Comparison of quantum confinement effect on the reduced effective mass of CdSe nanocrystals prepared by different methods

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Based on Effective Mass Approximation (EMA) and Hyperbolic Band Model (HBM), the effect of quantum confinement upon the energy band gap and reduced effective masses of CdSe nanoparticles has been examined. The size of nanoparticles were used from experimental data, such as X-ray diffraction (XRD), Scanning and transmission electron microscopy and the band gap also derived from optical spectroscopy. Also preparation of CdSe nanocrystals was achieved via ultrasound-assisted method. X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Uv-visible spectroscopy were used to characterize the structural and optical properties of as-prepared nanostructures. The experimental results showed that the as-prepared CdSe nanostructures are formed with very small nanometer size, which showed a blue shift of about 0.4eV in energy gap. Theoretical study showed that the value of the reduced effective mass of charge carriers in quantum sized CdSe materials differs from its bulk crystal. The comparative analyses and the main reasons of the changes in reduced effective mass value in the case of CdSe nanoparticles are briefly discussed.

1. Introduction

Nanoscale materials are expected to possess different physical properties compared to their corresponding bulk materials. Specially, semiconductor quantum dots deserve particular attention, as they are expected to play an important role as building blocks of optoelectronic devices [1-6]. Between different types of semiconductors, II-IV group materials, have been attracted more attentions due to their different applications [7]. CdSe, is one of the important and interesting material which are both in cubic and hexagonal structures. The direct band gap of bulk CdSe is 1.74 eV [8]. CdSe has potential applications in various fields such as: optoelectronic devices [9-12], biological surfaces [13-14], solar cells [15-19], blue photoemission and laser diodes [20]. Theoretical interpretation of experimentally observed quantum confinement effect is one of the most important problems in physics. This type of studies can help us to understand more the physics of such fundamental quantum effects. The particle in quantum box is one of the elementary and important problems in quantum mechanics, which presented in basic quantum mechanics books. Charge carriers in semiconductors are electron and hole pairs (excitons). More ever, it is also well known that, in the case of semiconductor nanostructures depending on the type of confinement (zero, one and two dimension), the reduced dimensionality and quantum size enhances the total energy of charge carriers (electron and holes). Much effort has been devoted to the theoretical calculations of the size dependent energies and reduced effective masses in low-dimensional semiconductor quantum systems.

Between them, two simple models (Effective Mass Approximation and Hyperbolic Band Model) have been used in literature more than others. The effective mass of charge carriers is usually derived from a cyclotron resonance, but we can also derive the effective mass of charge carriers from quantum mechanical models. Research in this area has focused often extensively on understanding the band structure of an exciton as a function of nanocrystal radius. Quantum confinement can affect every energy spectrum within low-dimensional system, but not equally. In this paper, using above-mentioned quantum mechanical models, we estimate the differences for the reduced effective masses within size, energy gap and preparation technology. In the case of CdSe nanocrystals, different experimental methods have been reported in literature, the comparative study in this field is important from a physicist and also an engineer's point of view. One of the main results of quantum confinement effect is variation of band structure in semiconductors with variation of quantum sizes, and in all cases a blue shift in absorption and transmission spectrum has been observed [21-25]. These are main result of quantum confinement effect. In this work we collect some experimental values about of size of CdSe nanoparticles from (SEM or TEM) and (XRD) analyses, and also we derive their band gaps from optical absorption spectroscopy, then we analyz quantum confinement effect using two known approximation (Effective Mass Approximation and Hyperbolic Band Model). Then we estimate the value of reduced effective mass from these two models and discussed more about obtained results.

2. Experimental details

Cadmium acetate dihydrate ($C_4H_6CdO_4.2H_2O$ extra pure), Se powder (purity $\geq$ 99%), sodium hydroxide (NaOH extra pure), sodium sulfite (Na_2SO_3 extra pure), (3-Mercaptopropionic acide) and absolute ethanol were obtained from Merck and directly employed without purification.

At room temperature, 20 ml of 0.2 M aqueous solution of cadmium acetate was prepared as cationic precursor solution then 20 ml of 1.1M of aqueous solution of sodium sulfite (Na_2SO_3) by magnetically stirring for 4 hours at 80 °C applying a reflux column system. . The pH of this solution brought to 9 by addition of NaOH. Sodium selenosulfide solution were added to 3 ml of the aqueous solution of 10%, 3-MPA in a flask and imposed to ultrasonic irradiation for 60 min. The orange precipitates were separated by centrifugation, washed at least four times with deionized water and ethanol. Production yield of the sample imposed to ultrasonic irradiation is considerably higher. The obtained products were characterized by X-ray diffraction (XRD, Philips X pert, Cu Kα radiation λ = 0.15406 nm), scanning electron microscope (SEM, LEO 1430VP), and Optical absorption measurement (UV–Visible spectrophotometer model Carry 5, Varian).

