

Optical Properties of Manganese-Doped Nanocrystals of ZnS

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We report for the first time that doped nanocrystals of semiconductor can yield both high luminescent efficiencies and lifetime shortening at the same time. Nanocrystals of Mn-doped ZnS with sizes varying from 3.5 to 7.5 nm were prepared by a room temperature chemical process yielding an external photoluminescent quantum efficiency 18% and a luminescent decay at least 5 orders of magnitude faster than the corresponding Mn^{2+} transition in the bulk crystals. The quantum efficiency increases with decreasing size of the particles. These results suggest that doped nanocrystals are indeed a new class of materials heretofore unknown.

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During the past few years, the preparation and characterization of materials in the nanometer scale has provided not only new physics in reduced dimensions, but also the possibility of fabricating novel materials. Buckyballs (C_{60}), porous Si, and quantum dots of semiconductors are examples of this new class of materials. Nanosize semiconductor crystallites have changed properties, such as an increased energy band gap, which results from quantum confinement [1,2]. Here we report on the optical properties of the first realization of ZnS semiconductor nanocrystals doped with Mn isoelectronic impurities [3]. The Mn^{2+} ion d -electron states act as efficient luminescent centers while interacting strongly with the s - p electronic states of the host nanocrystal into which external electronic excitation is normally directed. Here we show that this electronic interaction provides an effective energy transfer path and leads to high luminescent efficiencies at room temperature. More generally, we feel that nanocrystals doped with optically active luminescence centers may create new opportunities in the study and application of nanoscale material structures.

Nanocrystalline ZnS powder was precipitated by reacting diethylzinc with hydrogen sulfide in toluene to form ZnS. Bulk ZnS is usually doped by thermal diffusion at high temperatures ($> 1100^\circ C$), but since nanocrystallites sinter at extremely low temperatures, they must be doped during precipitation. To dope the ZnS, manganese chloride is reacted with ethylmagnesium chloride to form diethylmanganese in a tetrahydrofuran solvent and added to the reaction. The separation of the particles is maintained by coating with the surfactant methacrylic acid. In the coated ZnS:Mn particle system we observe a gradual but significant increase in the luminescent intensity of Mn^{2+} emission when exposed to exciting 300 nm UV light (UV curing) and the photoluminescent efficiency of 27–33 Å ZnS:Mn nanocrystalline powder is about 18% at room temperature [3]. Our hypothesis is that this enhancement in efficiency results from the passivation of

surface of the ZnS:Mn nanocrystals and is related to the photopolymerization of the surfactant.

The optical properties of these doped nanocrystals were studied at room temperature with the band-to-band excitation in ZnS being used to excite the Mn^{2+} emission. The subsequent transfer of electron and hole into the electronic level of the Mn ion leads to the characteristic emission of Mn^{2+} in ZnS [4]. This yellow emission observed in the photoluminescence of bulk ZnS:Mn is associated with the Mn^{2+} $4T_1-6A_1$ transition and it peaks at around 2.12 eV (585 nm) with a half width of 0.23 eV at room temperature. The photoluminescence (PL) and photoluminescence excitation (PLE) data for the nanocrystals of ZnS:Mn are compared to bulk ZnS:Mn powder in Fig. 1. The perturbation by the host crystal fields renders the otherwise spin forbidden d - d intraion transition partially electric dipole allowed (through the mixing of opposite spin states). The large linewidth of the yellow emission is due to a combination of inhomogeneous

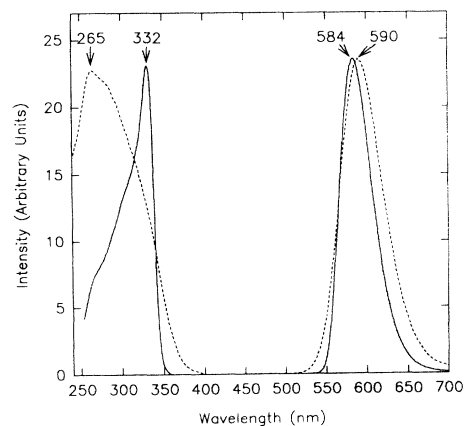


FIG. 1. The PLE and PL spectra of bulk (solid lines) and nanocrystalline (dashed lines) ZnS:Mn. Note that the position of the PLE peak reflects the band edge of the host.

