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ZnS nanoparticles doped with Cu(I) by controlling coordination and precipitation in aqueous solution

Lingdong Sun, Changhui Liu, Chunsheng Liao and Chunhua Yan*

State Key Laboratory of Rare Earth Materials Chemistry & Applications, PKU-HKU Joint Laboratory on Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing 100871, China. E-mail: chyan@chemms.chem.pku.edu.cn

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A novel method for the synthesis of ZnS:Cu colloids has been studied in aqueous solution, in which the Cu^+ ions were incorporated into the ZnS matrix by the assistance of a sulfur-containing ligand, *i.e.* thiourea or thiosulfate. The optical properties of the colloids (absorption, emission and excitation spectra) were studied. Compared with the bulk materials, the absorption band-edge is blue-shifted, which is attributed to a quantum size effect. The average ZnS nanoparticle size, deduced from the absorption spectra by an effective mass approximation, is about 4 nm. Upon excitation at 325 nm, a broad green emission band is observed, while for samples doped with 0.2% Cu, a blue emission band at 450 nm is also observed, which is quenched at higher dopant concentrations. It is concluded that Cu^+ ions occupy Zn^{2+} sites in the lattice of ZnS nanocrystals and act as both green and blue luminescent centers at different dopant concentrations. The sulfur-containing ligand (thiourea or thiosulfate) plays an important role in the synthesis as both ligand and surfactant; it stabilizes the Cu^+ ions, reduces the solubility difference between ZnS and Cu_2S, and protects the particles surfaces.

Optical properties of semiconductor nanocrystals have been studied extensively in recent years.[1–10] Quantum confined effects make these materials behave remarkably differently from the bulk and this has stimulated much research interest. Furthermore, semiconductor nanocrystals are potential luminescent materials in both photoluminescence (PL)[1–8] and electroluminescence (EL).[9,10] A report on the doping of a luminescent center (Mn^{2+} ions) into a nanosized ZnS matrix has made this a more vigorous and attractive subject.[1–5] As well as ZnS:Mn nanocrystals, efforts were also dedicated to investigating the synthesis and optical properties of copper doped ZnS nanocrystals, not only because ZnS:Cu is a widely used luminescent material, but also on account of the stronger interaction of copper ions with the host, ZnS. Larger emission shifts compared with that of the bulk are expected, and nanosized ZnS:Cu is more important for fundamental research.

Most of the reported work utilised the inorganic synthesis method described elsewhere[6] and Cu^{2+} ions were doped as the luminescent centers. It is important to investigate the incorporation of Cu^+ ions as the luminescent centers and study the characteristic optical properties which should differ from that of Cu^{2+} incorporation. For the synthesis of ZnS:Cu colloids by the normal inorganic method, Cu^+ ions are not stable in aqueous solutions and can only exist in some complex species. The solubility of Cu_2S ($K_{sp} = 2.5 \times 10^{-48}$) is far less than that of ZnS ($K_{sp} = 2.2 \times 10^{-22}$), which makes it difficult for Cu^+ and Zn^{2+} ions to be coprecipitated with S^{2-} ions, *i.e.* Cu^+ ions can not enter the lattice of ZnS crystals, unlike Mn^{2+} ions in a previous study of ZnS:Mn.[5]

In the present paper, we adopted a coordination chemistry method to solve these two problems. Thiourea or thiosulfate were used as both ligand and surfactant, and acted to stabilize Cu^+ ions in aqueous solution and minimize the solubility difference between Cu_2S and ZnS. By the use of these sulfur containing ligands, nanosized ZnS:Cu particles were obtained and their optical properties (absorption, excitation, and emission spectra) were studied.

ZnS colloid was prepared as described previously,[5,6] with only minor modifications. Freshly prepared $ZnCl_2$ and ligand solutions (thiourea or sodium thiosulfate) were stoichiometrically mixed together. Under continuous stirring, freshly prepared sodium sulfide solution was added to the above mixture. The addition rate was controlled at 1.0 ml min^{-1} by a fixed-flow console pump (Gilson, M312). Immediately after adding the Na_2S solution, a slightly opaque white, stable colloid was obtained which contained well dispersed ZnS nanoparticles. The Cu^+ complex solution was prepared by addition of CuCl to a stoichiometric quantity of thiourea or sodium thiosulfate. The preparation procedure of ZnS:Cu colloid was similar. The only difference was that the corresponding Cu^+ complex solution was mixed with $ZnCl_2$ solution at a molar ratio of 100:1 ($Zn^{2+}:Cu^+$) before sodium sulfide was added. There are no obvious differences between the ZnS:Cu colloid and ZnS colloid synthesized using the two different sulfur-containing ligands. The colloids were stable for several days before visible precipitation occurred.

