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Lixin Cao, Jiahua Zhang, Shanling Ren, and Shihua Huang

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# Luminescence enhancement of core-shell ZnS:Mn/ZnS nanoparticles

Lixin Cao,[a] Jiahua Zhang, Shanling Ren, and Shihua Huang
*Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun, 130021, China and Changchun Institute of Optical, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, 130021, China*

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$Mn^{2+}$-doped ZnS nanoparticles and $Mn^{2+}$-doped ZnS nanoparticles coated with a shell of ZnS were prepared in reverse micelles. $Mn^{2+}$ emission at 580 nm in the coated nanoparticles was seven times stronger than that in the uncoated ones. Ultraviolet light treatment enhanced the luminescence at 580 nm in the uncoated nanoparticles, but led to no luminescence enhancement in the coated ones. Some calculations indicated that $Mn^{2+}$ ions were not randomly distributed in the particle, but preferred to occupy the sites close to the surface. The experiment results indicated that ZnS shell and UV treatment could block the nonradiative transition paths and led to the enhancement of luminescence.

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Nanoparticles have large amounts of vacancies arising from their large surface-to-volume ratio. Since the vacancies usually act as luminescence killers, it is necessary to modify the surface of nanoparticles for better optical properties. For $Mn^{2+}$-doped ZnS nanoparticles, organic molecules with carboxylic functional groups are often used as passivating agents. Enhancements of 4, 10, and 30 times in photoluminescence intensity have been observed from $Mn^{2+}$-doped ZnS nanoparticles passivated by methacrylic acid,[1] polymethymethacrylate,[2] and 3-methacryloxypropyl trimethoxysilane,[3] respectively. Similar phenomenon has also been reported for core-shell quantum dots structures.[4,5] A core nanoparticle of one material was coated by a shell of another having a large band gap, eliminating nonradiative relaxation pathways and enhancing photoluminescence (PL) from the core. Another useful method for obtaining highly luminescent $Mn^{2+}$-doped ZnS nanoparticles is UV light treatment,[2,6–8] which "passivates" the nanoparticle surface, removes unwanted nonradiative relaxation paths, and thus enhances the overall luminescence quantum yield. Several processes have been proposed as the mechanisms of the irradiation-induced luminescence enhancement effect. One of them is irradiation with suitable wavelengths, causing filling of empty surface states with electrons.[2] The other is UV light inducing the polymerization of the methacrylic acid stabilizer, leading to a better surface passivation.[7,8]

In this paper, we studied optical properties of $Mn^{2+}$-doped ZnS nanoparticles and $Mn^{2+}$-doped nanoparticles coated with a shell of ZnS prepared in reverse micelles.

$Mn^{2+}$-doped ZnS nanoparticles and the nanoparticles covered by a shell of ZnS were prepared with inverted micelles method.[9–11] Dioctylsulfosuccinate sodium salt (AOT) was used as a surfactant. Standard solutions of $Zn^{2+}$ (1.0 M) and $Mn^{2+}$ (0.5 M) were prepared from $Zn(CH_3COO)_2$, $Mn(CH_3COO)_2$, and purified water. The usual procedure was: 0.04 M AOT heptane solution was mixed with an amount of 1.0 M $Zn(CH_3COO)_2$ aqueous and 0.5 M $Mn(CH_3COO)_2$ aqueous with a certain mole ratio of water-to-surfactant ($W$) and a mole ratio of $Mn^{2+}$-to-$Zn^{2+}$ ($V$). The mixture was stirred magnetically until a homogeneous microemulsion was obtained. After 30 min $N_2$ gas bubbling, excess $H_2S$ was injected to lead to the formation of $Mn^{2+}$-doped ZnS nanoparticles. Then the nonreacted $H_2S$ was blown out by $N_2$ gas bubbling. The calculated amount of $Zn^{2+}$ ions were added to the solution containing $Mn^{2+}$-doped ZnS nanoparticles by several steps while the mole ratio $W$ was raised to a given value. Every step was followed by an injection of $H_2S$ and a removal of nonreacted $H_2S$. Finally $Mn^{2+}$-doped ZnS nanoparticles coated with a shell of ZnS were produced in AOT in heptane. In this letter, the two samples were made under $W=11$ and $V=0.013$. Equal amounts of $Zn^{2+}$ ions, $Mn^{2+}$ ions, and AOT heptane solution were used. For the ZnS shell coating particles, the core was made under $W=7$ and the final $W$ is 11. The radius of the nanoparticles could be estimated from $W$. The radius is about 2.89 nm when $W=11$. For the coated particles, the radius of the core was estimated to be 2.15 nm and the thickness of the shell was estimated to be 0.75 nm. Fluorescence spectra were taken by a Hitachi F-4500 fluorescence spectrophotometer and the PL scan took only a few seconds.

