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Double Surfactants-assisted Hydrothermal Synthesis of $Cd_{1-x}Zn_xS$ Solid Solution as an Efficient Visible-light-driven Photocatalyst for Hydrogen Production

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1 Introduction

Photocatalytic hydrogen production from water splitting under visible light by semiconductor has attracted increasing attention for its many advantages [1-4]. In view of practical application of photocatalytic hydrogen production technique, reduction of the photocatalyst cost is one of the key issues. CdS, as one of the most well-known semiconductor photocatalysts, has been used for water splitting due to its proper band gap of approximately 2.4 eV and good absorption properties of visible light [5, 6]. However, CdS is prone to produce photocorrosion in aqueous solution under light irradiation. Lots of efforts have been made to improve the stability of metal sulfide, for example, by loading noble metal (Pt, Ru et al.) [7, 8], incorporating the nanoparticles of metal sulfides into the interlayer photocatalysts [9-11], and compound with oxide, for example, TiO_2 [12]. It has been reported that CdS could also be modified by ZnS to form a solid solution, resulting in enhanced stability and photoactivity. This method required no noble metal loading, which means low cost [13-16]. Thus, active photocatalysts free of noble metal like $Cd_{1-x}Zn_xS$ is valuable in this consideration. However, the activity of $Cd_{1-x}Zn_xS$ prepared by traditional methods is still far from being satisfactory for commercial utilization. Development of new approach for the preparation of $Cd_{1-x}Zn_xS$ with improved activity and stability is thus highly valued.

In present work, a series of nano-$Cd_{1-x}Zn_xS$ solid solution were prepared by a double surfactants-assisted hydrothermal method. Results showed that the as-prepared photocatalysts had a very high activity for hydrogen production under visible light from Xe lamp. The factors for this high activity were investigated and the amount of catalyst for the photocatalytic reaction was optimized.

2 Experiment

2.1 Preparation of photocatalysts

The details are as follows: NaOH aqueous solution (4 M, 10 mL), SDS (0.1 M,10 mL), SDBS (0.025 M, 9 mL) were sequently spilled into a aqueous solution (20 ml) containing stoichiometric $Cd(Ac)_2\cdot 2H_2O$ and $Zn(Ac)_2\cdot 2H_2O$ (n(Cd)+n(Zn)=0.02 mol), then thioacetamide (0.025 mol) were added to the previous mixture. The whole process was carried out under magnetic stirring. The reaction mixture was stirred for 20 min, and then was sealed in a 60mL capacity Teflon-lined stainless steel autoclave. Mixtures of different molar ratio for Cd and Zn were heated under autogenous pressure at 130℃ for 24 h; mixtures of the molar ratio 1:1 for Cd and Zn were heated under temperatures of 130℃, 150℃, 170℃, 180℃, 190℃, 210℃ and 230℃ for 24h, respectively. After cooling, the products were separated by centrifugation, washed with deionized water and ethanol several times, and dried at 80 ℃ for 5 h in a vacuum oven.

2.2 Characterization

These as-prepared $Cd_{1-x}Zn_xS$ photocatalysts were characterized by X-ray diffraction (XRD) confirmed by an X'Pert PRO diffractometer using Cu Ka irradiation; diffuse reflectance UV-vis spectra measured on a Hitachi U-4100 instrument employed with a lab-sphere diffuse reflectance accessory; and a JEOL JSM-6700F field emission scanning electron microscopy (SEM). Surface areas were determined by a Beckman Coulter SA3100 instrument.

2.3 Photocatalytic reaction

Photocatalytic reactions of hydrogen production from water were conducted in a gas-closed system with a side irradiation Pyrex cell. The effective area for the cell is 12.56 cm2. The photocatalyst powder (0.2 g) was dispersed by a magnetic stirrer in an aqueous (200 mL) containing Na_2S (0.35 M) and Na_2SO_3 (0.25 M) as electron donors. The photocatalysts were irradiated with visible light (λ≥ 430 nm) through a cutoff filter from a 350 W Xe lamp. The amount of H_2 gas was determined using online thermal conductivity detector (TCD) gas chromatography (NaX zeolite column, TCD detector, N_2 carrier). Apparent quantum yields defined by eq 1 were measured using a 425 nm band pass filters and an irradiatometer.

