Research Article

Annealing Effects on Photocatalytic Activity of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ Films Prepared by Chemical Bath Deposition

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$\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films were prepared on glass substrates at room temperature using chemical bath deposition method. The obtained films were annealed at temperatures ranging from 200°C to 500°C with heating rate of 5°C/min and annealed at 400°C with heating rate of 2°C/min and 10°C/min. The films were characterized by X-ray diffraction, scanning electron microscopy, energy-dispersive spectroscopy, and UV-VIS spectrophotometer. The increasing of annealing temperature increases the crystallinity and the mean grain size of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films and significantly enhances the absorption in the visible region. The efficient visible light photocatalytic activity for annealed $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films is associated with the larger size grain and the higher crystallinity.

1. Introduction

Semiconductor assisted photocatalysis has received increasing attention owing to its potential in simultaneously solving the energy shortage and environmental problems [1–3]. Among the various semiconductors for photocatalysis, TiO_2 is undoubtedly the most widely used photocatalyst. However, the wide band gap and rapid electron-hole recombination of TiO_2 largely limits its application as a photocatalyst [4–6]. In order to utilize the abundant solar energy, the development of visible light active photocatalysts with high activities under visible light irradiation is of great importance. To date, many semiconductor photocatalyst systems have been reported to be active under visible light, such as modified TiO_2 and its composites [7, 8], CdS [9, 10], ZnS [11, 12], SrSnO_3 [13], Bi_2WO_6 [14], SrTiO_3 [15], $\text{CdS}_x\text{Se}_{1-x}$ [16], Oxide- $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ [17], AgInS_2 [18], Ag_3PO_4 [19], and $\text{ZuS-CuInS}_2\text{-AgInS}_2$ [20]. Among them, $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solution photocatalyst has been extensively studied due to its controllable band structure and excellent performance in the photocatalytic hydrogen production process under visible light irradiation [21, 22]. In our previous work, it is found that the alloyed $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films show enhanced photocatalytic activity when $x = 0.20\sim 0.29$ [23, 24].

Heat treatment is often used to tune the structure and properties of materials. By using appropriate parameters for heat treatment, different shapes [25] or colors [26] of nano-materials with controllable properties can be produced. However, the systematic effects of annealing on the structural and photocatalytic properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ alloyed films were rarely reported. In order to clarify this issue, $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films are synthesized by a simple chemical bath deposition and the effects of annealing temperature and heating rate on the morphology, composition, and optical properties are comprehensively explored in this work. It is interesting that shape and particle size can be controlled by annealing temperature and heating rate which greatly influences the photocatalytic activity of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films. The photocatalytic activity of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films under visible light irradiation is greatly enhanced by increase of annealing temperature and heating rate.

2. Experimental

2.1. Preparations of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ Thin Films. All the chemicals are analytical reagents and used without further purification. The glass slides were cleaned with acetone, alcohol, and deionized water, respectively. 0.005 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and

FIGURE 1: SEM micrographs of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films at different annealing conditions are as follows: (a) 200°C and 5°C/min, (b) 300°C and 5°C/min, (c) 400°C and 5°C/min, (d) 500°C and 5°C/min, (c1) 400°C and 2°C/min, and (c2) 400°C and 10°C/min.

0.02 M CdCl_2 were mixed in a beaker together with appropriate amount of $\text{SC}(\text{NH}_2)_2$ and NH_4Cl . The pH of the aqueous solution was adjusted to about 12 with ammonia water. A clear and homogeneous solution was obtained after stirring for several minutes. Then, the glass slides were put into the above solution and the deposition was kept at 80°C for 3 h. Finally, the synthesized films were dried in vacuum at 60°C for 1 h. The nominal molar ratios of Zn/Cd were 1/4, and the prepared films were marked as $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$. The as-prepared $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ films were annealed at different temperatures and heating rates for 1 h in the 98% Ar + 2% H_2 atmosphere.

2.2. Characterization. The structure was characterized by X-ray diffraction (XRD, D8). The morphologies of the products

were characterized by scanning electron microscopy (SEM, Hitachi S-4800) and the components were measured by energy-dispersive spectroscopy (EDS). The fluorescence (FL) spectra were obtained by fluorescence spectrophotometer (F-2500) with an excitation wavelength of 380 nm laser line. The absorption spectra of the films were determined using a double beam UV-VIS spectrophotometer (TU-1901) in the wavelength range of 300–800 nm.

2.3. Photodegradation Tests. The photocatalytic activity of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ films was evaluated by photodegradation of aqueous solution of methyl orange under the irradiation of 55 W LED lamps. The catalytic experiments were carried out with 60 ML methyl orange solution and annealed $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$

FIGURE 2: XRD patterns of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films (a) annealed at 200°C, 300°C, 400°C, and 500°C, respectively, with heating rate of 5°C/min. (b) Annealed at 400°C with heating rate of 2°C/min, 5°C/min, and 10°C/min, respectively.

films. The suspension was magnetically stirred and placed at 3 cm from the lamp. During irradiation, the samples were withdrawn at regular time intervals and centrifuged to remove the catalysts. The absorption spectra of the solution were determined using UV-VIS spectrophotometer.

