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Hydrothermal synthesis and highly visible light-induced photocatalytic activity of zinc-doped cadmium selenide photocatalysts

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ABSTRACT

Novel Zn-doped CdSe photocatalysts were synthesized by a mild hydrothermal route. The as-prepared products were characterized by X-ray powder diffraction (XRD), UV–vis absorption spectroscopy, and Brunauer–Emmett–Teller (BET) surface area analysis. The as-synthesized photocatalysts efficiently catalyzed the photodegradation of methylene blue (MB) in aqueous solutions under visible light irradiation, exhibiting higher photocatalytic activity than commercially available photocatalysts such as P25 and CdSe. The effects of the treatment temperature of the photocatalysts, the different zinc contents, the quantity of the photocatalysts, and the concentration of MB on photocatalytic performance were also investigated.

1. Introduction

Environmental problems such as toxic organic pollutants provide the impetus for fundamental and applied research into environmental areas. Semiconductor photocatalysts have attracted considerable attention for a long time in the fields of photochemistry [1–10] because of their usefulness with regard to solving environmental problems. Over the last few years, considerable efforts have been made in the controlled synthesis of various nanoscaled materials to improve their properties for photocatalysis. More recently, many groups have synthesized CdSe nanomaterials with high photocatalytic activity in the degradation of organic pollutants under UV light irradiation, such as CdSe–Pt nanorods and nanonets [11], hybrid CdSe–Au nanodumbbells [12], CdSe/ZnS-photosensitized nano-TiO_2 film [13]. Therefore, as an important semiconductor, CdSe is an effective catalyst for photocatalytic degradation of organic pollutants. Furthermore, the exploration of new visible light-responsive CdSe photocatalysts with high photoactivity is a research topic that is gaining increasing interest. Modification to nanomaterials by doping has been shown to be an effective method that improves photocatalytic activity.

In this paper, a series of Zn-doped CdSe photocatalysts were prepared through a simple hydrothermal method. The intrinsic characteristics of the photocatalysts were studied by X-ray powder diffraction (XRD), UV–vis spectroscopy, and the determination of Brunauer–Emmett–Teller (BET) surface areas. The photocatalytic activity of the as-synthesized samples was evaluated by degrading methylene blue (MB) under visible light irradiation. The reasons for the improved photocatalytic activity of the Zn-doped CdSe photocatalysts are explained in detail in the remainder of this paper.

2. Experimental procedure

2.1. Synthesis of Zn-doped CdSe photocatalysts

In a typical synthesis, zinc acetate ($Zn(Ac)_2{\cdot}2H_2O$, 0.001 mol) and cadmium chloride ($CdCl_2{\cdot}2H_2O$, 0.001 mmol) were added into 20 mL ammonia ($NH_3{\cdot}H_2O$, 25 wt%), which was then stirred to form an even solution. Hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 80 wt%, 40 mL) was then added dropwise to the above solution by vigorous stirring for 15 min. Afterward, 0.002 mol selenium powder (Se) was sequentially added to the solution. The resulting mixture was sonicated until a clear solution was obtained. The above solution was transferred into a Teflon-lined stainless steel autoclave that was sealed. The contents were then warmed to 110 °C. After 10 h, the contents were cooled to room temperature. The products were collected using a centrifuge, washed several times using distilled water and absolute ethanol, and dried under a vacuum at 80 °C for 6 h.

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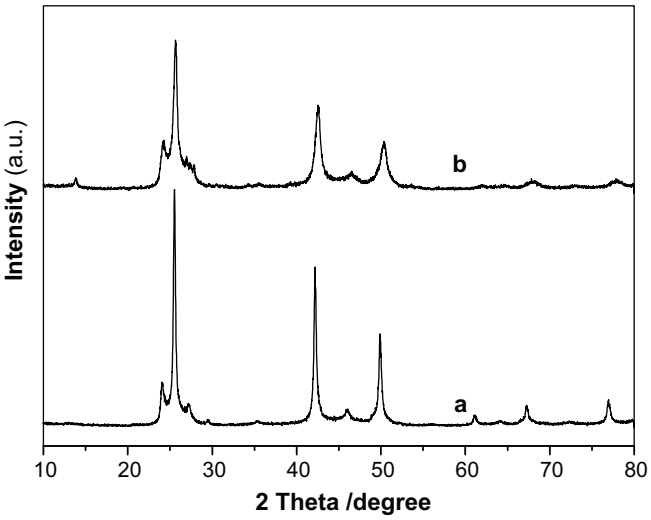

Fig. 1. X-ray diffraction patterns of (a) undoped CdSe and (b) Zn-doped CdSe treated at 110°C.

