Supercritical Microemulsions as Nanoreactors for Manufacturing ZnS Nanophosphors

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The nanometer-sized zinc sulfide (ZnS) as a blue-emitting phosphor was prepared in a water-in-supercritical CO_2 microemulsion. The nanoparticles were characterized by XRD, TEM, and PL. XRD analysis shows that the average crystalline size of ZnS nanometer-scale samples is about 2–3 nm. Emission intensity of the ZnS nanophosphors obtained by the process is higher than that micrometer-sized ZnS.

Semiconductor nanocrystals have attracted much attention in the past few years because of their unique physical properties such as nonlinear optical behaviors,[1] size quantization,[2] and unusual luminescence.[3] Numerous methods for preparation of nanoparticles have been reported in the literature.[4,5] Using water-in-oil microemulsions as templates is one method of synthesizing semiconductor nanoparticles. One problem of using water-in-oil microemulsions for nanoparticle synthesis is the removal of solvent from products. In recent years, supercritical CO_2 has been extensively studied as a solvent for chemical synthesis. The advantages of using supercritical CO_2 for chemical reactions and synthesis are described in a number of recent publications.[6,7] Some reports show that fluorinated surfactants,[8–14] such as perfluorinated polyether (PFPE), polyether phosphate ($PFPE-PO_4$), ammonium carboxylate perfluoropolyether ($PFPE-COONH_4$), and fluorinated AOT (F-AOT), dissolved in supercritical CO_2 suggest the feasibility of forming supercritical microemulsion. Water-in-supercritical CO_2 microemulsions have been investigated as a reaction system for synthesizing inorganic nanoparticles such as silver,[9,10] silver halide,[11] copper,[12] CdS,[13] and ZnS.[14]

The ZnS nanoparticle could have some attractive luminescence performance.[15] The supercritical microemulsion appears to offer a new method for synthesizing a variety of nanoparticles in supercritical CO_2 using particular chemicals as surfactants. Synthesizing semiconductor nanoparticles in supercritical CO_2 offers several advantages over the conventional water-in-oil microemulsion approach including the fast reaction speed, rapid separation, and easy removal of solvent from nanoparticles. In this paper, we report the synthesis of the ZnS nanoparticles in the water-in-supercritical CO_2 microemulsion by using a novel bis(2,2,3,3,4,4,5,5-octafluoropentyl) maleate (BOFM) prepared as the surfactant in supercritical CO_2 fluid. The synthesis of ZnS nanoparticles is initiated by mixing two water-in-supercritical CO_2 microemulsions containing S^{2-} ions and Zn^{2+} ions separately in the water core. By collision, exchange of ions between the microemulsions takes place, leading to the formation of ZnS in the water core. The microemulsions thus act like nanoreactors for the synthesis of these metal sulfide nanoparticles.

The BOFM was synthesized by the procedures given by our laboratory. A mixture of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol, malonic acid, and toluol-4-sulfonic acid monohydrate as the catalyst in toluene was refluxed with Dean–Stark trap for 4 h. The reaction was stopped when approximately 90% of the theoretical amount of water was collected in the trap. Subsequently, the solvent was evaporated and the residue was extracted with ethyl acetate three times. A colorless liquid product was obtained by fractional distillation.

Zinc chloride and sodium sulfide of a minimum purity of 98% were purchased from Aldrich. The experimental apparatus used in this study is illustrated in Figure 1. The reverse micellar solutions were prepared by utilizing the BOFM at the water-to-surfactant weight ratio (W) value of 9, 12, and 15, $W = [H_2O]/[BOFM]$. A known amount of the Zn^{2+} aqueous solution and BOFM were placed in the autoclave reactor, and liquid carbon dioxide was compressed and sent to the reactor by pump. The reactor was pressurized to 100 atm first for making the CO_2 microemulsion and stirred at 35 °C for 1 h to ensure the formation of a homogeneous optically transparent microemulsion. The aqueous solution containing S^{2-} and BOFM were placed in the buffer tank, the buffer tank was pressurized to 200 atm and the microemulsion containing the S^{2-} solution was pushed into the reactor containing Zn^{2+} by opening an interconnecting valve. Supercritical microemulsions containing Zn^{2+} and S^{2-} were mixed together with continuous stirring at 35 °C for 1 h.

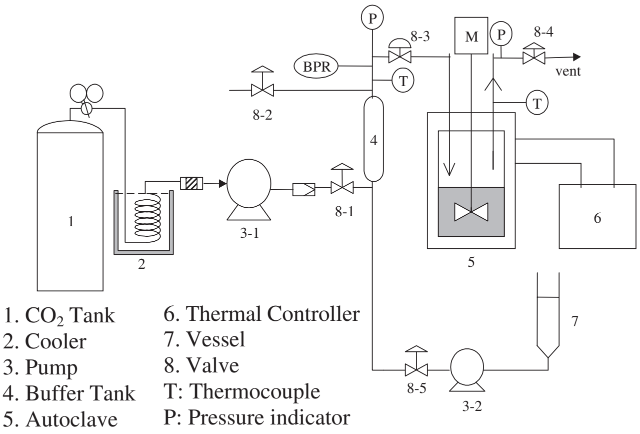


Figure 1. Experimental apparatus diagram of the supercritical CO_2 microemulsion reaction system.

