

# Strong and Weak Quantum Confinement and Size Dependent Optoelectronic Properties of Zinc Oxide

PIJUS KANTI SAMANTA

Post Graduate Department of Physics, Prabhat Kumar College, Contai-721404, West Bengal, India

E-mail: pijush.samanta@gmail.com, Tel: +91-97755-50907

## Abstract

We have studied here the effect of quantum confinement of carriers on the optical properties of nanocrystals with special reference to ZnO. We have discussed in detail the strong and weak quantum confinement regime of ZnO nanocrystals and used the theoretical results to explain the observed optical properties of ZnO nanoparticles of different sizes.

**Keywords:** Nanoparticles, Quantum-confinement, Bandgap, Photoluminescence

## Introduction

Electronic and optical properties of a semiconductor material depend on the carrier dynamics of the system. To understand the carrier dynamics of a material, it is very much essential to know about the different energy levels, energy gap and degeneracy. These properties differ in case of a nanomaterial compared to their bulk counter because of the confined motion of carriers in nanoscale regime. This is called quantum confinement. This leads to the enhancement of band gap of the material [1]. As a result the optical and electronic properties change drastically in nanoscale. Zinc oxide (ZnO) is a very well investigated nanostructured semiconductor metal oxide having band gap  $\sim 3.4$  eV and large excitonic binding energy (60 meV) at room temperature [2]. It usually exhibits UV emission leading to its potential application in UV-laser source fabrication. However during low temperature growth, several defect states like zinc vacancy and interstitials, oxygen vacancies and interstitials, zinc and oxygen antisites are developed in the crystal leading to the existence of lower energy shallow levels between the conduction band and the valence band of ZnO crystals [3-7]. These defect states of lower energy lead to visible emission from ZnO. Due to quantum confinement effect the band gap of ZnO is reported to be enhanced up to 4.2 eV [8]. Thus the quantum confinement phenomenon in this case will be quite strong. To understand the degree of the confinement and calculate different energy levels and band gap in a material, it is necessary to solve the Schrodinger equation under appropriate boundary conditions.

## Theory of Quantum confinement in nanocrystals

Let us start with a simple system consisting of an electron and a hole. In such a system the Hamiltonian ( $\mathcal{H}$ ) has three components: (i) kinetic energy possessed by the electron and hole, (ii) Coulombic interaction between electron-hole pair (EHP) and (iii) the confinement

potential arising due to the dimension of the material. The Hamiltonian of this system can thus be written as [9]

$$\mathcal{H} = -\frac{\hbar^2}{2m_e^*} \nabla_e^2 - \frac{\hbar^2}{2m_h^*} \nabla_h^2 + V_C^e(\vec{r}_e) + V_C^h(\vec{r}_h) - \frac{e^2}{\epsilon r_{eh}}$$

Here,  $m_e^*$  and  $m_h^*$  denotes the effective mass of the electron and hole respectively,  $r_{eh}$  represents the EH separation,  $\epsilon$  being the dielectric constant of the material. The potentials  $V_C^e(\vec{r}_e)$  and  $V_C^h(\vec{r}_h)$  denotes the confinement potentials for electron and hole respectively. For simplicity, let us consider that the confinement potentials are centrosymmetric in nature and have constant values for large value of  $r_{eh}$ . Using the conventional Hartree-Fock equation, the energy eigen value equation for electron and hole can be formulated as [10, 11]:

$$\begin{aligned} \left[ \frac{p_e^2}{2m_e^*} + V_e(r_e) \right] \varphi_e(r_e) &= \widetilde{E}_e \varphi_e(r_e) \quad (\text{Electron}) \\ \left[ \frac{p_h^2}{2m_h^*} + V_h(r_h) \right] \varphi_h(r_h) &= \widetilde{E}_h \varphi_h(r_h) \quad (\text{Hole}) \end{aligned}$$

