International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Short Communication

Controllable Preparation of Zn_xCd_{1-x}S Films by Chemical Bath Deposition for Enhanced Photocatalytic Activity

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Received: 18 February 2021 / Accepted: 3 April 2021 / Published: 31 May 2021

Composition-tunable $Zn_xCd_{1-x}S$ alloy films were synthesized using the method of chemical bath deposition (CBD). When the Zn/Cd molar ratios were tuned based on the initial materials, their film structures ranged from primarily hexagonal CdS to primarily cubic ZnS, accompanied by gradual macromorphological changes from leaf-like to rod and spherical particles. Moreover, with an increase in the proportion of Zn, blue shift was observed in both the photoluminescence spectrum and the ultra violet absorption spectrum, which indicates the highly controlled properties of $Zn_xCd_{1-x}S$ when the composition of the materials was tuned. It was found that $Zn_xCd_{1-x}S$ alloy films showed significant enhancement in photocatalytic activity for methyl orange degradation under visible irradiation. The degradation efficiency was 2.3 times higher than that of pure ZnS under visible light irradiation.

Keywords: Thin films, Metals and alloys, Photocatalytic, Blue shift, Semiconductors

1. INTRODUCTION

ZnS and CdS have attracted tremendous attention and are well-known wide and direct band gap II–VI semiconductor materials [1]. They are extensively studied today owing to their distinctive semiconductor properties. However, their application is limited because of their settled energies of band gap, i.e., 2.42–2.50 eV for CdS and 3.60–3.91 eV for ZnS [2]. The good news is that the properties of CdS could be enhanced by introducing new materials such as ZnS [3]. CdS and ZnS can form alloys of different compositions by adjusting the Zn/Cd molar ratios [4]. It has been demonstrated that the catalysis, electronics, photonics, and chemical properties of the Zn_xCd_{1-x}S films can be optimized by adjusting their chemical composition [5]. Importantly, by adjusting the Zn content, the composites can be accurately adjusted to optimize their optical absorptivity and photocatalytic activity. However, manipulation of the morphology and chemical composition of the Zn_xCd_{1-x}S alloyed films is still in its infancy.

Considerable efforts have been made to synthesize $Zn_xCd_{1-x}S$ alloyed nanocrystals or nanowires by using the microwave-assisted route [6], mix–solvothermal route, precipitate–hydrothermal method, and Langmuir monolayer technique. These methods have some limitations in that they require high temperature, poisonous reagents, and expensive equipment. In comparison to the other methods, the chemical bath deposition (CBD) techniques offers numerous advantages such as uniformity, affordability, and simplicity for large deposition areas of the compound films made of semiconductor material [7].

In this paper, $Zn_xCd_{1-x}S$ alloyed films were prepared through the facile and effective CBD method. It was found that $Zn_xCd_{1-x}S$ alloyed films with adjustable composition, morphology, and optical properties could be prepared by controlling the Zn/Cd molar ratios. The obtained samples displayed high visible light catalytic activity and stability for the decomposition of MO. Moreover, CBD was suitable for fabricating other solid solution semiconductor films.

2. EXPERIMENTAL

2.1 Thin films prepared from $Zn_xCd_{1-x}S$

Every chemical, when not used with adequate purification, reacts like an analytical reagent. The used glass slides were first cleaned using acetone, followed by alcohol and then deionized water. Different molar ratios of ZnSO₄.7H₂O and CdCl₂ were mixed together in a beaker with NH₄Cl and SC(NH₂)₂ in appropriate quantities. The pH of the aqueous solution was adjusted using ammonia water. A homogeneous and clear solution was obtained after stirring for some time. The cleaned glass slides were then immersed in the prepared solution. This deposition was kept for 3 hours at 80^oC. The synthesized films were then dried at 60^oC in vacuum for 1 h and annealed at 350°C for 1 h in an argon–hydrogen atmosphere.

2.2 Characterization

X-ray diffraction (XRD, D8) was used for structure elucidation. The product morphology was then analyzed using scanning electron microscope (SEM, Hitachi S-4800), and its components were estimated using energy-dispersive X-ray spectroscopy (EDS,). The fluorescence spectrum was obtained using an F-2500 fluorescence spectrophotometer with 380 nm excitation wavelength laser light. The absorption spectrum of the films was estimated using TU-1901 UV-Vis double beam spectrophotometer with 300 – 800 nm range of wavelength.

