

Nano Particle Size Effect on Photo-Luminescence

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Introduction

The term “nanotechnology” has evolved over the years via terminology drift to mean “anything smaller than microtechnology”. Such as nano powder and other things that are nanoscale in size, but not referring to mechanisms that have been purposefully built from nanoscale components. This evolved version of the term is more properly labeled “nanoscale bulk technology,” while the original meaning of nanotechnology.

Nanophase materials generally include original meaning is now properly labeled “molecular nanotechnology”(MNT), or “nanoscale engineering,” or “molecular mechanics,” or “molecular machine systems,” or “molecular manufacturing.” Recently, the Foresight Institute has suggested an alternate term to represent the nanocrystalline thin films, sintered materials with an ultra fine grain structure and loosely aggregate nanoparticles. Size reduction affects most of the physical properties (structural, magnetic, optical, dielectric, 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 counterparts. The interest in the study of size effect in semiconductors of reduced dimensions (in nanometer scale) is due to their application in solar cells, light emitting diodes, resonant tunneling devices, laser catalyst etc.

When the radius R of the crystallites is smaller than ~ 2 exciton Bohr radii, electrons and holes are considered as two confined particles bound by an enforced coulomb interaction and when crystallite radius is larger than ~ 4 exciton radii, the ground exciton is treated as a rigid sphere, confined as a quasiparticle. In between these two limiting cases both the electron and hole confinement and their coulomb interaction are considered. In case of nanocrystals, the electron, holes and exciton have limited space to move and their motion is possible for definite values of energy. As a result, the continuum of states in the conduction and valance band are broken down into discrete states with energy spacing relative to band edge, which is inversely proportional to the square of the particle radius resulting in the widening of the band gap as compared to the bulk. Quantum dots or nanoclusters exhibit discrete electron energy levels with high oscillator strength and strong luminescence. These systems

have a very high surface to volume ratio and hence surface defects play an important role in their properties. The main aim of present paper is to analyze the size dispersion of nanoparticle gives PL peak at different energies.

Broadening in Photo-Luminescence Peaks

As the optical properties are strongly dependent on particle size, a particle size distribution is expected to cause inhomogeneous broadening of optical spectra. The PL spectra often exhibit well defined peaks associated with band-edge luminescence and recombination at defects. These are also broadened in homogeneously due to particle Size distribution; however there have been few attempts to analyze the spectra quantitatively. Here we will present simple and elegant method for analysis of in homogeneously broadened band edge PL line shape for different particle size distributions.

In order to keep the number of adjustable parameters minimum, the measured PL spectrum of bulk film is used as input. So, considering the photoluminescence arising from the recombination of carriers at the band-edge in the bulk of direct-gap semiconductor with band-gap E_0 . the resulting line shape can be representing by a Gaussian profile.

$$g_{qd}(E, R_0) = \frac{A}{\Gamma\sqrt{2\pi}} \exp\left[-\frac{(E - E(R_0))^2}{2\Gamma^2}\right] \quad \text{-----(1)}$$

where Γ is the parameter representing the intrinsic line width of the PL spectrum arising from the vibronic coupling. The full width at half maximum (FWHM) of Gaussian profile is equal to $(2.354)\Gamma$. Due to quantum confinement effect, the electronic energy levels of a semi-conductor nano-particle (quantum dots) are shifted with respect to bulk. The lowest direct inter-band transition energy of a spherical quantum dot of radius R_0 has been obtained by Brus effective mass approximation as

$$E(R_0) = E_0 + \frac{\hbar^2\pi^2}{2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \frac{1}{R_0^2} - \frac{1.8e^2}{\epsilon_2} - \frac{1}{R_0} + \frac{e^2}{R_0} \sum_{n=1}^{\infty} \alpha_n \left(\frac{S}{R_0} \right)^{2n} \quad \text{-----(2)}$$