Here,  $V(r)$  is the field effectively influencing electron and hole. These fields can be expressed as [11, 12, 13]:

$$\begin{aligned} V_e(r_e) \varphi_e(r_e) &= \left[ V_0^e(r_e) - \frac{e^2}{2\epsilon} \int dr_h \frac{|\varphi_h(r_h)|^2}{|r_e - r_h|} \right] \varphi_e(r_e) + \frac{e^2}{2\epsilon} \int dr_h \frac{\varphi_h^*(r_h) \varphi_e(r_h)}{|r_e - r_h|} \varphi_h(r_e) \\ V_h(r_h) \varphi_h(r_h) &= \left[ V_0^h(r_h) - \frac{e^2}{2\epsilon} \int dr_e \frac{|\varphi_e(r_e)|^2}{|r_e - r_h|} \right] \varphi_h(r_h) + \frac{e^2}{2\epsilon} \int dr_e \frac{\varphi_e^*(r_e) \varphi_h(r_e)}{|r_h - r_e|} \varphi_e(r_h) \end{aligned}$$

Several approaches have been made to solve these types of equations. Three dimensional fast Fourier transformation technique is commonly used by the researcher. However a simple potential-morphing method (PMM) is used by some researcher to solve these iterative Hartree-Fock equations [11, 12]. Bohr radius is an important parameter in the context of defining the quantum size effect in nanostructures and is defined as the mean radius of the ground state electronic orbit in an atom. In case of an e-h pair it assumes the form [12, 13]:

$$a_0 = \frac{\epsilon \hbar^2}{2\pi \mu e^2}$$

Where,  $\mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*}$ , is the conventional reduced mass of the e-h pair. In case of ZnO nanocrystals we have the following data:  $\mu = \frac{1}{2} \mu_e$  and  $\epsilon = 3.7 \epsilon_0$  [13]. This leads to the value of Bohr radius to be  $\sim 2$  nm. So to observe the strong confinement effect the size of the synthesized ZnO nanocrystals should be around 10-15 nm or less otherwise the confinement will be much weaker.

### Strong confinement

In case of strong quantum confinement, the confinement energy is much larger than the Coulomb energy of the system. Hence electron and hole are individually confined and their motion movement is also independent. The confinement energy in this case can be represented by [9-11]:

$$E_{n,l}^{e,h} = \frac{\hbar^2 \alpha_{n,l}^2}{2m_{e,h}^* R^2}$$

Here,  $\alpha_{1,0} = \pi$ ,  $\alpha_{1,1} \approx 1.43\pi$ ,  $\alpha_{2,1} \approx 1.83\pi$  etc. In case of any allowed optical transition in this case  $n$  and  $l$  are conserved and guided dipolar transition selection rules. The total energy corresponding to the first allowed transition ( $n_e = n_h = 1, l_e = l_h = 0, m_e = m_h = 0$ ) can thus be expressed by [10, 11]

$$E_{1s-1s} = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{e^2}{\epsilon R} \frac{1.8}{R}$$

Researchers have reported the size ( $R$ ) dependence of the band gap under strong quantum confinement regime. In our method we have we have synthesized ZnO nanoparticles using a soft chemical technique and the detail of the method is reported elsewhere in [14]. Briefly, in methanolic solution of zinc nitrate (0.1 M) was mixed with methanolic solution of NaOH (0.225 M) and stirred continuously for 1.5 hr. PVA was used to control the particles size. A white precipitate was deposited at the bottom of the flask. The precipitate was washed and dried for further characterization. By this process we obtained fine ZnO nanoparticles of size ranges from 17 nm to 7 nm. This causes the band gap to increase from 3.4 eV to 3.84 eV. The variation of band gap with particle size is tabulated in table-1 and also shown in Fig. 1. The nanoparticles exhibit strong photoluminescence peaked at  $\sim 427$  nm as shown in Fig. 2. This corresponds to recombination of electrons in zinc interstitials and holes in the valance band. This visible emission from ZnO nanostructures indicates that the PL emission is dominated by the defect states emission over direct band edge transitions.

