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Research Article

Solvothermal Synthesis of Well-Disperse ZnS Nanorods with Efficient Photocatalytic Properties

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Well-disperse short-range-ordered ZnS nanorods with efficient photocatalytic property for photodegradation of Rhodamin B have been successfully synthesized through a solvothermal method. Solvent used can be recovered and reused, which makes the route environment-friendly. Dodecylamine was found effective in organizing nanorods to ordered monolayer. Characterization showed that these nanorods were uniform with the diameter of about 3 nm and length of nearly 30 nm. And it is expected that these monodisperse ZnS nanorods have potential applications in electroluminescence materials.

1. Introduction

Over the past decades, nanocrystals which are monodisperse in size and shape have received substantial attention due to their unique optical and physical properties compared to bulk materials [1]. However, it is still a great challenge to fabricate monodisperse nanorods. Among various nanomaterials, semiconductor nanomaterials, especially metal chalcogenide nanomaterials, have been studied in depth due to their optical and electronic properties arising from the quantum confinement effect and large surface area [2]. In this paper, a solvothermal method is used to synthesize high-quality ZnS nanorods, an important wide bandgap (E_g of 3.66 eV at room temperature) II-VI group semiconductor, which is highly desirable in potential applications such as electroluminescence devices, photoluminescence devices, and semiconductor quantum well devices, flat-panel display, infrared windows, sensors, and lasers [3–10].

Various approaches have been explored to pursue a simple and shape-controllable synthetic method for semiconductor monodisperse nanocrystals, including irradiation method, solution-phase synthetic route, and solvothermal synthesis [11–14]. Among these methods, it is well established that synthetic routes utilizing organometallic/nonmetallic precursors enable production of high-quality monodisperse semiconductors, metals, and metal oxide nanocrystal dispersions [15]. Since the first synthesis for monodisperse ZnS nanoparticles by size selective photocorrosion [16], some similar approaches in synthesizing monodisperse nanoparticles have been reported [17, 18]. However, seldom effort is devoted to synthesizing ZnS monodisperse nanorods using a simple and nontoxic solution route without tedious size selection processes [19].

In this paper, a long-chain alkylamine is introduced in the traditional solvothermal method, which is conducted simply by the reaction of zinc sulfate and S powder in nontoxic dodecylamine. Due to the special reactivity under high temperature and high pressure, S powder can be directly used as S sources, which avoids usage of its toxic precursors. In addition, the sample shows good photocatalytic effect on the degradation of Rhodamin B.

2. Experimental

2.1. Synthesis of ZnS Nanorods. In a typical synthesis, 0.15 g $ZnSO_4 \cdot 7H_2O$ was put into a 25 mL round bottom flask, then 5 mL dodecylamine was added, and the mixture was stirred for 3 h at 80°C. 0.032 g sulfur powder was put into the mixture quickly and stirred heavily for 10 min. Consequently, the mixture was transferred into a Teflon-lined autoclave of 10 mL capacity. Then the autoclave was sealed and heated at 200°C for 1.5 h and was left to cool to room temperature

naturally. The products were collected by filtration, washed with deionized water and absolute ethanol. A white powder was obtained after 3 h dry at 70°C in a vacuum drying oven and was preserved in absolute ethanol for further characterization.

2.2. Synthesis of ZnS Microspheres. 0.15 g $ZnSO_4 \cdot 7H_2O$ and 0.032 g sulfur powder were mixed in water, and then the mixture was stirred and transferred into a Teflon-lined autoclave of 10 mL capacity. The autoclave was sealed and heated at 200°C for 1.5 h and was left to cool to room temperature naturally. The products were collected by filtration, washed with deionized water and absolute ethanol. A white powder was obtained after 3 h dry at 70°C in a vacuum drying oven and was preserved in absolute ethanol for further characterization.

2.3. Characterization. The phase purities of the obtained samples were measured on a Bruker D8-advance X-ray powder diffractometer with Cu K_α radiation ($\lambda = 1.5418$ Å). A small amount of products was dispersed in ethanol by ultrasonic treatment for about 5 min, and then one drop of the resulting solution was placed onto a carbon-coated copper grid and dried at room temperature for TEM visualization. Morphology analysis of the samples was conducted with JEOL JEM-1230 transmission electron microscopy (TEM) operated at 80 kV. Room temperature photoluminescence (PL) of as-prepared sample was observed under excitation by UV light at 365 nm with a Perkin-Elmer LS-55 fluorescence spectrophotometer. The UV-Vis absorption spectrum was recorded on an Agilent 8453 UV-visible spectrophotometer.