Where m_e^* and m_h^* are the effective mass of electron and holes respectively, e is the electron charge, ϵ_2 is dielectric constant of medium and α_n is a function of dielectric constant and S is electron-hole separation. The second term on right hand side of equation (2) represents quantum localization energy. The third and the fourth term correspond to coulomb potential and the polarization energy respectively. Hence blue shift in interband electronic transition is

$$\Delta E(R_0) = E(R_0) - E_0 \quad \text{-----(3)}$$

In view of the shift of the direct interband transition energy, the PL spectrum of quantum-dot will also be shifted by same amount. The PL spectrum for nanoparticles of radius R_0 can thus be given by

$$= \frac{A}{\Gamma \sqrt{2\pi}} g_{qd}^*(E, R_0) \quad \text{-----(4)}$$

If the particle size is not uniform but has a distribution the observed spectrum of the quantum dot system can be taken as the superposition of the contribution from each individual particle. As each particle would exhibit a peak at a position dictated by its diameter, this would result in an inhomogeneous broadening of PL spectrum. The overall line shape can be determined by integrating $g_{qd}(E, R)$ over size distribution $P(R)$ as

$$G(E) = \int P(R) \cdot g_{qd}(E, R) dR \quad \text{-----(5)}$$

In order to keep calculation simple, the distribution $P(R)$ is taken to be Gaussian with mean R_0 and standard deviation σ_R .

$$P(R) = \frac{1}{\sigma_R \sqrt{2\pi}} \exp\left[-\frac{(R - R_0)^2}{2\sigma_R^2}\right] \quad \text{-----(6)}$$

$$= \frac{1}{\sigma_R \sqrt{2\pi}} P^*(R)$$

Therefore,

$$G(E) = \frac{A}{2\pi\sigma_R\Gamma} \sum_{R=R_0-3\sigma_R}^{R=R_0+3\sigma_R} [P^*(R) \cdot g_{qd}^*(E, R)] dR$$

$$= F \cdot \sum_{R=R_0-3\sigma_R}^{R=R_0+3\sigma_R} [P^*(R) \cdot g_{qd}^*(E, R)] dR \quad \text{-----(7)}$$

PL Peak Broadening in CdS and ZnSNANOPARTICLES

I. Using Equation (1) the line shape of bulk CdS can be obtained by substituting the constants for CdS. The constant have been taken in present calculations are $\Gamma=0.1$ and $E_0=2.43$ eV, for ZnS $E_0=3.68$ eV. The value of A has been taken by, considering the maximum PL intensity, as unity i.e.,

$$\frac{A}{2\pi\Gamma\sigma_R} = 1 \text{ and } \Gamma = 0.1$$

$A = 0.25$ Therefore this gives

$$g_b(E) = \frac{0.25}{\sqrt{2 \times 3.14 \times 0.1}} \exp\left[-\frac{(E - 2.43)^2}{2(0.1)^2}\right] \text{ for CdS} \quad \text{-----(8)}$$

$$g_b(E) = \frac{0.25}{\sqrt{2 \times 3.14 \times 0.1}} \exp\left[-\frac{(E - 3.68)^2}{2(0.1)^2}\right] \text{ for ZnS} \quad \text{-----(9)}$$

For nanoparticles of average size 2nm, E(R) is first evaluated with the help of equation(2). Now $g_b(E)$ is calculated for different values of E=2.0, 2.1,.....3.8. Figure (1) shows the PL spectrum of CdS according to equation (8). Figure (4) shows PL spectrum of ZnS according to equation (9).