$$\begin{aligned} \text{A.Q.Y(\%)} &= \frac{\text{The number of reacted electrons}}{\text{The number of incident photons}} \times 100 \\ &= \frac{\text{The number of evolved } H_2 \text{ molecules } \times 2}{\text{The number of incident photons}} \times 100 \end{aligned} \qquad (1)$$

3 Results and Discussion

3.1 Crystal structure and morphology of nano-$Cd_{1-x}Zn_xS$

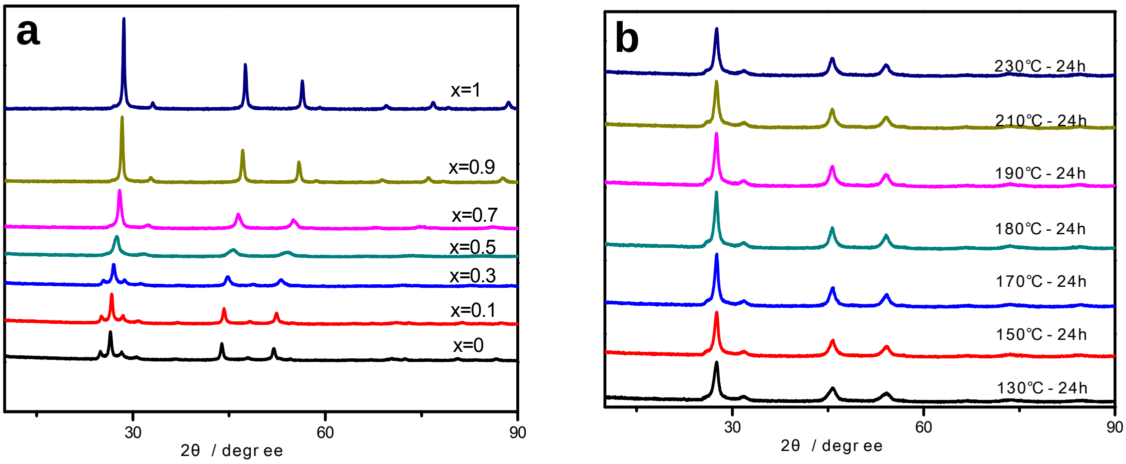

Figure 1: XRD patterns of nano-$Cd_{1-x}Zn_xS$ solid solution. a) $Cd_{1-x}Zn_xS$ solid solution of different molar ratio for Cd and Zn prepared at 130 ℃. b) $Cd_{0.5}Zn_{0.5}S$ prepared under different temperature.

