

# Irradiation-induced luminescence enhancement effect of ZnS:Mn<sup>2+</sup> nanoparticles in polymer films

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Received January 27, 1997

The effects of irradiation-induced luminescence enhancement by ZnS:Mn<sup>2+</sup> nanoparticles in poly(vinyl butyral) films are reported. The luminescence intensity increases several times when fresh samples are irradiated by a 248-nm excimer laser. The decay time also increases with exposure time. The increase in the initial intensity of the slow component of luminescence makes the main contribution to the enhancement effect. A tentative model is proposed in which the efficiency of the energy transfer to Mn<sup>2+</sup> ions increases with exposure. States at interfaces are expected to play an important role in this process. © 1997 Optical Society of America

The optical properties of semiconductor nanoparticles have been studied extensively in recent years.<sup>1-3</sup> These materials behave differently from bulk semiconductors and have stimulated great interest in both basic and applied research, especially in the study of the intrinsic optical properties of pure materials. Papers on the optical properties of transition-metal-ion-doped semiconductor nanoparticles have emerged recently.<sup>4-7</sup> These doped nanoparticles have interesting properties worth studying for both basic research and applications. Bhargava *et al.* reported high luminescent efficiencies of nanocrystals of ZnS:Mn<sup>2+</sup> and claimed that doped nanocrystals are a new class of material.<sup>4</sup> The mechanisms that drive the new phenomena are still unclear, and the rich field of doped nanoparticles of semiconductors needs further exploration. In this Letter we report, for the first time to our knowledge, on the effects of irradiation-induced luminescence enhancement (IILE) of ZnS:Mn<sup>2+</sup> nanoparticles embedded in polymer films. This report adds new elements to this field and may deepen our understanding of the properties of these materials. For application purposes, understanding the mechanism of IILE effects may provide a method to increase the luminescence efficiency of this new class of material.

Nanoparticles of ZnS:Mn<sup>2+</sup> were made by the same method described in Ref. 7. Poly(vinyl butyral) (PVB) was used as the polymer matrix. The excitation peak of the sample is at 297.5 nm, as shown in the inset of Fig. 1. The sample showed a significant blue shift compared with that at 350 nm of the conventional ZnS:Mn<sup>2+</sup> powder, which originates from the well-known quantum-confinement effect. The size of the ZnS:Mn<sup>2+</sup> nanoparticles was estimated to be ~3.6 nm.<sup>8</sup> The emission spectra at 7.8 K under 248-nm excitation are shown in Fig. 1. Curve 1 is the emission spectrum of the sample after 15-min exposure to a 248-nm laser beam, and curve 2 is the emission spectrum after 130-min exposure. The emission band with a peak at 600 nm is typical, well known to be due to the <sup>4</sup>T<sub>1</sub>-<sup>6</sup>A<sub>1</sub> transition of Mn<sup>2+</sup> in ZnS. The band at the high-energy side is discussed below.

An interesting phenomenon of the IILE effect that we observed is shown in Fig. 2. In this experiment a 248-nm excimer laser was employed as the excitation source. The repetition rate of the laser pulse was 2 Hz. A photon counter was used to measure the emission intensity. For a fresh sample under irradiation the luminescence intensity increased rapidly with total exposure time in the initial stage, then slowed and gradually approached a saturation value of approximately seven times the initial intensity. The intensity enhancement is so obvious that it can easily be seen by the naked eye. The stronger the irradiation intensity, the greater the saturation intensity, and the

