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Bionic synthesis of ZnS : Mn nanocrystals and their optical properties

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Transparent ZnS : Mn(II) nanocrystal solution was obtained by the reaction of Na_2S with a histidine-coordinated Zn^{2+} and Mn^{2+} solution with a sulfide/(Zn + Mn) ratio of 1.0 under stirring at room temperature. Nanocrystals of 8.3 nm in size were precipitated by addition of ethanol. The optical properties and structural characteristics of the nanocrystals are reported.

Nanometer-sized fluorescent materials used as bio-labels have attracted considerable attentions in recent years.[1–4] In comparison with common organic dyes, nanometer-sized fluorescent materials are more stable with high luminescent intensity, low photobleaching and large Stokes' shift.[2] However, the synthesis of most fluorescent nanocrystals with small size (for example, 5–20 nm) and narrow size distribution remains problematic. In addition, their aqueous insolubility, and how to attach them to biomolecules are also problems.[2]

ZnS : Mn is a favorable phosphor which exhibits better optical properties such as high luminescent intensity, narrow emission band *etc.*[5–9] In this paper, ZnS : Mn nanocrystals were synthesized by utilizing histidine as the capping material. Histidine is a favorable chelator for Zn, Cd *etc.*[10] For example, zinc coordinated by cysteine and histidine exists most notably in zinc-finger proteins. Peptide-coated CdS nanocrystals have been produced in organisms through chelation of Cd with histidine.[11] ZnS : Mn nanocrystals with narrow size distribution were difficult to synthesize in aqueous solution because of the different dissociation constants (K_d) for ZnS and MnS. In this procedure, when adding sulfide into the preformed zinc–histidine complex and manganese ions, competition for metal between the sulfide and histidine is introduced. The K_d of the zinc–histidine complex (in water at 25 °C) was 8.7×10^{-13}.[5] Zinc sulfide has greater stability with a K_d value of 1.1×10^{-24},[12] while manganese sulfide has a K_d value of 2×10^{-13}. With the coordination of Zn^{2+} by histidine, the solubility of ZnS can be increased from 1.1×10^{-24} to 1.26×10^{-12}, the possibility of co-precipitation of ZnS and MnS is greatly improved during the preparation, which makes it possible to obtain well doped ZnS : Mn nanocrystals. Moreover, on titration of sulfide, due to the formation of histidine capped ZnS : Mn, agglomeration is prevented by the steric barrier introduced by the capping group.

To a flask containing 0.25 M histidine in 1 M Tris buffer solution were added 4.3 ml 1 M $ZnSO_4$ (in 0.01 M HCl) and 1.76 ml 0.05 M $MnSO_4$ (in 0.01 M HCl), followed by injection of 4.4 ml 1 M Na_2S to achieve a sulfide/(Zn + Mn) ratio of 1.0 under stirring. The sample was sealed and incubated for 60 min at room temperature. The solution of ZnS : Mn nanocrystals looked transparent in the presence of histidine. Ethanol was introduced to the solution to precipitate ZnS : Mn nanocrystals. The deposition was collected and washed with ethanol, and dried overnight in vacuum.

Fig. 1 shows a typical TEM image of ZnS : Mn (2% Mn as the best doping concentration) nanocrystals; nearly spherical nanocrystals aggregated, whereas the recognizable isolated particles in size range from 7 nm to 10 nm. According to TEM and particle size analysis results, we estimate the average nanocrystal size is ~8.3 nm. XRD study indicates that ZnS : Mn nanocrystals are cubic.

When excited by an ordinary UV lamp (wavelength of 254 nm or 365 nm), orange fluorescence could be seen from the sample, which could not be observed in the undoped samples. Fig. 2 is the photoluminescent excitation (PLE) spectrum (a) and the photoluminescent (PL) spectrum (b) of ZnS : Mn nanocrystals. From the PLE spectrum, two main excitation peaks centered at 387 nm and 412 nm could be observed. The PL peak centered around 581 nm, which is similar to that of ZnS : Mn bulk crystal, is the characteristic emission of Mn^{2+} ion due to the d–d transition.

The ZnS : Mn nanocrystals could be redissolved in Tris buffer in the presence of histidine or cysteine. This is because the capping amino acid is full of water-soluble groups such as $-NH_2$ or –COOH. With the capping amino acid, the solubility

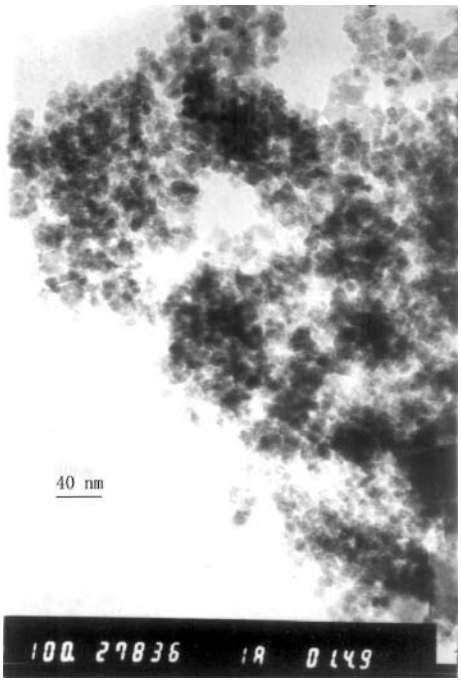

Fig. 1 TEM image of ZnS : Mn nanocrystals.

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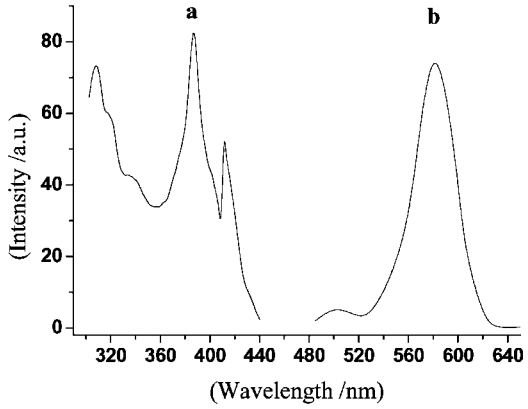

Fig. 2 PLE (a) and PL (b) spectra of ZnS : Mn nanocrystals.

of the nanocrystals increased. On the other hand, the presence of $-NH_2$ and –COOH on the surface of ZnS : Mn nanocrystals makes it easier to link to biomolecules such as protein and DNA molecules. These nanocrystals therefore show promise as fluorescent labels, and studies in this direction are under way.

By utilizing an amino acid, histidine, as the capping material, ZnS : Mn nanocrystals were formed with high reactant concentrations and mild reaction conditions. The size of the nanocrystals was measured to be 8.3 nm through TEM and particle size analysis. PL and PLE spectra were recorded. The emission spectrum exhibited a peak centered at 581 nm, which is the characteristic emission of Mn^{2+}. The product can be redissolved in Tris buffer, thus making it a promising fluorescent bio-label.

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