spectrometer ($BaSO_4$ was used as a blank).

Photocatalytic hydrogen evolution was performed in home-made photoreactor, consisting of a 500-W power-tunable Xe lamp (Ushio xenon short arc lamp, Tokyo, Japan) and a double

-walled cylindrical glassy vessel equipped with a temperature-controlling bath circulator (WCR-P6). In the typical experiment, 50 ml of 0.5 M aqueous NaOH solution in the reactor dispersed with 0.2 g of the photocatalyst powder, stirred and thermostated at 25℃ was first purged with nitrogen for 1 h to eliminate the dissolved oxygen and then with bubbling H_2S for about 90 min until saturation of the alkali solution. Then aqueous dispersion in the reactor was irradiated with light from a 500 W xenon lamp. The volume of gas being evolved during the test was measured under atmospheric conditions at 298 K by leading the released gas into an inverted burette (±0.1 cc) filled with water.

3. Results and discussion

The XRD patterns of the solid solution and the standard diffraction patterns of cubic ZnS are depicted in Fig. 1. Sample showed diffraction pattern at 2θ angles of 28.8, 47.9 and 57.4 corresponding to the (111), (220), (311) planes of cubic zinc-blend structure [9]. Compared with the pure ZnS, XRD data shows that the peaks position of alloy photocatalyst shift toward larger values.

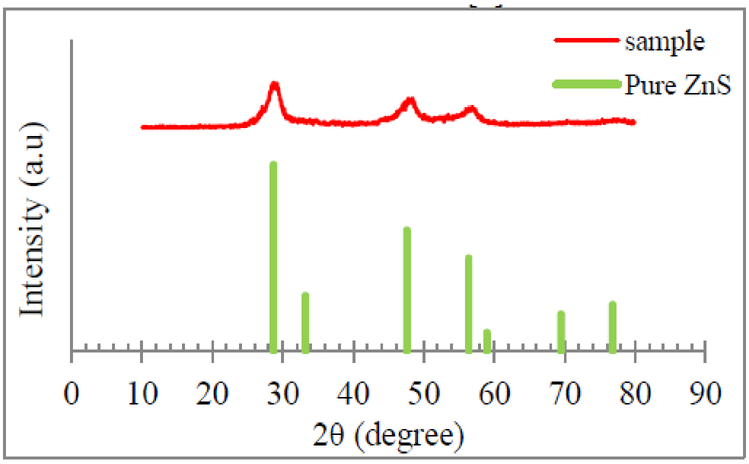

Fig.1. XRD pattern of the alloy photocatalyst synthesized in this work

The successive shift clearly indicates that solid solution was formed. No other peaks were detected, indicating the purity of the solid solution. No CdS, SnS_2 and Ag_2S derived peaks were observed, suggesting that the Cd, Sn and Ag dispersed well in the ZnS crystal [5]. The average crystal size of alloy semiconductor was determined by Scherrer's formula and was calculated as 4 nm [8]. Figure 2 shows the optical absorbance spectrum of alloy semiconductor. The spectrum indicated that the photocatalysts have good absorption in the region 300-700 nm. This means that photocatalysts can absorb visible light. The values of Eg were determined through Kubelka–Munk method [8].

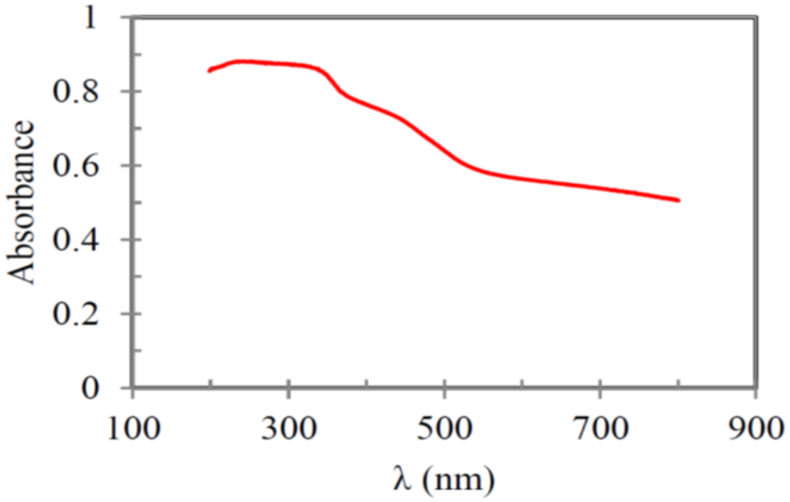

Fig.2. Diffuse reflectance UV –visible spectra of the photocatalyst

The values of Eg was 2.64 eV for the photocatalyst. The FESEM images of a solid solution photocatalyst at different magnification are presented in Figure 3. It can be observed that the photocatalyst consists of nanospheres, nanoplatelets, and dense microspheres (nanoparticles aggregated to form microspheres) in the range of 400-500 nm.