II. Now by using equation (4), the line shape of monodisperse CdS can be obtained by substituting value for $\sigma_R = 0$, $m_e^* = 0.19$, $m_h^* = 0.8$, $\epsilon_2 = 5.7$, $e = 1.6 \times 10^{-19} \text{C}$, $h = 6.63 \times 10^{-34} \text{J-S}$. For ZnS the value of constants are $\sigma_R = 0$, $m_e^* = 0.14$, $m_h^* = 0.61$, $\epsilon_2 = 8.3$, $e = 1.6 \times 10^{-19} \text{C}$, $h = 6.63 \times 10^{-34} \text{J-S}$. To calculate the value for $g_{qd}(E, R)$ it is necessary to find the value of E(R_0) as shown below

$$E(R_0) = E_0 + \frac{\hbar^2 \pi^2}{2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \frac{1}{R_0^2} - \frac{1.8e^2}{\epsilon_2} - \frac{1}{R_0} + \frac{e^2}{R_0} \sum_{n=1}^{\infty} \alpha_n \left(\frac{S}{R_0} \right)^{2n}$$

Here we see that for calculating E(R_0), last term is neglected because its calculation is not straight forward.

$$E(R_0) = 2.43 + \left(\frac{h}{2\pi} \right)^2 \frac{\pi^2}{2} \left(\frac{1}{0.19} + \frac{1}{0.8} \right) \frac{1}{1.6 \times 10^{-19} \times 9.1 \times 10^{-31} \times 10^{-18} \times R_0^2} - \frac{1.8e^2}{\epsilon_2} \cdot \frac{1}{R_0}$$

Now, $\epsilon_2 = 4\pi\epsilon_0\epsilon_r = 5.7 \times 4\pi\epsilon_0$, but $4\pi\epsilon_0 = \frac{10^7}{c^2}$ therefore,

$$(E, R_0) = 2.43 + \frac{2.44}{R_0^2} - \frac{0.4547}{R_0} \quad (\text{in case of CdS})$$

$$(E, R_0) = 3.68 + \frac{3.31}{R_0^2} - \frac{0.312}{R_0} \quad (\text{in case of ZnS})$$

From reported results it is found CdS with radius 1-4 nm the polarization term is typically one third of coulomb term with opposite sign Therefore,

$$\frac{0.3031}{R} = \frac{0.45}{R} - \frac{0.45}{3R}$$

For both CdS and ZnS the value of $R_0 = 2 \text{ nm}$, thus for CdS

$$E(2) = 2.43 + \frac{2.44}{(2)^2} - \frac{0.3031}{2} = 2.89 \text{ eV}$$

And for ZnS nanocrystalline

$$E(2) = 3.68 + \frac{3.31}{(2)^2} - \frac{0.312}{2} = 4.35 \text{ eV}$$

Substituting the value of Γ , A and E(R_0), for different values of E, $g_{qd}(E, R_0)$ is calculated by equation (4). Figure (2) shows the PL spectrum of monodisperse CdS nanoparticles. Figure (5) shows the PL spectrum of monodisperse ZnS nanoparticles.

III Using Equation (2) (4) (6) and (7), the line shape of polydisperse CdS and ZnS can be obtained by substituting the constants for CdS and ZnS nanoparticles. following constants are in present calculation.

$$1. \frac{\sigma_R}{R_0} = 25\%, \frac{A}{2\pi\Gamma\sigma_R} = F = 0.8, dR = 0.2, R = 0.5 - 3.5nm$$

Substituting the above values in equation (7). $P^*(R)$ is calculated for different values of $R = 0.5$ to $3.5nm$. Similarly $E(R)$ is calculated by equation (8 and 9) energy $R=R_0 + 3\sigma_R$ for different value of $R=0.5$ to $3.5 nm$. Then $g^*_{qd}(E,R)$ is calculated by Equation (4) for different values of E . Substituting the value $P^*(R)$ and $g^*_{qd}(E,R)$ for specific value of R and E in equation (6). Substituting $dR = 0.2$, $\frac{A}{2\pi\Gamma\sigma_R} = 0.8$, we get different values of $g^*_{qd}(E,R) \times P^*(R) \times F \times dR$. The Equation (5) for CdS and ZnS is given by [polydisperse]

$$G(E) = \int P(R).g_{qd}(E.R)dR$$

$$= \frac{A}{2\pi\sigma_R\Gamma} \left\{ \sum_{R=R_0-3\sigma_R}^{R=R_0+3\sigma_R} [P^*(R).g^*_{qd}(E.R)_{E=2} + P^*(R).g^*_{qd}(E.R)_{E=2.2} + \dots + P^*(R).g^*_{qd}(E.R)_{E=3.8}] \right\}$$