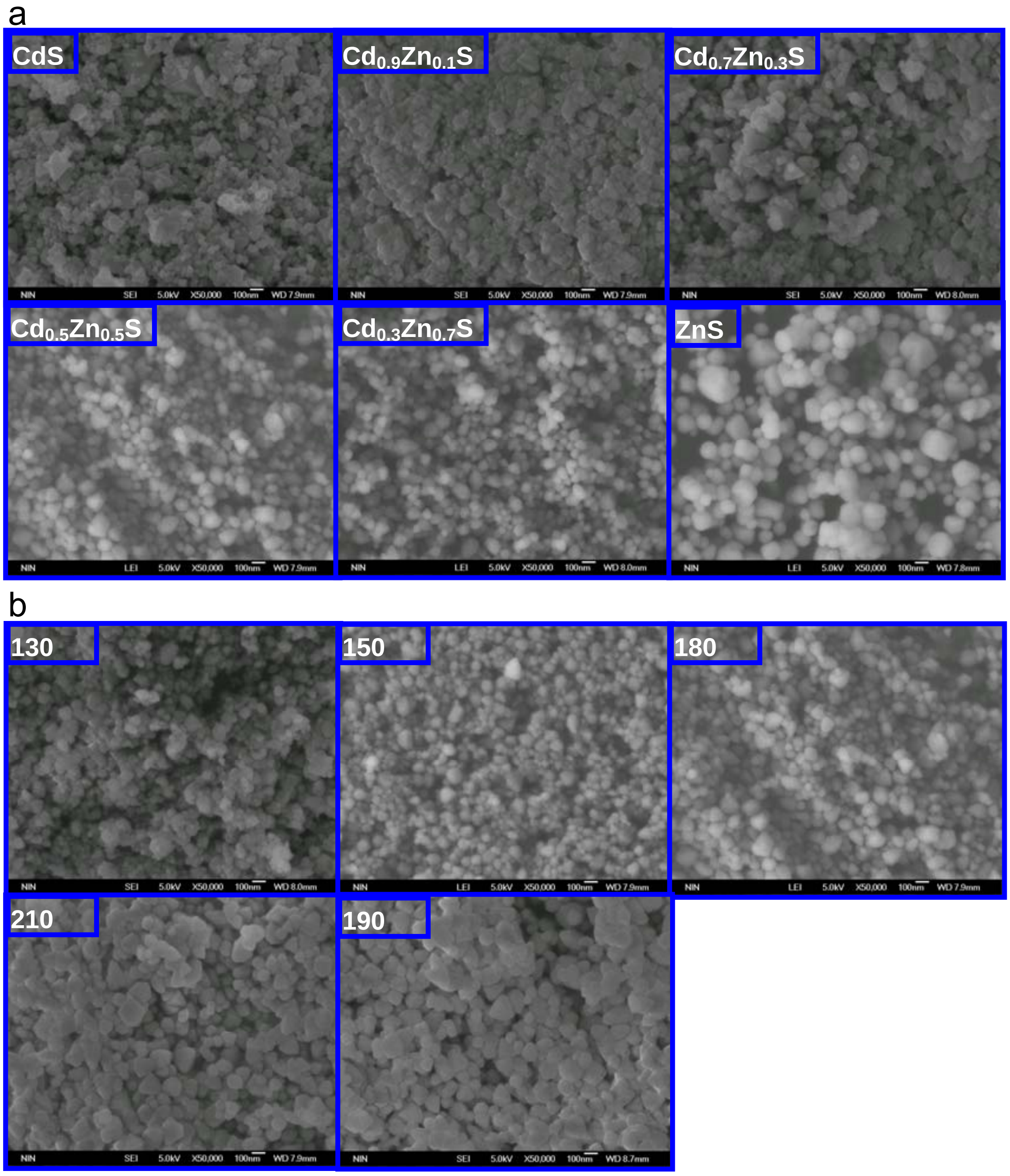

Figure 2: SEM patterns of nano-Cd$_{1-x}$Zn$_x$S solid solution. a) Cd1-xZnxS solid solution of different molar ratio for Cd and Zn prepared at 130 ℃ for 24h. b) Cd$_{0.5}$Zn$_{0.5}$S prepared under different temperature.

The crystal structure of Cd$_{1-x}$Zn$_x$S photocatalysts was investigated by X-ray diffraction as shown in Figure 1. As shown in Figure 1(a), it is found that the peaks are gradually shifted to a higher-angle side with the increase of Zn concentration from hexagonal CdS to cubic ZnS. Similar phenomenon had also been reported by Zu [17] and Nien [18]. This successive shift indicates that CdS and ZnS a not mechanically mixed but formed a solid solution. The radii of Zn^{2+} ion (0.74 Å) is smaller than Cd^{2+} ion (0.97 Å), so Zn^{2+} ion could easily insert into the CdS Lattice or enter its interstitial sites [19-21]. Moreover, the electronegativities of Cd (1.69) and Zn (1.65) are very close to form a solid solution [22]. The interplane spacing of Cd$_{1-x}$Zn$_x$S solid solution became smaller with the increase of Zn concentration for the smaller radii of Zn^{2+} ion than Cd^{2+} ion, which means a decrease in crystal lattice parameters (a, b, c). As a result, the peaks are shifted to the higher-angle side with the increase of Zn concentration. It is also found that the intensity of the peaks is enhanced by the increase of Zn concentration, which indicated that, from CdS to ZnS, more cubic crystals with better crystallization are formed. The temperature has little impact on the photocatalysts' X-ray diffraction property as shown in Figure 1(b). The SEM pictures of the as-prepared photocatalysts are shown in Figure 2. As shown in Figure 2(a), Well-crystallized particles with estimated particle sizes of ~100nm are observed. Interestingly, the surface morphology of the crystals is a mixture of polyhedrons and near-nano-sphere; moreover, the higher content of Zn, the more sphere-like crystals obtained. So it can be inferred that the formation of these near-nano-spherical particles is mostly because of the existence of the cubic phase, while the formation of nano-polyhedron particles is a result of hexagonal phase. The nano-particles, with uniform size, shape, will enhance the separation of electrons and holes, increase the transfer rate of electrons, and decrease their body composite [23]. So the activity of the photocatalyst can be greatly increased. Temperature is another important factor that impacts the growth of the crystals. As shown in Figure 2(b), the crystals grow with the increase of temperature, indicating better crystallinity.

