Effect of irradiation on the luminescence in ZnS:Mn²⁺ nanoparticles

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Abstract

Mn^{2+}-doped ZnS nanoparticles were prepared in AOT micelles and the $^4T_1$-$^6A_1$ emission at 580 nm of Mn^{2+} ions incorporated within the ZnS nanoparticles was obtained. The irradiation-induced luminescence enhancement effect was observed that not only the luminescence at 580 nm was largely enhanced, but also the shape and the position of the excitation band was changed after a 305 nm irradiation from a Xe lamp. Different from the work reported previously, the irradiation-induced luminescence enhancement effect was not persistent and the irradiation resulted in the size decreasing of the nanoparticles. The experiments preferred to the electrons filling model.
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1. Introduction

Semiconductor nanomaterials have been a new generation of advanced materials due to their novel electronic and optical properties, originating from size quantization [1–2]. The properties of such nanomaterials are determined not only by their atomic scale structures but also by their interface and surface structures. Due to the large surface-to-volume ratio, nanoparticles have large amounts of vacancies which usually act as luminescence killers. So over the last 20 years especially the last decade since Bhargava et al. [3–4] suggested the discovery of a new class of luminescence materials of doped nanocrystals combining high luminescence efficiency and decay time shortening, not only the preparation and photoluminescence of II–VI semiconductor nanocrystals, as isolated particles, clusters or doped-particles in colloids, sol–gel glasses and polymer hosts, but also the methods of surface modification have been extensively investigated [3–23]. Though

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the discovery has been disputed by Bol and Meijerink [15], and Murase et al. [16] with the experiments which confirmed that the shortened decay time to several nanoseconds originated from the blue emission of ZnS nanocrystals, not related to Mn^{2+} centers in ZnS nanocrystals, the photoluminescence of Mn^{2+}-doped ZnS nanocrystals still remains an interesting research field [8,11,19–23]. In order to obtain better optical properties in Mn^{2+}-doped ZnS nanoparticles, organic molecules with carboxylic functional groups are often used as passivating agents. Enhancement of 4, 10 and 30 times in photoluminescence intensity has been observed from Mn^{2+}-doped ZnS nanoparticles passivated by methacrylic acid (MA) [17], poly methy methacrylate (PMMA) [10] and 3-methacryloxypropyl trimethoxysilane (MPTS) [11] respectively. Another useful method for obtaining highly luminescent Mn^{2+}-doped ZnS nanoparticles is UV light treatment [4,10,14,18,19], 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 that the irradiation with suitable wavelengths caused filling of empty surface states with electrons [10]. The other is that the UV light induced the polymerization of the methacrylic acid stabilizer, leading to a better surface passivation [4,18]. The third is that the UV curing made the surface of the nanoparticles photo-oxidated, which provided a more efficient passivation [24]. In this paper, Mn^{2+}-doped ZnS nanoparticles were prepared in AOT micelles and the irradiation-induced luminescence enhancement effect was observed too. The experiments preferred to the electrons filling model.

2. Experimental

Mn^{2+}-doped ZnS nanoparticles were prepared with inverted micelles method [25–27]. Dioctylsulfosuccinate sodium salt (AOT) was used as 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 in AOT in heptane. Then the nonreacted H_2S was blown out by N_2 gas bubbling. In this paper, the samples were made under $W = 11$ and $V = 0.013$.

Fluorescence spectra were taken by a HITACHI F-4500 Fluorescence Spectrophotometer and the PL scan took only a few seconds. The irradiation light was from 150 W Xe lamp of the F-4500 Fluorescence Spectrophotometer. Absorption spectra were measured with a Shimadzu Recording Spectrophotometer.

3. Results and discussion

The semiconductor particles are assumed to have grown to approximately the same size as the water pools of the reverse micelles in which they are prepared [25,26]. The size of the water pools can be estimated roughly by the water-to-surfactant mole ratio (W). A more precise relationship between W and the radius of the micelle water pool (r) is given in Eq. (1):

$$[(r + 15)/r]^3 - 1 = 27.5/W. \tag{1}$$

In our experiments, ZnS nanoparticles were prepared at $W = 11$. Thus the radius of the ZnS nanoparticles was estimated to be 2.89 nm. In the article, AOT was used as a microreactor which controlled the size of the nanoparticles. Because the high AOT concentrations interfered with the microscopy of the particles, the particle's images of TEM were not obtained. The size of the ZnS nanoparticles was also calculated from the excitation spectrum (Fig. 3, spectrum a) using the effective mass model of Brus [28]. For ZnS, the effective mass of the electron and the hole are $0.42 m_e$ and $0.61 m_e$ respectively. The dielectric constant is 8.0. Then the radius of the ZnS

nanoparticles was calculated to be 2.97 nm which was consistent with the values estimated by W (2.89 nm).