geneous broadening and phonon assisted transitions [5]. The PL peak of the Mn^{2+} transition in the nanocrystal is 2.10 eV, which is slightly shifted to a lower energy when compared to the peak in the bulk sample. The PLE spectrum for the bulk ZnS:Mn powder peaks at 3.73 eV (332 nm). This PLE peak should be compared with the room temperature energy band gap (E_g) of 3.66 eV for the cubic ZnS single crystal. In contrast, the PLE spectrum for 30 Å nanocrystals peaks at 4.68 eV (265 nm). This large shift of 1.02 eV to a higher energy is interpreted [4] as being due to an increase in the value of s - p electron band gap in the ZnS nanocrystals from quantum confinement. The exciton Bohr radius (a_B) for ZnS is estimated to be ~ 25 Å [6]. For ZnS nanocrystals smaller than 50 Å in diameter (D), the size dependent shift of E_g to higher energies is estimated within the framework of the effective mass theory [1] and for $D=30$ Å particles the estimated energy shift is 0.55 eV [6]. This should be compared with experimental value of 1.02 eV. There are several possible causes for this discrepancy. (i) The theoretical estimate of E_g begins to deviate from the real value as the particle size gets significantly smaller than a_B . (ii) The size of the particle as estimated from transmission electron microscopy only provides an approximate value of particle size within a given range of size distribution. (iii) The PLE yields an approximate value of the s - p energy band gap.

These results become clearer when we look at the dependence of peak position and intensity of PLE on the size of the nanocrystal. First, the highest energy peak in the PLE spectra is indicative of the band edge absorption of the smallest particle. This is consistent with the observation that in a given sample, the peak of the PLE spectrum shifts to higher energy under UV exposure. Second, the highest energy peak of the PLE spectra in UV cured sample has the highest intensity suggesting that the smallest particles are contributing the most to the Mn^{2+} emission. This is again confirmed by measuring increased efficiency as a function of decreased particle size [3] and is discussed later. The key feature in the present work for Mn doped ZnS nanocrystallites, apart from increasing E_g with decreasing size, is that the spatial confinement of the electron hole at the nanocrystal also profoundly affects the recombination kinetics of the Mn^{2+} ion d -electron luminescence.

The correlation between E_g , as measured through PLE spectra using yellow emission from Mn ion as a probe, and different sizes of the nanocrystals confirms that the energy transfer occurs from s - p electron-hole pair band states to the d states of Mn ion. This establishes beyond doubt that the Mn ion is an integral part of the ZnS nanocrystal. Based on earlier experiments performed on bulk powders [5], we suggest that Mn^{2+} is occupying the Zn^{2+} cation site in ZnS nanocrystals. Recent extended x-ray-absorption fine structure (EXAFS) experiments [7] also confirms that Mn is occupying a Zn site. This also has been observed in nanocrystals of $ZnMnS$ [8]. The

determination of E_g of the host crystal by measuring the PLE peak responsible for the impurity emission gives us an elegant and rapid technique to assess the size distribution and their relative contribution to total luminescent efficiency in a given multiple size nanocrystal sample.

