Quantum Confinement in Quantum Dots: Theory and Experiment

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Abstract

Quantum confinement is an important phenomenon in low dimensional materials especially in quantum dots where, carriers are confined within the small dimension of the nanocrystal. This results in the changes in energy states and band gap of materials. Therefore, optoelectronic properties of quantum dots get changed. It is therefore, very important to understand this quantum confinement effect. Understanding the electronic theory of quantum dots is very complicated. This article uses an existing model to study different degree of quantum confinement and its effect on the electronic absorption property and band gap of the nanostructure and compare the theoretical model with the experimental observation.

Keywords: Quantum dot, Quantum confinement, Band gap, Absorption, Coulomb interaction.

1. Introduction

Nanomaterials are in the forefront of materials research because of their unique properties as compared to their bulk counterpart [1]. The two major phenomena that make them significantly different from the bulk phase are- enhanced *surface to volume ratio (S/V)* and *quantum* confinement [2]. The *S/V* ratio vary inversely with size of the nanoparticles [3]. Therefore, in nanomaterials more hidden surfaces are exposed. Therefore, more number of surface atoms come in contact with the surrounding materials resulting in the enhanced surface properties such as- catalytic activity, gas and chemical sensing, hydrophobicity, chemical reactivity and many more [4-8]. For example, bulk gold is chemically inactive and cannot influence rate of a reaction. However, nano-gold has significant catalytic activity [9]. Furthermore, in bulk structure, gold is yellow (golden) in colour. But gold nanoparticles exhibit excellent size dependent colour and this happens due to a phenomena known as *surface plasmon resonance* [10]. Similarly, cadmium selenide (CdSe) semiconductor heterostructure quantum dots also exhibit size dependent light emission when excited by a UV-light source [11]. Similar property is also observed in case of CdS, and ZnO [12, 13]. This happens due to size dependent band gap at nanoscale. Therefore, in nanostructure, the carrier confinement (quantum confinement) has significant influence on the optical, electrical and thermal properties of materials. Therefore, it is very crucial to understand the theoretical perspective of quantum confinement to predict the observed size dependent electronic properties.

Here, in this paper, a theoretical formulation of the confinement effect has been discussed supported by the analysis of the optical properties of ZnO quantum dots. This will help the

beginner and intermediate researchers to understand the effect from both theoretical and experimental point of view

2. Theory of quantum confinement

Let us consider a quantum dot consisting of few tens of atoms. In these nanocrystals, the carriers (electrons and holes) are confined within the small diameter of the nanocrystal. To find the energy levels of the carriers lets us first write the Schrodinger's equation as follows [14]:

$$\mathcal{H}_{QD} = -\frac{\hbar^2}{2m_e^*}\nabla_e^2 - \frac{\hbar^2}{2m_h^*}\nabla_h^2 + V_C^e(\overrightarrow{r_e}) + V_C^h(\overrightarrow{r_h}) - \frac{e^2}{\varepsilon r_{eh}}$$

Here, r_{eh} represents Bohr radius of *e-h* excitons, the electron-hole confinement potential V_C and ε, the dielectric constant. The eigen value equation of the *e-h* system will be [15]:

$$\left[\frac{p_e^2}{2m_e^*} + U_e(r_e)\right]\psi_e(r_e) = \widetilde{E_e}\psi_e(r_e) \qquad \text{(for electron)}$$

$$\left[\frac{p_h^2}{2m_h^*} + U_h(r_h)\right]\psi_h(r_h) = \widetilde{E_h}\psi_h(r_h) \qquad \text{(for hole)}$$

The effective potential *U(r)* associated with the electron and hole usually takes the form [15]-

$$U_e(r_e)\psi_e(r_e) = \left[V_O^e(r_e) - \frac{e^2}{2\varepsilon}\int dr_h \frac{|\psi_h(r_h)|^2}{|r_e - r_h|}\right]\varphi_e(r_e) + \frac{e^2}{2\varepsilon}\int dr_h \frac{\psi_h^*(r_h)\,\psi_e(r_h)}{|r_e - r_h|}\psi_h(r_e)$$

$$U_h(r_h)\psi_h(r_h) = \left[V_O^h(r_h) - \frac{e^2}{2\varepsilon}\int dr_e \frac{|\psi_e(r_e)|^2}{|r_e - r_h|}\right]\psi_h(r_h) + \frac{e^2}{2\varepsilon}\int dr_e \frac{\psi_e^*(r_e)\,\psi_h(r_e)}{|r_h - r_e|}\psi_e(r_h)$$

Here, we have taken a centro-symmetric potential. Further, it has been assumed that the carriers experience a constant potential outside the QD. The strength of the confinement potential determines the energy of the system.

