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Facile synthesis of hierarchical ZnS microspheres and their photocatalytic properties

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Abstract. Hexagonal ZnS nanostructured spheres self-assembled from ZnS nanocrystals were successfully synthesized through a facile hydrothermal method using 1-butyl-3-methlyimidazole thiocyanate ([BMIM][SCN]) as both sulfur source and capping ligand. By combining the results of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FE-SEM), ultraviolet–visible (UV–vis) absorption spectra, a structural and morphological characterization of the products was performed. The photocatalytic activity of ZnS microspheres had been tested by degradation of Rhodamine B (RB) under UV light compared to commercial ZnS powders, which indicated that the as-syntherized ZnS spheres exhibited enhanced photocatalytic activity for degradation of RB.

Introduction

Zinc sulfide is an important II-VI group compound semiconductor with a band gap energy (E_g) of 3.6 eV [1] and it has been extensively studied for a variety of applications. Recent studies have revealed that ZnS nanospheres displayed excellent photocatalytic activity toward the photodegradation of eosin B under the irradiation of UV [2-5]. Therefore, much effort has been made in the past decade to the controlled preparation of ZnS nanostructures with various forms including nanorods [6,7], nanowires [8], nanosheets [9], nanobelts [10], nanotubes [11], nanosaws [12], and nanoparticles [13]. For photocatalysts, the high-energy conversion efficiencies as well as large light-harvesting capacities can be achieved by constructing the complex architectures. Thus, it is expected that the complex 3D ZnS architectures would show superior photocatalytic efficiency.

Herein, in this paper, we have reported the synthesis of novel ZnS microspheres with matte surface by a facile hydrothermal method using 1-butyl-3-methlyimidazole thiocyanate ([BMIM][SCN]) as both sulfur source and capping ligand in aqueous solution. The photocatalytic activity of the synthesized photocatalysts was investigated using Rhodamine B (RB) as a model pollutant under UV irradiation. The obtained ZnS microspheres show strongly structure-induced enhancement of photocatalytic performance and exhibit much better photocatalytic property than that of commercial ZnS powders.

Experimental

In a typical experiment, required amount of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 15mL of water and required amount of [BMIM][SCN] was separately dissolved in another 15mL of water. The molar ratio of Zn^{2+}:SCN^- was maintained at 1:2 in the experiment. Then, they were mixed together with vigorous magnetic stirring for another 30 min at room temperature to form a homogeneous solution and transferred into a Teflon container with 50ml capacity. The autoclave was heated to and

maintained at 180 ^{o}C for 24 h, and allowed to cool to room temperature gradually air. The products were collected by filtration, washed several times with distilled water and ethanol, and then dried in a vacuum at 70 ^{o}C for 8 h. The synthesized sample was characterized using appropriate analytical techniques.

The as-prepared sample was characterized by X-ray power diffraction (XRD) on a D8 Advance X-ray diffractometer with Cu Kα irradiation at λ=1.5406 Å. X-ray photoelectron spectroscopy (XPS) measurement was performed on a PHI-5300/ESCA system. The field-emission scanning electron microscope (SEM) images were taken with Japan Hitachi S-4800 field-emission scanning electron microscope to observe the morphologies and microstructures. The UV-vis absorption spectra were measured on a Shimadzu UV–2550 spectrophotometer. The concentration of RB was also monitored by a Shimadzu UV–vis spectrophotometer (UV-2550). The Brunauer-Emmett-Teller (BET) surface area of the powders was computed from the results of Nitrogen physisorption.

Results and discussion

The powder XRD pattern in Fig. 1 revealed that the as-prepared ZnS could be indexed as the hexagonal wurtzite structure with lattice parameters a=3.80 Å and c=6.23 Å (JCPDS card no. 75-1534). No other impure diffraction peaks were detected, indicating that the as-synthesized products were high pure. In order to confirm the chemical purity of synthesized ZnS, the XPS analysis was studied and the results were presented in Fig. 2. The XPS data of the sample indicated the presence of Zn and S. No other obvious impurities were found on the surface of the samples, indicating that they were relatively pure. The binding energies of Zn 2p3/2 and Zn 2p1/2 for the product were observed at 1022.0 eV and 1045.0 eV (Fig.2(a)), while the peak located at 162.5 eV (Fig.2(b)) corresponded to the binding energy of S 2p3/2. All of the observed binding energy values for Zn 2p and S 2p agreed with the literature data [14,15].