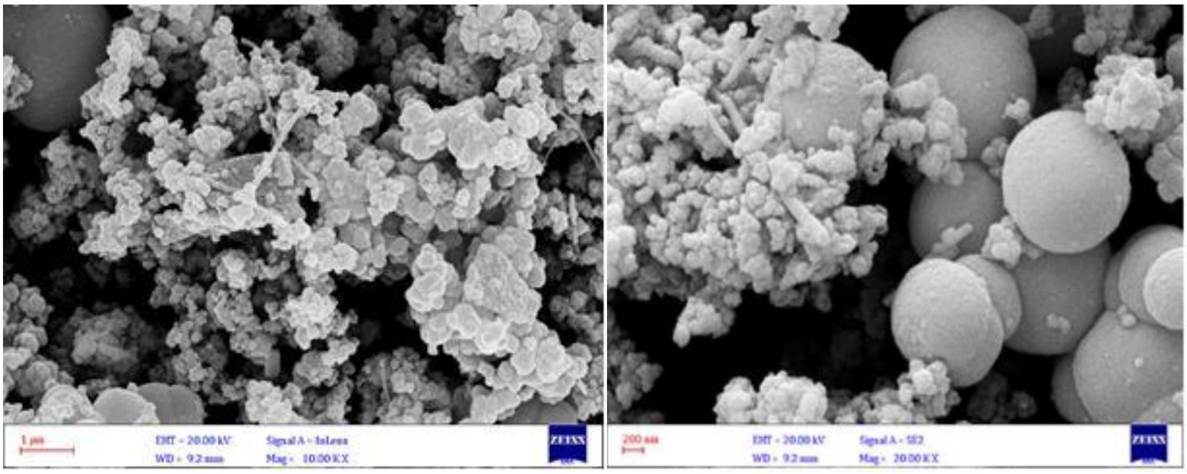

Fig.3. Field emission scanning electron micrograph (FE-SEM) of alloy semiconductor

The energy dispersive x-ray spectroscopy analysis (Table1) revealed that the obtained solid solution is composed of Ag, Sn, Cd, Zn and S.

Table1. Energy dispersive X-ray spectroscopy (EDS/EDX) data (Wt. %).

Semiconductor	**Cd**	**Zn**	**Sn**	**Ag**	**S**
$Cd_{0.1}Zn_{0.87}Sn_{0.01}Ag_{0.02}S$	4.4	70	0.8	0.1	24.7

Hydrogen production rates from the photodecomposition of hydrogen sulfide solution are shown in Fig. 4. The figure indicates that the semiconductor synthesized here have an excellent photocatalytic performance with average hydrogen production rate of 15 ml/h.

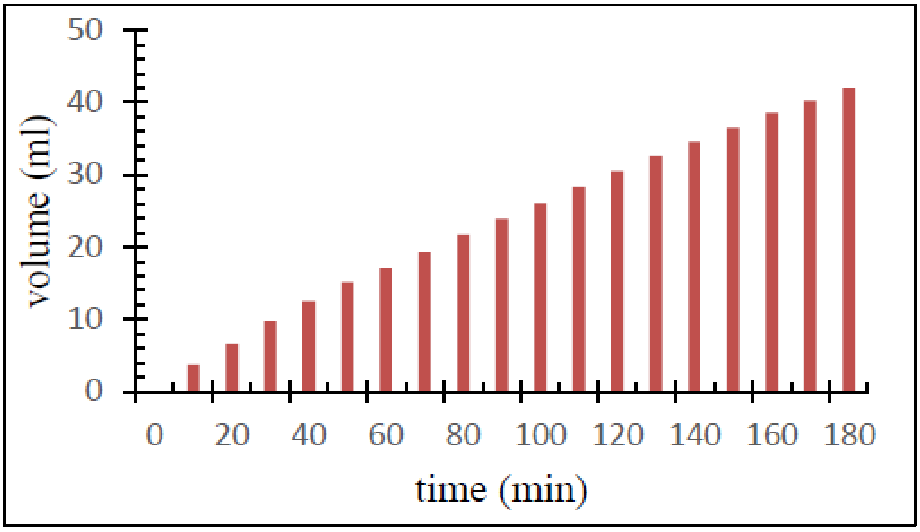

Fig.4. The volume of hydrogen gas being evolved over the semiconductor photocatalyst in alkaline solution.

4. Conclusions

Using a facile hydrothermal method, an efficient nanostructured semiconductor was synthesized and was applied as alloy photocatalyst to generate hydrogen fuel via a hydrogen sulfide photodecomposition process. The nanostructured solid-solution compound photocatalyst was confirmed by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDX/EDS) analyses. The crystallite sizes of the solid solution samples are in a range of 3–4 nm. Solid-solution semiconductor exhibited a fairly good photocatalytic performance with average hydrogen production rate of 15 ml/h.

Acknowledgment

The authors are thankful to Zanjan University and Center for Research in Climate Change and Global Warming for the partial support to carry out this work.

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