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Facile Synthesis Of $Cd_xZn_{1-x}S$ Photocatalyst With Enhanced Photocatalytic Hydrogen Production Under Visible Light Irradiation

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ABSTRACT

$Cd_xZn_{1-x}S$ -based photocatalysts for the hydrogen evolution under visible light ($\lambda=405$ nm) irradiation from aqueous solutions containing sodium sulfide and sodium sulfite as sacrificial agents have been synthesized by co-precipitation and solvothermal methods. The effects of Cd/Zn molar ratios and doped PdS as cocatalyst on the rate of photocatalytic hydrogen production have been investigated.

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INTRODUCTION

As a potential answer to the global energy crisis and environmental pollution, the application of hydrogen energy has attracted great attention. Extensive work has been devoted to the efficient production of hydrogen at low cost. Since Fujishima and Honda firstly reported the decomposition of water on illuminated TiO_2 electrodes in 1972 (Fujishima A., 1972), photocatalytic water splitting has been considered as a promising strategy of converting solar energy into hydrogen energy. Because of the advantages of photocatalytic H_2 production, such as pollution-free and low energy consumption, researchers have made enormous efforts to improve the efficiency of H_2 production by modifying TiO_2 nanostructures (Kato, H., 2003; Zong, X., 2008), as well as developing new photocatalysts (Kim, H.G, 2004; Maeda, K. 2005; Shen S.H 2008). However, most of the photocatalysts could only respond to UV irradiation that takes up ~4% of solar energy, which limits the application of photocatalysts to a great extent.

Cadmium sulfide was the first photocatalyst to be employed in hydrogen production by irradiation of its aqueous solutions with visible light using sulfide ions as electron donors. Cadmium sulfide is characterized by a band gap of 2.4 eV, and the positions of its valence and conduction bands are suitable for the photocatalytic decomposition of water (Zhu, J., 2009). However, the sulfide ion is readily oxidized to sulfate by the photogenerated holes, with Cd^{2+} ions escaping into the solution. Use of sulfides as electron donors diminishes the photocorrosion of the catalyst. A possible way of enhancing the photocatalytic activity of cadmium sulfide is to develop composite materials based on CdS and broader band semiconductors, for example, ZnS (Chen, J., 2008). Zinc and cadmium sulfides have similar crystal structures, so they fairly readily form $Cd_xZn_{1-x}S$ solid solutions. As well-known, $Cd_xZn_{1-x}S$ solid solution photocatalyst has been studied extensively due to its controllable band structure and excellent performance in photocatalytic hydrogen production under visible-light irradiation. Thus lots of efforts have been made to improve the photocatalytic activity of $Cd_xZn_{1-x}S$ (Zhang, W. 2008; Liu, G 2008; Zhang, X. 2008). Herein, we report on effect of the preparation method, Cd/Zn molar ratios and metal sulfide as cocatalyst loaded onto $Cd_xZn_{1-x}S$ for the photocatalytic H_2 production under visible light.

Experimental:

Preparation of photocatalyst:

Co-precipitation method:

All the reagents are analytical grade and used without further purification. A heat resistant 500 mL beaker containing a 0.1 M NaOH solution (100 mL) was placed on a magnetic stirrer, and a mixed solution (100 mL) of cadmium chloride and zinc chloride in proportions corresponding to $x = 0.3$ was added. Precipitation was carried out with a 0.1 M Na_2S solution at a twofold excess of sodium sulfide. The mixture was then stirred for 20 min.

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The resulting suspension was placed in Teflon beakers and centrifuged. The precipitate was washed with distilled water about 10 times. Thereafter, the precipitate was decanted and was kept in a drying oven at 70 °C for 15 h.

Solvothermal Method:

The composite photocatalysts $Cd_xZn_{1-x}S$ were synthesized as follows (Wang, Y. 2012). Firstly, the single-source precursor was prepared by dropwise addition of 100 mL of a sodium diethyldithiocarbamate aqueous solution (0.2 M) to 50 mL of an aqueous solution containing zinc acetate and cadmium acetate with a certain molar ratio of metal ions and a total metal concentration of 0.2M. After stirring for 24 h at room temperature, the resulting precipitate was centrifuged, washed with deionized water for a few times and dried in an oven at 60 °C overnight. Subsequently, as-prepared single-source precursor was added into a 100 mL PTFE-lined stainless steel autoclave containing 60 mL of ethylenediamine. The autoclave was kept in an oven at 180 °C for 24 h. After cooling to room temperature naturally, the obtained precipitate was centrifuged, washed with ethanol and deionized water for several times and then dried at 60 °C overnight.