We now turn to the energy transfer process and its dynamics in the ZnS:Mn nanocrystals. The best external quantum efficiency measured to date in 30 Å nanocrystals has been about 18% [3]. Such efficiency is to our knowledge the highest observed in nanocrystals and we propose that it is a direct consequence of fast transfer of the excited electron-hole pairs into the Mn-ion impurity, and a subsequent efficient and fast radiative recombination of the d -electron excitation. This contrasts with the circumstance usually encountered with undoped nanocrystals where the surface provides a very effective nonradiative path for the electron-hole pairs [9]. The problem is acute in the small particle limit (such as considered here), since the surface to volume ratio of a nanocrystal is quite large. Therefore, even with the partial passivation provided by the UV-cured polymer coating, it is still remarkable that these high luminescent efficiencies are observed in our experiments.

In bulk crystalline material, the partially spin-forbidden Mn^{2+} $4T_1-6A_1$ transition has a lifetime of about 1.8 msec [5]. In our nanocrystals, we find dramatic shortening of this decay time by several orders of magnitude. Figure 2 shows the transient yellow luminescence for 30 Å size particles, measured by exciting the host ZnS nanocrystal above the band gap by a picosecond pulsed laser. The laser pulse is also shown as a reference. In the inset we have plotted the luminescence decay on a semilog scale. Two distinct decay time constants of 3.7 and 20.5 nsec are identified, suggesting that perhaps two different recombination centers may be involved. In PLE spectra, frequently several peaks are also observed which suggests that we have distinct and discrete size distribution. The different sizes of particles as observed in PLE spectra during the UV curing process, probably contrib-

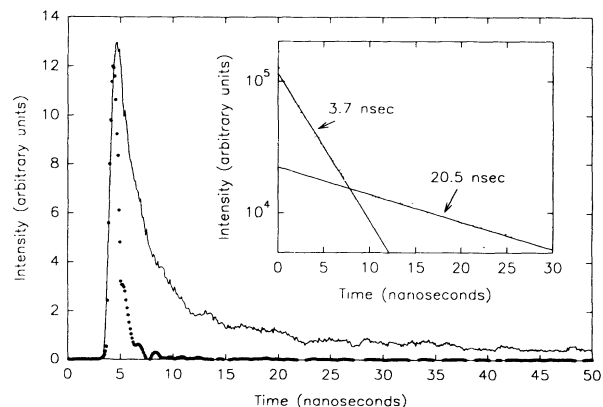


FIG. 2. The time decay of the light emission from 30 Å nanocrystalline ZnS:Mn. Inset: The time decay is separated into its exponential decay components.

ute to these two separate decay times. We have carefully examined any remaining longer lived components in the PL, and conclude that the occurrence of the dominant radiative decay on a nanosecond time scale is indeed a characteristic of the small ZnS:Mn nanocrystals.

On the other hand, we have not been successful in measuring the transfer rate of the electron-hole pairs or exciton to Mn^{2+} luminescence because the energy transfer occurs on a picosecond time scale [10] and is below our experimental resolution. This transfer time is an important parameter towards understanding the size dependence of the internal efficiency. In our discussion we have simply assumed that the external efficiency is related to internal efficiency by a constant factor and it does not depend on size. Additional information about the relationship between the s - p band states and the d electrons has been sought in magnetoluminescence experiments [11]. These experiments are motivated by the fact that the ZnS:Mn system is also a diluted magnetic semiconductor in which the p - d and s - d exchange interaction can give rise to the so-called giant Zeeman effects at the band gap at low temperatures [12]. Figure 3 shows the influence of a magnetic field on the band edge, identified from the PLE spectrum of the yellow luminescence, at $T=2$ K for bulk ZnS:Mn powder and a 35 Å nanocrystalline sample. Note that while the bulk material shows a Zeeman effect (of several tens of meV), this is not observed in the nanocrystal (of comparable average Mn concentration) within the spectral resolution of the experiment (~ 5 meV).

