



REVIEW OF LUMINESCENCE PROPERTIES OF SEMICONDUCTOR NANOCRYSTALS

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ARTICLE INFO

Article History:

Received 10<sup>th</sup> November, 2018

Received in revised form 2<sup>nd</sup>

December, 2018

Accepted 26<sup>th</sup> January, 2018

Published online 28<sup>th</sup> February, 2019

Key words:

Photoluminescence, Quantum Confinement Effect, nanocrystals.

ABSTRACT

This paper reviews recent advances in luminescence properties of semiconductor nanocrystals. The onset of absorption takes place at longer wavelength with reducing the size of the semiconductor nanocrystals. Such blueshift with reducing size of the nanocrystals is the reflection of bandgap increase owing to the quantum confinement effect. In most cases blueshift in the peak of photoluminescence (PL) spectra is observed with reducing size of the nanocrystals, but the luminescence from certain surface states may give rise to the red-shift with reducing size of the nanocrystals. Whereas the decay time of luminescence decreases, the quantum efficiency of luminescence and Stokes shift increase with reducing size of the nanoparticles. The photoluminescence intensity of nanocrystals decreases with increasing temperature. It is optimum for a particular concentration of the dopants in the nanoparticles. The luminescence of semiconductor nanoparticles is exciting to the researchers and it has several important potentials

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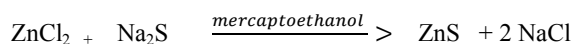
INTRODUCTION

In the recent past, nanomaterials have drawn greater attention of scientific community due to their size specific properties that are different from the bulk materials. 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. 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 studies we have investigated the energy conversion and stokes shift properties of semiconductor nanoparticles.

Experimental Details

The most important step in the studies of the nanoparticles is their synthesis. Nanophase materials generally include nanocrystalline thin films, sintered materials with ultrafine grain structure and loosely aggregate nanoparticles.

Nanoparticles can be prepared by chemical and physical methods. Khosravi *et al* [1] have reported a simple chemical bath deposition method of preparing ZnS and doped ZnS nanocrystals from the aqueous solution of ZnCl<sub>2</sub>, mercaptoethanol (C<sub>2</sub>H<sub>5</sub>OSH) and sodium sulphide (Na<sub>2</sub>S) in which the following reaction takes place:



Lokhande *et al* [2] have reported the preparative conduction for nanocrystalline thin films of CdS, CdSe, HgS, MnS, In<sub>2</sub>S<sub>3</sub>, ZnS, Bi<sub>2</sub>S<sub>3</sub>, and As<sub>2</sub>S<sub>3</sub>. Nanoparticles can be characterized using high resolution transmission electron microscopy (HRTEM), small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), X-ray diffractions (XRD), low frequency Raman scattering, optical absorption, photoluminescence spectroscopy and longitudinal-optic(LO) phonon Raman scattering. The concentration of dopants in bulk can be determined using atomic absorption method. So far as the luminescence measurement is concerned, all the conventional techniques used for phosphors can be used also for the nanoparticles.

Optical Absorption in Nanoparticles

The nanocrystalline semiconductors exhibit the quantum confinement effect market by the absence of excitonic radius. Table 1 show the Bohr structure, when the crystalline size is comparable to exciton Bohr exciton radius, bulk and effective band gap (depending upon the crystalline sizes) of some important semiconductors. Depending upon the crystalline size, two limiting confinements can be observed in practice.

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When the radius of the crystalline  $R$  is smaller than  $\sim 2$  exciton Bohr radii, electrons and holes are considered as two confined particles, bound by an enforced Coulomb interaction, where the confinement energy becomes larger than the Coulomb energy. When the crystallite radius is longer than  $\sim 4$  exciton radii, the ground exciton is treated as a rigid sphere, confined as a quasi particle.