Addition of metal sulfides and photocatalytic reaction

40 mg of prepared $Cd_xZn_{1-x}S$ powder was dispersed in 30 mL aqueous solution containing Na_2S/Na_2SO_3 with stirring and N_2 purge. Then, 10 mL of various metal ions were added into the solution at 0.5 mL/min to load metal sulfides [13]. After loading, the suspension was irradiated for 7 h by a 405 nm LED lamp. The light intensity for the reactor was 25.5 mW/cm². The reactant solution was maintained at room temperature during the photocatalytic reaction. The amount of hydrogen evolved was determined by a gas chromatography.

RESULTS AND DISCUSSION

Phase Structure:

Fig.1 shows the XRD patterns of as-prepared $Cd_{0.3}Zn_{0.7}S$ samples from the co-precipitation method. Three diffraction peaks are detected in all samples, corresponding to the (111), (220), (311) planes of cubic phase. The XRD patterns for all the samples in Fig.1 did not any change because of a small amount of metal sulfide.

The XRD patterns displayed in Fig. 2 show that hexagonal phase CdS prepared by solvothermal synthesis of good crystallinity is formed. The three diffraction peaks at 24.9°, 26.6° and 28.3° can be assigned to (100), (002) and (101) planes, respectively. The hexagonal phase is maintained in $Cd_xZn_{1-x}S$ at higher x values of 0.7 and 0.6 the diffraction peaks shift to higher 2θ values as the Zn^{2+} content increases due to a smaller ionic radius of Zn^{2+} than that of Cd^{2+} . The above observations indicate that hexagonal phase $Cd_xZn_{1-x}S$ solid solutions are formed, while the blending of Zn^{2+} cations into the structure causes the change in both the growth orientation and the crystallinity. When the x value is decreased to 0.5, the resulted samples are no longer single-phase solid solutions. As it can be seen from Fig. 2, cubic phase ZnS starts to appear when Cd^{2+} is 0.5 and becomes dominant at 0.3. All the samples prepared by coprecipitation method showed the lower crystallinity than those by solvothermal method.

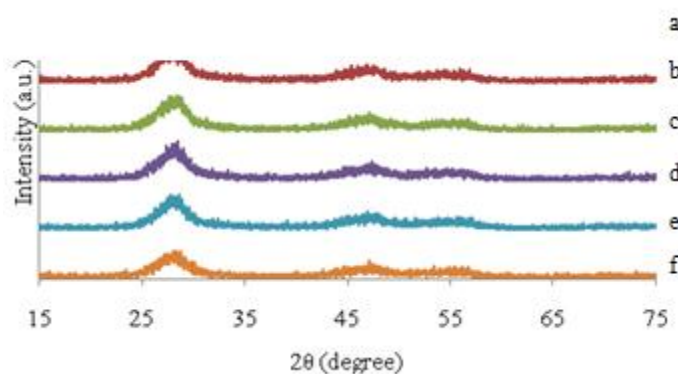


Fig. 1: XRD patterns of as-prepared $Cd_{0.3}Zn_{0.7}S$ samples from the co-precipitation method. (a) CoS, (b) Ag_2S , (c) NiS, (d) Ru_2S_3 , (e) PdS and (f) without as cocatalyst

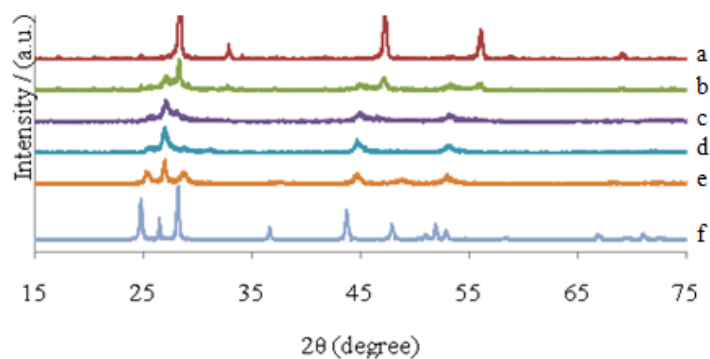


Fig. 2: XRD patterns of as-prepared $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ samples ($X=0-1.0$) from the solvothermal synthesis. The values of x : (a) 0, (a) 0.1, (b) 0.3, (c) 0.5, (d) 0.6, (e) 0.7 and (f) 1.0

