

Visible luminescence mechanism in nano ZnO under weak confinement regime

Litty Irimpan,^{a)} V. P. N. Nampoory, and P. Radhakrishnan

International School of Photonics, Cochin University of Science and Technology, Cochin, Kerala 682022, India

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We describe the structure of luminescence spectrum in the visible region in nano-ZnO in colloidal and thin film forms under weak confinement regime by modeling the transition from excited state energy levels of excitons to their ground state. Measurements on nanocrystallites indicate the presence of luminescence due to excitonic emissions when excited with 255 nm. The relevant energy levels showing the transitions corresponding to the observed peaks in the emission spectrum of ZnO of particle size 18 nm are identified. © 2008 American Institute of Physics.
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I. INTRODUCTION

Nanostructures of II-VI semiconductor compounds, such as CdS and ZnO, and the III-V compound GaN are currently attracting a strong interest due to their intriguing optical properties.¹ The interest in ZnO is fueled and fanned by its prospects in optoelectronics applications owing to its direct wide bandgap ($E_g=3.3$ eV at 300 K). Some of the optoelectronic applications of ZnO overlap with that of GaN ($E_g=3.4$ eV at 300 K), which is widely used for the production of green, blue-ultraviolet, and white light-emitting devices. However, ZnO has some advantages over GaN, among which are the availability of fairly high-quality ZnO bulk single crystals and a large exciton binding energy (60 meV). ZnO also has a much simpler crystal-growth technology, resulting in a potentially lower cost for ZnO-based devices.

ZnO crystals possess remarkable optoelectronic properties such as three exciton resonances (A, B, and C exciton) due to spin-orbit coupling in the crystal field with a large oscillator strength and an exciton binding energy up to 60 meV.² The large exciton binding energy paves the way for an intense near band edge excitonic emission at room and even high temperatures because this value is 2.4 times that of room temperature thermal energy ($k_B T=25$ meV). As a consequence, it is expected that the exciton emissions are strong, which could lead to lasing action based on exciton recombination even above room temperature.

The possibility of tailoring the bulk material properties by varying the size, structure, and composition of constituting nanoscale particles makes them candidates for various important applications in the field of material research. Optical methods give rich experimental information about an energetic structure of these finite-size solids. Understanding the size dependent optical properties of semiconductor clusters has been achieved in a number of theoretical publications for a long time.³

The ZnO bulk particles or nanoparticles have various luminescence transitions since different preparation techniques lead to varying structures and surface properties in

ZnO. Generally, ZnO exhibits two kinds of emissions: one is an ultraviolet near band edge emission at approximately 380 nm and the other is a visible deep level emission with a peak in the range from 450 to 730nm.⁴ Out of the different reported emission peaks, the origin of the green emission is the most controversial. In samples with low impurity concentrations, the free excitons can also exhibit excited states, in addition to their ground state transitions. In this article we present the mechanism of visible luminescence in nano-ZnO in colloidal and thin film forms under weak confinement regime by modeling the transition from excited state energy levels of exciton to ground state with a “particle in a box” problem.

II. THEORY

Optical properties of semiconductor nanocrystals depend on the structure of valence and conduction electronic states. One of the most interesting effects of low dimensional semiconductor quantum structures is the size dependent bandgap.⁵ In the effective mass approximation (EMA), the Hamiltonian for the electron-hole ($e-h$) system contains kinetic energy of electron and hole, confinement potential for electron and hole, and their Coulomb interaction energy.⁶ It can be written as

$$H = -\frac{\hbar^2}{2m_e^*} \nabla_e^2 - \frac{\hbar^2}{2m_h^*} \nabla_h^2 + V_0^e(\vec{r}_e) + V_0^h(\vec{r}_h) - \frac{e^2}{\epsilon r_{eh}}, \quad (1)$$

where $m_e^*(m_h^*)$ is the effective electron (hole) mass, ϵ is the effective dielectric constant, $r_{eh}=|\vec{r}_e-\vec{r}_h|$ is the $e-h$ distance in three dimensions, and $V_0^e(\vec{r}_e)[V_0^h(\vec{r}_h)]$ is the confinement potential of electron (hole). For quantum dots (QDs) the potential is assumed to be centrosymmetric; it has a constant value $V_0^e[V_0^h]$ for distances larger than the QD radius and it vanishes inside the dot. The Bohr radius of the electron and hole pair in a QD a_B^{QD} is given by

$$a_B^{QD} = \frac{\hbar^2 \epsilon}{2\pi \mu e^2}, \quad (2)$$

where μ is the effective mass and $1/\mu=1/m_e^*+1/m_h^*$.