2.4. Photocatalytic Activity Measurement. Seven cylindrical Pyrex flasks (capacity ca. 10 mL) were used as the photoreactor vessels. The reaction system containing Rhodamine B ($C_{28}H_{31}N_2O_3Cl$) (Sigma-Aldrich Chemical Co.; 1×10^{-4} M, 10 mL) and ZnS nanorods as catalyst (10 mg) was magnetically stirred in the dark for 12 h to reach the adsorption equilibrium of Rhodamine B with the catalyst and then exposed to light from a Xujiang middle-pressure Hg lamp (300 W), and the maximum intensity of the light irradiated on the solution is 365 nm. UV-Vis absorption spectra were recorded at different intervals to monitor the reaction.

3. Results and Discussion

The crystalline structure and purity were examined by X-ray diffraction analysis (XRD). As shown in Figure 1, all diffraction peaks can be indexed to face-centered cubic Sphalerite ZnS phase (JCPDS 05-0566), with lattice constants of $a = 5.406$ nm. An obvious broadening can be observed from the XRD curve which may be caused by the small grain size of the sample [20]. No characteristic peaks ascribing to other phases were observed, which indicates high purity of the prepared ZnS nanorods.

The size and shape of the products were examined by TEM imaging. Figure 2 shows typical images of ZnS nanorods, which have very narrow size distributions. These

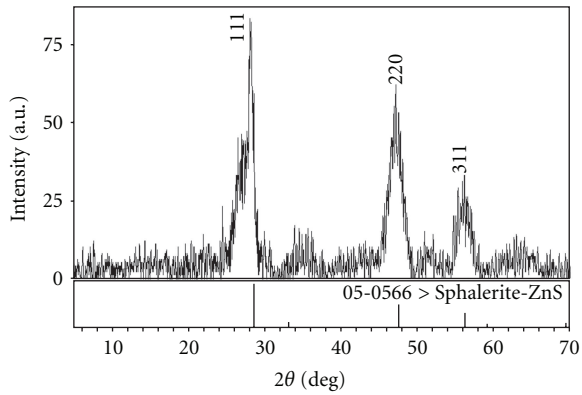

Figure 1: XRD curve of ZnS nanorods.

nanorods have diameters of about 3 nm and length of nearly 30 nm. The shape and size are uniform and it is observed that all the nanorods are well dispersed. These nanorods can be used as conducting wires in microelectronic devices. Keeping other reaction conditions the same, the morphology of the sample is sphere when dodecylamine is not added (shown in Figure 2(c)). The diameter of these spheres is nearly 2 μm. It was found that dodecylamine played important role in the formation and dispersion of 1D ZnS nanorods. Dodecylamine is long-chain molecule with $-NH_2$. The N atom has strong coordination ability, which could coordinate with Zn^{2+}, which will control the nucleation velocity of ZnS. Consequently, it limits the crystal growth at high temperature and direct forming well-disperse ZnS nanorods.

In order to investigate the optical properties of the products, UV-Vis absorption spectrum was also studied as shown in Figure 3. The as-obtained nanorods have the maximum absorption at 269 nm. There is about a 70 nm blue shift from the bulk counterparts (E_g of 3.66 eV). That may contribute to the quantum size effect of nanomaterials caused by the photogenerated electron-hole pairs [21].

As we all know, the study of luminescence properties can shed some light on defects in the ZnS crystals and their potential as photonic materials. Figure 4 shows the room-temperature photoluminescence spectrum of the sample excited with UV-light at 365 nm. The slight difference was also observed in the PL spectrum. The band position centered at about 410 nm is the stable and strong purple emission. This broad emission peak may be due to the band to band transition of ZnS.