### Weak confinement

When the size of the nanoparticles is quite larger compared to the Bohr radius, the confinement is very weak. In this case the interaction potential of  $e-h$  system due to quantum confinement is also very negligible in comparison to the Coulomb potential. To calculate the band energies, we need to solve Schrodingers equation for the  $e-h$  system. Several researchers have reported the solution of the equation and the energy associated with the optical transition of the nanocrystals in weak quantum confinement regime and can be expressed as [9, 10, 13]:

$$E_n = E_{bulk} - E_{ex} + \frac{\hbar^2 \pi^2}{2MR^2} n^2$$

Here,  $M$  is the total mass of  $e-h$  pair and  $R$  is the centre of mass of the  $e-h$  system.

To study the weak confinement we need ZnO nanocrystals of large size. For this purpose we followed a reduction chemical reaction process as reported elsewhere in [15]. In brief, under vigorous stirring of triethylamine (60 mM), in 30 ml aquatic solution, benzene-1,3,5-tricarboxylic acid (20 mM) was added and the stirring was continued. Then Zinc(II) acetate dihydrate (30 mM) solution was added dropwise. After mixing, the stirring was continued for further 2 hr. A white precipitate was observed. The precipitate was filters, washed with de-ionized water and dried in an oven at 550 °C for decomposition of the precursor complex to obtain ZnO.

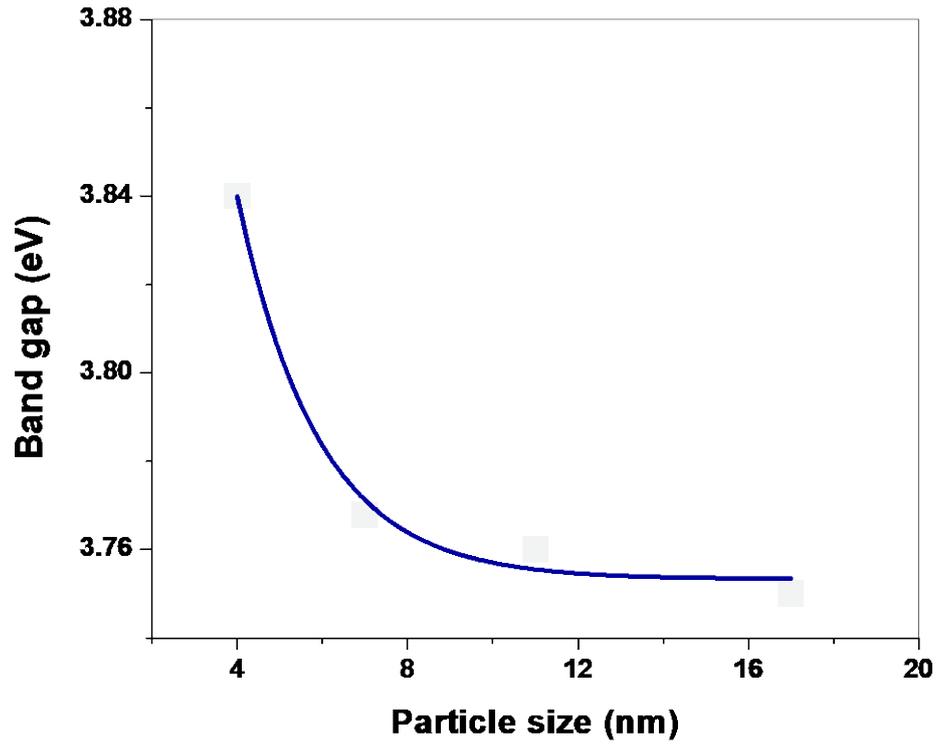


Fig. 1: Variation of band gap with particle size obtained from the data of table-1