3. RESULTS AND DISCUSSION

3.1 Morphology and structure

For obtaining information regarding product structure, Zn_xCd_{1-x}S alloyed films were categorized

by XRD. Fig. 1 depicts the XRD patterns of the samples. All patterns exhibited some degree of size broadening impact, suggesting the finite size of the films. For the CdS samples, the patterns were indexed as hexagonal structures (JCPDS No.49-1302) as per five different characteristic peak matches with the (100), (002), (101), (110), and (112) plane of crystallization for CdS. On the other hand, for ZnS, the XRD pattern exhibited a cubic structure (JCPDS No.79-0043), with three major peaks of diffraction that matched with the (111), (220), and (311) ZnS crystalline plane. The diffraction sample peaks shifted gradually on a higher angle and underwent a phase transition to cubic ZnS from hexagonal CdS with an increase in the Zn content. It could be stated that the Zn²⁺ particles entering the CdS lattice caused a lattice distortion, resulting in the larger radii of the Cd²⁺ ion (0.97Å) than the Zn²⁺ ion (0.74Å) [8, 9]. The continuous shifts in the XRD patterns ed that the obtained crystals were not a mixture of CdS and ZnS but were Zn_xCd_{1-x}S alloyed structures.



Figure 1. X-ray diffraction patterns of the $Zn_xCd_{1-x}S$ alloyed film (from top to bottom: x = 1, 0.75, 0.5, 0.25, 0.15, and 0)



Figure 2. Energy-dispersive X-ray spectroscopy images of the Zn_xCd_{1-x}S alloyed films ((a): x = 0.15, (b): x = 0.75)

Int. J. Electrochem. Sci., 16 (2021) Article ID: 210755

The compositions of the $Zn_xCd_{1-x}S$ alloyed films were determined by EDS, and the typical patterns are shown in Fig. 2. The atomic ratio of the $Zn_xCd_{1-x}S$ alloyed films and the molar ratio of Zn/Cd are listed in Table 1. It was noteworthy that the molar ratios of the Zn/Cd samples were a little lower than the nominal ratios of the reactants. This finding can be attributed to the fact that the reaction between Cd and S is more rapid as compared to that between Zn and S in the same system [10].

Sample	Х	Zn	Cd	Zn/Cd
Zn _x Cd _{1-x} S		atomic %	atomic %	molar ratios
CdS	0	0	49.92	-
Zn _{0.15} Cd _{0.85} S	0.15	2.85	48.81	0.03
Zn0.25Cd0.75S	0.25	9.59	47.12	0.12
Zn _{0.5} Cd _{0.5} S	0.5	22.12	34.15	0.37
Zn _{0.75} Cd _{0.25} S	0.75	47.67	34.36	0.80
ZnS	1	48.50	0	-

 Table 1. Parameter and Reactant Solution Compositions of the Products



Figure 3. Scanning electron microscopy images of the $Zn_xCd_{1-x}S$ alloyed films (a \rightarrow f :x = 0, 0.15, 0.25, 0.5, 0.75, and 1)

The SEM images of the $Zn_xCd_{1-x}S$ alloyed films are depicted in Fig. 3. It is obvious that the pure CdS films (sample a) displayed a fine leaf-like surface morphology, while the pure ZnS films (sample f)

were composed of spherical particles. With regard to the $Zn_xCd_{1-x}S$ alloyed films, different Zn contents resulted in morphological variations. It is interesting that the surface morphologies of $Zn_xCd_{1-x}S$ were composition-tunable, which gradually evolved from leaf-like to rods and finally to nanospheres with increase in the Zn contents.

The reason for the composition-induced morphology transition of the $Zn_xCd_{1-x}S$ alloyed films could be as follows: for ZnS, it was easy to produce spherical particles since a sphere is the thermodynamically favored shape of the particle with low energy on the surface. The rates of nucleation and growth of CdS were much higher than those of ZnS since the reaction between Cd and S was more rapid than that between Zn and S in the reaction system. The outgrowth of the cards resulted in the crystals not having sufficient time to form spherical particles to satisfy the lowest surface energy and therefore led to the leaf-like surface morphology. As for the $Zn_xCd_{1-x}S$ alloyed film formation, the two reactants Zn^{2+} and Cd^{2+} were dissolved in the solvent and were mixed at a molecular level with each other. Thus, the $Zn_xCd_{1-x}S$ ternary nanocrystals were formed during the CBD processes, and their growth included the competition between ZnS-like (spherical particles) and CdS-like (leaf like morphology) growth modes. Hence, the Zn/Cd molar ratio of the reactants influenced the nucleation and growth process and led to different surface morphologies of the formed Zn_xCd_1-xS nanocrystals.

More interestingly, these $Zn_xCd_{1-x}S$ nanocrystals exhibited special composition-tunable properties, which are likely to improve their photocatalytic performance.