Fig. 1 shows the emission spectra of the Mn^{2+}-doped ZnS nanoparticles excited at 305 nm before and after 1.5 h exposed under 305 nm irradiation. It can be seen that an emission at 580 nm, which can be assigned to the ${}^4T_1$–${}^6A_1$ emission of Mn^{2+} ions which are incorporated within the ZnS nanoparticles, was observed. It also can be seen that the Mn^{2+} ions emission at 580 nm was strongly enhanced after the nanoparticles were exposed under 305 nm irradiation for 1.5 h.

The changes of luminescence intensity at 580 nm with exposure time under 305 nm irradiation are shown in Fig. 2. The luminescence intensity of the Mn^{2+}-doped ZnS nanoparticles increases rapidly with total exposure time at the initial stage, then slows down and finally approaches a saturation value which is about seven times the initial intensity.

As the particles being exposed under the UV irradiation, the population of the surface quench centers decreases due to either photochemical or photophysical processes. Assume X be the rate constant of the process, and N_s be the population of the surface quench center with initial value N_s $(t = 0) = N_{s0}$, N be the population of excited Mn^{2+} ions, $N(t = 0) = 0$. Assume W_1 be the intra-ion transition rate and $W_2(R_i)$ be the energy

Fig. 2. The changes of luminescence intensity at 580 nm with exposure time under 305-nm irradiation for Mn^{2+}-doped ZnS nanoparticles. (a) Experimental curve; (b) the fitting curve.

transfer rate to all the surface quench centers, where R_i is the distance of the ith ion from the origin. We chose an average W_2 for all the Mn^{2+} ions, obviously, $W_2 = wN_s$. The set of rate equations for the UV irradiation induced luminescence enhancement can be written as

$$\frac{dN}{dt} = G - W_1 N - w N_s N,$$

$$\frac{dN_s}{dt} = -X N_s,$$

$$N(0) = 0, \quad N_s(0) = N_{s0}.$$

Solutions of the equations are

$$N_s = N_{s0} \exp(-Xt),$$

$$N = G \int_0^t \exp\left[-W_1(t - t') - \frac{wN_{s0}}{X}\right.$$
$$\left. \times (e^{-Xt'} - e^{-Xt})\right] dt'.$$

Since $W_1 \gg X$, $e^{-Xt'} - e^{-Xt} \approx e^{-Xt} X(t - t')$, N can be approximated by

$$N \approx G \frac{1 - \exp[-(W_1 + wN_{s0}e^{-Xt})t]}{W_1 + wN_{s0}e^{-Xt}}.$$

After several ms, the numerator approaches to 1, the equation reduced to

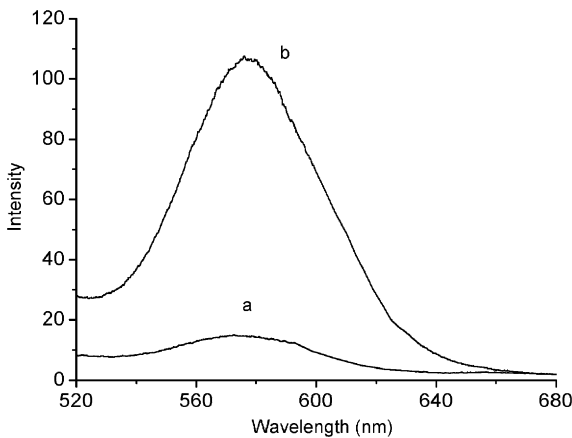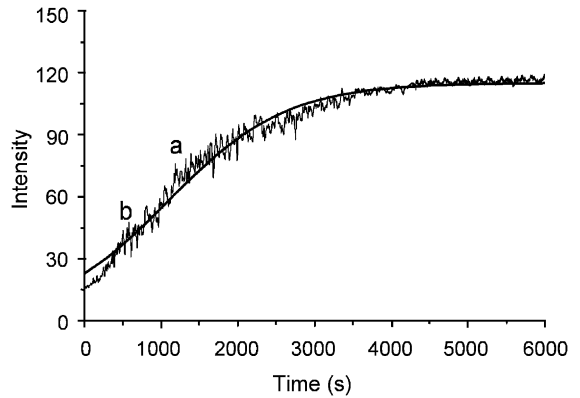$$N \propto \frac{1}{1 + \frac{wN_{s0}}{W_1} e^{-Xt}}.$$

Fig. 1. The emission spectra of the Mn^{2+}-doped ZnS nanoparticles excited at 305 nm (a) before and (b) after 1.5 h exposed under 305 nm irradiation from a Xe lamp.