When the dot size (*R*) is much smaller than the excitonic Bohr radius (a_B) $(i.e., R \gg a_B)$, the confinement is weak . In this case the solution of Schrodinger's equation yields:

$$E_n^{QD} = E_B - E_{e-h} + \frac{\hbar^2}{2M}\left(\frac{n^2\pi^2}{R^2}\right)$$

Therefore, the energy associated with the electronic transition from $(n+1)^{th}$ state to n^{th} sate, will results in photon emission (assuming direct semiconductor) of energy:

$$E_{n+1}^{QD} - E_n^{QD} = \frac{\hbar^2\pi^2}{2MR^2}[(n+1)^2 - n^2] = \wp(2n+1), \text{ where, } \wp = \frac{\hbar^2\pi^2}{2MR^2}$$

When the dot size is much smaller than the excitonic Bohr radius, $(i.e., R \ll a_B)$, the Coulombic potential can be ignored compared to the confinement potential. In this case the solution of the Hamiltonian has been reported by many researchers and the energy states can be expressed in terms of the quantum numbers *n* and *l* as [14, 15]

$$E_{n,l}^{QD} = \frac{h^2 \alpha_{n,l}^2}{8\pi^2 m R^2}, \quad \alpha_{1,0} = \pi, \alpha_{1,1} \approx 1.43\pi, \alpha_{2,1} \approx 1.83\pi$$

Considering the dipolar transition selection rules and perturbation energy calculation, the total energy associated with the transition 1S→IS (*n=1, l=0*) will be

$$E_{1S-IS}^{QD} = E_g^{bulk} + \left(\frac{\hbar^2 \pi^2}{2\mu R^2}\right)_{QC} - \left(\frac{1.8e^2}{\varepsilon R}\right)_{Coulomb}$$

3. Materials synthesis and characterization

All chemicals used in this synthesis were of analytical grade and was used as supplied. Ethanolic solution of 0.01M of zinc acetate and 1.0 M of NaOH was put under constant vigorous stirring for 30 min. At the end of the reaction a transparent solution was obtained. The solution was centrifuged and the quantum dots were collected for further characterization. Transmission electron microscopy (TEM) was carried out in a JEOL high resolution TEM (HRTEM) operating at 5 kV. UV-visible absorption spectroscopy was carried out in Perkin Elmer Spectrophotometer.

4. Results and discussions

Typical transmission electron microscopic image is shown in Fig. 1. Small size quantum dot is found to form. The size of the quantum dot is ~ 12 nm. Clear lattice fringes are also seen which indicates the high crystallinity of the synthesized ZnO quantum dots. The *d*-spacing was calculated to be ~ 2.46 Å which corresponds to (101) plane of ZnO hexagonal nanocrystals.

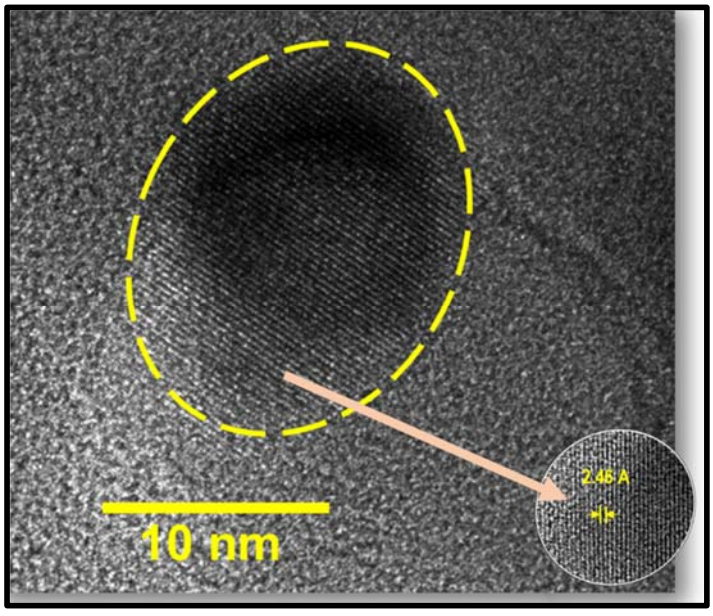

Figure-1: HRTEM image of the synthesized ZnO quantum dots. Inset shows the lattice fringe.

Typical UV-visible absorption spectra of the synthesized ZnO QDs are shown in Fig. 2. The absorbance is found to decrease with increased wavelength and is more pronounced in the visible region. Band gap of a semiconductor can be estimated from its absorption spectra using Tauc equation [16]-

$$(\alpha h\upsilon)^n = B\left(h\upsilon - E_g\right)$$

Here, B is a constant, $h\upsilon$ is the energy of the exciting photon and n is an exponent and takes vales ½ and *2* for indirect and direct band gap semiconductors respectively. As ZnO is a direct semiconductor, Tauc equation takes the form [16]:

$$(\alpha h\upsilon)^2 = B\left(h\upsilon - E_g\right)$$

A plot of $(\alpha h\upsilon)^2$ against $h\upsilon$ is shown in Fig. 3. A slope drawn from the high absorption region and intercept to $h\upsilon = 0$ axis will give the band gap and was found to be 3.42 eV. The excitonic Bohr radius of ZnO is ~ 2.34 nm. The size of the synthesize ZnO quantum dot is larger than the Bohr radius. Therefore, the quantum confinement can be treated as weak in this case. The energy contribution to the band gap of ZnO due to quantum confinement effect is ~ 0.09 eV which is a positive contribution. However, the negative contribution from the Coulomb energy is calculated to be ~ 0.03 eV. Therefore, the band gap of the synthesized ZnO QDs will have a net positive contribution of ~0.06 eV. The band gap of bulk ZnO is ~ 3.37 eV and the calculated band gap of the synthesized ZnO QDs is 3.42 eV. The enhancement of and gap is very much consistent with the theory. Therefore, the theory can successfully explain the observed band gap enhancement in quantum dots.