After separation and washing with water, the final products were examined by X-ray diffraction (XRD). XRD patterns of the samples synthesized with different conditions are shown in Figure 2. It reveals that the ZnS nanoparticles exhibit a zinc blende crystal structure. The three diffraction peaks correspond to (111), (220), and (311) planes of the cubic crystalline ZnS. The average crystallite size of ZnS nanophosphors, estimated from the Debye–Scherrer formula, is about 2–3 nm. The ZnS nanoparticles synthesized by the water-in- supercritical CO_2 microemulsion with $W = 9$ tend to agglomerate and form an aggregates (Figure 3a). High-resolution TEM pictures were also taken for the ZnS nanoparticles. The image in Figure 3b shows the lattice fringe indicating ZnS nanoparticles with crystalline cores and the sizes of the ZnS nanoparticles are in the range of 3–6 nm in diameter.

The results of photoluminescence (PL) studied on the samples synthesized with different conditions are shown in Figure 4.

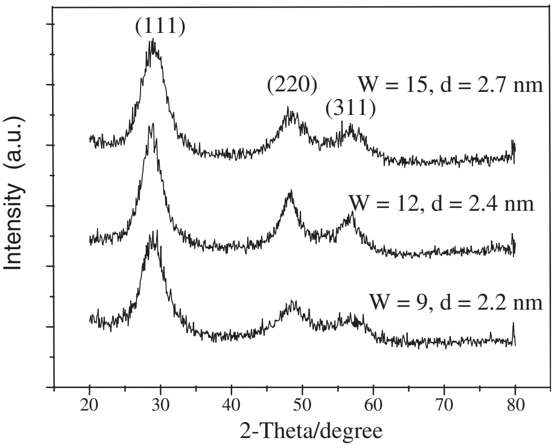
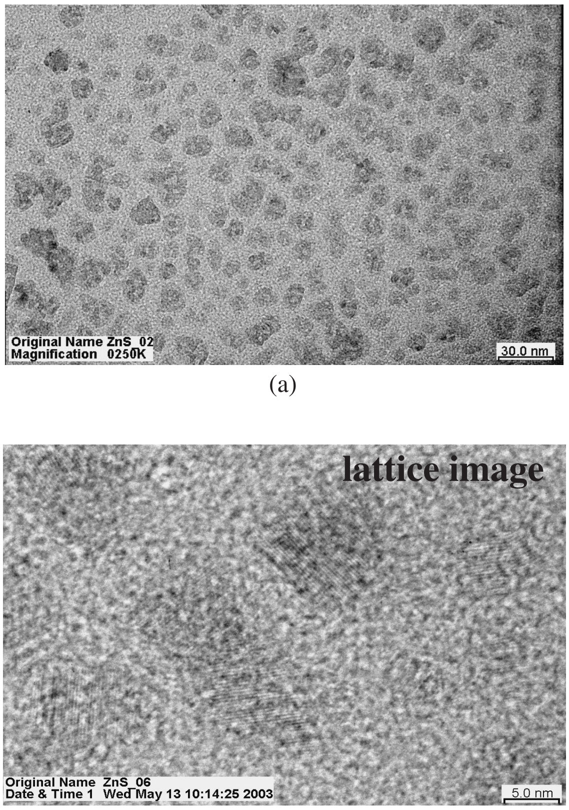


Figure 2. XRD patterns of the dried ZnS nanoparticles synthesized by supercritical CO_2 microemulsion method with different water-to-surfactant ratio (W) (average crystallite size).



(a)

(b)

Figure 3. TEM images of the dried ZnS nanoparticles ($W = 9$). (a) Aggregates of the ZnS nanoparticles; scale = 30.0 nm, (b) A high-resolution TEM image of a single ZnS nanoparticle; scale = 5.0 nm.

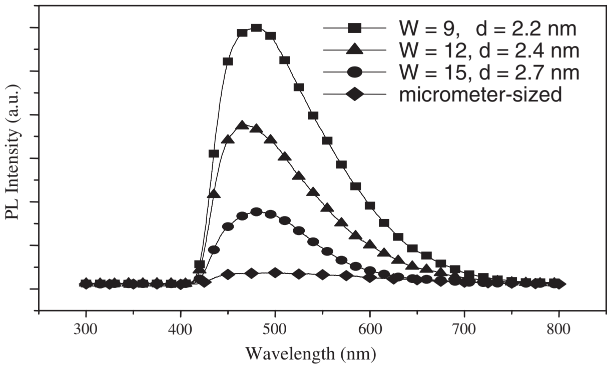


Figure 4. Emission spectra of the dried ZnS nanoparticles synthesized by supercritical CO_2 microemulsion method with different water-to-surfactant ratio (W) and ZnS microparticles synthesized by solid-state method ($\lambda_{\text{xcitation}} = 373$ nm).

For ZnS nanoparticles, blue emission band centered at 470 nm can be observed, which arises from the recombination of vacancies. Compared with the micro-sized particle phosphor prepared by solid-state reaction method, the emission intensity of the nanometer-sized ZnS phosphor obtained by this processing is higher than that micrometer-sized phosphor. The nanophosphor particle synthesized by supercritical microemulsion processing has quantum confinement and regular shape, while scattering of light evolved from the phosphor decrease, so the luminescence intensity is higher.

In summary, we successfully synthesized BOFM by the procedures given by our laboratory. Stable water-in-supercritical CO_2 microemulsions containing electrolytes can be formed using the BOFM surfactant. The non-ionic surfactant BOFM makes the much finer ZnS than the ionic surfactant fluorinated AOT.[14] The supercritical CO_2 microemulsions have emerged as a new type of nanoscale reactors for synthesizing ZnS in supercritical carbon dioxide. Nanometer ZnS phosphor can be manufactured by the supercritical microemulsion process. It is fine enough for application without grinding or milling. This water-BOFM-supercritical CO_2 approach offers a simple method for synthesizing various nanoparticles using water-soluble reagents as starting materials.

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