

SIZE DEPENDENCE OF LUMINESCENCE EFFICIENCY OF SEMICONDUCTOR NANOPARTICLES

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ABSTRACT

This paper review recent advances in luminescence of semiconductor nanoparticles. With reducing size of the semiconductor nanoparticles the luminescence of low dimensional systems i.e. two dimensional, one-dimensional and zero dimensional systems has become important and interesting topic of research in the field of material science. Two dimensional systems include quantum wells and layered materials, quantum wire and linear chain like materials constitute one-dimensional systems and quantum dots and microcrystalites are zero-dimensional. In low dimensional systems electron and holes are spatially confined causing quantum confinement effects. It has been found that the efficiency of low dimensional system increases with decreasing size R of the semiconductor nanoparticles. The luminescence efficiency of ZnS:Mn nanocrystals increases with decreasing size R and follows the relation :

$$\eta = \frac{1}{(1 + \beta R^2)}$$

KEY WORDS: Semiconductor nanoparticles, Luminescence.

INTRODUCTION

Nanoparticle or an ultrafine particle is a small solid whose dimension lies in the approximate range of a few nm to a few hundred nm. Semiconductor nanoparticles having size less than the critical size M of charge carriers are called quantum dots or q particles. Nanophase materials generally include nanocrystalline thin films, sintered materials with ultra-fine grain structure, and loosely aggregate nanoparticles.

Size reduction affects most of the physical properties (structural, magnetic, optical, dielectric, and thermal, etc.) due to surface effects and quantum size effects. Owing to the extremely small dimensions, these materials exhibit properties, which are fundamentally different from, and often superior to those of their conventional counterpart. In recent past, there has been considerable interest in the study of size effect in semiconductors of reduced dimension (in nanometer scale) due to their applications in optoelectronic devices, single electron devices, resonant tunneling devices, memory devices, magnetic sensors, catalysis, etc ((Singh and John, 1997; Itoh et al., 1988; John and Singh, 1996; Bhargava et al., 1994; Wang and Herron 1991). Optical spectroscopy being the non-contact method, has proved to be the most suitable technique to monitor the size-evolution of the electronic structure. The present paper reports the energy conversion, characteristics of semiconductor nanoparticles.

THEORY

In bulk crystalline ZnS:Mn, the partially spin-forbidden $Mn^{2+} 4T_1 \rightarrow 6A_1$ transition has a lifetime of 1.8 ms at room temperature. In ZnS:Mn of 3nm size there are two lifetimes $\tau_1=3.7ns, \tau_2=20.5ns$ In ZnS : Cu $\lambda_{em}=480nm, \tau_1=2.9ns, \tau_2=20.5ns$, , two different recombination centers may be involved in nanoparticles firstly the recombination centers lying on surface and secondly the recombination centers lying inside the bulk.

To interpret these observation it is suggested that the hybridization of s-p electron state of host with the d-electron state of Mn^{2+} , is caused to a significant extent by the spatial overlap of these states owing to the confinement.

The luminescence efficiency η may be expressed as:

$$\eta = \frac{\alpha_r}{\alpha_r + \alpha_{nr}} \quad \dots(1)$$

α_r and α_{nr} are radiative and non-radiative rates, respectively.

The radiative recombination takes place at the surface. Thus, α_{nr} should depend on the number of surface atoms per units volume and it may be expressed as:

$$\alpha_{nr} \propto \frac{4\pi R^2}{\frac{4}{3}\pi R^3} \propto \frac{1}{R} \quad \dots(2)$$

α_r should depend on the number of Mn^{2+} at Zn^{2+} sites. In case of a single Mn^{2+} ion within a Nano crystal may expressed as:

$$\alpha_r \propto R^{-3} \quad \dots(3)$$

Thus from Eqs (1), (2) & (3) we get:

$$\eta = \frac{\frac{C_1}{R^3}}{\frac{C_1}{R^3} + \frac{C_2}{R}} = \frac{1}{(1 + \beta R^2)} \quad \dots(4)$$

where $\beta = \frac{C_2}{C_1}$

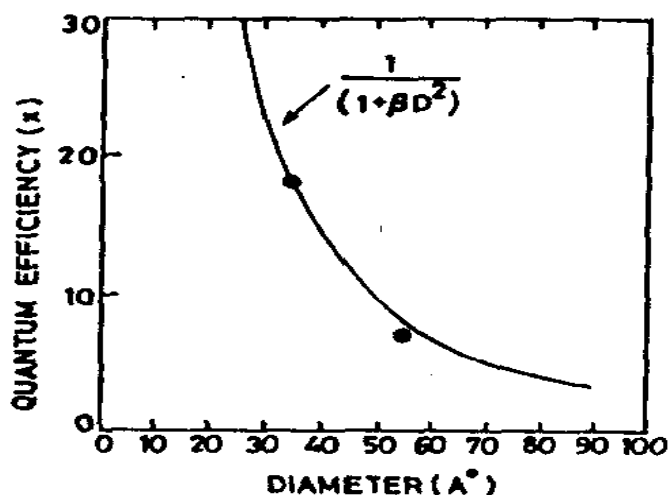


Fig.- 01 Variation of luminescence quantum efficiency of ZnS:Mn²⁺ nanocrystals as a function of the radius.

The solid line represents the equation $\frac{1}{(1 + \beta R^2)}$

EXPERIMENTAL SUPPORT TO THE PROPOSED THEORY

Fig. (1) shows the size dependence of the luminescence efficiency of ZnS:Mn nanoparticles. It is seen that the dependence of η or R of Eq (4). To perform this experimental [4] precipitated, nanocrystalline ZnS powder by reacting diethylzinc with hydrogen sulfide in toluene to form ZnS. Bulk ZnS is usually doped by thermal diffusion at high temperatures [$>1100^\circ\text{C}$] 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 a gradual but significant increase is observed in the luminescent intensity of Mn²⁺ emission when exposed to exciting 300nm UV light (UV curing) and the photo luminescent efficiency of 27-33Å ZnS:Mn nanocrystalline powder is about 18% at room temperature.

CONCLUSIONS

The important conclusions are drawn from the present investigation

- (i) It is found that the luminescence efficiency of ZnS:Mn nanocrystals increases with decreasing size R and follows the relation :

$$\eta = \frac{1}{(1 + \beta R^2)}$$

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