Figure 1 gives the emission spectra of the two samples excited at 305 nm. It can be seen that the $^4T_1-^6A_1$ emission of $Mn^{2+}$ ions is at ~580 nm, and the intensity of the 580 nm

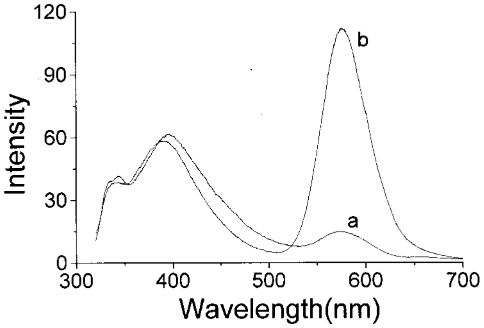

FIG. 1. The emission spectra of the (a) uncoated and the (b) coated $Mn^{2+}$-doped ZnS nanoparticles excited at 305 nm.

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[a] Author to whom correspondence should be addressed; electronic mail: 9990629@sina.com

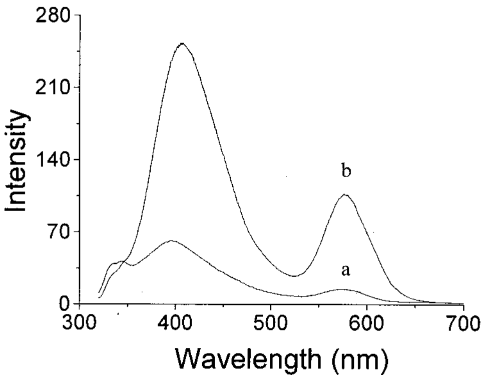

FIG. 2. The emission spectra of the uncoated $Mn^{2+}$-doped ZnS nanoparticles excited at 305 nm (a) before and (b) after 1 h exposed under 305 nm irradiation from a Xe lamp.

emission of the coated nanoparticles is seven times that of the uncoated nanoparticles. The emission peak centered at ~400 nm is attributed to the self-activated emission caused by Zn vacancies in the lattice.

Both types of samples were subjected to UV treatment. No significant change is observed in the emission spectra of the coated nanoparticles excited at 305 nm before and after exposed under 305 nm irradiation from a Xe lamp. Figure 2 shows the emission spectra of the noncoated nanoparticles excited at 305 nm before and after 1 h exposed under 305 nm irradiation. It can be seen that the $Mn^{2+}$ ions emission at 580 nm was strongly enhanced.

The changes of luminescence intensity at 580 nm with exposure time under 305 nm irradiation are shown in Fig. 3. The decrease in the luminescence intensity of the coated nanocrystals is less than 15%, while that of the uncoated nanoparticles increases rapidly with total exposure time at the initial stage, then slows down, and finally approaches a saturation value. The saturation value is about seven times the initial intensity, and approximately equals the initial intensity of the coated nanoparticles. The concentrations of the $Mn^{2+}$ ions are equal in the two samples; the only difference is their distribution. In the uncoated particles, $Mn^{2+}$ ions are distributed in the whole volume; among them some are close or even at the surface. On the other hand, $Mn^{2+}$ ions in the coated particles are within the core, away from the surface.

The average radius of the nanoparticles is 2.89 nm, and the average radius of the core in the sample A (coated nanoparticles) is 2.15 nm. The lattice constant of ZnS is $a=0.541$ nm, and the distance between two closest cations is $a/(2)^{1/2}$. We assume the surface states are located at the outer shell of the particle, i.e., $2.51\ \text{nm}<r<2.89$ nm. Assuming the particle is a sphere, there are $n_2=986$ cation sites at the surface, $n_0=1055$ sites within the core, and $n_1=546$ sites in between.