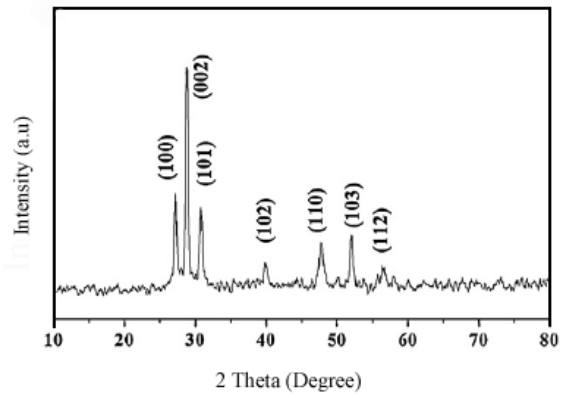

Fig.1. X-ray diffraction (XRD) patterns of ZnS samples

The size and morphology of the ZnS were examined by FE-SEM. It could be seen from Fig. 3(a) that the as-prepared ZnS showed spherical morphologies with diameters of approximate 1 to 8 μm. Higher magnification SEM images were shown in Fig. 3(b), which offered a clearer view of the exterior morphology. Fig. 3(b) revealed that the microsphere surface was assembled by small nanoparticles size ranging from 10 to 50 nm.

To demonstrate the potential applicability in photocatalysis of the obtained ZnS microspheres, we investigated their photocatalytic activity by choosing photocatalytic degradation of Rhodamine B. Fig. 4(a) indicated the absorption spectra of an aqueous solution of Rhodamine B (initial concentration is 1.0×10^{-5} M, 75 mL) in the presence of 10 mg microspheres under UV light irradiation. The characteristic absorption peak at 553 nm corresponds to the Rhodamine B

molecules. The intensity of absorption diminishes rapidly with extension of the exposure time and the absorption peak completely disappears after 60 min. No new absorption bands appeared in either the visible or ultraviolet regions, which indicated the effective photodegradation of RB.

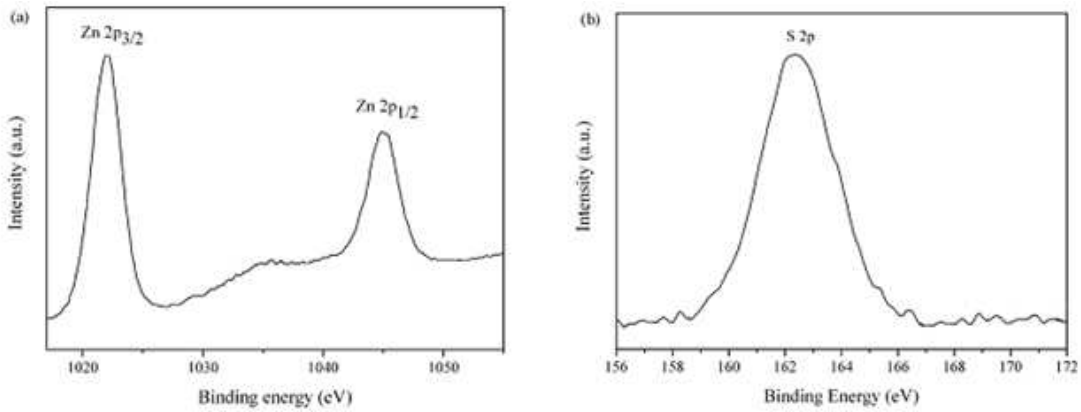

Fig.2. XPS spectra of as-synthesized ZnS samples: (a) Zn 2p spectrum; (b) S2p spectrum