3.2 Optical properties of nano-$Cd_{1-x}Zn_xS$ solid solution

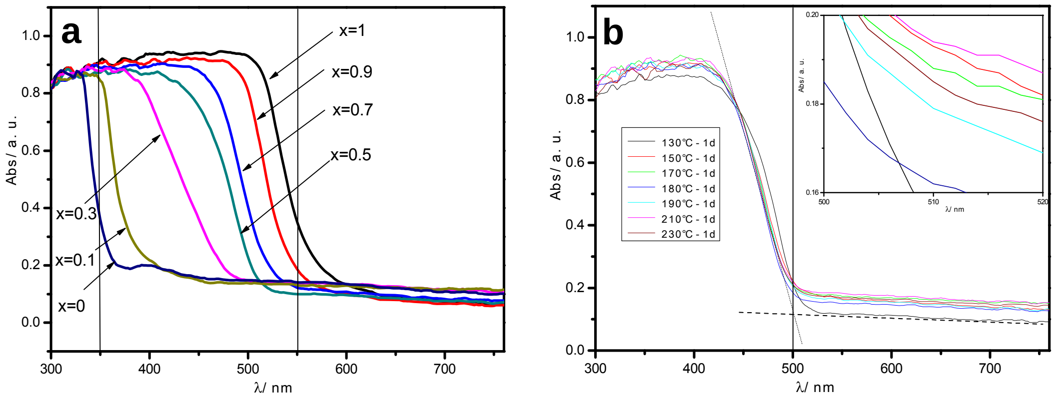

Figure 3: **UV-Vis spectrum of nano-$Cd_{1-x}Zn_xS$ solid solution. a) $Cd_{1-x}Zn_xS$ solid solution of different molar ratio for Cd and Zn prepared at 130 ℃ for 24h. b) $Cd_{0.5}Zn_{0.5}S$ prepared under different temperature.**

Figure 3 shows the UV-Vis absorption spectra of nano-$Cd_{1-x}Zn_xS$ photocalalysts. As shown in Figure 3(a) the absorption edges are gradually red shift with the increase of x, from about 350 nm to about 560 nm, which also prove that CdS and ZnS have formed a solid solution. Figure 3(d) shows the nearly same absorption spectra of $Cd_{0.5}Zn_{0.5}S$ photocatalysts prepared at different temperatures, indicating that synthesized temperature has little influence on band structures of the as prepared photocatalysts. The band structures of solid solution are schematically shown in Figure 4. The band gap size of $Cd_{1-x}Zn_xS$ solid solution shift monotonously in energy (from 2.2eV to 3.5eV, calculated by the UV-Vis absorption spectra with the Kubelka-Munk method [24]). This variation in the band structure of the solid solution is a result of Cd^{2+} ion, which offers a lower conduction band, incorporated in the Zn Lattice. The sharp absorption curve indicates the absorption almost purely due to the band-gap transition of electrons.

3.3 Photocatalytic activity of nano-Cd_1-xZn_xS

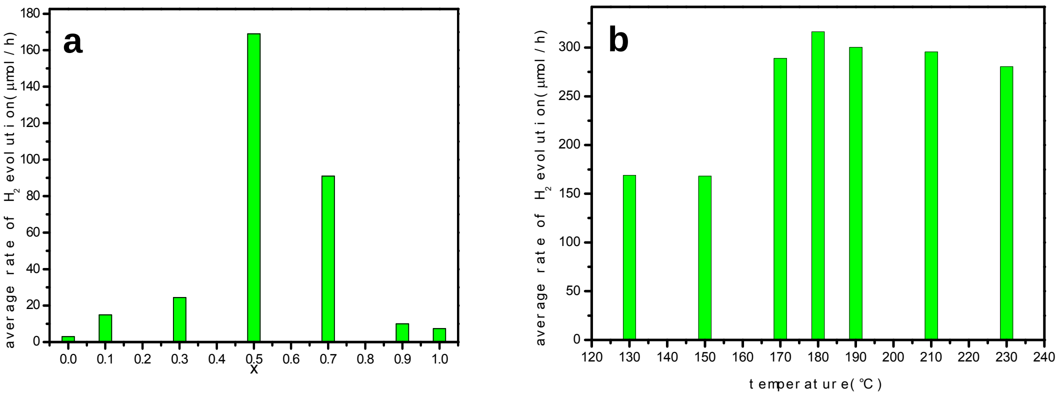

Figure 4: **Rate of H_2 evolution by nano-$Cd_{1-x}Zn_xS$ solid solution. a) $Cd_{1-x}Zn_xS$ solid solution of different molar ratio for Cd and Zn prepared at 130 ℃ for 24h. b) $Cd_{0.5}Zn_{0.5}S$ prepared under different temperature.**