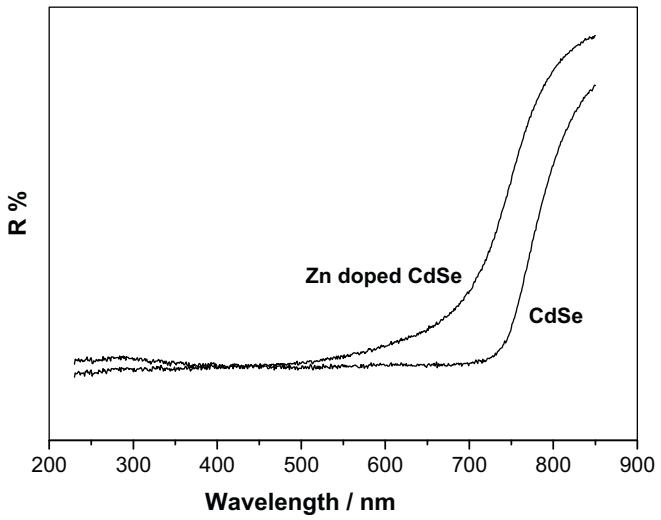

Fig. 2. UV–vis diffuse reflectance spectra of samples treated at 110 °C.

2.2. Characterization

The products were characterized by XRD recorded on a Rigaku D/Max 2500 powder diffractometer with monochromatic high-intensity CuKα radiation (λ = 1.5406 Å). UV–vis spectra were recorded on an HP8453 spectrophotometer at room temperature. BET surface areas (S_{BET}) were measured by N_2 adsorption at −196 °C using an automatic surface area and pore size analyzer (Autosorb-1-MP 1530 VP).

2.3. Photocatalytic decomposition of methylene blue

The photocatalytic activity under visible-light irradiation of the Zn-doped CdSe samples was evaluated by using methylene blue (MB) as the model substrate. In a typical process, 250 mL MB (10 mg/L) aqueous solution and 1.0 g of photocatalyst powder were mixed in a quartz photoreactor. Prior to a photocatalytic reaction, the photocatalyst suspension was sonicated to reach adsorption equilibrium with the photocatalyst in darkness. The above solution was photoirradiated by using a 300 W Xe lamp as light source under continuous stirring. At a defined time interval, the concentration of MB in the photocatalytic reaction was analyzed by using an UV–vis spectrophotometer at 665 nm.

3. Results and discussion

XRD analysis was used to determine the phase purity of the samples. Fig. 1 shows the XRD patterns of the resulting undoped and Zn-doped CdSe samples obtained at 110 °C. As shown in Fig. 1a and b, all of the peaks in the XRD pattern can be readily indexed to the cubic CdSe, with lattice constants of lattice constants of 6.05 Å. Indeed, this result agrees with previously reported data (JCPDS file no. 65–2891). In Fig. 1b, no peaks for Zn and ZnSe were detected. Compared with Fig. 1a and b, it can be observed that the widths of the Zn-doped CdSe sample's peaks become larger than those of the undoped sample. The average crystallite sizes of the two samples were calculated using the Debye–Scherrer equation:

$$D = \frac{0.94\lambda}{\beta \cos \theta},$$

where D is the average crystallite size in angstroms, λ is the wavelength of the X-ray radiation (CuKα, λ = 1.5406 Å), β is the full width at half-maximum, and θ is the diffraction angle. The calculated results are 28 and 12 nm for the undoped and doped CdSe particles, respectively. It is suggested that the particle size decreases after Zn doping, which indicates that the Zn dopants can restrain the agglomeration of CdSe crystals and improve the surface areas of CdSe particles.

The UV–vis diffuse reflectance spectra of the as-synthesized undoped and doped CdSe at 110 °C are illustrated in Fig. 2. The reflectance characteristics of the Zn-doped CdSe sample were quite similar to that of the undoped sample. It can be seen from Fig. 2 that the two samples showed a strong photoabsorption at visible light range. However, the Zn-doped CdSe specimens exhibited a greater light absorption throughout the visible wavelengths due to the Zn dopants. As is shown in Fig. 2, the absorption edge of the Zn-doped CdSe was found to have shifted towards the shorter wavelength side (blue shift). This indicates an increase in the band gap of CdSe due to the Zn dopants.

The photocatalytic activities of the catalysts were evaluated by the photodegradation of MB aqueous solution under visible light irradiation. The decreasing concentration of MB in the photocatalytic reaction was used to evaluate the activity of the photocatalyst. The specific area of the undoped and doped CdSe (Zn: 0.005 mol) at 110 °C for 10 h were 24 and 35 $m^2\ g^{-1}$.