Fig. 2(a) is fitted by this equation and the fitting curve is presented in Fig. 2(b). It is fitted well and some constants are obtained. wN_{s0}/W_1 equals to 4.08 ± 0.03 and X equals to $0.0013 \pm 0.00001 \, \text{s}^{-1}$. wN_{s0}/W_1 is the ratio of nonradiative transition rate to radiative transition rate at $t = 0$. The fitting results indicate that about 80.3% of the energy transferred to Mn^{2+} relaxed by nonradiative transition in the Mn^{2+}-doped ZnS nanoparticles. If the nonradiative recombination paths were blocked, the luminescence of Mn^{2+} would be enhanced by a factor of 5.08.

Fig. 3 shows the excitation spectra of the Mn^{2+}-doped ZnS nanoparticles monitored at 580 nm. (a) and (b) were tested before and just after exposed under 305 nm Xe lamp irradiation for 1.5 h. (c)–(f) were laid for 1 h, 6 h, 3 and 8 day, respectively after exposed under 305 nm Xe lamp irradiation for 1.5 h before testing. Generally, in doped semiconductors, there are two channels for luminescence excitation. One is indirect excitation, i.e., excita-

tion into the excited levels of the host, followed by an energy transfer from the host to the impurity ions to cause the luminescence. The other is direct excitation of the impurity ions. From the excitation spectra, two excitation peaks at 303 and 266 nm, respectively were obtained. It is indicated that luminescence from indirect excitation of the host is much more efficient, which proves that energy transfer from ZnS to Mn^{2+} is taking place. For the absorption band being effective to the excitation, it is in correspondence with the excitation band. Similar to the absorption spectrum, the excitation spectrum of nanoparticles is also size-dependent. It can be seen that after the nanoparticles were exposed under 305 nm Xe lamp irradiation for 1.5 h, not only the luminescence was enhanced by several times, but also the excitation band was changed. The excitation peaks at 303 and 266 nm, respectively before the irradiation were shifted to 292 and 254 nm, respectively after the irradiation, and the excitation onset at
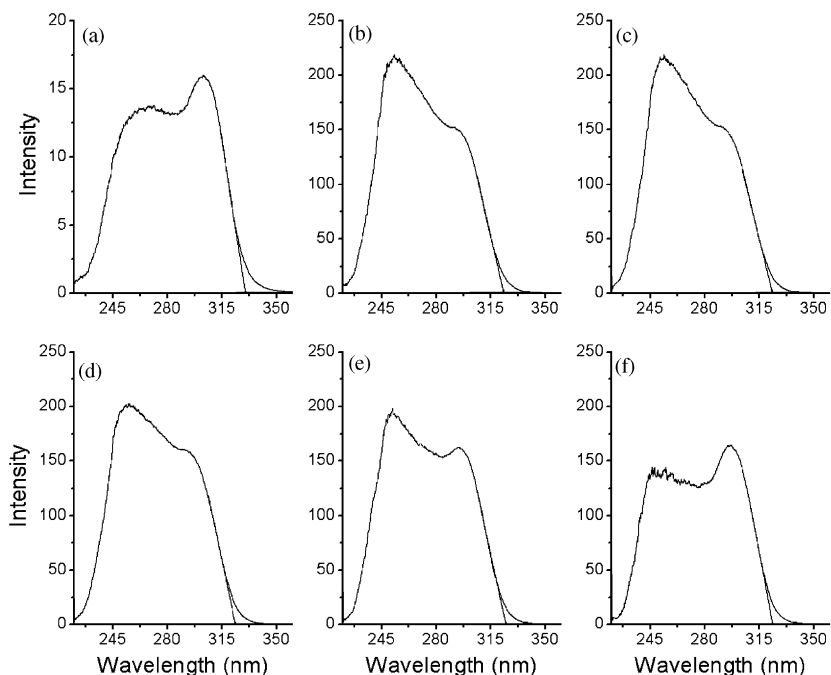

Fig. 3. The excitation spectra of the Mn^{2+}-doped ZnS nanoparticles monitored at 580 nm. (a) and (b) were tested before and just after exposed under 305 nm Xe lamp irradiation for 1.5 h. (c)–(f) were laid for 1 h, 6 h, 3 and 8 day respectively after exposed under 305 nm Xe lamp irradiation for 1.5 h before testing.