We now argue that the decay time measurements of the d -electron luminescence and the (null) magnetoluminescence result at the s - p band gap are consistent with a strongly coupled sp - d electron system in the nanocrystals. Given the high external quantum efficiency of the yellow emission, the extraordinary shortening in the d -electron decay time must include a significant degree of hybridization of the s - p host states with those of the d

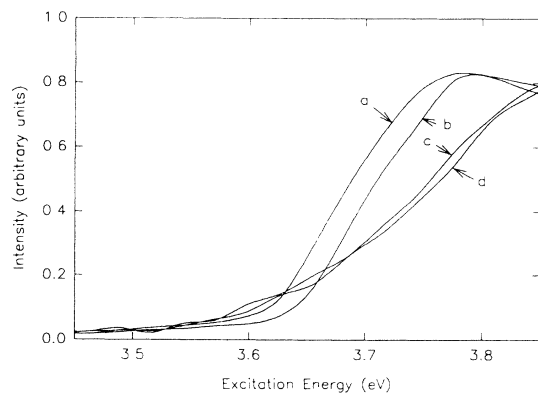


FIG. 3. Magnetic field shifts of the PLE spectra (band edge 590 nm) of ZnS:Mn at 1.6 K. (a) is bulk with $H=4.5$ T, (b) is bulk with $H=0$, (c) is nanocrystalline with $H=4.5$ T, and (d) is nanocrystalline with $H=0$.

electron. It is unlikely that modified crystal fields, given the proximity to a surface in a nanocrystal, can alone be responsible for such admixing. Rather, we believe that the electronic confinement experienced by the s - p states and the corresponding increase in their spatial overlap with the localized d -electron states promotes the process of hybridization. An immediate benefit of the mixing is, of course, an enhanced energy transfer (capture) rate of the electron-hole pairs at the d -electron sites.

In an undoped quantum dot, the external band edge as well as impurity related luminescent efficiency at room temperature is too low to be of any practical consequence [13]. In the case of undoped nanocrystals, in the limit of a strong confinement case when $D < a_B$ [1], the electron and hole in a nanocrystal occupy the individual lowest eigenstate with relatively little spatial correlation. These separately trapped electrons and holes at different locations recombine through a combination of radiative and nonradiative tunneling and show long decay time [1,14]. The efficiency of such e - h recombination at room temperature is rather low and surface recombination probably remains the dominant nonradiative path. This is schematically represented in Fig. 4(a). The quantum efficiency η_{bb} , for the band-to-band recombination is given by $\eta_{bb} = \tau_{bb}^{-1} / (\tau_{bb}^{-1} + \tau_{NR}^{-1})$ where τ_{bb}^{-1} and τ_{NR}^{-1} are the band-to-band recombination and nonradiative surface recombination rate, respectively. The capture rate τ_{NR}^{-1} should depend on the number of surface atoms per unit volume which is inversely proportional to the size of the particle (i.e., D^{-1}). τ_{bb}^{-1} should be weakly dependent on the size of the particle [14]. From above it follows that $\eta_{bb} \rightarrow 0$ as $D \rightarrow 0$.

But in doped quantum dots of size less than a_B , we observe a large increase in external efficiency with decreasing size of the nanocrystal. We believe this effect is related to modulation of electron-hole transfer rates in a nanocrystal due to electron-hole localization near the impurity. For the recombination process shown in Fig. 4(b), the internal efficiency η is simply given by $\eta = \tau_R^{-1} / (\tau_R^{-1} + \tau_{NR}^{-1})$ where τ_R^{-1} and τ_{NR}^{-1} are the radiative and nonradiative rates related to Mn and surface states, respectively. The radiative capture rate τ_R^{-1} is proportional to the number density of Mn^{2+} at the Zn site within the nanocrystal [15], hence, it is inversely proportional to the volume of the nanocrystal (i.e., D^{-3}) for the case of a single Mn ion within a nanocrystal. The nonradiative decay rate τ_{NR}^{-1} varies as D^{-1} as expressed above. Thus, the internal efficiency can be expressed as $\eta = (1 + \beta D^2)^{-1}$ where β is related to the ratio τ_R / τ_{NR} . In the case of all surface related nonradiative recombination, where $D \rightarrow \infty$, $\eta \rightarrow 0$; and in the limit $D \rightarrow 0$, the internal efficiency goes to unity.