Fig. 3 illustrates the photocatalytic decomposition of MB on the photocatalysts with different zinc contents under visible light irradiation (λ > 400 nm). From Fig. 3, the photocatalytic activity of the Zn-doped samples was higher than that of CdSe. In this experiment, the photodegradation ratio of MB over the undoped CdSe sample was less than 62% after 60 min irradiation (Fig. 3d). However, the photodegradation efficiency of the Zn-doped sample can reach 93.4% (Fig. 3h), which is probably related to the decrease in crystalline size and the increase in surface area. From Fig. 3e–h, it is very obvious that the degradation rate of MB increased and reached a maximal value at Zn 0.005 mol, even as the doping amount of zinc increased. According to Fig. 2, the increased photocatalytic activity of the Zn-doped samples can partly be due to this increase in absorption. In addition, an excessive Zn is inferred to cover many active centers of the photocatalysts, thus decreasing their activity remarkably.

It should also be noted that the adsorption of MB into the Zn-doped CdSe sample in the dark, degrading MB over P25 and MB photolysis were performed under the same conditions (Fig. 3a–c). As shown in Fig. 3, the adsorption capacity of MB into the Zn-doped CdSe sample is very little in the dark. The MB photolysis in the absence of photocatalysts only produces about 10.4%

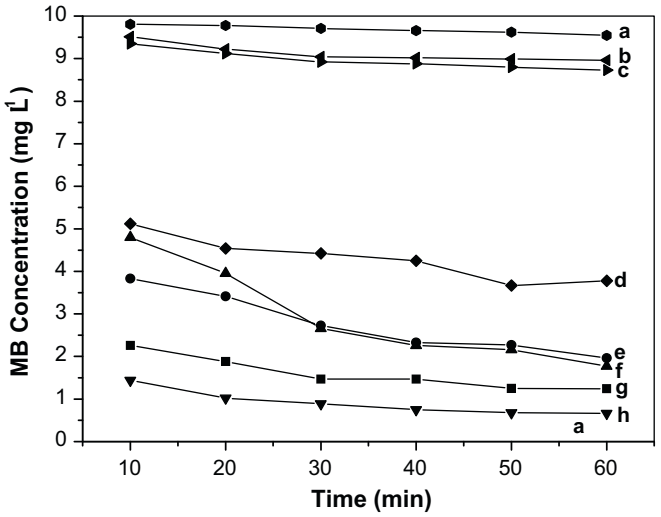

Fig. 3. Degradation of MB under visible-light irradiation of (a) adsorption of MB into Zn-doped CdSe in dark, (b) MB photolysis, (c) P25, (d) undoped CdSe, and Zn-doped CdSe treated with different zinc contents of (e) 0.001, (f) 0.0025, (g) 0.0035, and (h) 0.005 mol at 110 °C.

decomposition of MB molecules, which can be attributed to the photosensitivity of the MB molecules. However, the photodegradation efficiency of P25 is only about 12.7%, which is obviously lower than that of the Zn-doped CdSe sample.

The photodegradation efficiency of the samples treated at 110–160 °C is shown in Fig. 4. An increase in the Zn-doped CdSe crystallization temperature does not enhance photocatalytic performance. It is well known that better crystallization of the sample at higher temperatures may lead to a lower specific surface area. To investigate this assertion, the specific areas of the samples obtained at 110, 120, 140, and 160 °C were measured. Their BET specific areas were found to be 35, 33, 23, and 20 $m^2 g^{-1}$, respectively. The BET specific areas increased as the crystallization temperature decreased. Indeed, this result is in agreement with the assertion that photocatalytic activity is enhanced as the crystallization temperature decreases.

Fig. 5 shows the effect of the quantity of the Zn-doped CdSe samples on the photocatalytic performance. From Fig. 5, it is obvious that 1.0 g of the sample gave much better results. However, when the quantity of the sample was increased to 1.5 g, the photocatalytic activity did not change. This demonstrates that the optimal quantity of the sample is 1.0 g.

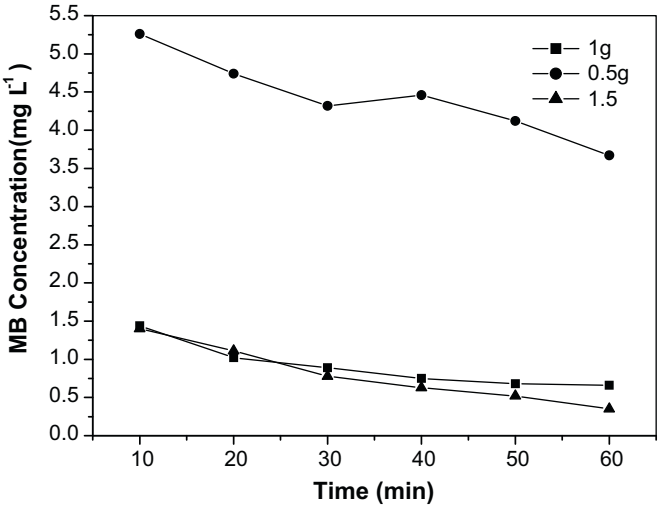

Fig. 5. Degradation of MB under visible-light irradiation for the Zn-doped CdSe samples with different quantity, zinc contents: 0.005 mol.

