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Invited feature article

Hydrothermal synthesis of cobalt-doped ZnS for efficient photodegradation of methylene blue



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ABSTRACT

A series of coral-like Co-doped ZnS were synthesized by hydrothermal method and used for efficient photodegradation of methylene blue. The chemical composition and microstructure of the Co-doped ZnS were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, UV–vis diffuse reflectance spectra, scanning electron microscope, and transmission electron microscopy. The results showed that the Co atoms were incorporated into the Zn–S lattice, forming solid solution-type phase. As the Co dopant concentration increases from 0 to 22.49 at.%, the calculated band gap energy of the doped ZnS decreases from 3.32 to 2.65 eV, which enables stronger absorption of visible light. Furthermore, the Co dopant could act as electron trapping center, which inhibits the recombination of the photoinduced electrons and holes. As such, the Co-doped ZnS micro-corals showed higher photodegradation efficiency for methylene blue compared with pristine ZnS. The optimized photocatalytic activity was achieved on 5.49 at.% Co-doped ZnS.

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1. Introduction

ZnS, as an important II–VI semiconductor, has been widely investigated owing to its excellent performance in the applications of photocatalysis, optical materials and sensor apparatus [1–5]. However, the usage of the ZnS as photocatalyst is greatly limited by its extremely wide band gap (3.54 eV) and high electron-hole recombination loss. Many efforts have been devoted to further improving the photocatalytic activity of the ZnS. One is to fabricate hybrid systems. For instance, the reduced graphene oxide (rGO) wrapped ZnS–Ag₂S composites show enhanced separation efficiency of the photoinduced electrons and holes because the rGO interlayer can easily transfer the electrons between ZnS and Ag₂S [6]. In addition, CuS modified ZnS porous nanosheets also exhibit efficient interfacial charge transfer from the valence band of ZnS to that of CuS, and therefore reduce the recombination of photoinduced carriers [7]. An alternative way to enhance the photocatalytic activity of ZnS is heteroatom doping [8–10]. The heteroatom doping reduces the band gap value of ZnS and therefore improves the visible light absorption. Furthermore, the

recombination of photoinduced carriers can be greatly inhibited, resulting in the improvement of the photocatalytic performance. To date, plenty of non-metallic inorganic elements- and transition metal-doped ZnS have been reported for enhanced photocatalytic activity. For instance, N-doped ZnS showed improved stability for photocatalytic hydrogen evolution [11]. Ni- and Cu-doped ZnS have been reported with high activity for hydrogen generation under visible light irradiation [12,13]. However, Co-doped ZnS photocatalyst has rarely been investigated.

Previous investigations primarily focused on the fluorescence property of Co-doped ZnS fabricated by pulsed laser ablation and deposition or chemical co-precipitation method [14–16]. It was noted that the Co atoms act as the electron trapping centers, photoelectrons easily transfer to the dopant level formed by the Co doping [14,17], which results in nonradiative recombination. However, the influence of the Co dopant on chemical structure and photocatalytic property of the ZnS is still unclear. Herein, Co-doped ZnS with coral-like microstructure was synthesized by one-step hydrothermal method and was then used for photodegradation of methylene blue (MB). The result showed that the Co-doped ZnS exhibited enhanced photodegradation activity under simulated solar light irradiation and the activity significantly depends on the Co dopant concentration.

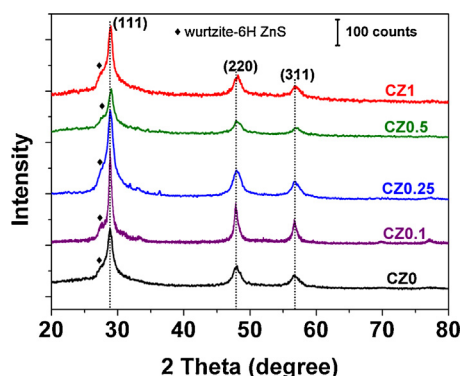
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Table 1

The elemental compositions of the Co-doped ZnS samples determined by XPS analysis.

