Colloid Polym Sci (2003) 281: 178–181
DOI 10.1007/s00396-002-0775-z

SHORT COMMUNICATION

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Synthesis and size control of monodisperse manganese-doped ZnS nanoparticles by methacrylate polymer

Received: 5 April 2002
Accepted: 15 July 2002
Published online: 14 November 2002

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Abstract A simple route to the fabrication of methacrylate polymer containing Mn-doped ZnS nanoparticles is described. The particles prepared have sizes as small as 1.8–2 nm, capped or modified by methacrylate polymer, and the thermal, mechanical, chemical stability, life and luminescence intensity are greatly improved. The particle sizes can be easily controlled by changing the number-average degrees of polymerization, which can be realized by adjusting the molar ratio of monomer to chain-transfer agent.

Keywords ZnS:Mn · Nanoparticles · Luminescence · Synthesis

Introduction

During the past few years, semiconductor nanocrystallites have been studied extensively [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. These materials behave differently from the corresponding bulk crystals because of the quantum confinement effect, a large surface-to-volume ratio and a high density of surface states as well as the geometrical confinement of phonons. Mn-doped ZnS crystallite has many special properties: it is one of the most important luminescence materials, and is widely used in electronics, light industry, military, and medical fields. It has therefore stimulated wide interest in both basic or in applied research. Bhargava et al. [12] first synthesized ZnS semiconductor nanocrystallites doped with Mn^{2+} ions, and found that the photoluminescence of Mn^{2+} doped in ZnS nanoparticles had a much higher quantum efficiency than bulk crystals. Mn-doped ZnS nanoparticles have been intensively studied from the viewpoint of the quantum size effects and the high luminescence efficiency since then [12, 13, 14, 15, 16]. A variety of methods are being developed for the manufacture of Mn^{2+}-doped ZnS nanocrystallites. Although considerable progress has been made in the synthesis of ZnS:Mn nanocrystallites, there are still many difficulties owing to high cost and difficult operation or production in organic solution which limit the mass production of ZnS:Mn nanoparticles. The study of an appropriate high-quality model system is essential for producing ZnS:Mn nanoparticles which must display a high degree of monodispersivity, high luminescence, low cost, easy operation and easily controlled size.

In this paper, we report, for the first time, a simple, rapid, and generalizable process for the synthesis of nanoparticles with precisely adjustable sizes, narrow size distribution, and high crystallinity as shown in Fig. 1. The desired nanoparticles are formed via two major steps: precise control of the number-average degrees of polymerization [17, 18, 19] followed by treating the

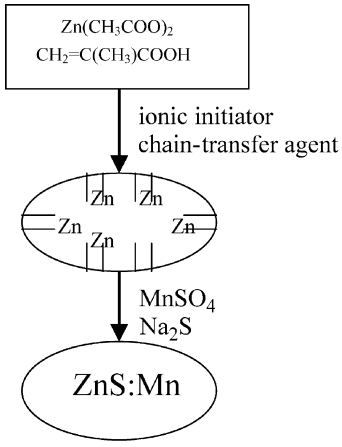


Fig. 1 Schematic outline of the experimental procedure to synthesize Mn-doped ZnS

polymer with sodium sulfide aqueous solution. Such reactions might yield high-quality, nearly monodispersed samples of Mn-doped ZnS nanometer-size crystallites. During the formation of the nanoparticles, the nanoparticles were capped by methacrylate polymer, which distributes on the surface to prevent them from agglomerating, and passivates, or modifies, the surface atoms, eliminates the energy levels inside the gap [1], and greatly increases the luminescence intensity. Provided each salt of methacrylate polymer forms one nanoparticle, the particle size can be estimated by a simple calculation. In our experiment, the calculated sizes are in agreement with experimental results.

Experimental

Chemicals

Methacrylic acid (99%) monomers were purified by distillation under reduced pressure prior to use. Zinc acetate dihydrate (99%), manganese(II) sulfate monohydrate (99%), sodium sulfide nonahydrate (98%), potassium persulfate (99.5%) ionic initiator, and mercaptoacetic acid (85%) chain-transfer agent were all purchased from Beijing Chemical Agent Corporation. The water was purified by deionization.