^{a)}Electronic mail: littyirimpan@yahoo.co.in.

For ZnO,

$$\mu \approx \frac{m_e}{2} \quad \text{and} \quad \varepsilon = 3.7\varepsilon_0 \quad \text{so that} \quad a_B^{\text{ZnO}} \approx 2 \text{ nm}. \quad (3)$$

Thus charged particles, electrons, and holes have two potentials: the interaction Coulomb potential and the spherical well potential that quantify the kinetic energies of the e - h pair. The Coulomb energy scales as $e^2/\varepsilon R$, whereas the e - h pair kinetic energy in the well of radius R scales as $\hbar^2/2\mu R^2$. The relative importance of these two potentials enables us to distinguish three different confinement regimes.

A. Case 1: Weak confinement regime ($R \gg a_B$)

When the Coulomb energy is much larger than the confinement energy, the regime is called weak confinement and the particle size is much larger than the Bohr radius. In this case, the e - h pair is confined as a whole and the quantification of the movement of the center of mass is accomplished. Then the envelope wave function of the e - h pair is the product of two wave functions describing the movement of the e - h pair with respect to the center of mass and the movement of the center of mass confined in the infinite spherical well. On solving the Schrödinger equation, we get the energies of possible related optical transitions as

$$E_n = E_g - E_{\text{exc}} + \frac{\hbar^2 \pi^2 n^2}{2MR^2}, \quad (4)$$

where $M = m_e^* + m_h^*$ is the total mass of the e - h pair, $R = m_e^* \vec{r}_e + m_h^* \vec{r}_h / m_e^* + m_h^*$ is the position of the center of mass, E_g denotes the bulk bandgap energy, E_{exc} is the exciton binding energy, and n is the quantum number. The energy of ($n+1$)th optical transition is

$$E_{n+1} = E_g - E_{\text{exc}} + \frac{\hbar^2 \pi^2 (n+1)^2}{2MR^2}, \quad (5)$$

$$E_{n+1} - E_n = \frac{\hbar^2 \pi^2}{2MR^2} (2n+1) = \frac{h^2}{4MR^2} \left(n + \frac{1}{2}\right) = \alpha \left(n + \frac{1}{2}\right), \quad (6)$$

where

$$\alpha = \frac{h^2}{4MR^2}. \quad (7)$$

B. Case 2: Strong confinement regime ($R \ll a_B$)

Here the Coulomb energy is negligible with respect to confinement energy and this regime appears when the particle size is much smaller than Bohr radius. In this case, both electron and hole are confined separately. The movement of both carriers is independent and they are considered separately confined in the infinite spherical potential. Confinement energies of the electron and hole depend only on n and l quantum numbers and can be written as

$$E_{n,l}^{e,h} = \frac{\hbar^2 \alpha_{n,l}^2}{2m_{(e,h)}^* R^2}, \quad (8)$$

with $\alpha_{1,0} = \pi$, $\alpha_{1,1} \approx 1.43\pi$, $\alpha_{2,1} \approx 1.83\pi$, etc.

Calculation of selection rules for dipolar transitions shows that in the optically allowed transitions, the quantum numbers n and l are preserved. By perturbation approach, the Coulomb energy is calculated and the total energy of the first optical transition 1S-1S ($n_e = n_h = 1$, $l_e = l_h = 0$, $m_e = m_h = 0$) is written as

$$E_{1S-1S} = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{e^2}{\varepsilon R}. \quad (9)$$

C. Case 3: Intermediate regime ($R \sim a_B$)

Here, the Coulomb energy is no longer negligible with respect to confinement energy. In general, the electron and the hole have different effective masses. The electron is the lightest particle, and only its movement is confined. To solve the problem in this situation, the results of strong confinement are taken as a departure point to diagonalize the Hamiltonian and to use a variational calculation or a perturbative calculation to take into account the Coulomb interaction.