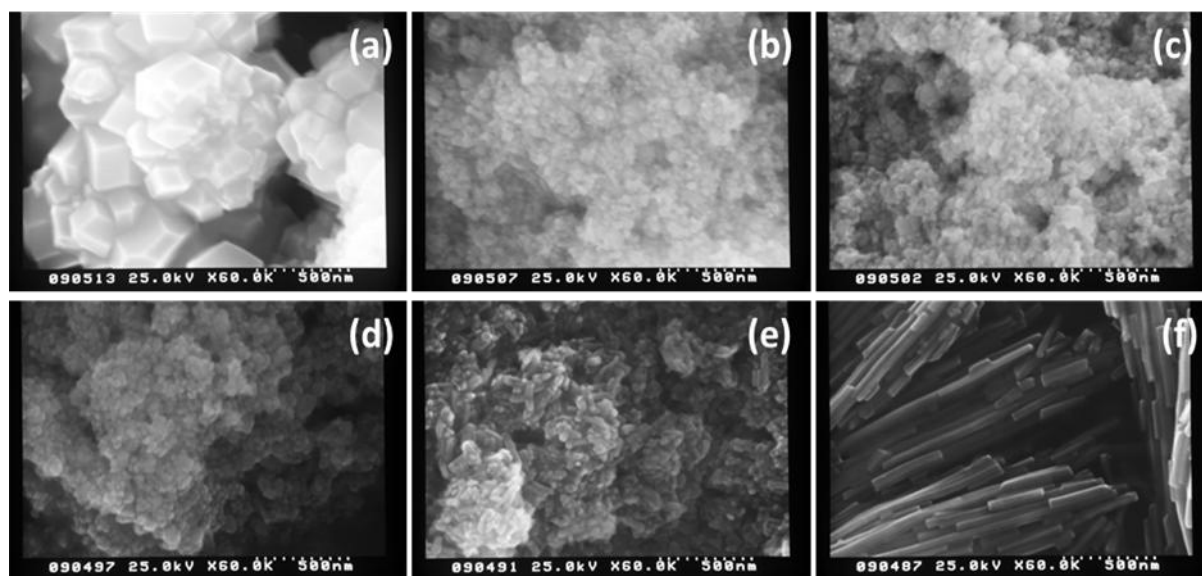


Fig. 3: SEM images of (a) $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}$, (b) $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$, (c) $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$, (d) $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$, (e) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$, (f) CdS .

SEM images:

Fig.3 shows the SEM images of as-prepared $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ samples from the solvothermal method. The morphology of photocatalysts turns to nanoparticles from nanowires with decreasing molar ratio. The sample $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}$ (Fig. 3a) presents the morphology of microspheres comprised of aggregated particles which is distinctively different from other samples. CdS nanowires of high aspect ratios are formed (Fig. 3f) due to the preferential growth along the c -axis direction in ethylenediamine solvent.

UV-vis Absorption Properties:

The UV-vis DRS spectra of as-prepared $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ samples by co-precipitation synthesis are displayed in Fig.4. Although PdS loaded onto $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ solid solution shows the high absorption at about 500 nm, other samples indicate a similar tendency.

The UV-vis DRS spectra of as-prepared $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ samples by solvothermal synthesis are displayed in Fig. 5. As shown in Fig.5, an obvious absorption edge shift can be observed with increasing x values.

Photocatalytic Activity:

Table 1 shows the photocatalytic activities of co-precipitation synthesized $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ solid solution for H_2 production from an aqueous solution containing $\text{S}_2^-/\text{SO}_3^{2-}$ as a sacrificial reagent.

The synthesized PdS(1.0 wt%)@ $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ showed a greatly enhanced photocatalytic activity, with the rate of H_2 production determined to be $1300 \mu\text{mol h}^{-1}\text{g}^{-1}$.

The synthesized PdS(1.0wt%)@ $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ showed a greatly enhanced photocatalytic activity, with the rate of H_2 production determined to be $2100 \mu\text{mol h}^{-1}\text{g}^{-1}$.