**Table 1** Physical parameters of different nanocrystalline semiconductors

Materials	Bulk Band Gap $E_g$ in eV	Crystalline size in Å	Band gap $E_{ng}$ in eV	Bohr radius $a_B$ in Å
ZnS	3.5	7	$\sim 5.2$	15
CdS	2.4	12	3.2	30
CdSe	1.7	18	2.4	$\sim 30$
ZnTe	2.26	40	3.2	$\sim 60$
PbS	0.47	13	2.4	Large

In between these limiting cases both the electron-hole confinement and their Coulomb interaction are considered. In the individual confinement limits, the lowest energy of an electron-hole pair can be written as [3].

$$E = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2} - 1.786 \left(\frac{e^2}{\epsilon R}\right) - 0.248 E_{ex} \quad \dots (1)$$

where  $\mu$ ,  $\epsilon$ ,  $E_g$ ,  $E_{ex}$  and  $R$  are the reduced mass, dielectric constant, band gap, exciton binding energy, and radius of nanocrystallites, respectively.

The exciton binding energy is  $E_{ex} = e^2/4\pi\epsilon_0$  and the corresponding Bohr radius is  $a_B = (4\pi e^2/\mu\epsilon^2)$ . In the weak confinement limit, the lowest energy is given by

$$E = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2} - E_{ex} \quad \dots (2)$$

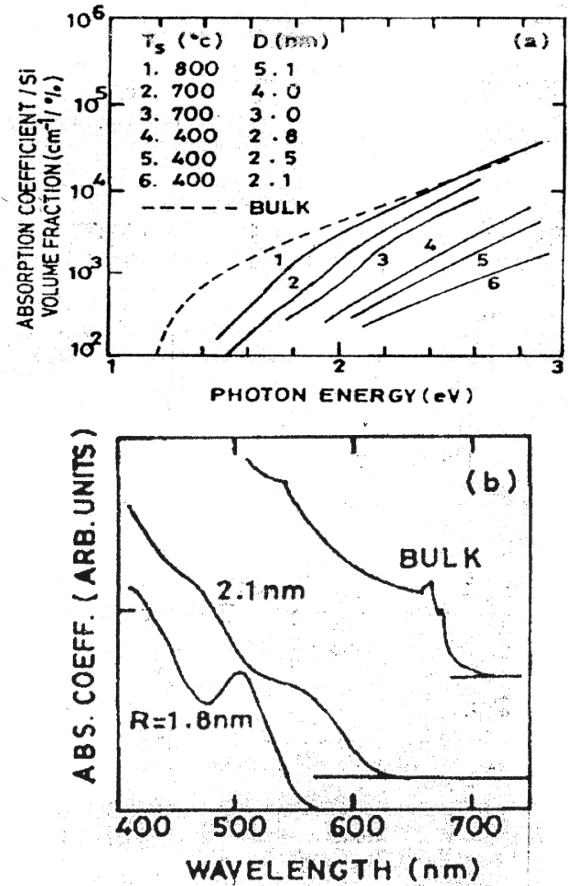
where  $M = (M_e + M_h)$ , is the translation mass,  $M_e$  and  $M_h$  being the electron and hole mass, respectively.

In case of nanocrystalline, the electrons, holes and excitons have limited space to move and their motion is possible for definite values of the energy. thus, their energy spectrum is required. As a result, the continuum of states in the conduction and valence band, respectively are broken down into discrete states with energy spacing relative to the band edge which is approximately inversely proportional to the square of particle size [4] and reduced mass as is evident from eq. (1). The third and fourth terms which originate from the Coulomb interactions and polarization provide the small correction to the energy. The highest occupied valance band and the lowest unoccupied conduction band are shifted to a more negative and positive values, respectively resulting in widening of the band gap. This leads to a effective band gap larger than its bulk value that can be observed through optical absorption studies. in all cases, as the crystalline size is narrowed down there will be a blue shift in the absorption spectra along with the oscillatory structure which is signature of the size quantization effect. From the blue shift the average radius of the nanocrystallites can be estimated. a hyperbolic band model has been proposed to explain the change of energy gap as a function of particles size [5]. The equation derived for the band gap  $E_{gn}$  of nanocrystallites according to this model is given by

$$E_{gn} = \left[ E_{gb}^2 + 2\hbar^2 E_{gb} \left(\frac{\pi}{R^2}\right)/m^* \right]^{1/2} \quad \dots (3)$$

where  $E_{gb}$  is the band gap for the bulk semiconductor,  $R$  is the particles radius, and  $m^*$  is the effective electron mass. If  $E_{gn}$  are known, the crystalline size can be estimated from eq. (3). The change in absorption followed by a change in colour with reducing size of nanoparticles is an interesting effect. For example, the bulk CdS semiconductor with energy gap of 2.42 eV is orange in colour. As the clusters become smaller and energy gap increases, it becomes yellowish and ultimately white. In fact, the observation of different colours due to CdSe in glass matrix led scientists to think that CdSe nanoparticles of different sizes may have been formed.