The XRD pattern of the as-prepared CdSe nanostructures is depicted in Fig. 1. The diffraction peaks reveal that all products have same crystal structure for the cubic type CdSe nanocrystal system.
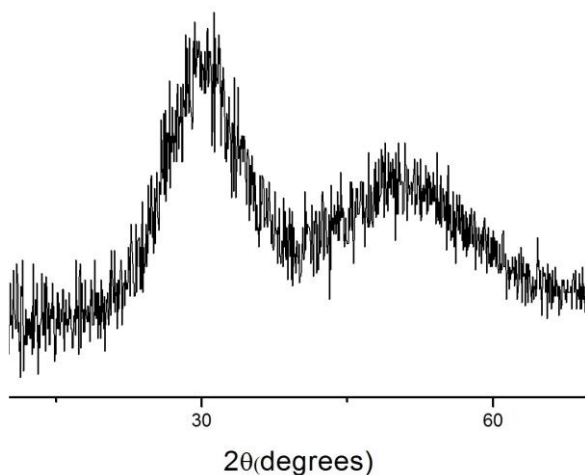

Fig. 1. XRD pattern of as-prepared 3-MPA capped CdSe nanostructures.

The SEM images of CdSe nanocrystals are exhibited in Fig. 2. It can be seen that the product mainly consist of small nanocrystals with average sizes less than 100nm, which aggregated in the form of polydispersive nanoclusters.
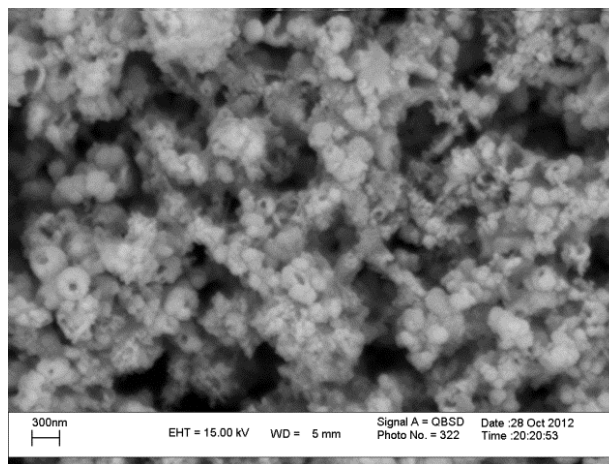

Fig. 2. The SEM image of the as-prepared 3-MPA capped CdSe nanostructures.

Optical absorption spectroscopy results showed that the band gap energy of the as-prepared 3-MPA capped CdSe nanocrystals is about 2.25eV, comparing to 1.74eV, corresponding to its bulk value, a blue shift of about 0.51eV is detected. This shift is due to quantum confinement of charge carriers which confined in a small volume.

3. Theory

In this section, first we review two famous theoretical models in the case of quantum confinement effect and then we should analyze estimated data from obtained results. In semiconductor materials, exciton Bohr radius is an important parameter, gives by:

$$a_B = \frac{\hbar^2 \varepsilon}{e^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right]$$

Where, ε is dielectric constant, m_e and m_h are the electron and hole effective masses respectively.

We can determine three types of quantum confinement regimes using a comparative estimation of excitons Bohr radius:

The first type is weak confinement: In week confinement we have these conditions:

$\overline{R} \rangle\rangle a_B$, $\overline{R} \rangle\rangle a_e$, $\overline{R} \rangle\rangle a_h$ SO: $a_B = a_e + a_h$.

$$a_e = \frac{\hbar^2 \varepsilon}{m_e^* e^2}$$

$$a_h = \frac{\hbar^2 \varepsilon}{m_h^* e^2}$$

Here a_e is the electron Bohr radius, and a_h is hole Bohr radius. In weak confinement regime coulomb energy is important. The kinetic term in this regime also blue shifted and the energy of confined systems was increased. The energy difference between quantum confined and bulk semiconductor material, in this regime is given by:

$$\Delta E \approx \frac{\hbar^2 \pi^2}{2MR^2}$$

Where in this relation, M is exciton mass, and $M = m_e^* + m_h^*$.

The second type of confinement is strong confinement regime, in this case, $\overline{R} \langle \langle a_h$ and also $\overline{R} \langle \langle a_e$, and the coulomb term is not more important and negligible. We can use coulomb term as a perturbation term and in some case we can consider electrons and holes as a confined separated particle. In this case, we cannot talk about excitons. One of the results of the strong confinement regime is decrease in energy level concentration and also more discretion in energy levels.