330 nm before the irradiation was shifted to
324 nm after the irradiation. Using the effective
mass model of Brus [28], the size of the ZnS
nanoparticles was calculated from the excitation
spectrum. The radius of the ZnS nanoparticles
before the irradiation was calculated to be 2.97 nm
and after the irradiation the radius was reduced to
2.36 nm. This indicates that the irradiation re-
sulted in the decreasing of the nanoparticles, as
was reported by Bol et al. [24], but different from
the results of Jin et al. [10] that the size of the
nanoparticles did not change after irradiation. It
also can be seen that the shape of the excitation
spectrum also changed. The excitation at 303 nm
was most effective before the irradiation and after
the irradiation the most effective excitation wave-
length was shifted to 254 nm. The higher-energy
part increased relative to the lower-energy part.
But the changes were not persistent, after the
irradiation, the higher-energy excitation became
less effective with the being laid time. When the
nanoparticles were laid for 8 days after exposed
under 305 nm Xe lamp irradiation for 1.5 h, the
most effective excitation wavelength returned to
297 nm again which corresponded to the lower-
energy part. The size of the nanoparticles did not
change with the being laid time after the irradia-
tion. So we prefer the electron filling model. Due
to the small particle size in nano-scale, surface
defects such as donors and acceptors are easily
formed on the ZnS nanoparticles surface. Usually,
these surface states are the major origin of the
nonradiative paths. The irradiation may fill some
of these surface states with electrons, then some of
the nonradiative paths are blocked, which led to
the luminescence enhancement. But these filled
surface states are metastable. The higher the
energy of the surface states, the faster the electron
relaxation. So after a long time, the surface states
with higher energy become unblocked and the
higher part of the excitation bands become less
efficient than the lower part of the excitation band.
It can be expected that after a long enough time,
the luminescence enhancement would disappeared.
Not as Yu et al. [14] suggested, the irradiation-
induced luminescence enhancement effect of
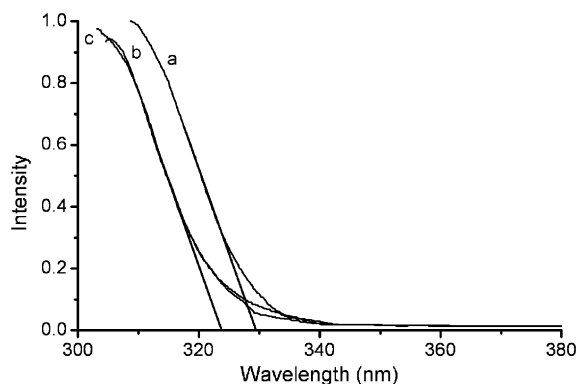ZnS:Mn nanoparticles in AOT micelles was not
persistent.

Fig. 4. The absorption spectra of the Mn^{2+}-doped ZnS nanoparticles. (a) and (b) were tested before and just after exposed under 305 nm Xe lamp irradiation for 1.5 h, (c) was laid for 8 day after exposed under 305 nm Xe lamp irradiation for 1.5 h before testing.

Fig. 4 shows the absorption spectra of the
Mn^{2+}-doped ZnS nanoparticles (a) and (b) were
tested before and just after exposed under 305 nm
Xe lamp irradiation for 1.5 h (c) was laid for 8 day
after exposed under 305 nm Xe lamp irradiation
for 1.5 h before testing. It can be seen that the
absorption onset was at about 329.5 nm before the
irradiation and was shifted to 323.7 nm after the
irradiation. The results were consistent with those
of the excitation spectra.

4. Conclusions

Mn^{2+}-doped ZnS nanoparticles were prepared
in AOT micelles and the $^4T_1$-$^6A_1$ emission at
580 nm of Mn^{2+} ions incorporated within the
ZnS nanoparticles was obtained. The irradiation-
induced luminescence enhancement effect was
observed that not only the luminescence at
580 nm was largely enhanced, but also the shape
and the position of the excitation band was
changed after a 305 nm irradiation from a Xe
lamp. Different from the work reported pre-
viously, the irradiation-induced luminescence
enhancement effect was not persistent and the
irradiation resulted in the size decreasing of
the nanoparticles. The experiments preferred to
the electrons filling model.

Acknowledgements

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