In any case, the boundaries of the different regimes are not really strict and it is common to extend the theory of strong confinement to describe transitions near the threshold of optical absorption. The main results in the EMA are the transformation of a band structure into a series of discrete levels for which their energy depends on nanocrystal size and the increase in first optical transition energy with respect to the bulk gap energy.

III. EXPERIMENT

In the present investigation, colloids of ZnO are synthesized by a modified polyol precipitation method.⁴ The ZnO film is prepared by the technique of spin coating. A stable hydrolyzed solution is prepared using stoichiometric quantities of zinc acetate dissolved in isopropyl alcohol, and the solution is used for spin coating ZnO thin film on quartz substrates by rotating the deposition system at 2000 rotations/min. The sample is then dried at 110 °C for half an hour and then placed in a furnace for annealing. The nano-ZnO colloids and film are characterized by optical absorption measurements recorded using a spectrophotometer (Jasco V-570 UV/visible/IR). The structural properties of the sample are investigated by x-ray diffraction (XRD) with Ni-filtered Cu $K\alpha$ (1.5406 Å) source. The fluorescence emission from ZnO colloids and film is recorded using a Cary Eclipse fluorescence spectrometer (Varian).

IV. RESULTS AND DISCUSSION

Figure 1 gives the room temperature absorption spectra of nano-ZnO colloids and thin film. The excitonic peak is found to be blueshifted with respect to that of bulk ZnO and this could be attributed to the confinement effects.⁷ In the case of nanocrystallites, the electrons, holes, and excitons have limited space to move and their limited motion be-

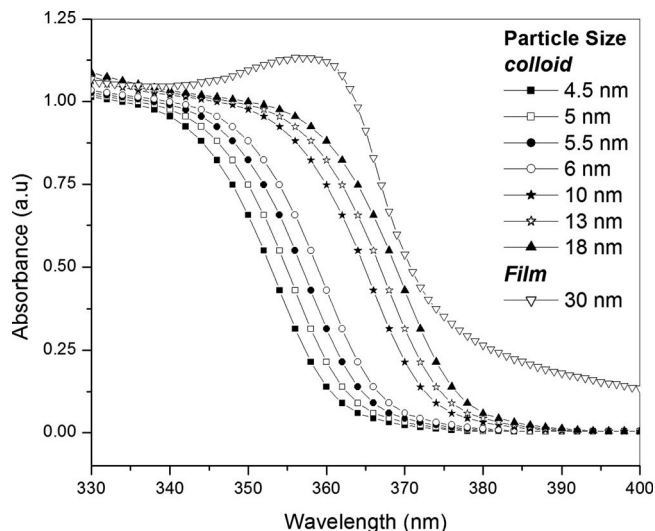


FIG. 1. Absorption spectra of nano-ZnO colloids and thin film.

comes possible only for definite values of energy. The highest occupied valence band and the lowest unoccupied conduction band are shifted to a more negative and positive values, respectively, resulting in widening of bandgap. This leads to a blueshift of absorption band, which can be observed through optical absorption and transmission studies. These size dependent shifts in absorption band edge are shown in Fig. 1. An order of magnitude estimate of particle size is obtained from the absorption spectra. The pronounced dependence of the absorption bandgap on the size of ZnO nanocrystals is used to determine the particle size. The cluster sizes are calculated from the absorption spectra using the analytical formula given by Viswanatha *et al.*⁸ The particle size is also estimated theoretically using potential morphing method from the UV absorption edge data.^{9,10}

The powder extracted from the colloid of large particle size is characterized by XRD. Typical XRD pattern of ZnO colloid is given in Fig. 2. The diffraction pattern and inter-plane spacings can be well matched to the standard diffraction pattern of wurtzite ZnO, demonstrating the formation of

