SHORT PAPER

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Synthetic effects on site symmetry and photoluminescence properties of Eu-doped ZnS semiconductor nanoparticles†

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Eu-doped ZnS semiconductor nanoparticles were successfully prepared by using a new method – single-phase precipitation and solid-state reaction.

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The search for nanosized functional materials for information storage has stimulated great interest in both materials science and information science.[1] The study of nanosized metal sulfide semiconductor materials doped with impurities has been an area of intense activity in recent years.[2] We have previously reported the photoluminescence and upconversion properties of Sm-doped CaS nanoparticles, which showed different properties compared to their bulk-counterparts.[3,4] Zinc sulfide is the best host for luminescent materials with the band gap of 3.7 eV. Bhargava *et al.* first reported that Mn-doped ZnS nanoparticles yield an external photoluminescence quantum efficiency of 18% at room temperature and a luminescent decay time several orders of magnitude faster than that of the corresponding Mn^{2+} emission in the bulk crystals.[5] Cu-doped ZnS nanoparticles and their optical properties were also reported.[6,7] These spectacular results suggested that doped ZnS semiconductor nanoparticles form a new class of luminescent materials, with a wide range of applications in displays, lighting, and lasers *etc*.[2] Since the rare-earth ions are excellent luminescence centres, nanosized ZnS doped with them is becoming a new kind of solid-state luminescent material though the radii of rare-earth ions is larger than that of zinc ions. In this paper, we report the synthesis of Eu-doped ZnS semiconductor nanoparticles, together with their photoluminescence behaviour.

ZnS:Eu nanoparticles **1** and **2** were prepared by two methods, A and B, respectively. In general, without solid-state reaction, dopant ions tend to adhere to the surface of the nanoparticles, rather than dope in the crystal lattice. We first developed a superior synthetic method – the combination of single-phase precipitation and solid-state reaction. Nanoparticles prepared by this method still retain well-formed crystal shape and uniform physical phase. In method A, Na_2S serves as the inorganic sulfur donor and S^{2-} ions from Na_2S react with Zn^{2+} ions immediately. Without stirring, the precipitates will aggregate. In method B, Zn^{2+} ions react with S^{2-} ions from the organic sulfur donor CH_3CSNH_2 gradually. The formation of ZnS precipitates in method B is therefore much slower than that in method A. No aggregation phenomenon of the precipitates is observed even after storing at room temperature for 24 hours. It is evident that the formation rate of precipitation will undoubtedly affect the dopant ions getting into the lattice and the particle size of the precipitate. However, the effect of the preparation methods on the nanoparticle size is not observed after the solid-state reaction, and the difference in the particle size is difficult to observe, at least by absorption spectra.

In order to characterise the particle size, the diffuse reflectance absorption spectrum of ZnS:Eu nanoparticles **1** was measured. It is noteworthy that the absorption spectrum of **1**, including the absorption band edge, is the same as that of ZnS nanoparticles prepared by the same method without Eu doping, which means that the doping Eu ions have little effect on ZnS:Eu particle size. Compared to the absorption maximum of ZnS bulk materials (3.7 eV),[8] the absorption maximum of ZnS nanoparticles is blueshifted to 320 nm (3.9 eV). It is well known that the quantum size effect is one of the most striking features of nanometre-sized materials.[9–11] In the quantum size region, the band gap of the semiconductor increases when the size of the particles is decreased, which results in the blueshift of absorption bands. The grain size of ZnS:Eu nanoparticles can be estimated according to the effective-mass approximation.[12–15] The calculated exciton energy $E(R)$ is based on

$$E(R) = E_g + \frac{\hbar^2\pi^2}{2\mu R^2} - \frac{1.786e^2}{\varepsilon R} - 0.248E^*_{Ry}$$

where R is cluster radius, $1/\mu = 1/m_e^* + 1/m_h^*$, m_e^* is the electron effective mass, m_h^* is the hole effective mass, ε is the dielectric constant, and E^*_{Ry} is the effective Rydberg energy, $e^4/2\varepsilon^2\hbar^2(m_e^{*-1} + m_h^{*-1})$. The first term in the above equation is the band gap of the bulk materials, the second represents the kinetic energy, the third term the Coulombic energy, and the last term is the result of the correlation effect. For the ZnS semiconductor, $\mu = 0.176\ m_e$, and $\varepsilon = 8.3$.[8] Estimated from the above equation and absorption spectrum of sample **1**, grain size of the ZnS:Eu nanoparticle (sample **1**) is 6.8 nm.