Figure 1(a) shows the optical absorption spectra of Si microcrystals doped into  $\text{SiO}_2$  glass film prepared by the rf magnetron sputtering technique [6]. In this case, the average diameter of microcrystals was estimated by transmission electron microscopy observation and the absorption spectra were recorded using Shimadzu or 3100 S spectrometer. It is seen from the figure that the energy corresponding to the onset of absorption increases with reducing size of the nanocrystals. Thus the blue shift is clearly evident with reducing size of the nanocrystals. Figure 1 (b) illustrates the optical absorption spectra of CdSe prepared by precipitation technique [7]. In this case, also the blue shift with decreasing size of the crystals is clearly observed. The blue shift has always been optical absorption spectra have been made on several nanocrystals whereby the blue shift has always been found with their reducing size.

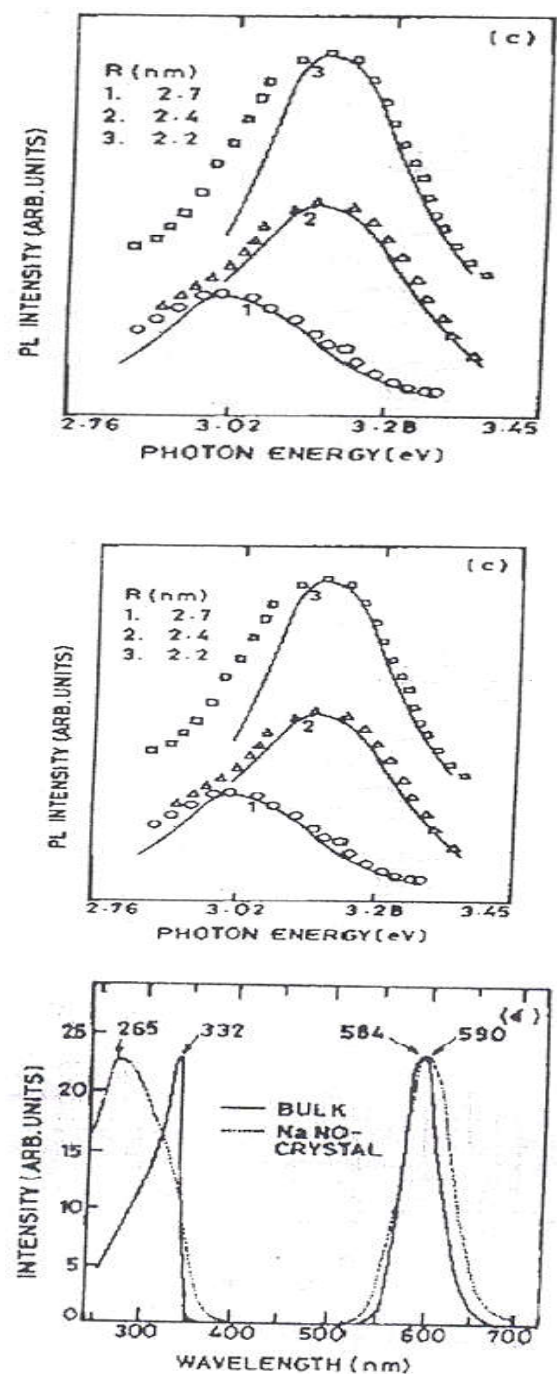
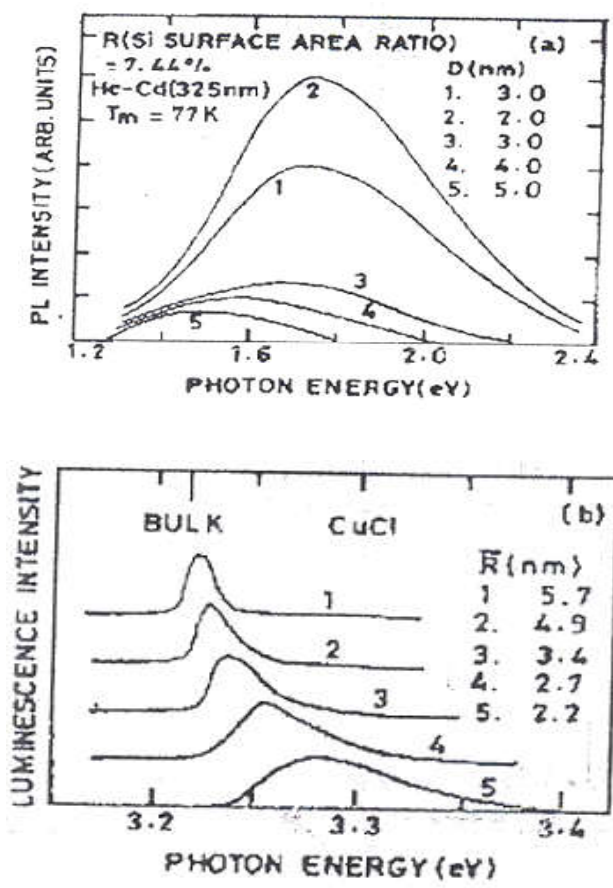