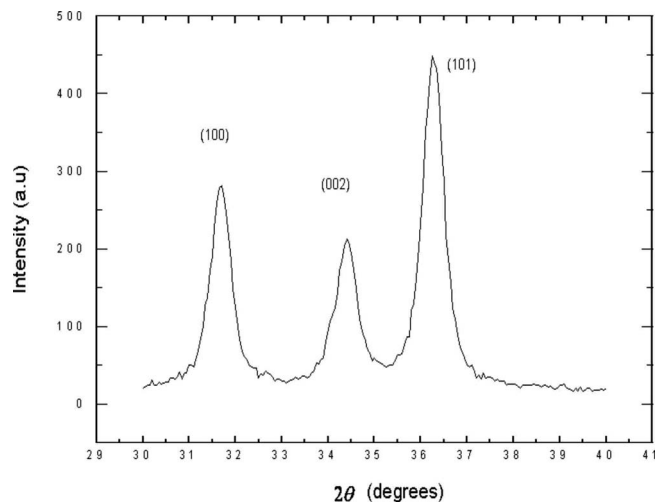


FIG. 2. XRD pattern of the powder extracted from ZnO colloid of size 18 nm.

wurtzite ZnO nanocrystals.⁴ The particle diameter d is calculated using the Debye–Scherrer formula $d=0.89\lambda/\beta \cos \theta$, where λ is the x-ray wavelength (1.5406 Å), θ is the Bragg diffraction angle, and β is the peak width at half maximum. The XRD peak at 36° in Fig. 2 gives the ZnO particle diameter of 18 nm and matches well with the size calculated from absorption spectrum using the analytical formula given by Viswanatha *et al.*⁸

From Eq. (2) it is clear that the Bohr radius a_B corresponding to ZnO is 2 nm. From Fig. 1, it is clear that ZnO colloids of size 4.5–6 nm lie in the intermediate regime ($R \sim a_B$) and ZnO colloids of size 10–18 nm lie in the weak confinement regime ($R > a_B$). The crystallite size of the ZnO film is 30 nm and lies in the weak confinement regime. In the following sections, we analyze the fluorescence spectrum of nano-ZnO based on weak confinement regime.

Figure 3 shows the excitation spectrum corresponding to the emission peak at 390 nm and exhibiting two excitation wavelengths at $\lambda_{ex}^{(1)}=255$ nm and $\lambda_{ex}^{(2)}=325$ nm. Since ZnO

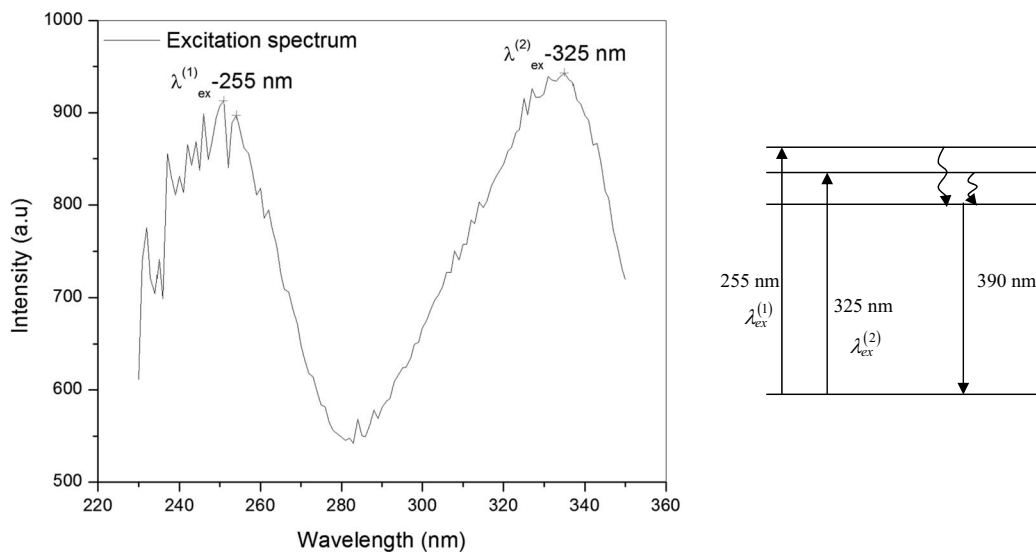


FIG. 3. Excitation spectrum of ZnO colloid for an emission peak of 390 nm.