The X-ray diffraction pattern of ZnS:Eu semiconductor nanoparticles **1** is shown in Fig. 1. All peaks can be ascribed

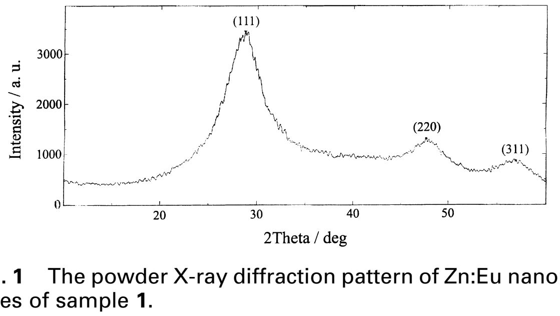

Fig. 1 The powder X-ray diffraction pattern of Zn:Eu nanoparticles of sample **1**.

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to a zinc blende crystal structure without extra phases and non-crystalline state. The peaks are markedly broad, which is characteristic of the nanoparticles. The average grain size of ZnS:Eu nanoparticles can be estimated by the Scherrer equation[16]

$$D_{\mathrm{h,k,l}} = k\lambda/(B_0 - b_0)\cos\theta$$

where k is a constant, about 1, generally considered as 0.89, λ the wavelength of Cu Kα radiation, 1.54 Å, B_0 the full width at half height of XRD peaks, b_0 the natural width of XRD spectrometer, generally replaced by full width at half height of a standard sample, and θ the diffraction angle. The average grain size of the nanoparticles is 6.9 nm estimated from Scherrer equation, which agrees well with the result from the diffuse reflectance spectrum.

The transmission electron microscopy image of ZnS:Eu nanoparticles of **1** is also measured (not showing). It is evident from the TEM image that the ZnS:Eu nanoparticles have a well-formed single-phase structure. The average size of the particles is about 8 nm according to the TEM image except for some aggregation of a few particles.

The photoluminescence spectra of **1** and **2** excited at 396 nm are shown in Fig. 2. No further splitting of the emission peaks is observed indicating that the site symmetry of Eu^{3+} belongs to the O_h group (zinc blende crystal belongs to the O_h group). Assignment of the emission peaks of **1** and **2** is given in Table 1. If the site symmetry of Eu^{3+} belongs to the O_h group, the emission at 590 nm originating from magneto-dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition is dominant. When the site symmetry of Eu^{3+} is reduced, the intensity of the emission band at 616 nm, which is the electric-dipole allowed $^5D_0 \rightarrow {}^7F_2$ transition, should increase. So it is evident that two emission peaks of Eu^{3+} centred at 590 and 616 nm are sensitive to site symmetry and can be used to study site symmetry, *i.e.* to study the microstructure around Eu^{3+} and the defects caused by doping of Eu^{3+} in the lattice of ZnS. The ion sizes of Eu^{3+} and Zn^{2+} are 0.95 and 0.77 Å, respectively. As the ion size of Eu^{3+} is much larger than that of Zn^{2+}, the defects and the deformation of the lattice must appear when Eu^{3+} gets into the lattice of ZnS, and the site symmetry of the doping Eu^{3+} ion must be decreased also. As the data in Fig. 2 show, the relative intensity of the emission peak at 616 nm is much larger than that at 590 nm in sample **2**, compared with the intensity ratio in sample **1**, and the sample **2** shows much larger total emission intensity than does the sample **1**. These comparisons indicate that it seems to be plausible that ZnS:Eu nanoparticles are doped by higher dopant concentration of Eu^{3+} in sample **2** than in sample **1**, even though the absolute contents of Eu^{3+} ions in the two samples are not measured in this paper, which is well agreement with our previous study.[17] The higher dopant concentration of Eu^{3+} in **2** than that in **1** is considered to relate to the different formation rate of the precipitate and therefore the different particle size of the ZnS precipitates obtained during the single-phase precipitation reaction. As mentioned above, in method A, S^{2-} ions from the inorganic sulfur donor Na_2S react with Zn^{2+} ions immediately. So Eu^{3+} ions tend to adhere to the surface of the ZnS precipitates. In method B, the organic sulfur donor CH_3CSNH_2 releases S^{2-} gradually, so the formation of ZnS precipitates is much slower, which is beneficial to getting the extra fine particles of ZnS precipitate with a much larger surface and therefore to admixing or adhering Eu^{3+} ions with/to the precipitates. It can be concluded that the slower the formation of the precipitate in the single-phase precipitation, the smaller the grain size of the precipitate and the easier doping of the ions in the solid-state reaction also.