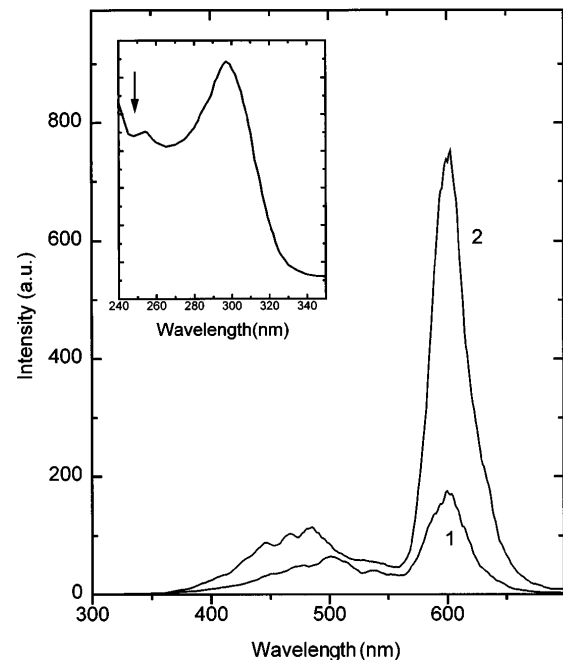


Fig. 1. Emission spectrum of ZnS:Mn<sup>2+</sup> nanoparticles in PVB film at 7.8 K excited at 248 nm. The inset is the excitation spectrum of ZnS:Mn<sup>2+</sup> nanoparticles in PVB film at room temperature monitored at 590 nm. Arrow, 248 nm.

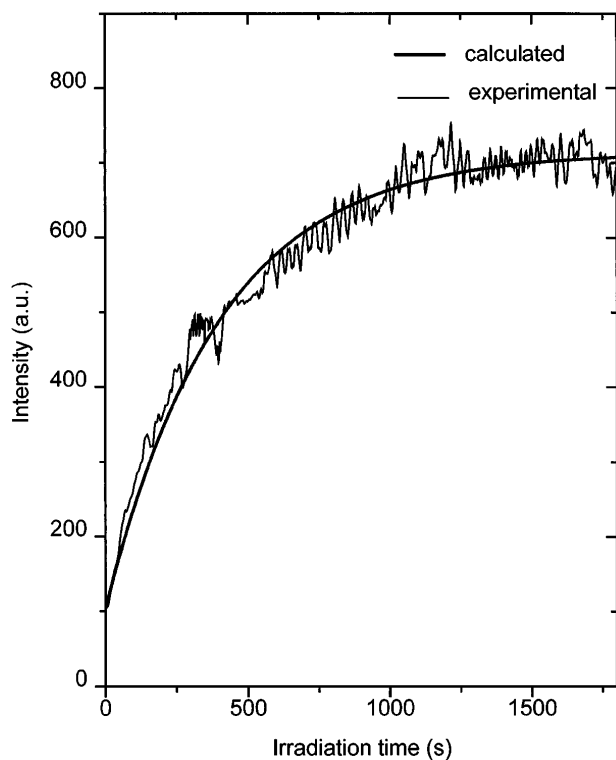


Fig. 2. Luminescence intensity at 590 nm versus exposure time under 248-nm irradiation.

shorter the time needed to reach the saturation value. This enhancement effect was found in all fresh samples measured, but the enhancement factor (the ratio of maximum to initial intensity) varied from sample to sample from several to tens of times. In comparison, we did not find a similar enhancement effect for conventional ZnS:Mn<sup>2+</sup> powder with micrometer-sized particles under the same irradiation conditions.

After exposure, a weak excitation light was used to monitor the change in luminescence. The luminescence intensity decreased slightly within hours and then reached a stable value, as shown in Fig. 3. The IILE effect of ZnS:Mn<sup>2+</sup> nanoparticles was found to be persistent in PVB films.

From Fig. 1 we can see that exposure to 248-nm laser light increases the intensity of the 600-nm band and produces a change in a new high-energy band. The new band appears in the range from 400 to 480 nm. This means that some new electron states are created by 248-nm irradiation.

The effect of irradiation on luminescence decay at room temperature was also investigated. The decay curves shown in Fig. 4 can be decomposed into two exponential decay components:

$$I = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2),$$

where  $I$  is the total intensity,  $I_1$  and  $I_2$  are the initial intensity of the slow component and the fast component, respectively, and  $\tau_1$  and  $\tau_2$  are decay times of the slow component and the fast component, respectively. The slow component makes the main contribution to the integrated intensity. The initial intensity  $I_1$  of the slow component increases dramatically with exposure. Curve 1 in Fig. 4 is for a sample after 15-min irradiation.