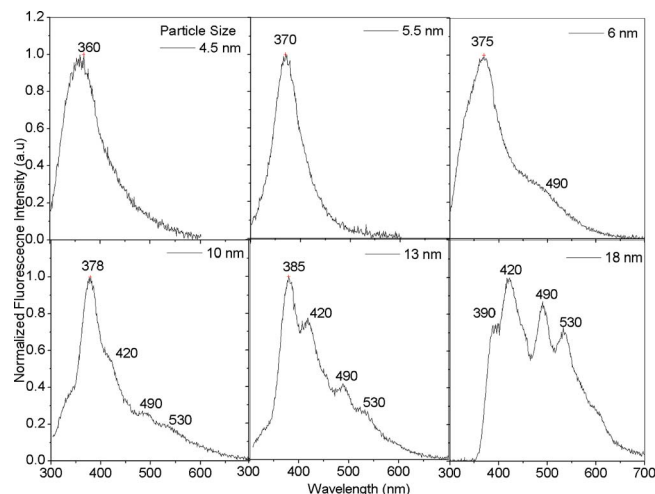


FIG. 4. (Color online) Steady state fluorescence spectra of nano-ZnO colloids of different particle sizes for an excitation wavelength of 255 nm.

has a broadband absorption, excitation spectrum is very significant in finding the excitation wavelengths at which it has maximum emission.

The fluorescence spectra of nano-ZnO colloids of different particle sizes for an excitation wavelength of 255 nm are shown in Fig. 4. Results show that additional emissions at 420 and 490 nm are developed with the increase in particle size along with reported emissions at 380 and 530 nm. Figure 5 shows the fluorescence spectrum of the powder extracted from ZnO colloid of 18 nm at an excitation wavelength of 255 nm. It exhibits all the characteristic emission peaks of the colloid. It confirms the fact that the emission peaks are of pure ZnO and there are no solvent effects. The fluorescence spectrum of thin film of nano-ZnO for an excitation wavelength of 255 nm is shown in Fig. 6. At larger particle sizes, the colloid, powder, and film show multiple emission peaks. These may be attributed to transitions from various excited state energy levels of exciton to the ground level corresponding to $R \gg a_B$ case.

For ZnO colloids of particle size 18 nm, we get emission

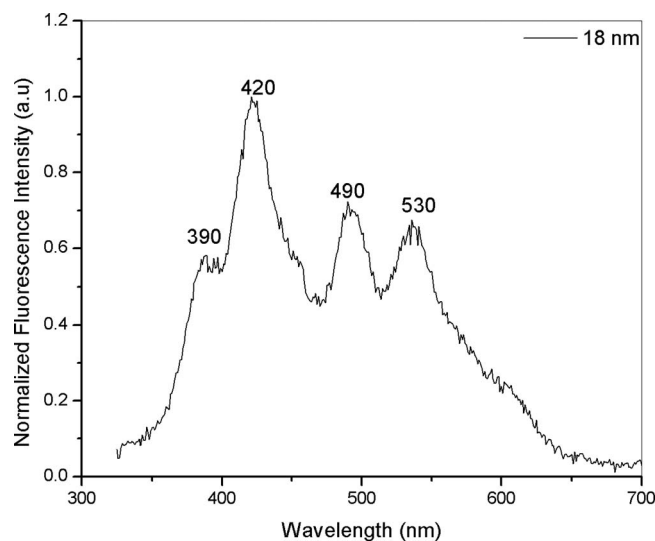


FIG. 5. Fluorescence spectrum of the powder extracted from ZnO colloid of size 18 nm at an excitation wavelength of 255 nm.