3.2. Optical properties



Figure 4. Fluorescence spectra of the $Zn_xCd_{1-x}S$ alloyed films (from top to bottom: x = 1, 0.75, 0.5, 0.25, 0.15, and 0)

Optical property is an important factor in determining the photocatalytic efficiency of the samples. Hence, II-VI semiconductors and their photoluminescence show two emission bands under

room temperature. Emission of light exists near the band edge and on a deeper level of emission. The former is related to an intrinsic emission near the band edge, and the latter is linked to a deep and extrinsic level of emission [11-13]. The fluorescence spectra of the $Zn_xCd_{1-x}S$ alloyed films are shown in Fig. 4. It can be found that all the $Zn_xCd_{1-x}S$ alloyed films demonstrated strong emissions at 550 nm and 570 nm. The fluorescence signal at 550 nm was enhanced with the addition of Zn^{2+} , which exhibited a little blue shift from pure CdS to pure ZnS [14]. This observation can be due to the interstitial states or vacancy states of a particular structure. In addition, crystallinity degree could also affect the fluorescence signal quality [15, 16]. As shown in Fig.4, the ZnS films were spherical and exhibited good crystallinity. These results indicate that the properties of the $Zn_xCd_{1-x}S$ alloyed films can be effectively adjusted, thereby augmenting the photocatalytic performance.



Figure 5. Diffuse reflectance spectra of the $Zn_xCd_{1-x}S$ alloyed films (from left to right: x = 1, 0.75, 0.5, 0.25, 0.15, and 0)

The edge was located at about 480 nm in Fig. 5. The absorption edge exhibited a blue shift with the increase in the amount of Zn. This sharpness in the curve depicted in above graph denotes an absence of absorption because of impure energy levels, which occurs due to the transitioning of the electrons in the band-gap from the valence to the conduction band of $Zn_xCd_{1-x}S$. Cd^{2+} was considered to be incorporated in the Zn lattice [17]. This proves once again that the $Zn_xCd_{1-x}S$ films have alloyed structures and therefore significant enhancement in photocatalytic activity.

3.3. Photocatalytic performance

Fig. 6 (a) shows the visible light catalytic degradation tests conducted in an aqueous solution of MO (10 mg/L, 80ml) with 20 mg of $Zn_xCd_{1-x}S$ alloy films. With the increase in the exposure time, the absorption peak corresponding to MO decreased rapidly, indicating MO decomposition. Accordingly, the MO concentration decreased significantly. MO photodegradation efficiency under visible light

irradiation of the $Zn_xCd_{1-x}S$ alloy films is shown in Fig. 6 (b). It is clear that after 240 min of irradiation, 80.2% of the MO in the $Zn_xCd_{1-x}S$ alloy films (x = 0.15) underwent photocatalytic degradation. However, in the pure ZnS and CdS samples, the degradation rates of MO were only 34.2% and 51.5%, respectively. These results assert that the $Zn_xCd_{1-x}S$ alloy films (x = 0.15) have excellent photocatalytic performance.



Figure 6. (a) The absorption spectra of MO (80 ml) in the presence of Zn_xCd_{1-x}S (20 mg) under visible light (b) Comparison of the photocatalytic activities of different samples for the photodegradation of MO



Figure 7. X-ray diffraction patterns of $Zn_xCd_{1-x}S$ (x = 0.15) before and after photocatalysis

No obvious change was observed in the XRD patterns of the $Zn_xCd_{1-x}S$ (x = 0.15) films before and after the photocatalysis (fig.7). These results prove that the films have excellent photocatalytic performance and stability.

4. CONCLUSIONS

The $Zn_xCd_{1-x}S$ alloy films were prepared using the method of CBD. The alloy film and its composition could be changed by tuning the molar ratio of Zn/Cd in the initial materials. The lattice structure ranged from primarily hexagonal CdS to primarily cubic ZnS, as "x" increased from 0 to 1. Meanwhile, the fluorescence intensity of the $Zn_xCd_{1-x}S$ alloyed films increased gradually, and the absorption edge exhibited a blue shift. The synthesized $Zn_xCd_{1-x}S$ films possessed excellent photocatalytic activity for MO degradation under visible light irradiation. The degradation efficiency of the $Zn_xCd_{1-x}S$ films was superior to that of pure ZnS and CdS. This enhanced photocatalytic activity could be attributed to the controllable morphology, chemical composition, and tunable optical properties.

ACKNOWLEDGMENTS

Grants for the work were received from "National Natural Science Foundations of China" (Grant No. 11704116 and 11704115) and "Natural Science Foundations of Hunan Province" (Grant No. 2019JJ50175).

CONFLICT OF INTEREST

The authors declare that no conflict of interest was faced in this work. The authors would also like to declare that no associative or commercial interest is linked to this paper; hence, there is no conflict of interest related to the submitted work.

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