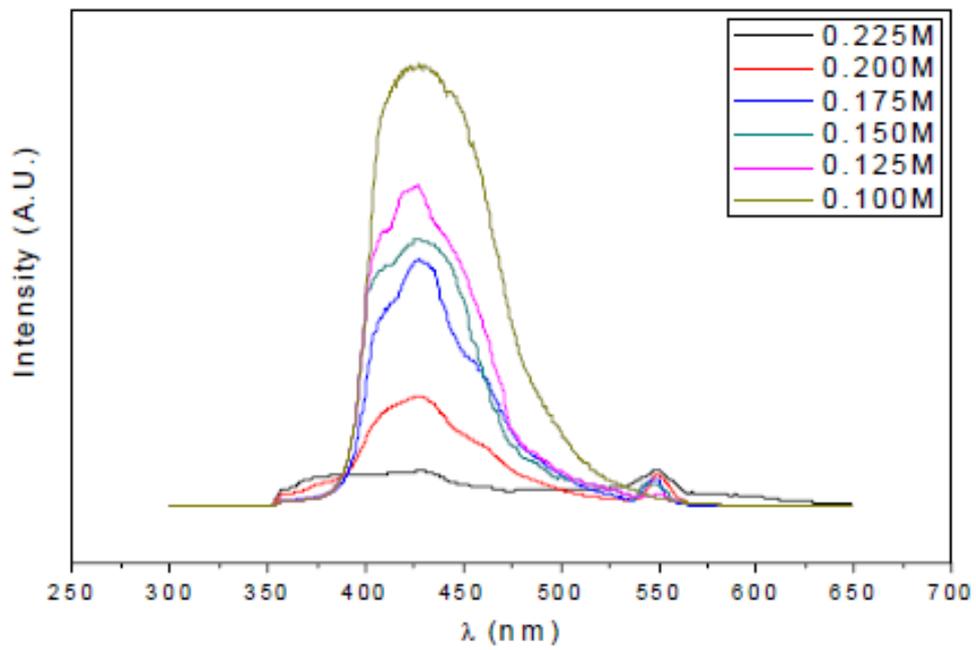


Figure 2: Room temperature photoluminescence of ZnO QDs

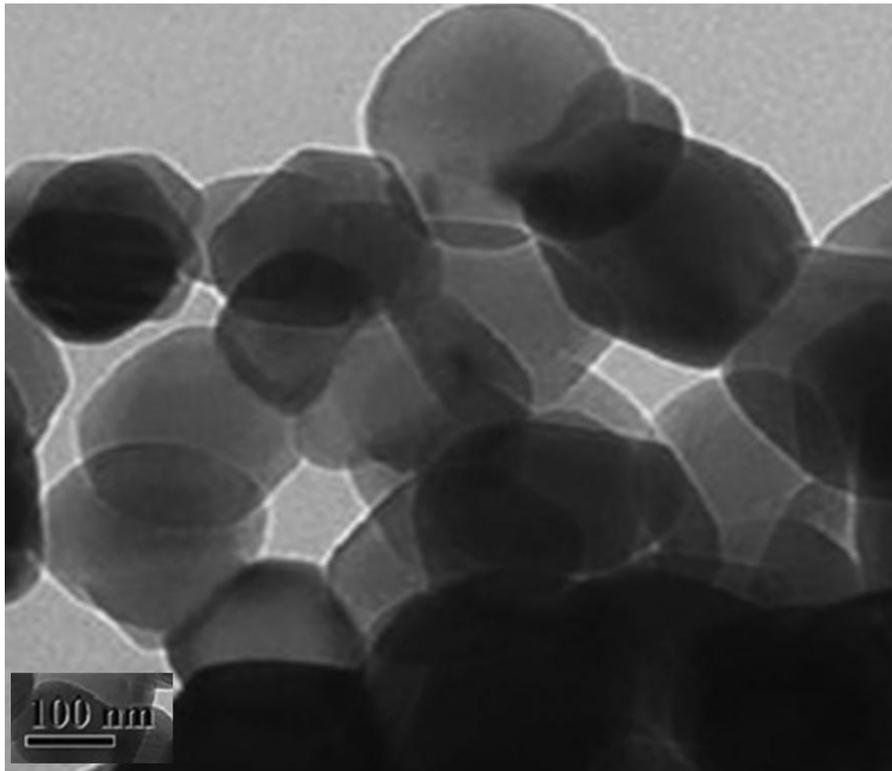


Figure 3: HRTEM image of ZnO nanoparticles

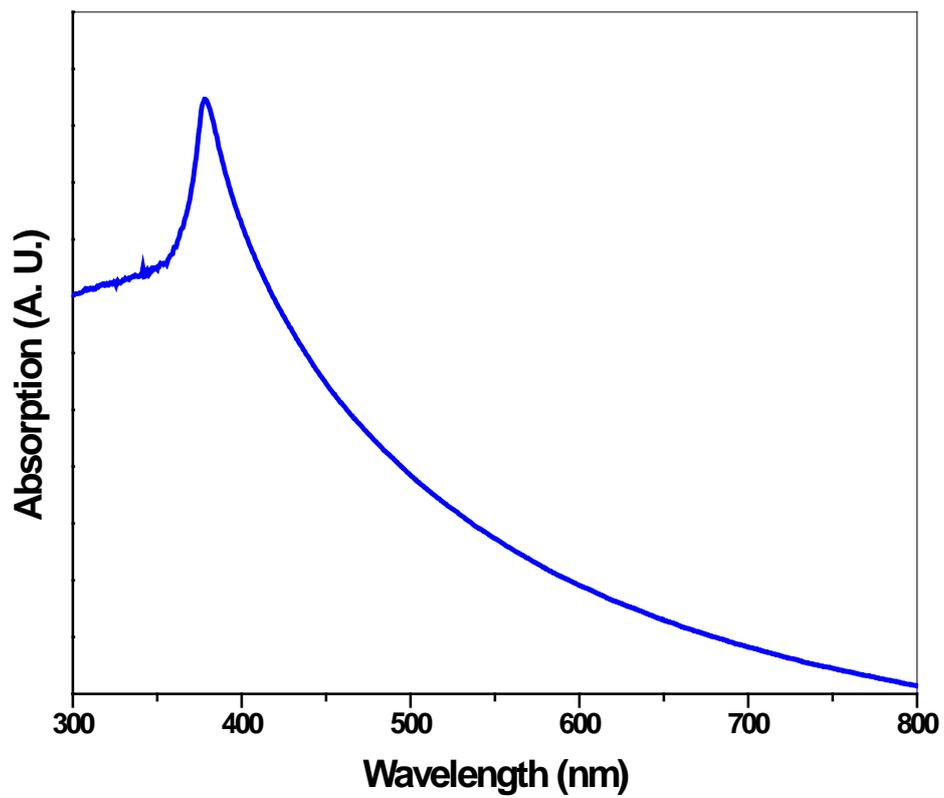


Figure 4: UV-visible absorption spectrum of ZnO nanoparticles

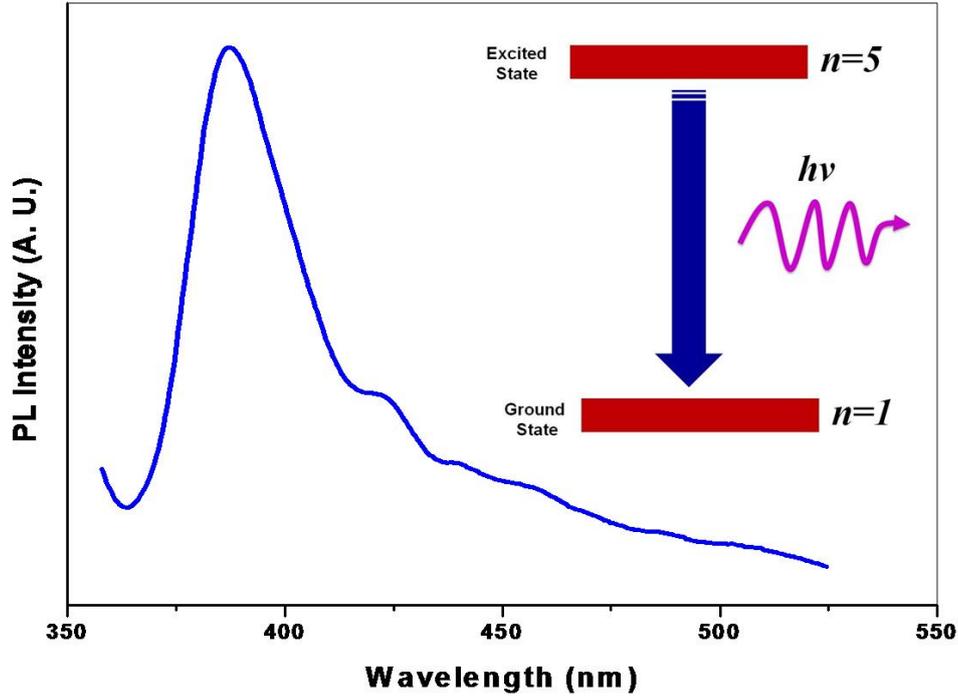


Figure 5: Room temperature photoluminescence of ZnO NPs. Inset shows the transition levels.

Table-1: Concentration dependence of particle size and band gap of ZnO NPs

NaOH concentration	Particle size (nm)	Band gap (eV)	PL peak position (nm)
0.075	4	3.84	427
0.1	7	3.77	
0.15	11	3.76	
0.225	17	3.75	

Typical HRTEM image of the synthesized ZnO nanoparticles is shown in Fig. 3. Well grown nanoparticles of diameter  $\sim 100$  nm is found to form. The UV-visible absorption spectrum is also shown in Fig. 4. The nanoparticles exhibit very low