It is well known that ZnS has been used as a semiconductor-type photocatalyst for the photoreductive dehalogenation of halogenated benzene derivatives, photocatalytic degradation of water pollutants, and photocatalytic reduction of toxic metal ions [22, 23]. To demonstrate the potential applicability of as-synthesized ZnS nanorods in these applications, their photocatalytic activity by choosing photodegradation of Rhodamin B at room temperature is investigated. The characteristic absorption of Rhodamin B at about 553 nm is chosen as the monitored parameter for the photo-degradation process.

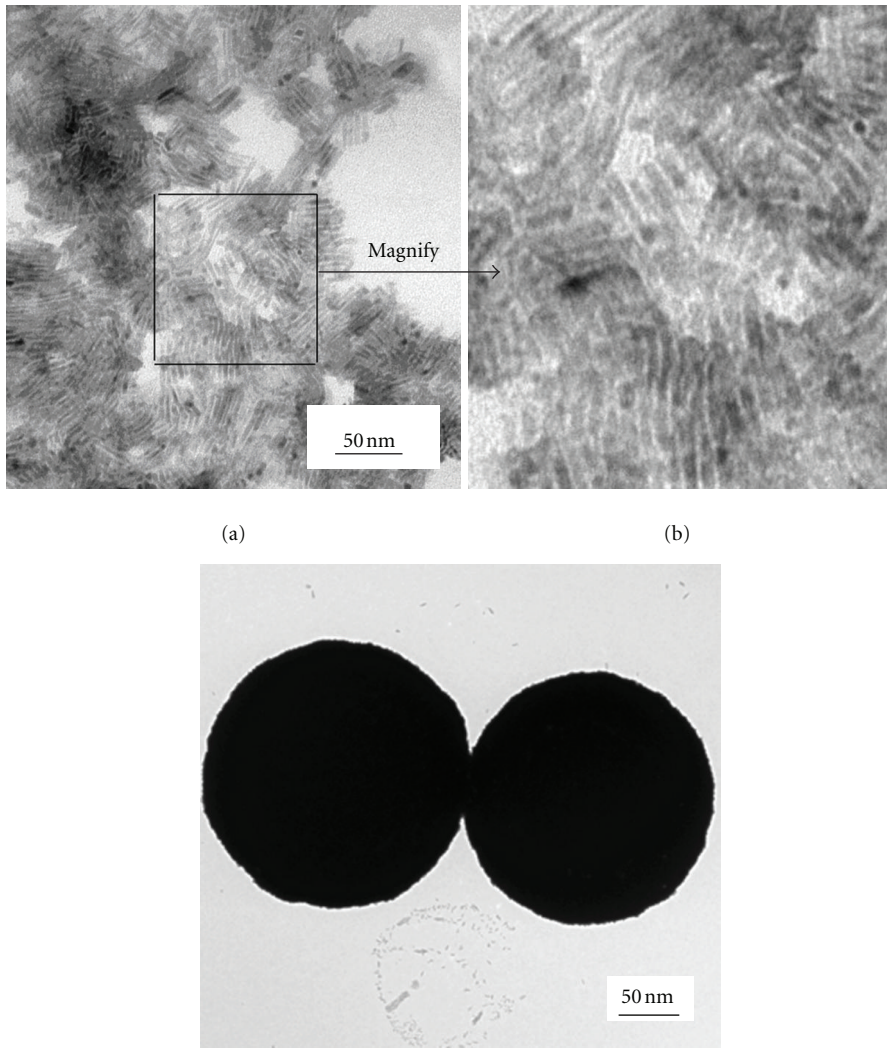

Figure 2: (a), (b) Typical TEM image of well-disperse ZnS nanorods synthesized with dodecylamine as template. (c) TEM image of ZnS spheres obtained without dodecylamine.

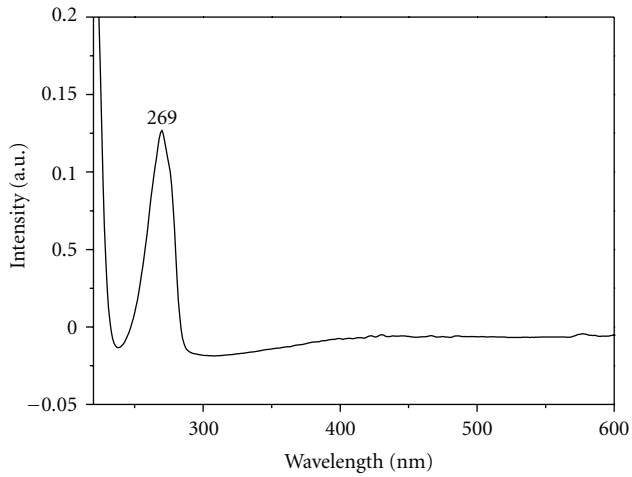

Figure 3: UV-Vis absorption spectrum of as-prepared ZnS nanorods.