-----(10)

Figure (3 and 6) shows the PL spectrum of CdS and ZnS nanoparticles respectively for 25% dispersion by curve 1.

$$2. \frac{\sigma_R}{R_0} = 15\%, \frac{A}{2\pi\Gamma\sigma_R} = F = 1.3, dR = 0.1, R = 1.1to2.9nm$$

Figure (3 and 6) shows the PL spectrum of CdS and ZnS nanoparticles for 15% dispersion by curve2.

$$3. \frac{\sigma_R}{R_0} = 5\%, \frac{A}{2\pi\Gamma\sigma_R} = F = 4, dR = 0.05, R = 1.7to2.3nm$$

Calculations for above case are similar as in 1. Figure (3 and 6) shows the PL spectrum of CdS and ZnS nanoparticles for 5% dispersion by curve 3.

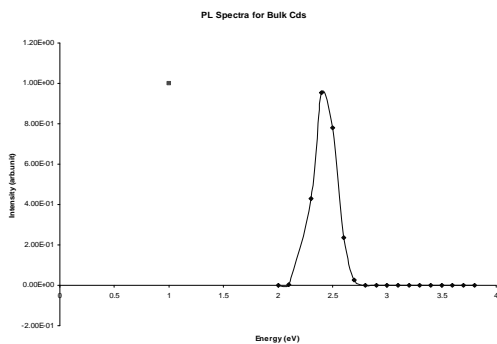


Figure 1

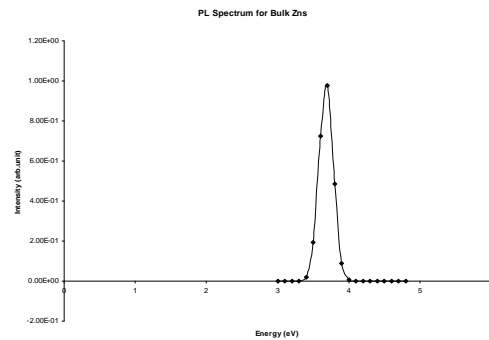


Figure 4

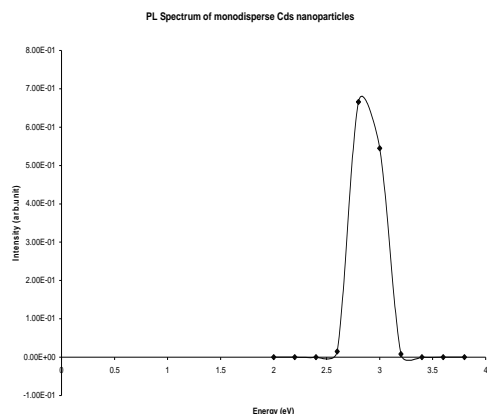


Figure 2

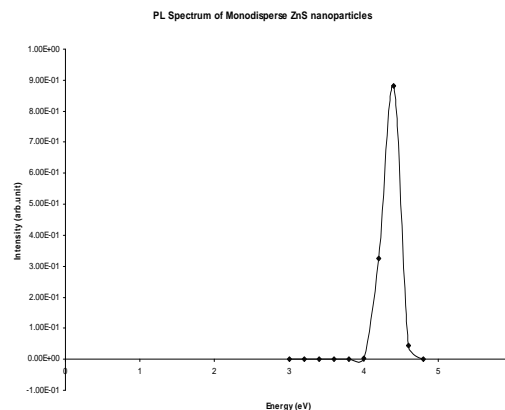


Figure 5

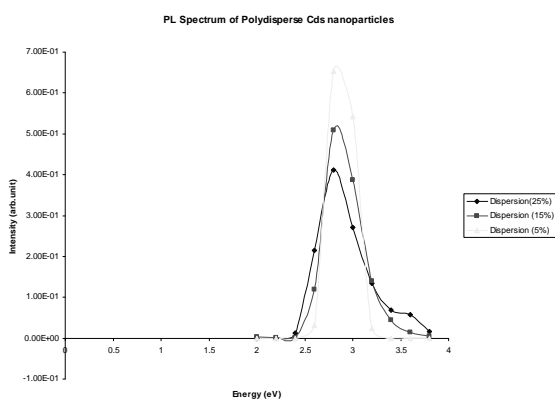


Figure 3

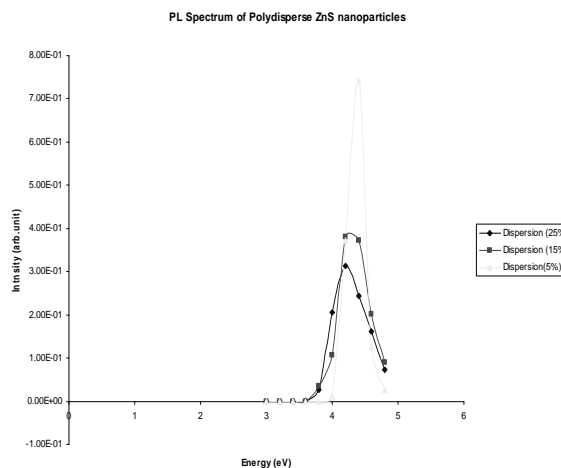


Figure 6

Discussion

Many workers have reported band to band PL for a number of materials. In case of nanocrystals the PL peak is observed at same energy as the absorption edge shift towards shorter wavelength for smaller particles. In general it is difficult to obtain monodisperse particles and PL spectrum can be taken as superposition of the contribution from each individual nanoparticle. The effect of particle size distribution of semiconductor nanoparticles on the band-edge photoluminescence spectrum is investigated. The calculations show inhomogeneous broadening of PL line shape. The measured PL spectrum which exhibit peaks arising from band-edge luminescence and recombination at defects can be analyzed by fitting the calculated line shape to it. Thus, the overall behaviour of PL spectrum is strongly affected by the size distribution of nanoparticles.

Result