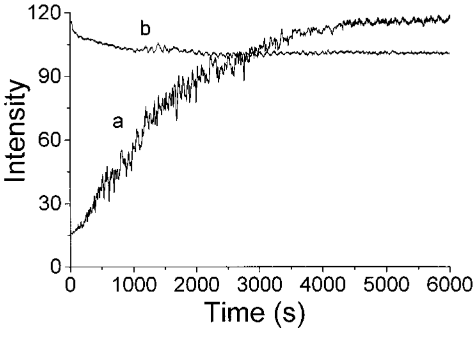

FIG. 3. The changes of luminescence intensity at 580 nm with exposure time under 305 nm irradiation for (a) uncoated $Mn^{2+}$-doped ZnS nanoparticles and (b) coated $Mn^{2+}$-doped ZnS nanoparticles.

If $Mn^{2+}$ ions are randomly distributed, in sample B (uncoated nanoparticles) a portion $[n_2/(n_0+n_1+n_2)=0.38]$ of the total Mn ions is at the surface and would have no or only a little contribution to the luminescence. Leeb *et al.*[12] reported that concentration quenching was observed at a $Mn^{2+}$ concentration of 1 at. % Mn incorporated in the nanoparticle, but Bol[13] stated that no concentration quenching was observed at the same $Mn^{2+}$ concentration. Reference 13 indicated that the $Mn^{2+}$ concentration in the nanoparticle was less than the $Mn^{2+}$ concentration present during the synthesis. For example, when the mole ratio of $Mn^{2+}$ to $Zn^{2+}$ in the solution was 5.0 at. %, the $Mn^{2+}$ concentration in the nanoparticle was only 0.25 at. %. In our experiments, the $Mn^{2+}$ concentration in the nanoparticle was estimated to be less than 0.25 at. % from Ref. 13, which is far below the quenching concentration. In addition, no concentration quenching took place when the mole ratio of $Mn^{2+}$ to $Zn^{2+}$ in the solution increased to 3.3 at. %.

If the $Mn^{2+}$ ions were randomly distributed in nanoparticles, in view of the large average Mn–Mn distances at a $Mn^{2+}$ concentration less than 0.25 at. %, energy migration among Mn ions could be ignored. Thus, the energy transfer from Mn to the surface quench centers would follow the static transfer mechanism. Assume $W_1$ be the intra-ion transition rate and $W_2(R_i)$ to be the energy transfer rate to all the surface quench centers. If $R_i$ is the distance of the $i$-th ion from the origin, the observed emission intensity is proportional to

$$I_B=\frac{1}{n_0+n_1+n_2}\sum_i^{n_0+n_1}\frac{W_1}{W_1+W_2(R_i)}$$

for the sample B, and to

$$I_A=\frac{1}{n_0}\sum_i^{n_0}\frac{W_1}{W_1+W_2(R_i)}$$

for the sample A. $I_B/I_A$ would lie between $(n_0+n_1)/(n_0+n_1+n_2)$ [if $W_1\gg W_2(R)$] and $n_0/(n_0+n_1+n_2)$ [if $W_2(R)\gg W_1$]. Substituting the values of $n_1$, $n_2$, and $n_3$, we have $0.62>I_B/I_A>0.40$. The observed ratio is about 0.143. This is an indication that the $Mn^{2+}$ ions are not randomly distributed in the particle, they prefer to occupy the sites close to the surface. The effect would be twofold. First, the average static transfer rate of $Mn^{2+}$ ions to the surface quench centers gets larger and second, enrichment of $Mn^{2+}$ ions in the surface layer makes energy migration among them easier. Both result in decreasing the emission quantum efficiency.

As the particles being exposed under the UV irradiation, the population of the surface quench centers decreases due to either photochemical or photophysical processes, luminescence of $Mn^{2+}$ ions is thus enhanced. The luminescence intensity of the coated nanoparticles does not change significantly under UV irradiation indicates that the ZnS shell blocked most of the nonradiative recombination paths.

In summary, a calculation based on uniform excitation of the $Mn^{2+}$ ions indicates a higher density of $Mn^{2+}$ ions near the surface of the particle. The luminescence at 580 nm in the coated nanoparticles can be enhanced by ZnS shell and UV treatment. Both ZnS shell and UV treatment can block most of the nonradiative transition paths leading to the enhancement of luminescence.

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