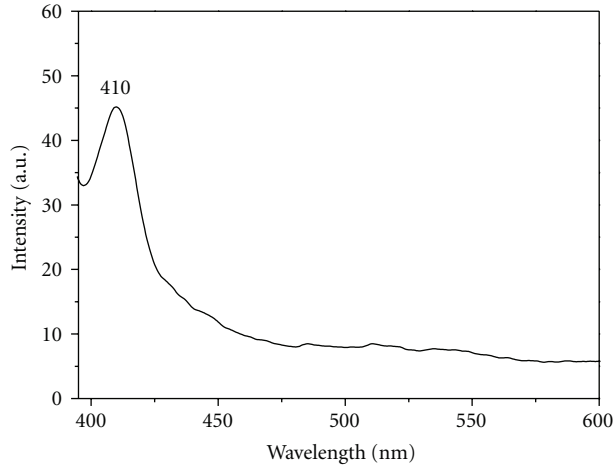

Figure 4: PL emission spectrum of as-prepared ZnS nanorods.

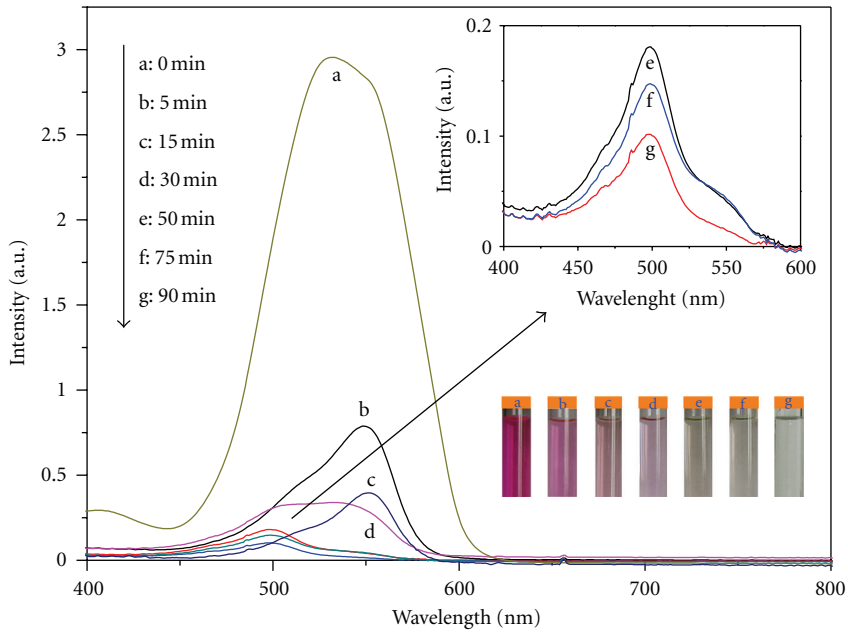

Figure 5: Time-dependent absorption spectra of a solution of Rhodamin B (1×10^{-4} mol/L, 10 mL) in the presence of monodisperse ZnS nanorods after its exposure to UV-light for (a) 0, (b) 5, (c) 15, (d) 30, (e) 50, (f) 75, and (g) 90 min. The inset (upper part) shows the enlarged temporal evolution of absorption (e–g).

Figure 5 shows the absorption spectra of an aqueous solution of Rhodamin B (initial concentration: 1.0×10^{-4} mol/L, 10 mL) in the presence of 10 mg ZnS nanorods under exposure to UV-light for different time. The absorption peaks almost diminish gradually as the exposure time increases and completely disappear after about 50 min. The results suggest that well-disperse ZnS nanorods can adsorb the dye molecules efficiently. A series of color changes (insert down part in Figure 5) corresponding to the sequential changes are detected by UV-Vis absorption measurements.