We have plotted the functional dependence of efficiency on the size of the doped nanocrystal in Fig. 4(c). The presence of an impurity within the nanocrystal and the localization of electron and hole wave function due to quantum confinement is schematically represented in Fig.

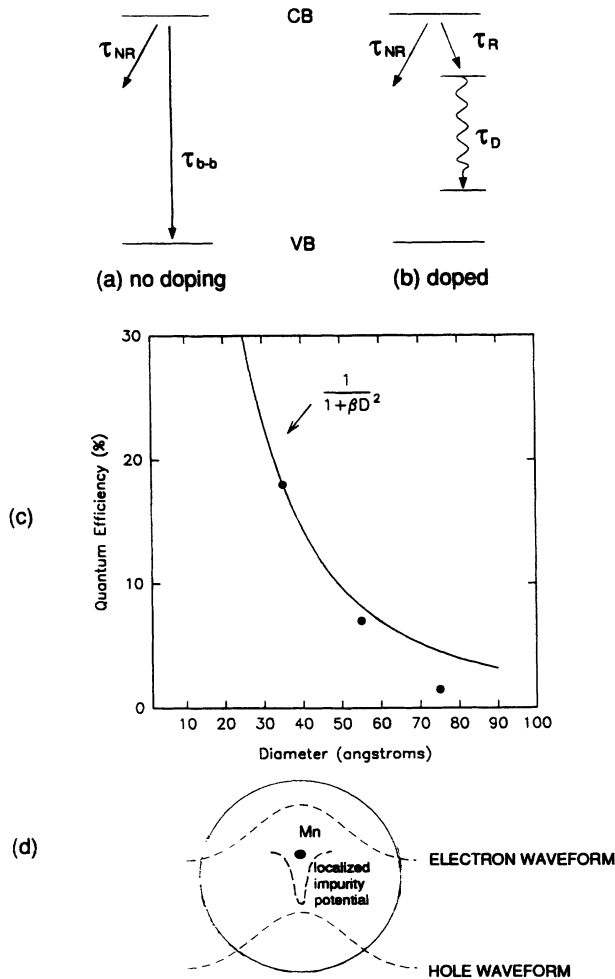


FIG. 4. (a) Schematic representation of the capture process in a nanocrystal without an impurity. (b) Same as (a) with an impurity. (c) Variation of external luminescent efficiency as a function of the size of the nanocrystals. Note that there is apt to be a significant error margin in the PL efficiency measurements, but the values are consistent with relative emission intensities measured separately. (d) A model depicting the overlap of electron-hole wave function with a localized impurity potential in a nanocrystal.

4(d). Because of this localization, smaller particles would have energy transfer to impurity faster than the transfer associated with either band-to-band or surface recombination. The measured values of the efficiency for 75, 55, and 30 Å nanocrystals are also plotted in Fig. 4(c).

The enhancement of external efficiency in Mn doped ZnS nanocrystals is not only a consequence of the faster energy transfer to Mn^{2+} ion but also is connected to the simultaneous change of the decay rate of Mn^{2+} emission. The faster decay time as a result of strong $sp-d$ mixing due to localization of electron and hole on Mn^{2+} , is necessary for this enhancement. If the lifetime of Mn^{2+} emission remained as long as in the bulk crystal (1.8

msec), faster transfer rate would not result in high internal efficiency because the light output would saturate at very low levels of excitation. In summary, we report large external luminescent efficiencies in doped nanocrystals accompanied by shortening of lifetime of the transition associated with the impurity. These results are explained on the basis of the interaction of the sp electron hole of the host (ZnS) and the d electrons of the impurity (Mn). Further theoretical and experimental work is needed to understand the detailed physics of these doped nanocrystals.

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