absorption in the visible region with strong absorption peak at 377 nm. Tauc plot enables us the information about the band gap of the material from the UV-visible absorption data and was calculated to be 3.52 eV. This enhancement in band gap clearly indicates the occurrence of quantum confinement in the ZnO nanocrystals. However the band gap enhancement is very small and hence this can be considered as the case of weak quantum confinement. The band gap of the bulk material ( $E_{bulk}$ ), exciton binding energy ( $E_x$ ) are related by the relation:

$$E_n = E_{bulk} - E_x + \frac{\hbar^2 \pi^2}{2MR^2} n^2$$

Where  $n$  represents the quantum number of the particular energy level. The energy of transition from  $(n+1)^{th}$  state to  $n^{th}$  state is thus given by:

$$\Delta E_{(n+1) \rightarrow n} = \frac{\hbar^2 \pi^2}{2MR^2} (2n + 1) = \frac{h^2}{4MR^2} \left( n + \frac{1}{2} \right)$$

Now the emission peak of PL can enable us to determine the quantum number  $n$ . The synthesized ZnO nanoparticles exhibit strong PL emission peak at 387 nm (see Fig. 5). This corresponds to transition from the quantum state  $n = 4$  to the ground state  $n = 1$  (see inset of Fig. 5).

## Conclusions

In conclusion, ZnO nanoparticles were successfully synthesized and characterized. The PMM model was analysed to explain the confinement behaviour. The case of strong and weak quantum confinement was discussed with reference to the synthesized ZnO nanoparticles. The results are very useful in understanding the photoluminescence from semiconductor in a different and simple way. This can also be used to explain the existence of several shallow level defect states in semiconductor nanostructures.

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