- (1) From the combined PL spectra of bulk, mono and polydispersed CdS particles, it is observed that:
 - (a) In case of bulk CdS, the peak point of PL is observed at 2.4eV.
 - (b) In Case of monodisperse nanoparticles of CdS for average size 2nm, the peak point is at 2.8eV.
 - (c) In case of polydispersed nanoparticles of CdS, we see that by increasing the standard deviation, there is slight red shift in PL peak.
 - (d) It is also observed that as the dispersion of nanoparticles increases the PL peak intensity decreases and the peak is broadened.
- (2) From combined PL spectra of bulk, mono and polydisperse ZnS nano particles, it is observed that following cases arise.
 - (a) In case of bulk ZnS the peak point is observed at 3.7 eV.
 - (b) In case of monodispersed particles of ZnS the peak point is observed at 4.4 eV with $R=2\text{nm}$ and $\sigma_R=0$.
 - (c) In case of polydispersed particles of ZnS, we see that for $R_o = 2\text{nm}$, the peak point is observed at 4.2eV, 4.2eV, 4.4 eV for $\sigma_R=5\%$ of R_o and 15% R_o , 25% of R_o respectively.

That is a marginal change in peak position with increase of broadening of PL peak is seen.

- (i) The PL peaks of nanoparticles are blue as compared to bulk.
- (ii) The blue shift in PL peaks of CdS is 0.46 eV and for ZnS, it is 0.72 eV when the particle size of both is same (2nm). Hence it can be said that blue shift in PL peaks is more for larger band gap materials.
- (iii) Our study indicates that 5% polydispersion does not affect the PL peak position and intensity as well as broadening. But when the dispersion is large the intensity is reduced and peak is broadened. This concludes that 5% dispersion is tolerable.

References

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