Preparation of nanoparticles

All the reactions were carried out in a three-neck flask equipped with a condenser, a mechanical stirrer, and inlets for nitrogen. Prior to reaction, the flask was purged with nitrogen.

Stage 1. Controlled degrees of methacrylate polymer

At the polymerization stage, 40 ml water, 0.03 mol zinc acetate, and 5.5 ml methacrylic acid were added into the reaction vessel, stirred, and then heated. When the temperature increased to about 60 °C, 40 ml 0.005 M potassium persulfate aqueous solution and 20 ml 0.017 M mercaptoacetic acid aqueous solution were added, respectively. The temperature was kept at 76–80 °C for 1 h.

Stage 2. Formation of nanoparticles

Upon cooling the reaction mixtures to 50 °C, 20 ml 0.06 M $MnSO_4$ aqueous solution was put into the reactor vessel, and then the mixture was stirred for 5 min. Sodium sulfide aqueous solution (40 ml, 0.8 M) was dropped into the reaction vessel containing the mixture for about 30 min, and then the mixture was continuously stirred for 30 min at 80 °C. The composites were separated from the solution by centrifuging. The separated compound was washed with methanol, then dewatered with butanol. Mn-doped ZnS nanopowders were obtained.

Studies of nanoparticles

The photoluminescence of Mn-doped ZnS nanopowders was recorded with a Hitachi F-4500 fluorescence spectrophotometer. The spectra were obtained by exciting the sample with a wavelength of 332 nm at room temperature. The X-ray powder diffraction patterns were obtained for the ZnS:Mn powders using a Rigaku RU-200B rotaflex diffractometer using Cu Kα $\lambda = 1.5406$ Å. The transmission electron microscopy (TEM) image and selected-area electron diffraction (SAED) patterns were taken using a JEOL-2010 transmission electron microscope operated at 200 kV. After completion of the reaction, several drops of the reaction solution were taken from the reaction vessel, and then the concentrated nanoparticle solution was diluted with water. Samples were prepared by placing a drop of the diluted aqueous solution on the surface of a copper grid (250 mesh).

Results and discussion

Particle size

Mn-doped ZnS nanopowder were synthesized by the chemical process. The particles are well dispersed, as shown in Fig. 2a. An individual nanocrystallite was characterized by SAED, as illustrated in Fig. 2c. The SAED pattern revealing the single crystalline nature of the nanocrystallite is zinc blende, and the corresponding spots are in the (111), (220) and (311) directions.

In this work, the precise control of the number-average degrees of polymerization plays an important role in controlling the mean particle size. To get narrow distributions of the degrees of polymerization, two measures were taken to control the polymer. First, we made the methacrylic acid react with zinc acetate to form the monomer precursor. Second, we chose a suitable chain-transfer agent. Both measures result in an increase in the speed of polymerization and narrow distributions of the degrees of polymerization. During the formation of the macromonomer, provided the polymerization process has an average distribution, that is, each polymer has an identical length, we can calculate the degree of polymerization, n, according to the molar ratio of monomer to the chain-transfer agent. The polymerization process is shown in Structure 1.

Mercaptoacetic acid is used as the chain-transfer agent, and can be used to adjust the degrees of