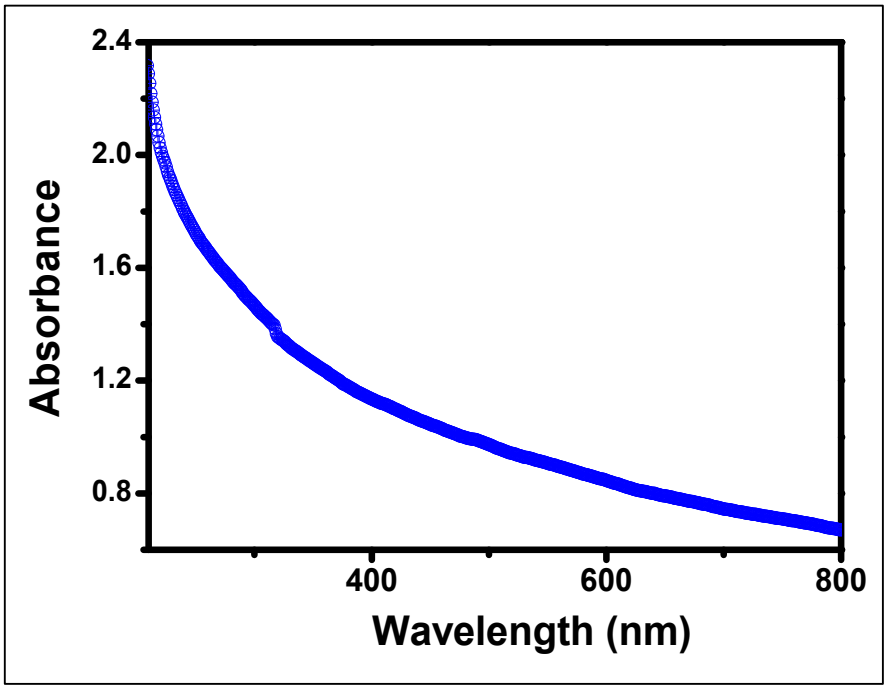

Figure 2. UV-visible absorption spectra of the ZnO QDs

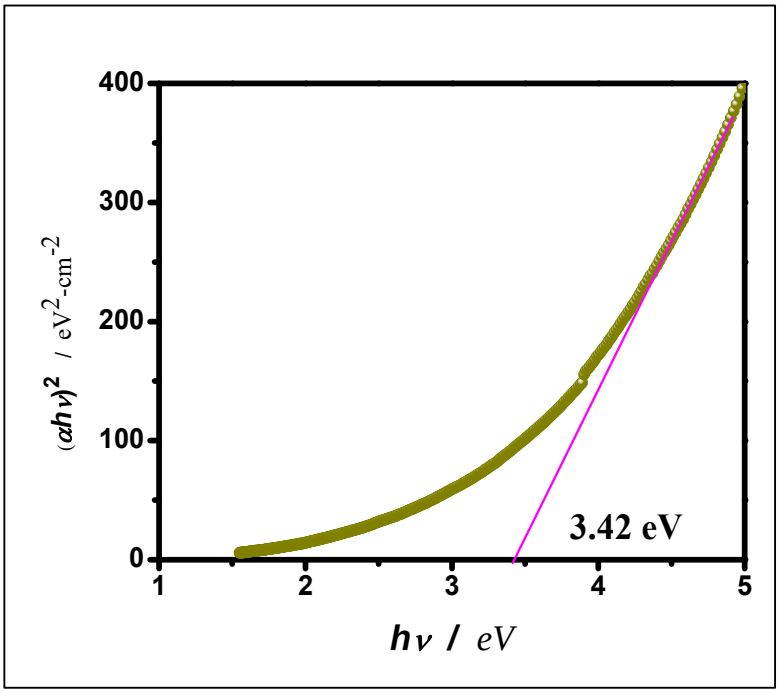

Figure 3. Tauc plot from Fig. 2 to estimate the band gap

5. Conclusions

In conclusion, a simple wet-chemistry has been successfully used to synthesized ZnO QDs. The dot size was measured from the HRTEM images. The optical absorption spectrum shows the occurrence of carrier confinement effect. Both the quantum confinement effect and Coulombic contribution are significant in this case to estimate the band gap and the observed data are very consistent with that predicted in the theory.

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