Sample	Co(Ac) ₂ ·4H ₂ O (mmol)	Zn(Ac) ₂ ·2H ₂ O (mmol)	Elemental composition (at.%)			Co/Zn atomic ratio
			Co	Zn	S	
CZ0	0	1	0	49.65	50.35	0
CZ0.1	0.1	1	1.72	46.55	51.73	0.04
CZ0.25	0.25	1	5.49	36.29	58.22	0.15
CZ0.5	0.5	1	13.56	31.74	54.70	0.43
CZ1	1	1	22.49	26.28	51.23	0.86

**Fig. 1.** XRD patterns of the Co-doped ZnS samples.

2. Experimental

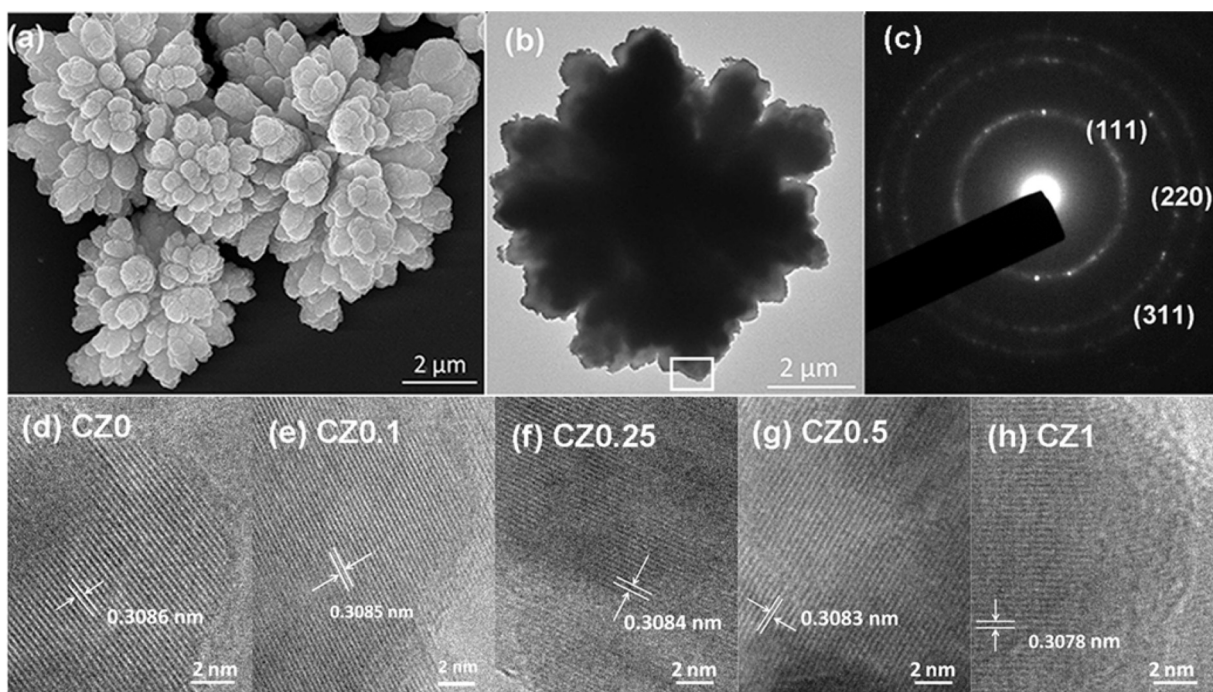
2.1. Sample preparation

All reagents were of analytical grade and used without further purification. In a typical synthesis, an appropriate amount of cobalt acetate (Co(Ac)₂·4H₂O, Ac = CH₃COOH) and 1 mmol of zinc acetate (Zn(Ac)₂·2H₂O) were dissolved in 60 mL deionized water under agitation. After stirring for 5 min, 0.2 mmol of tetra-*n*-butyl

ammonium bromide (TBAB) and thiourea were added into the above solution, respectively. The final molar ratio of the Co:Zn:thiourea was fixed at $x:1:(1+x)$ ($x=0, 0.1, 0.25, 0.5$ and 1). Then the solution was transferred to a Teflon-lined stainless steel autoclave with 100 mL capacity, sealed and heated at 200 °C for 24 h. After the reaction was finished, the autoclave was cooled down to room temperature in air. The obtained products were filtered and washed for several times using distilled water and absolute ethanol. Finally, drying these products in a vacuum oven at 60 °C for 6 h.

2.2. Characterization

The phase structure of the Co-doped ZnS samples was characterized by powder X-ray diffraction (XRD, Rigaku Ultima IV) using a Cu K α radiation as X-Ray source ($\lambda = 1.54056 \text{ \AA}$). The morphologies were examined using a field-emission ZEISS Sigma scanning electron microscope (SEM) with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) patterns were obtained by JEOL JEM-2100 (accelerating voltage of 200 kV). X-ray photoelectron spectroscopy (XPS, PHI QUANTUM 2000) was employed to determine the elemental compositions and chemical bonding states of the samples. Optical characterization was performed at room temperature over a wavelength range of 200–800 nm using Shimadzu 2550 spectrometer. In order to investigate the charge

**Fig. 2.** (a) SEM image, (b) TEM image, and (c) the corresponding SAED pattern of sample CZ0.25; (d–h) HR TEM images of samples CZ0–CZ1.

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