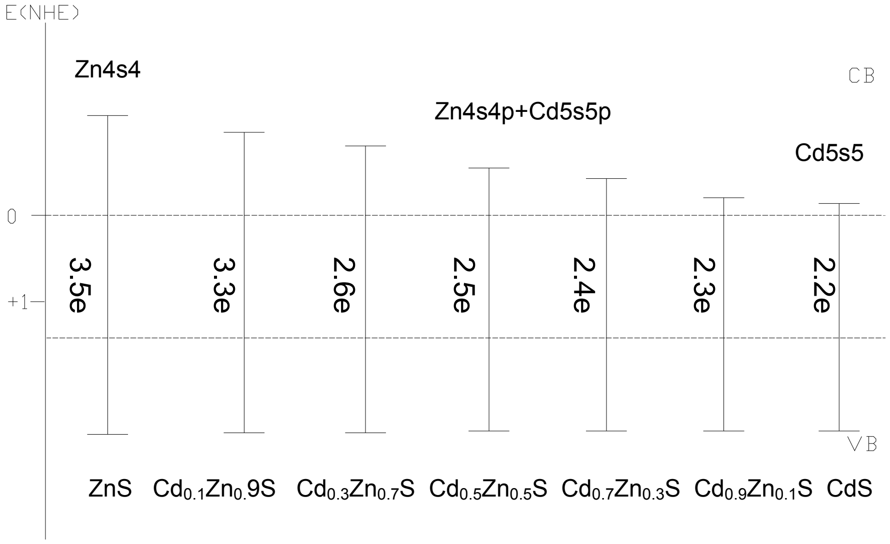

Figure 5: **Band structure of nano-$Cd_{1-x}Zn_xS$ solid solution**

It was found that the nano-$Cd_{1-x}Zn_xS$ solid solution prepared by precipitate-hydrothermal method showed a good activity for water splitting hydrogen production under visible light. As shown in Figure 6(a), $Cd_{0.5}Zn_{0.5}S$ had the highest activity for hydrogen production. The band gap energy can be increased with the increase of Zn content, along with the elevation of the conduction band position, which will enhance the mobility of the photogenerated carriers, thus promoted the photocatalytic activity [19]. However, the ability of absorbing and the utilizing photons by the catalysts will be decreased. So an appropriate Zn or Cd content could balance the two factors to gain a good solid solution with the highest-activity. As we can see, the critical concentration of Zn is 50% in molar ratio. The crystallinity is another important factor for the photocatalytic activity. As analysed above, better crystallinity can be obtained at higher temperature. $Cd_{0.5}Zn_{0.5}S$ photocatalysts prepared at different temperatures were used to investigate the impact of temperature. It is found that the photocatalytic activity increases with the temperature rised as shown in Figure 5(b). When the temperature got to 180 ℃, the rate of hydrogen production under visible light reached the highest, 316 μmol/h, without loading noble metal. And the apparent quantum yield of it at 425 nm reached 30%. Go on increasing the temperature will not promote the activity. As we known, crystallinity will be better when temperature increased. However, the surface area of the crystal will be decrease in this process, which is not favorable for photocatalytic reaction. Thus a critical temperature for the synthesis of nano-$Cd_{1-x}Zn_xS$ solid solution is needed to balance the conflict of crystallinity and surface area to gain the highest photocatalytic activity.

In summary, a series of nano-$Cd_{1-x}Zn_xS$ solid solution were synthesized by a precipitate-hydrothermal method. The visible-light-driven catalysts exhibited a very high activity for hydrogen production by water splitting. The activity of the solid solution was greatly influenced by Zn content, which attributed to its impact on the crystallinity, conduction band and light absorption and electron transferred ability associated to changes in band gap, etc. The photocatalytic activity of the photocatalyst reached the highest when x=0.5 ($Cd_{0.5}Zn_{0.5}S$) and prepared at 180 ℃, corresponding to the average rate 316 μmol/h for hydrogen production under visible light without loading noble metal, and the apparent quantum yield at 425 nm reached 30%, which is one of the highest quantum efficiencies reported in the literature for naked photocatalyst without loading noble metal to the best of our knowledge.

Acknowledgements

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