PL and photoluminescence excitation (PLE) spectra of the colloids were recorded with a Hitachi F-4500 fluorescence spectrophotometer. The absorption spectra were recorded using a Shimadzu UV-1206 spectrophotometer. All of the A.R. grade reagents used in the experiments were commercially obtained without any further purification. All of the syntheses and experiments were performed at room temperature.

The absorption spectra of ZnS and ZnS:Cu colloids are given in Fig. 1. For the same ligand system, the absorption spectra of ZnS and ZnS:Cu colloids resemble each other. This implies that the minor amount of additional Cu^+ ions does not result in obvious changes of the colloid size. The onset of the absorption spectra and the extent of the shoulder peaks are remarkably different for the two ligand systems. The absorption spectrum of the ZnS:Cu thiourea system showed a shoulder at about 287 nm (4.32 eV), but for the thiosulfate system, the shoulder is red-shifted to 295 nm (4.20 eV). It is concluded that the particles formed in the thiourea system are a little smaller than in the thiosulfate system. Compared with the bulk materials, the nanosized ZnS:Cu colloidal particles demonstrate an apparent quantum size effect and are blue-shifted by about 0.6–0.7 eV. According to an effective mass approximation,[11–13] the average sizes of the ZnS and ZnS:Cu particles are about 3.4 nm in the thiourea system and 3.8 nm in the thiosulfate system.

In bulk ZnS:Cu materials, copper ions can act as different kinds of luminescent centers, such as blue, green or even red emission centers, which give off the corresponding visible col-

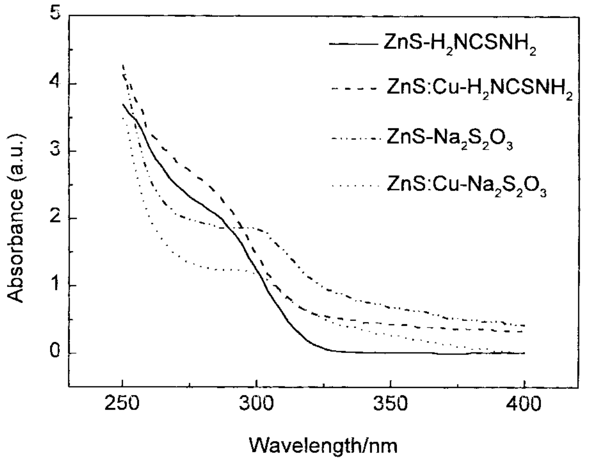

Fig. 1 Absorption spectra of ZnS and ZnS : Cu colloids stabilized by thiourea or thiosulfate.

oured light. It is reported that blue center emissions correspond to the Cu ions lying in the interstices of the ZnS lattice, and green centers appear when the Cu ions substitute for Zn^{2+} ions in the lattice.[14] Hence, blue, green, and even red emitting materials can be obtained by modifying the synthesis conditions. In the ZnS : Cu colloid system, which is stabilized by thiourea or thiosulfate, the emission peaks and intensities also change with the concentration of Cu^+ dopant ions as shown in Fig. 2. By changing the dopant concentration and the ligand, the evolution of the emission and the intensities of ZnS : Cu nanoparticles obvious differ. For both systems, there is a green emission band, which lies around 510–520 nm. When the dopant concentrations are identical, the emission intensity of the thiosulfate system is higher than that of the thiourea system. A blue emission band, which lies around 450 nm, can also be observed in samples doped with 0.2% Cu^+ and this is quenched at higher dopant concentrations. It is postulated that in the nanosized ZnS : Cu system, the copper ions form blue centers before green ones, and the former can only exist in small amounts in samples with lower dopant concentrations. This is consistent with the behaviour observed for bulk materials. It also means that our coordination doping method is effective for doping Cu^+ ions into the ZnS matrix, and the doping element, Cu, has entered the lattice by substitution for Zn^{2+} ions or occupation of the interstices of the lattice. As for the green emission band, the strongest emission appears at 0.6% dopant concentration, and is quenched at higher dopant concentrations. In comparison, for Cu^{2+} ions incorporated into ZnS nanoparticles, only a green emission band is observed with a maximum at approximately 500 nm. However, the incorporation of Cu^+ ions into ZnS nanoparticles is more complicated and different kinds of luminescent centers exist. The probability is that the Cu^+ complex is more stable and efficient during the doping process, and stable interstitial ions are expected to give rise to the blue emission band.