Curve 2 is for the sample after 130-min irradiation. The ratio of  $I_1$  of the slow component of curve 2 to that of curve 1 is  $\sim 5$ . The decay time  $\tau_1$  of the slow component also increases with exposure. The decay time of the slow component of curve 1 is  $4.3 \times 10^{-5}$  s, and that of curve 2 is  $5.4 \times 10^{-5}$  s.

Because the integrated intensity of an exponential decay is proportional to the product of the initial intensity and the decay time, we conclude that the increase in the initial intensity of the slow component makes the main contribution to the luminescence enhancement and that the contribution of increased decay time is secondary.

Decay curves were also measured at 7.8 K. Behavior similar to that at room temperature was found, indicating that the increase in initial intensity is

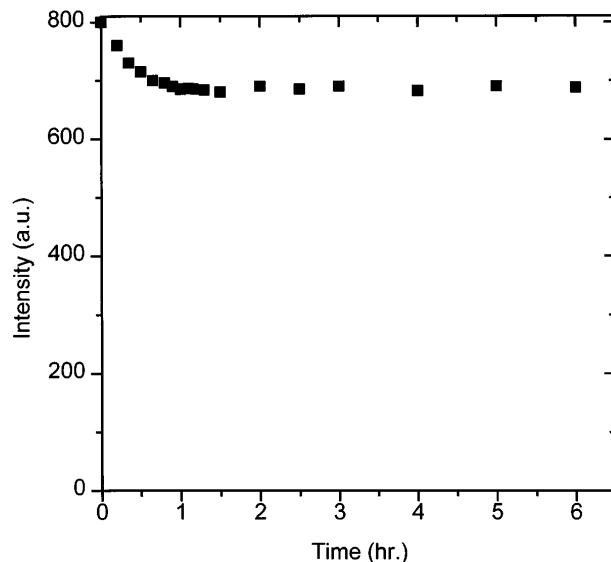


Fig. 3. Luminescence intensity at 590 nm versus time after irradiation.

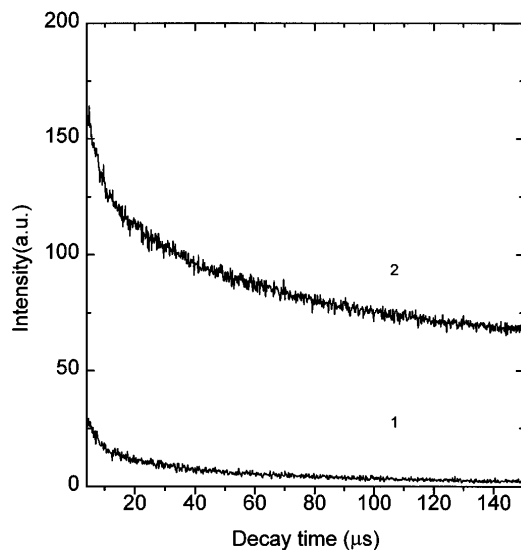


Fig. 4. Decay curve of 590-nm luminescence under 248-nm excimer laser excitation with a pulse width of 40 ns at 3 Hz. Curve 1, after 15-min exposure; curve 2, after 130-min exposure.

mainly responsible for luminescence enhancement; the increase of decay time has a minor effect.

Several mechanisms have been considered as the cause of the IILE effect. The first is the laser annealing effect. However, even weak light from a Xe lamp at an appropriate wavelength can produce the IILE effect. So the laser annealing effect is ruled out as a cause of IILE. There are three possible ways to increase luminescence intensity under weak excitation: (1) increasing the radiative transition probability of  $\text{Mn}^{2+}$  ions, (2) decreasing the nonradiative transition probability or even blocking the nonradiative path, and (3) increasing the efficiency of the energy transfer to  $\text{Mn}^{2+}$  ion. Because the main cause of the IILE effect is the increase in initial intensity of the slow component of luminescence, the first of these possibilities can be ruled out. Furthermore, we could not fit the experimental data theoretically by decreasing the nonradiative transition or blocking the nonradiative path but could fit them by using the following model, in which the increase in efficiency of the energy transfer to  $\text{Mn}^{2+}$  ions with irradiation is considered.