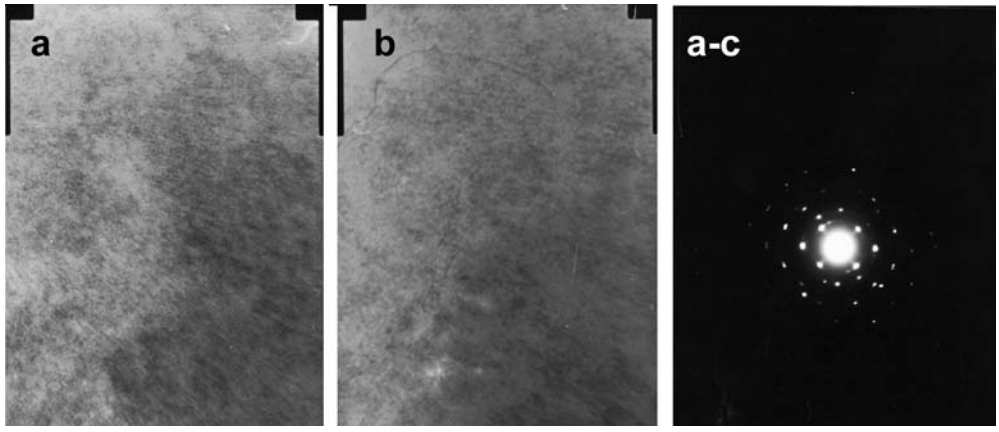
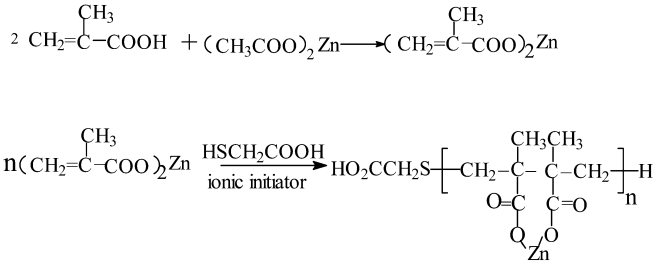


Fig. 2 **a**, **b** Transmission electron microscopy (*TEM*) images of Mn-doped ZnS nanoparticles. The molar ratios of monomer precursor to mercaptoacetic acid are 100:1 (**a**) and 150:1 (**b**), respectively. **c** Selected-area electron diffraction of Mn-doped ZnS taken from the particles in **a**



Structure 1

polymerization. When the molar ratio of monomer precursor to mercaptoacetic acid is about 100:1, according to single molecular volume, we can calculate the volume of a nanoparticle to be about 4 nm^3. The theoretical diameter of the nanoparticle corresponding to the experimental result from TEM is about 2 nm. (Fig. 2a). By changing the molar ratio of the monomer precursor to mercaptoacetic acid to 150:1, the theoretical diameter of the nanocrystallite corresponding to the experimental result of transmission electron microscopy is about 2.3 nm. (Fig. 2b)

X-ray powder diffraction probes a large number of crystallites that are statically oriented.(Fig. 3). Sample a exhibits a predominantly zinc blende crystal structure with planes in the (111), (220) and (311) directions. The diameter of the nanoparticle was estimated from the X-ray powder diffraction peak widths observed in Fig. 3, curve a, through the Scherrer formula. The diameter of the nanoparticle is about 2.1 nm, paralleling the result from TEM. Figure 3, curve b, shows the diameter of ZnS:Mn to about 2.4 nm, which also coincides with the TEM results. Sample c exhibits the bulk material of Mn-doped ZnS, which was patterned by a conventional calcine method. The previous discussion disclosed the relation between the nanosizes and the degrees of polymerization. By changing the ratio of monomer to chain-transfer agent, nanoparticles of exact size can be obtained. To the best of our knowledge, we precisely controlled the diameter of the nanoparticles for

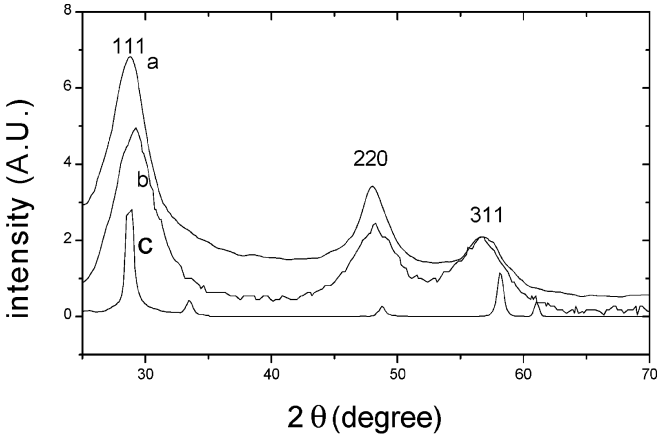


Fig. 3 Powder X-ray diffraction (*XRD*) spectra of Mn-doped ZnS. The molar ratios of monomer precursor to mercaptoacetic acid are 100:1 (*a*) and 150:1 (*b*). *c* XRD pattern of bulk ZnS:Mn

the first time. However, in our experiment, the diameter of the particle can be well controlled between 1.8 and 3 nm.