To evaluate the stability of $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ and $\text{PdS}(1.0\text{wt}\%)\text{@Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ photocatalysts, a recycling test was performed on the H_2 production determined to be $1300 \mu\text{mol h}^{-1} \text{g}^{-1}$.

Table 2 shows the photocatalytic activities of solvothermal synthesized $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ solid solution for H_2 production from an aqueous solution containing $\text{S}_2^{2-}/\text{SO}_3^{2-}$ as a sacrificial reagent. The synthesized $\text{PdS}(1.0\text{wt}\%)\text{@Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ showed a greatly enhanced photocatalytic activity, with the rate of H_2 production determined to be $2100 \mu\text{mol h}^{-1} \text{g}^{-1}$.

To evaluate the stability of $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ and $\text{PdS}(1.0\text{wt}\%)\text{@Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ photocatalysts, a recycling test was performed on the H_2 production activity. Fig.6 shows the Time course of photocatalytic H_2 production for $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ and $\text{PdS@Cd}_{0.6}\text{Zn}_{0.4}\text{S}$.

The reaction system was bubbled with N_2 for 30 min every 7 h to remove the H_2 inside. After 5 recycles, the catalyst did not exhibit any loss of activity, indicating its good stability during the photocatalytic reaction. Total amount of H_2 production after 35 h produced 68.3 mmol g^{-1} corresponding to 1.5 L g^{-1} .

Photocatalytic mechanism

Photocatalytic activity was improved by using the mixed solution containing both Na_2S and Na_2SO_3 in the present work. Using this mixed solution, the photocatalytic reaction should proceed as follows:

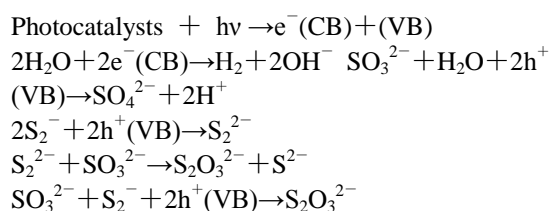


Table 1: Summary of the photocatalytic activities and QE of $\text{Cd}_{0.5}\text{Zn}_{0.7}\text{S}$ photocatalysts prepared by the co-precipitation method.

<u>$\text{Cd}_{0.5}\text{Zn}_{0.7}\text{S}$ photocatalysts prepared by the co-precipitation method.</u>			
sample	Band gap (eV)	H_2 production ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	QE (%)
$\text{Cd}_{0.5}\text{Zn}_{0.7}\text{S}$	2.59	740	5.9
$\text{PdS@Cd}_{0.5}\text{Zn}_{0.7}\text{S}$	2.48	1300	10.6
$\text{Ru}_2\text{S}_3\text{@Cd}_{0.5}\text{Zn}_{0.7}\text{S}$	2.62	1100	9.1
$\text{NiS@Cd}_{0.5}\text{Zn}_{0.7}\text{S}$	2.60	1100	8.8
$\text{Ag}_2\text{S@Cd}_{0.5}\text{Zn}_{0.7}\text{S}$	2.58	300	2.4
$\text{CoS@Cd}_{0.5}\text{Zn}_{0.7}\text{S}$	2.60	510	4.0

Fig.7 shows the H_2 production mechanism. When the catalyst was irradiated visible light, electrons in the valence band are excited to the conduction band, and generated electron-hole pairs. The generated holes can be transferred to PdS, which could efficiently oxidize the sulfide ion and sulfite ion, generating the proton. The proton are reduced by photogenerated electrons, and H_2 is produced.

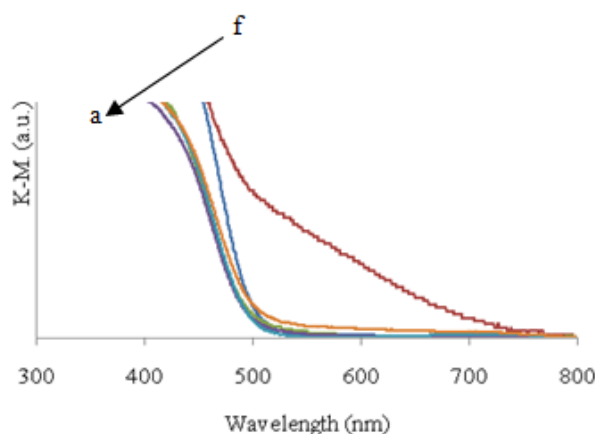


Fig. 4: UV-visible diffuse reflectance spectra of $\text{Cd}_{0.5}\text{Zn}_{0.7}\text{S}$ samples. The values of x: (a) NiS, (b) Ru_2S_3 , (c) CoS, (d) Ag_2S , (e) without and (f) PdS as cocatalyst along the direction of the arrow.