**Figure 1** (a) Optical absorption spectra for Si nanocrystals (6) and (b) the optical absorption spectra of CdS nanoparticles prepared by precipitation (7)

**Luminescence Properties of Semiconductor Nanoparticles**

**Spectral Characteristics**

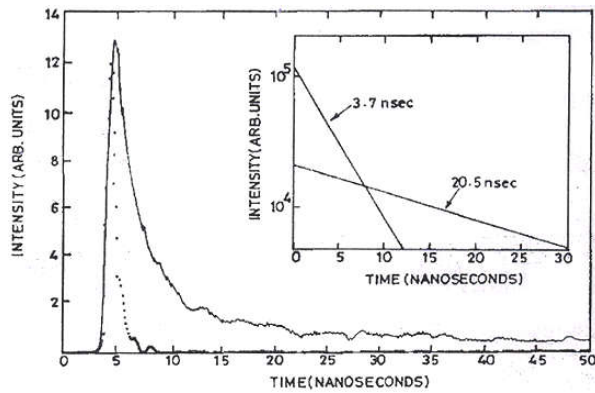
Figure 1(a) shows the effect of particle size on the photoluminescence spectra of Si nanocrystals embedded in SiO<sub>2</sub> glass films (6). It is evident that the peak position of PL exhibits mark blue-shift with reducing size of the nanocrystals. Figure 1 (b) shows the excitation luminescence spectra of CuCl for different microcrystallites [8]. In this case, also a blue shift is observed with decreasing size of the nanocrystals. The observed blue shift in nanocrystals is a reflection of the band-gap increase owing to the quantum confinement effect. The PL spectrum of ZnSe shown in Figure1 (c) also indicates the blue shift with reducing size of the nanocrystals [9]. Figure1 (d) shows the luminescence and excitation spectra of ZnS: Mn<sup>2+</sup> bulk and nanocrystals [10]. In the luminescence spectrum of nanocrystals the peak is only slightly different from that of the bulk, but in the excitation spectrum it is considerably shifted to the high –energy side. The peak position of 332 nm (3.73 eV) of bulk corresponds to the band gap energy of the ZnS host. The observed blueshift to 265 nm (4.68 eV) in nanocrystals is a reflection of the bandgap increase owing to the quantum confinement effect.



**Figure 1** (a) PL spectra of (a) Si nanocrystals (ref.(6)), (b) CuCl nanocrystals (8), (c) ZnSe films deposited on quartz at 20 Pa and at different substrate temperature (9), and (d) Luminescence and excitation spectra of ZnS:Mn<sup>2+</sup> at room temperature. Solid line-bulk phosphors, dashed line- nanocrystals (10).