Suppose that states  $S$  at interfaces are coupled to upper level  $C$  in the conduction band. For a fresh sample, while some of the electrons excited to high-energy states  $C$  in the conduction band will be trapped by states  $S$ , some electrons will relax to lower-energy states of the conduction band, contributing to the normal luminescence of  $\text{Mn}^{2+}$ . Suppose that states  $S$  act as sensitizers after they are filled by electrons, with the coefficient of energy transfer from states  $S$  to  $\text{Mn}^{2+}$  being proportional to  $n_s$ , the number of states  $S$  filled with electrons. The dynamical equation for  $n_s$  is

$$\frac{dn_s}{dt} = w_{cs}n_c(N - n_s) - w_s n_s,$$

where  $w_{cs}$  is the transition coefficient of electrons from states  $C$  to states  $S$ ,  $n_c$  is the number of filled states  $C$ ,  $N$  is the number of states  $S$ , and  $w_s$  is the leakage coefficient of filled electron states  $S$ . The IILE effect is persistent, so  $w_s n_s$  can be omitted. We used 40-ns pulses to irradiate the sample. In this case  $n_c$  can be approximately expressed as  $Id$ , where  $d$  is the pulse width and  $I$  is a constant proportional to excitation intensity. The luminescence intensity  $L$  can therefore be expressed as  $L = L_0 + b[1 - \exp(-w_{cs}n_c)]$ , where  $b$  is a constant. The solid curve labeled calculated in Fig. 2 represents theoretical fitting with the above equation.

The change in the emission spectra seems to favor use of the above model. The emission bands in the high-energy side of the 600-nm band are likely to be emission from states  $S$ . As they are filled by electrons after exposure, their valence states are changed, so a new emission band in the range from 400 to 480 nm appears.

We studied the luminescence enhancement effect of  $\text{ZnS:Mn}^{2+}$  nanoparticles in colloids<sup>7</sup> and in various polymers. We found that the luminescence intensity and the enhancement effect are strongly affected

by the surrounding media. This implies that states  $S$  at interfaces between nanoparticles and the surrounding media play an important role in luminescence and in the enhancement effect. The properties of states  $S$  depend on the interaction between surroundings and nanoparticles.  $\text{Mn}^{2+}$  ions in  $\text{ZnS}$  nanoparticles are located close to these interface states and hence are strongly affected by them. This effect is consistent with the fact that the portion of ions near the surface increases rapidly with a decrease in the size of the nanoparticles. 65.7% of the ions are near the surface within one lattice constant in 3.6-nm  $\text{ZnS}$  nanoparticles size, and 33.6% of the ions are within the distance between nearest ions, compared with only 0.04% of ions near the surface within one lattice constant for a powder of 5- $\mu\text{m}$  size. So electron states at the interface have a much stronger effect on the properties of nanoparticles than in bulk materials.

In summary, IILE by  $\text{ZnS:Mn}^{2+}$  nanoparticles of PVB films has been observed for the first time to our knowledge. The enhancement of the luminescence was due mainly to an increase of the slow component of luminescence with the laser irradiation. A tentative model was proposed in which the efficiency of energy transfer to  $\text{Mn}^{2+}$  ions increased with exposure. The electron states at the interface are expected to play an important role in this process. From the applied point of view, the IILE effect may provide a means to raise the luminescence efficiency of nanoparticles. Further study is under way to clarify the physics that underlie the IILE effect of  $\text{ZnS:Mn}^{2+}$  nanoparticles in PVB films.

This research was supported by the U.S. Army Research Office (DAAH 04-96-10416), the U.S. Department of Energy (DE-FRO2-94ER757640), and NASA (MURC-NCCW-00088).

The authors from the Changchun Institute of Physics thank the National Foundation of Natural Sciences of China for funding.

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