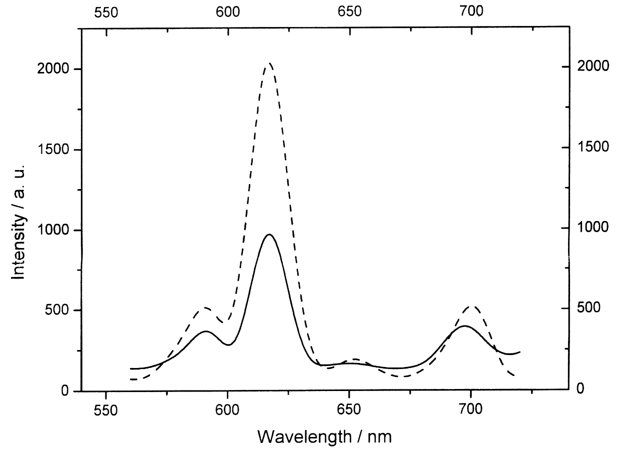

Fig. 2 The photoluminescence spectra of sample **1** (solid line) and **2** (dashed line). Excitation wavelength: 396 nm.

Table 1 Assignment of the emission peaks of **1** and **2** (Excitation wavelength: 396 nm)

1		2		Assignment
λ (nm)	*R*[a]	λ (nm)	*R*[a]	
591	1.00	590	1.00	$^5D_0 \rightarrow {}^7F_1$
617	2.65	616	3.96	$^5D_0 \rightarrow {}^7F_2$
652	0.46	651	0.37	$^5D_0 \rightarrow {}^7F_3$
697	1.09	700	1.01	$^5D_0 \rightarrow {}^7F_4$

[a] R: relative intensity of the transition $^5D_0 \rightarrow {}^7F_J$ / $^5D_0 \rightarrow {}^7F_1$

In summary, we have synthesised Eu-doped ZnS semiconductor nanoparticles successfully by the single-phase precipitation and the solid-state reaction method that was first developed in our laboratory. This new method opens a possible route for synthesis of doped semiconductor nanoparticles, even when the radius of the dopant ions is much larger than that of the host ions. We found that slow formation of the ZnS precipitates is beneficial to doping of Eu^{3+} in the crystal lattice. The ZnS:Eu nanoparticles prepared by this method are about 8 nm particle size and the crystalline structure is zinc blende crystal. The site symmetry of Eu^{3+} is well shown in the photoluminescence spectra, and the contents of Eu^{3+} in the crystal of sample **1** and **2** could be related to the intensity ratio of the emission at 616 nm to that at 590 nm. We believe these results will be helpful to the exploration of new kind of luminescence materials and further studies on optical upconversion materials based on the valence change of rare earths.

Experimental

The diffuse reflectance absorption spectrum was recorded on a Shimadzu UV-2010 spectrophotometer in the range of 220–700 nm. The powder X-ray diffraction was performed with a Rigaku X-ray diffractometer (model D/max-B) with Cu Kα radiation (40 kV, 120 mA). The transmission electron microscopy was carried out with Philips EM 400 ST electron microscope operating at 200 kV, and TEM images were recorded at a magnification of 100,000×. The photoluminescence spectra of the doped europium ions were measured by an Acton Research SpectraPro-300i spectrophotometer with a xenon arc lamp as an excitation source.

Syntheses of ZnS:Eu nanoparticles **1** (method A): To a stirred aqueous solution (150 ml) containing $Zn(CH_3CO_2)_2$ (30 mmol) and $Eu(CH_3CO_2)_3$ (0.3 mmol), Na_2S (30 mmol) aqueous solution (150 ml) was added dropwise at the rate of 1.5 ml per minute. The precipitate appeared immediately. The mixture was kept stirring for 30 min and then filtered and washed. The specimen was dried at 50°C for 24 h, and then mixed with equal amount sulfur and fired at 450°C for 2h in air atmosphere with carbon protection avoiding the oxidation and the formation of S^{2-} defects in the lattice during firing.

Syntheses of ZnS:Eu nanoparticles **2** (method B): To a stirred aqueous solution (150 ml) containing $Zn(CH_3CO_2)_2$ (30 mmol) and $Eu(CH_3CO_2)_3$ (0.3 mmol), CH_3CSNH_2 (30 mmol) ethanol solution (150 ml) was added dropwise at the same rate as in method A. The mixture was kept stirring and then the precipitate appeared gradually. After stirring for 24 h, the precipitate was filtered, washed, dried at 50°C for 24 h, and then fired at the same condition as those in method A.

It is worthy of note that the addition of sulfur does not affect the measurement of the sample because the sulfur sublimes below the firing temperature. In order for this to come true, however, it is important that the crucible with the samples are taken out of the bake oven at the firing temperature.

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