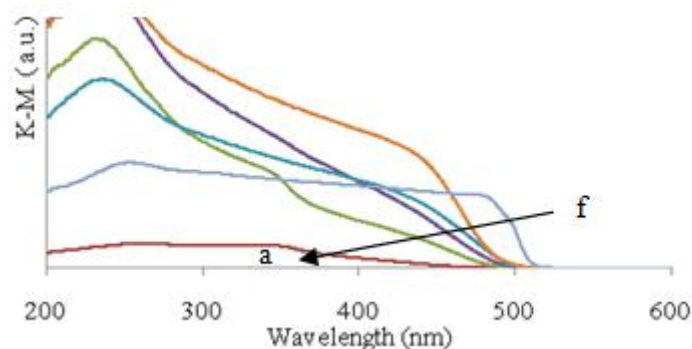


Fig. 5: UV-visible diffuse reflectance spectra of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ samples from the solvothermal synthesis. The values of x :(a) 0.1, (b) 0.3, (c) 0.5, (d) 0.6,(e) 0.7and (f) 1.0 along the direction of the arrow.

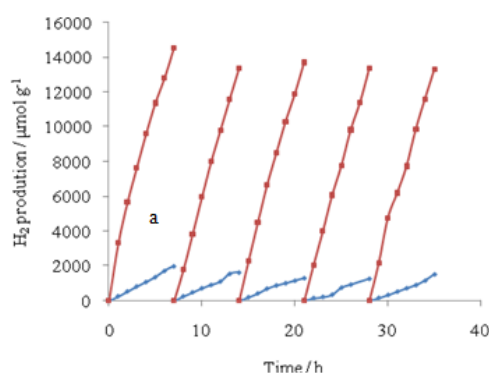


Fig. 6: Time course of photocatalytic H_2 production for (a) $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ and (b) $\text{PdS}@ \text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$.

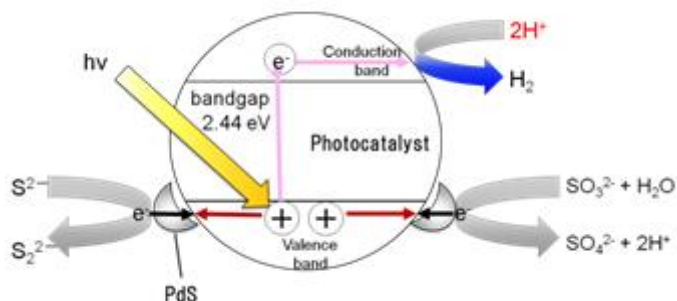


Fig. 7: H_2 production mechanism.

Table 2: Summary of the composition, photocatalytic activities and QE of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ photocatalysts prepared by the solvothermal method.

Cd	Zn	PdS (wt%)	Band gap (eV)	H_2 production ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	QE (%)
1	9	—	2.60	930	7.4
3	7	—	2.48	330	2.6
5	5	—	2.46	280	2.2
6	4	—	2.44	290	2.3
7	3	—	2.41	340	2.7
10	0	—	2.38	22	0.2
1	9	1	—	780	6.2
3	7	1	—	1700	13.3
5	5	1	—	1500	12.1
6	4	1	—	2100	16.6
7	3	1	—	1900	14.9
10	0	1	—	1600	12.7

Conclusions:

$Cd_xZn_{1-x}S$ photocatalysts have been successfully prepared by coprecipitation and solvothermal methods. The effects of composition of the photocatalysts and the photoreaction conditions were investigated. The photocatalytic hydrogen production was drastically improved in the presence of PdS. The maximum H_2 production of the PdS(1.0 wt%)($Cd_{0.6}Zn_{0.4}S$) solid solution reached $2100 \mu\text{mol g}^{-1} \text{h}^{-1}$ with a corresponding QE of 16.6% at 405 nm in the presence of S^{2-} and SO_3^{2-} as sacrificial reagents under visible light irradiation. It was proposed that PdS could serve as the accommodation centers for photogenerated charge carriers, which enhance the charge separation and the photocatalytic activity.

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