**Temporal Characteristics**

Figure 2 shows the transient yellow luminescence for 3 nm size particles measured by exciting the host ZnS nanocrystals above the band gap by a picoseconds pulsed laser [11]. Two distinct decay constants of 3.7 and 20.5 ns are identified, suggesting that two different recombination centres may be involved. Because the quantum efficiency is high, almost the same as in bulk phosphors, the observed shorting of decay time has to mean that there is an extremely larger enhancement of oscillator strength.



**Figure 2** The time decay of the PL from 3 nm nano-crystalline ZnS: Mn<sup>2+</sup>. The last pulse is shown by dots as a reference. Inset: the time decay is separated into its exponential decay components (10).

To interpret this observation it is suggested that the hybridization of the S-P electron state of the host with the d-electron state of Mn<sup>2+</sup> is caused to a significant extent by the spatial overlap of these states owing to the confinement. However, assuming this kind of hybridization does not completely account for the observed extraordinary shortening of the decay time corresponding to the exceedingly large enhancement of the oscillator strength. One concludes that some unknown dominant mechanism must be involved in this surprising phenomenon in luminescence of zero dimension systems.

$$\eta = \frac{1}{1 + \beta D^2} \quad \dots (1)$$

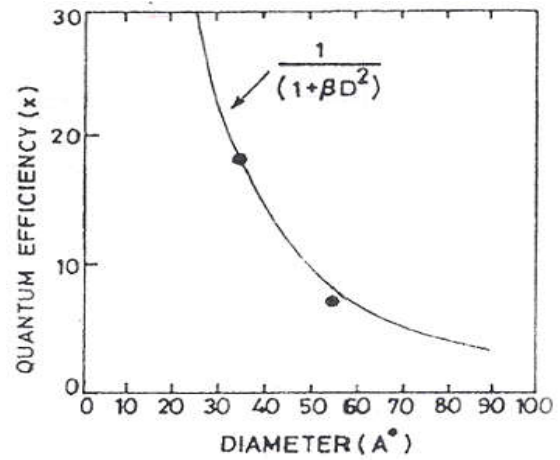
where  $\beta$  is a constant.

In ZnS:Mn<sup>2+</sup> nanocrystals electrons and holes produced by the band-to-band excitation are either captured by Mn<sup>2+</sup> centre to produce luminescence or recombine non-radiatively. The quantum efficiency is expressed as

$$h = \frac{R_r}{R_r + R_{nr}} \quad \dots (2)$$

Where  $R_r$  and  $R_{nr}$  are radiative and non-radiative recombination rates respectively. In nanocrystals, non-radiative recombination is considered to take place at the surface. Thus,  $R_{nr}$  should depend on the number of surface atoms per unit volume, which is inversely proportional to the size  $D$  of the nanocrystals, i.e.  $R_{nr} \propto D^{-1}$ .

$R_r$  is regarded as equal to the electron-hole capture rate, which is proportional to the number density of Mn<sup>2+</sup> at the Zn<sup>2+</sup> sites. In case of a single Mn<sup>2+</sup> ion within nanocrystals, it should be inversely proportional to the volume of the nanocrystals, i.e.  $R_r \propto D^{-3}$ . In this way,  $D$ -dependence of  $h$  can be expressed by Eq. (1).



**Figure 3** Variation of luminescence quantum efficiency of ZnS: Mn<sup>2+</sup> nanocrystals as a function of the diameter. The solid line represents the equation  $\frac{1}{1 + \beta D^2}$  (11).

## CONCLUSIONS

The blue shift with reducing size of the nanocrystals is the reflection of band-gap increase owing to the quantum confinement effect. In most cases blueshift in peak of the PL spectra is observed with reducing size of the nanocrystals. But the luminescence from certain surface states may give rise to the red-shift with reducing size of the nanocrystals. Whereas the decay time of luminescence decreases, the quantum efficiency with the decreasing size of nanoparticles. The PL intensity is optimum for a particular dopant concentration in the nanocrystals. The PL intensity decreases with decreasing size of the nanocrystals.

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