During the particle formation, the zinc (manganese) methacrylate polymers turned into methacrylate polymer and ZnS:Mn nanoparticles. The polymers capped and were distributed on the surface of the nanoparticles to prevent them from aggregating.

Photoluminescence spectra

Photoluminescence spectra of ZnS:Mn nanoparticles and commercial bulk are shown in Fig. 4. Two effects are clearly visible from these spectra. First, the ZnS:Mn nanoparticles show extremely enhanced optical emission of 20–25% over that of the commercial bulk. Second, the peaks of the nanoparticles exhibit a distinct redshift compared with that of the bulk. Both effects can be understood in terms of quantum size effects. As the particle size increases, the luminescence efficiency in the nanoparticles decreases with increasing crystallite size,

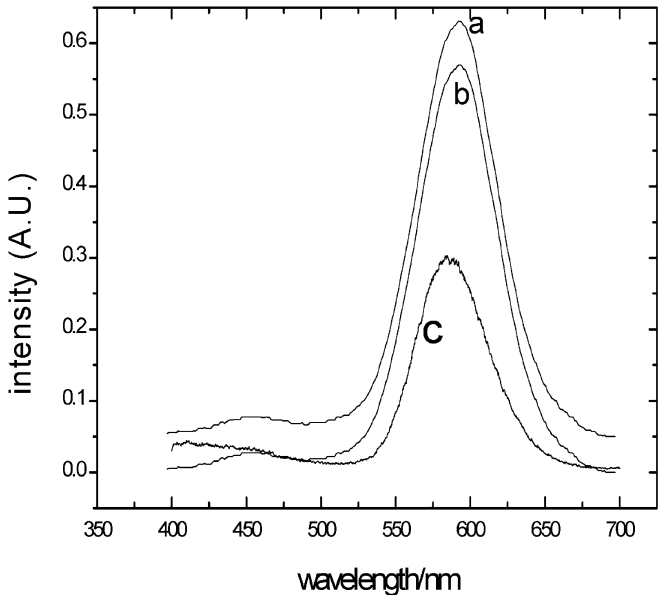


Fig. 4 Room temperature photoluminescence spectra of ZnS:Mn. 2 nm (*a*), 2.3 nm (*b*), commercial bulk ZnS:Mn (*c*)

but there is no obvious decrease in our experiment. A more important feature is that the photoluminescence intensity of the ZnS:Mn nanoparticles is stable for several months even when the particles are exposed to air directly; this is attributable to the methacrylate polymer coating the nanoparticles, which greatly improves their chemical stability, durability and lifetime. The polymer effectively passivates the surface of ZnS:Mn nanoparticles, and also results in a great improvement in the luminescence efficiency.

Conclusion

We have demonstrated the synthesis of relatively monodisperse ZnS:Mn nanocrystallites. The method proposed here focused on a strategy for separating these nanoparticles by methacrylate polymer that can distribute on the surface of the nanoparticles to prevent them from agglomerating. The particles prepared are capped or modified by methacrylate polymer, so their thermal, mechanical, chemical stability, durability, lifetime and luminescence intensity are greatly improved. We found that the methacrylate polymer plays an important role in controlling the growth of nanoparticles, and the number-average degrees of polymerization of the nanoparticles precisely control the nanosizes. The combination of TEM imaging and X-ray diffraction spectra provides a self-consistent description of the crystal structure. The nanocrystallites have better monodispersivity.

The schematic outline opens a broad range of potential uses and applications. The method can be extended to synthesize other kinds of metal-doped nanopowders, and can also be extended to prepare nearly monodisperse II–VI semiconductor nanopowders for which only suitable material needs to be selected.

Acknowledgements This work was supported by the innovation funds of the Chinese Academy of Sciences. We thank Mei Li and other members for their assistance in using X-ray diffraction, TEM and photoluminescence facilities.

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