In order to exclude the contribution of the decomposition of Rhodamin B itself, a test of the decomposition of RhB itself under light irradiation without photocatalyst was performed. The result was shown in Figure 6. It indicated that RhB itself was not decomposed in 180 min under the same light irradiation.

As illustrated in Figure 7, we plot the degradation rate under different exposure time. Curve a shows degradation rate of Rhodamin B by as-synthesized nanorods. It is obvious that degradation rate is high at the first 5 min, indicating high catalytic activity. After exposed about 15 min, the conversion reaches nearly 90%, which is better than that of TiO_2 as reported by Shao et al. [24]. With the time extending to 90 min, the conversion is 98%, indicating the nearly complete degradation. However, in the latter 75 min, the conversion increases only about 8%.

In comparison with the effect of spheres (curve b in Figure 7), the performance of nanorods is much better.

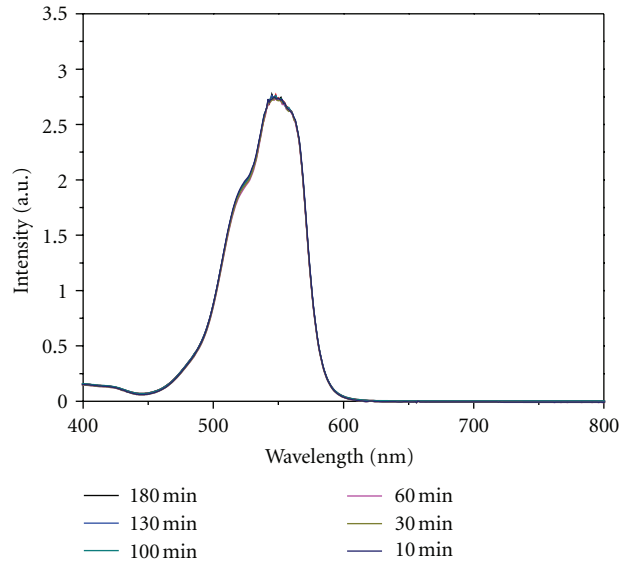

Figure 6: Time-dependent absorption spectra of a solution of Rhodamin B (1×10^{-4} mol/L, 10 mL) without ZnS catalyst after its exposure to UV-light for180 min.

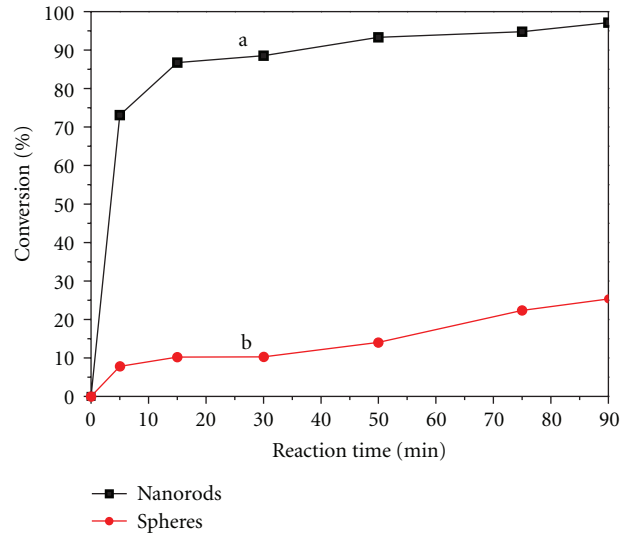

Figure 7: Degradation rate of Rhodamin B.

Dodecylamine used in the reaction is an effective stabilizer which prevents small nanorods from aggregation. In the degradation of RhB, the reaction was performed in the surface of photocatalyst and the reaction temperature is higher than room temperature. So the degradation rate can be reduced if the aggregation happens. It is believed that one-dimensional nanostructure can avoid aggregation at higher temperature; therefore well-disperse nanorods could provide much more activation site which can accelerate the degradation efficiently.

4. Conclusion

In conclusion, monodisperse ZnS nanorods have been synthesized with a solvothermal method. Instead of using expensive and toxic organometallic/nonmetallic precursors, the simple reaction between zinc sulfate and sulfur powders in nontoxic solvent suggests a safe and cheap route for monodisperse nanorods. These well-dispersed nanorods exhibit high photocatalytic activity, which makes it useful in the treatment of polluted water.

Acknowledgments

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