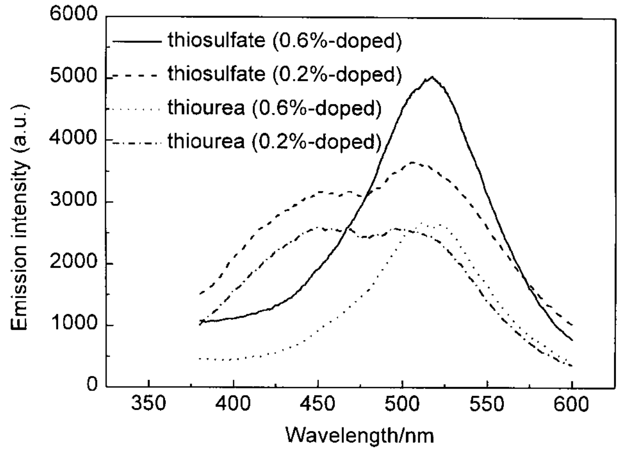

Fig. 2 Typical photoluminescence spectra of ZnS:Cu colloids stabilized by thiourea or thiosulfate with different doping concentrations. Green and blue emission bands were observed by UV excitation for 0.2% copper ion doping, only green emission bands were observed for 0.6% copper ion doping.

The excitation spectra of ZnS and ZnS : Cu (doped with 1% Cu^+) colloids are shown in Fig. 3; the detection wavelengths (λ_{em}) are 410 nm and 520 nm for ZnS and ZnS : Cu colloids, respectively. From Fig. 3, it is clear that the excitation spectra of ZnS and ZnS : Cu colloids are quite similar in the thiourea system; their excitation peaks are both centered at about 318 nm. However, for the thiosulfate system, the excitation spectrum for ZnS is much narrower than that for the ZnS : Cu colloid. The higher energy part of the excitation spectrum of the ZnS colloid seems weaker than that of ZnS : Cu, and the peak position is slight different. By comparing the excitation spectra of the two systems, it can be concluded that the green emission band of ZnS : Cu colloids and the violet emission band of ZnS colloids have the same origin. The luminescence mechanism of ZnS : Cu nanoparticles can be described as follows: the nanosized ZnS matrix absorbs ultraviolet photons, the electrons are excited from the valence band to the conduction band and are trapped by defects; recombination of the defects and the t_2 level induced by the copper center occurs and visible light emission is observed. Furthermore, the emission band depends on not only the doped copper concentration but also the particle size.

As for the synthesis of nanosized ZnS : Cu particles, the thiourea or thiosulfate plays an important role in the doping procedure. Firstly, thiourea or thiosulfate coordinates with Cu^+ ions thus improving their stability in aqueous solution.