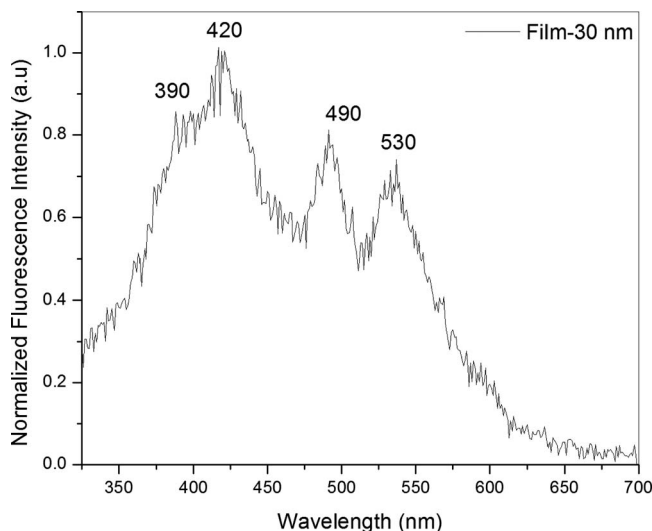


FIG. 6. Fluorescence spectrum of thin film of nano-ZnO for an excitation wavelength of 255 nm.

peaks at 390, 420, 490, and 530 nm. Additional shoulders at 455, 570, and 600 nm are present along with the emission peaks. This series of peaks can be modeled as a particle in a box problem. Assume that the emission peak at 600 nm (2 eV) results from the transition from a higher energy level corresponding to quantum number n to the lowest one corresponding to $n=1$. From Eq. (4), transition energy from n to 1 is

$$E_n - E_1 = \frac{\hbar^2 \pi^2}{2MR^2}(n^2 - 1) = \frac{h^2}{2 \times 4MR^2}(n^2 - 1) = \frac{\alpha}{2}(n^2 - 1). \tag{10}$$

Therefore, $\alpha/2(n^2-1)=2$ eV corresponds to 600 nm emission and for ZnO colloids of particle size $R=18$ nm,

$$\alpha = \frac{h^2}{8m_e R^2} = 1.85 \times 10^{-22}, J = 0.0012 \text{ eV} \\ = 9.6 \text{ cm}^{-1} \text{ so that } n = 59. \tag{11}$$

Thus 600 nm transition corresponds to $n=59$ to $n=1$ level. Similarly for other emission peaks, transitions are identified based on this model and is shown in Fig. 7.

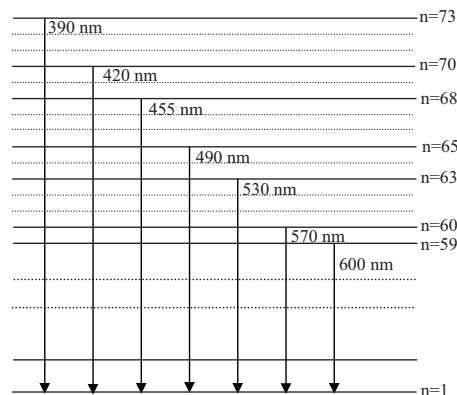


FIG. 7. Relevant energy level diagram showing the transitions corresponding to the observed peaks in the emission spectrum of ZnO of particle size 18 nm under 255 nm excitation.

The results obtained support the fact that exciton levels in the weak confinement regime can be modeled as those related to particle in a box. We used an empirical formula to calculate the size of the nanoparticle and hence the theoretical analysis (strong, weak, and intermediate regime classifications) as well the formula for the particle size are approximations. The spectra are not of sufficient resolution to get the transition peaks from all the consecutive energy levels.

V. CONCLUSIONS

In the present work, we discuss the mechanism of visible luminescence in nano-ZnO in colloidal and thin film forms under weak confinement regime by modeling the transition from excited state energy levels of exciton to ground state with a particle in a box problem. Systematic studies on nanocrystallites have indicated the presence of luminescence due to excitonic emissions when excited with 255 nm. The colloid and the film show multiple emission peaks for larger particle size. These may be attributed to transition from various excited state energy levels of exciton to the ground level

corresponding to weak confinement regime. The relevant energy levels showing the transitions corresponding to the observed peaks in the emission spectrum of ZnO of particle size 18 nm under 255 nm excitation are calculated.

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