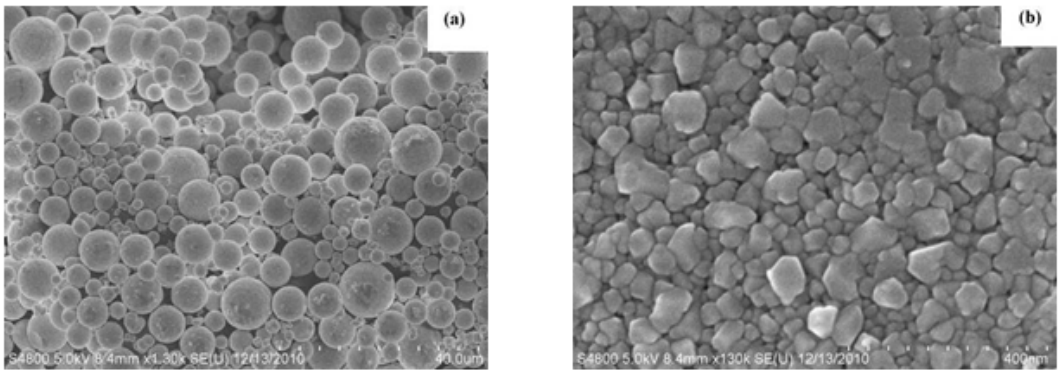

Fig.3. The FE-SEM pictures of synthesized ZnS samples

To further understand the photocatalytic properties of microspheres, as a comparison, we used 10 mg of the commercially available ZnS to degrade Rhodamine B at the same conditions. The results were shown in Fig. 4(b). Without any catalyst, the concentration of Rhodamine B solution almost did not change after 60 min (curve 1). The activity increased in turn for commercially available ZnS (curve 2), as-prepared ZnS microspheres (curve 3). The Rhodamine B solution was decolorized completely by using the ZnS microspheres after UV irradiation more than 60 min, which was apparently shorter than that of commercial ZnS powders.

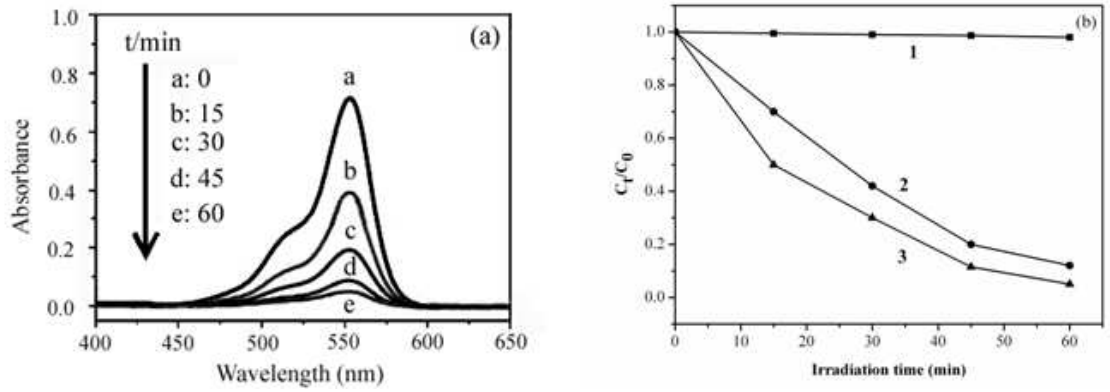

Fig.4. (a) Absorption spectrum of a solution of Rhodamine B (1.0×10^{-5} M, 75 mL) in the presence of ZnS microspheres (10 mg) under UV light irradiation. (b) Photodegradation of Rhodamine B (1.0×10^{-5} M, 75 mL) under UV light with different photocatalyst: (1) without any photocatalyst; (2) with commercially available ZnS (10 mg); (3) with as-synthesized ZnS microspheres (10 mg)

The superiority of photocatalytic performance of the ZnS microspheres should be attributed to their special structural features. The rough surface of ZnS microspheres should possess high specific surface area [16]. To evaluate the surface area of the obtained products, full nitrogen sorption isotherms were measured. The specific surface area was thus evaluated to be 52.6 $m^2 \cdot g^{-1}$ from data points in this pressure range by the BET equation. The result showed that the obtained microspheres possess higher specific surface area than that of commercial ZnS powders (36.1 $m^2 \cdot g^{-1}$), which was obviously beneficial for the enhancement of photocatalytic performance. Moreover, good dispersity and uniformity also can provide a large active surface area. On the basis of the above results, compared with the commercial ZnS powders, the advantages of ZnS microspheres are (1) a high surface-to-volume ratio with effective prevention from further aggregation to maintain the high catalytic activity area arising from the rough surface structure; (2) more easy separation and recycling than the common nanocrystals because of the larger size of the products.

Conclusions

In conclusion, based on facile hydrothermal method, 3D ZnS monodisperse spheres had been prepared via a simple convenient approach using 1-butyl-3-methlyimidazole thiocyanate ([BMIM][SCN]) as both sulfur source and capping ligand. The XRD pattern reveals the formation of wurtzite phase ZnS. The obtained ZnS microspheres display very high photocatalytic activity and are much more efficient than that of the commercial ZnS powders. The good photocatalytic performance of the ZnS microspheres should be attributed to their special structures and implied potential applications in other fields, such as solar cell and so on.

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