

Invited

Doped Nanocrystals of Semiconductors— A New Class of Luminescent Materials

R.N.Bhargava

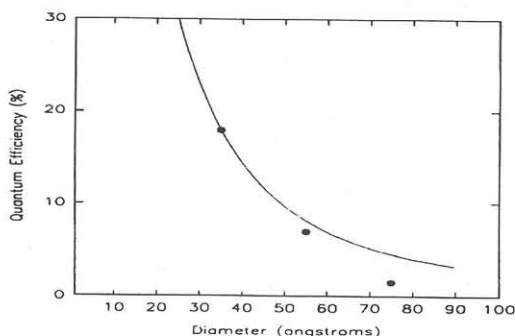
Nanocrystals Technology
P.O.Box 820 Briarcliff Manor, NY 10510 USA

Recently we have reported efficient impurity-induced luminescence in ZnS:Mn nanocrystals at room temperature. The interaction of the s-p electrons of the host with d-electrons of the impurity and their hybridization results in high luminescent efficiency accompanied by shortening of the lifetime of the Mn^{2+} d-d transition. This dramatic reduction of life-time without any loss of efficiency is a direct consequence of the strong e-h localization and impurity confinement in a 0-D quantum dot.

In the quantum dot limit, the surface dominates the recombination process thus yielding a very low quantum efficiency. By incorporating a *single impurity in a quantum confined structure* the dominant recombination process can be transferred from the surface to the impurity. If the impurity-induced transition can be localized as in the transition metals or rare-earth elements, the radiative efficiency of the impurity induced emission becomes high.

Recently, we have fabricated and characterized the properties of *doped nanocrystals* (DNC) of the $ZnS:Mn^{2+}$ [1]. The DNC's were prepared by an organometallic reaction chemistry at room temperature. The DNC's, ranging in size from 35Å to 70Å, were passivated using monomer to prevent agglomeration. The surface passivated quantum dots were characterized optically for its efficiency and its recombination kinetics.

To date, we have observed that the room temperature quantum efficiency is size dependent, increasing from <1% at 70Å to >20% at 35Å.



The energy transfer between the host and Mn impurity in 35Å DNC particle occurs in time less than 20psec.

The luminescence decay time of the Mn^{2+} emission in DNC's varies between 300 psec and 20 nsec. This widely differs from the corresponding Mn decay time of 1.8 msec in bulk ZnS. This change in six orders of magnitude in the decay time is a consequence of the e-h localization and the hybridization between host s-

p and impurity d-electrons. Given the high efficiency of the yellow emission of the Mn, 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-electron. It is unlikely that the 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 of the impurity.

The e-h localization in a confined quantum structure is also responsible for the enhanced external luminescent efficiency of the impurity transition. This is a direct consequence of the modulation of the e-h transfer rates in a nanocrystal due to e-h localization near the impurity. In this system, the

nonradiative capture of the free carriers by the extended surface states remains slow while the carrier capture /transfer to impurity increases as the size of the nanoparticle decreases. This results in a size dependent efficiency observed in figure 1. It is thus critical to prepare DNCs in the size less than the Bohr radius a_B before they become efficient.

We have also studied EXAFS and EPR in these samples. The EXAFS results show that Mn dopant occupy the Zn sites of ZnS in the nanocrystals but with substantial local lattice distortion depending on the nanocrystal size distribution. These results also indicate that the effective valence of Mn in these samples is close to +2 as in the bulk ZnS:Mn samples. The EPR data also identifies the presence of isolated Mn^{2+} on a Zn-site with the splitting due to hyperfine structure from ^{55}Mn nucleus. However, the spectrum differs markedly from that of Mn in single crystal ZnS. The differences are possibly due to the removal of the cubic-symmetry due to orientational disorder associated with the random orientation of the nanocrystals. Secondly, there is a disorder arising from the distribution in the position of the Mn^{2+}

within the nanocrystal. Axial or lower crystal fields arise when Mn is near the surface and are responsible for the broad background signal.

The band structure changes, the electron-hole localization and the hybridization describes a new material system where the semiconductor quantum dots behave like a quasi-atomic like system and yields an ultrafast, efficient luminescent material. These new luminescent materials should impact many applications where high-efficient phosphors are used. Both the physics and the applications of doped nanocrystals will be presented.

[1] R.N.Bhargava, D. Gallagher, X. Hong and A. Nurmikko "Optical Properties of Manganese-Doped Nanocrystals of ZnS", Phys. Rev. Letters **72**, 416 (1994)

Collaborators:

Efim Goldburt_(Nanocrystals Technology, Briarcliff Manor NY), D. Gallagher (Philips Laboratories), P. Klein , T.Norris (University of Michigan, Ann Arbor), J.Soo and Y.H.Kao (State University of New York, Buffalo), T.Kennedy (Naval Research Lab.)