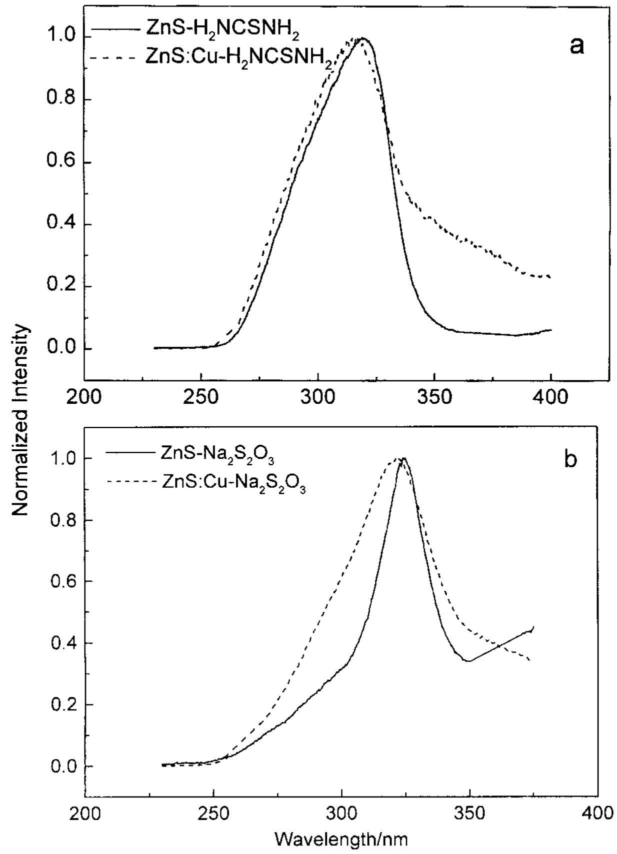

Fig. 3 Excitation spectra of ZnS and ZnS : Cu colloids stabilized by thiourea (a) or thiosulfate (b). The detection site was set to the corresponding emission peak. A UV cutoff filter was used to cut off wavelengths shorter than 350 nm.

The complex of Cu^+ ions with thiourea or thiosulfate is stable, with a stability constant of $\beta_4 = 2.5 \times 10^{15}$ in the thiourea system and $\beta_3 = 6.9 \times 10^{13}$ in the thiosulfate system. The coordination between Cu^{2+} and thiourea or thiosulfate can be neglected. For a system containing both Cu^+ and Cu^{2+} ions, the electric potential can be affected greatly by introducing a certain ligand. If the concentrations of thiourea and thiosulfate are both 1.0×10^{-2} mol L^{-1}, and the concentrations of Cu^+ and Cu^{2+} ions are 1.0×10^{-4} mol L^{-1}, the electric potential of $Cu^+ + e = Cu$ will decrease from 0.52 V to −0.15 V and −0.18 V for the thiourea and thiosulfate systems, respectively. At the same time, the electric potential of $Cu^{2+} + e = Cu^+$ will increase from 0.17 V to 0.61 V and 0.63 V, respectively. This result also means that the corresponding cell potential of $2Cu^+ = Cu + Cu^{2+}$ in the thiourea and thiosulfate systems will decrease from +0.35 V to −0.76 V and −0.81 V. Hence, the coordination effect will retard the spontaneous reaction of $2Cu^+ = Cu + Cu^{2+}$, *i.e.* thiourea or sulfate will stabilize Cu^+ ions in aqueous solution.

Secondly, thiourea and thiosulfate will reduce the solubility difference between ZnS and Cu_2S. The solubility of Cu_2S will increase from 8.5×10^{-17} mol L^{-1} to 3.4×10^{-9} mol L^{-1} or 1.4×10^{-9} mol L^{-1} with the existence of 1.0×10^{-2} mol L^{-1} thiourea or thiosulfate, and the solubility of ZnS increases just a little. Furthermore, the possibility of coprecipitation of ZnS and Cu_2S can be greatly improved during the synthesis, and this makes it possible to obtain ZnS:Cu nanoparticles in which Cu^+ ions replace the Zn^{2+} ions in the lattice.

Lastly, for ZnS nanocrystals, luminescence can only be observed with a Zn:S ratio of less than unity. This means that the luminescence of ZnS comes from the recombination of anion defects and the valence band. In most cases, there are insufficient S^{2-} ions present and the S^{2-} defect on the surface makes it attractive for sulfur-containing species or other kinds of species which can coordinate with Zn^{2+} ions. In our system, only S^{2-} and sulfur-containing species can combine with Zn^{2+} ions, and the insufficient S^{2-} means that thiourea or thiosulfate can bind to the surfaces of the crystals, forming a protective layer. So thiourea and thiosulfate can also act as surfactants for stabilizing ZnS nanoparticles.[15,16] This layer prevents the further agglomeration of nanoparticles and enables us to obtain more stable ZnS colloids.

In conclusion, we have synthesized Cu^+ doped ZnS nanoparticles by adopting a coordination method, with thiourea or thiosulfate as ligands. The ligand stabilizes the Cu^+ ions, reduces the solubility difference between ZnS and Cu_2S, and forms a protective layer on the particles surface. It is a more effective doping procedure using Cu^+ than the normal inorganic method, so that different kinds of Cu^+ emission can be observed.

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