3. Results and Discussions

3.1. Crystal Structure and Morphology. SEM images of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films at different annealing conditions are delineated in Figure 1. As can be seen in Figures 1(a) and 1(b), as the annealing temperature is lower than 300°C, $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films are dense, uniform, and homogeneous without detectable pores and covered well with glass substrate. However, the grains become bigger and cracks appear with increasing the annealing temperature or the heating rate as shown in Figures 1(c), 1(d), and 1(e), which may be due to the increasing stress with the increasing temperature, which is similar to that reported for ZnS [11].

$\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films were characterized by XRD to obtain information about the structure of the products. Figure 2 shows that the XRD patterns can be indexed as hexagonal structures (JCPDS No.49-1302) with the five characteristic diffraction peaks matching with the (100), (002), (101), (110), and (112) crystalline plane of CdS. The strong diffraction peaks indicate that all samples showed good crystalline structure and large mean grain size. With increasing the annealing temperature and heating rate, the CdS diffraction peaks become more distinct and the full width at half maximum narrows. This implies the increase of the crystallinity and the mean grain size of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$.

3.2. Optical Properties. The optical absorption spectra of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films annealed at different temperatures with different heating rates are illustrated in Figure 3. The absorption edge of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films is about 520 nm and obviously shifts to longer wavelength, with increasing

the annealing temperature and heating rate, which greatly enhance the absorption of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films in the visible region.

The degradation efficiency is shown in Figure 4. The plot inserted in Figure 4(a) illustrates the typical irradiation time dependent UV-vis spectra of methyl orange solution during photocatalytic degradation. The spectra of methyl orange exhibit a main band with a maximum at 464 nm in the visible region. The absorption peaks of methyl orange gradually decrease with irradiation time during the photocatalytic reaction, indicating the degradation of methyl orange. Therefore, the decrease of absorbance corresponding to the decrease of methyl orange concentration is recorded. The degradation efficiency (%D) is calculated according the following equation:

$$D\% = 100 \times \left[\frac{C_0 - C}{C} \right]. \quad (1)$$

Here C_0 is the initial concentration of methyl orange (10 mg/L) and C is the concentration of methyl orange after an irradiation time. It can be clearly seen from Figure 4(a) that the degradation efficiency increases continuously with irradiation time. The degradation efficiency of methyl orange for $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ films is 18.50%, 51.08%, 57.01%, and 63.75%, respectively, for the samples annealed at 200°C, 300°C, 400°C, and 500°C after 4 h visible light irradiation. The degradation efficiency of methyl orange for $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films is 32.64%, 57.01%, 65.78%, respectively, for the samples annealed at 400°C with heating rate of 2°C/min, 5°C/min, and 10°C/min (Figure 4(b)) after 4 h visible light irradiation. It is obvious that the degradation efficiency increases with an increase of heating rate. These results suggest that the photocatalytic activity of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films can be extremely improved by appropriate annealing conditions.

It is known that the photoactivity of semiconductors is particle size-dependent [27, 28] and crystallinity-dependent [29, 30]. The grain size increases in Figure 1 and the peak

FIGURE 3: Optical absorption spectra of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films (a) annealed at 200°C, 300°C, 400°C, and 500°C, respectively, with heating rate of 5°C/min. (b) Annealed at 400°C with heating rate of 2°C/min, 5°C/min and, 10°C/min, respectively.

FIGURE 4: Photocatalytic degradations of methyl orange in the presence of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films under visible light irradiation. (a) Annealed at 200°C, 300°C, 400°C, and 500°C, respectively. The inset figure is a typical absorption spectral change. (b) Annealed at 400°C with heating rate of 2°C/min, 5°C/min, and 10°C/min, respectively.

intensity of XRD patterns in Figure 2 increases with the increasing temperature and heating rate, suggesting the larger grain size and the higher crystallinity. Thus, the higher photoactivity can be attributed to the larger size and the higher crystallinity of annealed $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films, which decreases electron-hole recombination centers, facilitates the separation of electron-hole pairs, and therefore enhances the photoactivity of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films.

4. Conclusions

$\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films prepared by simple chemical bath deposition method were studied as photocatalysts for degradation of methyl orange under visible light irradiation. The grain size increases and crystallinity is enhanced for the $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films with increasing annealing temperature and heating rate. Moreover the absorption edge

obviously shifts to longer wavelength with increasing the annealing temperature and the heating rate. Increasing the annealing temperature and the heating rate can enhance photocatalytic activities of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ alloyed films under visible light irradiation. This work provides a simple and efficient method to enhance the photocatalytic activity of semiconductors.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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