Fig. 6 represents the photocatalytic decomposition of MB over Zn-doped CdSe (the sample treated at 110 °C) as a function of the original MB concentration under visible light irradiation. For different concentrations of the original MB aqueous solution, the level of photodegradation is quite different after 60 min illumination. After illumination for 60 min, the photodegradation efficiency of the 10 mg/mL MB concentration was 93.4%. However, for the 30 mg/mL MB concentration, only about 47.5% was degraded after 60 min. Therefore, it seems that the photodegradation efficiency of the MB photocatalyzed by the Zn-doped CdSe samples decreased as the original MB concentration increased. The main reason is that he initial dye concentration may affect strongly the rate of the photocatalytic process.

According to the above experimental data, the Zn-doped CdSe samples show much more photocatalytic activity than the undoped CdSe samples. This is due to the charge separation that takes place at the semiconductor interface. Indeed, this charge separation can effectively compete with rapid electron–hole recombination in the semiconductor [11,14–16]. In this study, MB was used as an electron acceptor and aqueous solution as a hole scavenger. The

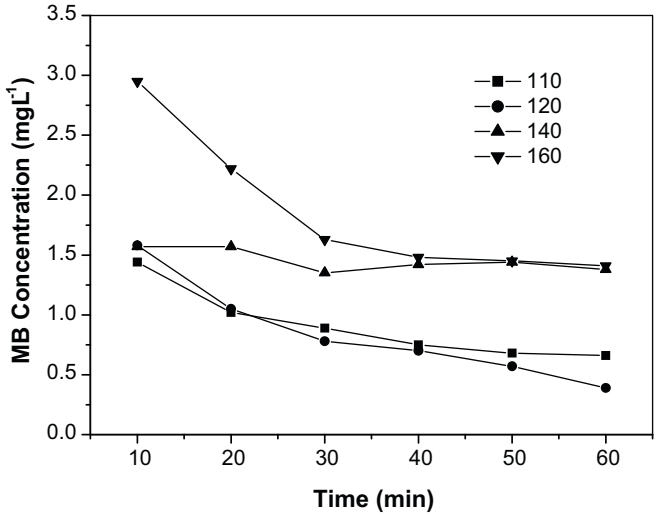

Fig. 4. Degradation of MB under visible-light irradiation for the Zn-doped CdSe samples treated at different temperatures, zinc contents: 0.005 mol.

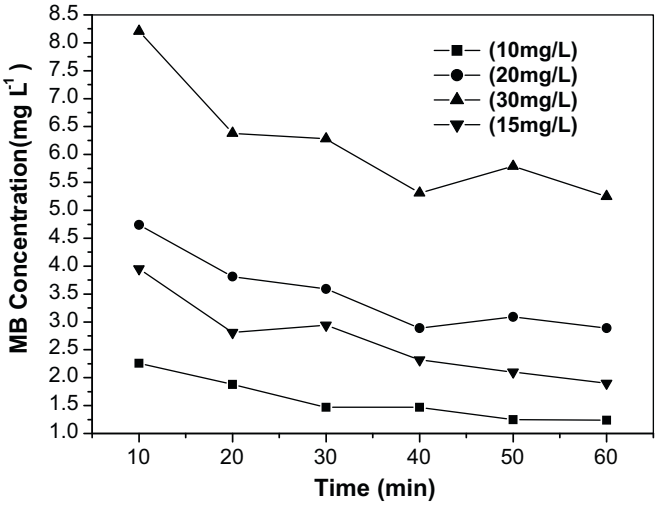

Fig. 6. Dependence of the concentration of the Zn-doped CdSe sample on time under visible-light irradiation, zinc contents: 0.005 mol.

photo-induced charge carriers in the Zn-doped CdSe particles form after visible light irradiation. The electron and hole relax to the lowest energy levels in the system, with the electron residing in the zinc and the hole in the CdSe particles. In this state, the hole may be transferred to the solution and the electron to the MB, which leads to the charge separation at the CdSe interface. For the above reason, improved photocatalytic activity was observed in the Zn-doped CdSe samples.

4. Conclusions

In summary, the Zn-doped CdSe prepared by a simple hydrothermal method exhibited high visible-light-driven activity. The zinc in the preparation increased the absorbance in the visible light region and reduced the recombination of electron–hole pairs, resulting in an increase in photocatalytic activity.

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