In the case of strong confinement regime, we have more discrete spectrum and the relation of band gap shift and nanoparticles size is given by:

$$\Delta E \approx \frac{\hbar^2 \pi^2}{2\mu R^2}$$

Where, μ is the reduced effective mass of electrons and holes and given by:

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

The third type is medium confinement regime, in this regime we have these conditions: $\overline{R} \langle \langle a_h$ and $\overline{R} \rangle \rangle a_e$, generally this type of confinement occurs for such crystal which has large difference between their electrons and holes effective masses [26].

It is known that the Schrodinger equation for a semiconductor material for two particles is given by:

$$\left[\frac{-\hbar^2}{2m_h} \nabla_h^2 + \frac{-\hbar^2}{2m_e} \nabla_e^2 + V(r_e, r_h) \right] \psi = E\psi$$

where

$$V(r_e, r_h) = \frac{-e^2}{\varepsilon |r_e - r_h|} \qquad \text{For inside R}$$

$$V(r_e, r_h) = \infty \qquad \text{For outside R}$$

Here, R is the radius of particles; the solution of above mentioned equation presented in general quantum mechanics books. The energy for first excited state is given by [27-31]:

$$E_{10} = \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{\varepsilon R}$$

Another model, which we use in this paper for investigation of quantum confinement effect, is Hyperbolic Band Model (HBM), this model is suitable for such materials, which has small exciton Bohr radius and also for such materials which coulomb interaction is weak. The relation between particle size, effective mass and shift in the frame work of HBM is given by:

$$E_{g,nano} = \left[E_{g,bulk}^2 + \frac{2\hbar^2 E_{g,bulk} \pi^2}{R^2 m^*} \right]^{1/2}$$

This is clear from HBM relation, that the model approximation with hyperbolic [32-34].

It is obvious from two above-mentioned equations the effective masses should increase with decreasing particle size as one would expect that the curvatures of the lowest conduction band and highest valence band decreases with decreasing nanoparticle size. We observed that the value of estimated reduced effective masses differ from those of bulk CdSe materials (Table 1). Analyze of the literature data showed that, in some cases the value of reduced mass near to its bulk, the reduced effective masses are higher than in most cases its bulk value (Figs. 3 and 4). Using two models (EMA and HBM), we analyzed the size dependent, reduced effective masses of charge carriers. Blue shifted energies in nanocrystalline CdSe semiconductor materials have been derived as well as their sizes from different experimental analyses techniques. Generally effective mass is an important parameter, which related to the periodic potential of a crystal, so this parameter may differ for nanometer sized same materials. Some experimental parameters such as techniques of nanostructure preparation, presence of impurities, and also analyzes manner and precision may effect on the physical parameters of materials. Mainly can changes the effective mass values in crystalline systems.

Table 1. Calculation of reduced effective masses of change carriers CdSe nanocrystals using available theoretical models prepared by different methods.

Ref	Method	E_g(eV)	Radius(nm)		Reduced mass/m_0 (EMA)		Reduced mass/m_0 (HBM)	
			TEM or HRTEM	XRD	TEM	XRD	TEM	XRD
[35]	Chemical	1.85	43	7.06	0.011	0.426	0.012	0.477
	Chemical	2.18	45	3.45	0.002	0.446	0.002	0.457
	Chemical	2.33	20	2.64	0.009	0.569	0.009	0.561
	Chemical	2.23	50	3.14	0.001	0.484	0.001	0.489
[36]	wet chemical	2.51	1.5	1.5	1.350	1.350	1.275	1.275
[37]	Solvothermal	2.25		1.3		2.714		2.730
	Solvothermal	2.25		1.9		1.270		1.278
	Solvothermal	2.25		2.5		0.734		0.738
	Solvothermal	2.43		3.95		0.217		0.209
	Solvothermal	2.43		3.3		0.311		0.299
	Solvothermal	2.43		2.1		0.769		0.740
[38]	Sonochemical	1.83	3.5	5.4	2.122	0.891	2.385	1.002
[39]	chemical	1.85	43	14.12	0.011	0.106	0.012	0.119
	chemical	2.18	45	6.9	0.002	0.111	0.002	0.114
	chemical	2.33	20.8	5.29	0.009	0.141	0.009	0.139
	chemical	2.33	50	6.28	0.001	0.100	0.001	0.099
[4o]	chemical	2.11	1.9		1.751		1.825	
[41]	colloidal	2	2.5	3.25	1.44	0.852	1.545	0.914
[42]	polymer	2.78	2		0.562		0.499	
[43]	ultrasonic	2.21		2.86		0.608		0.618
[44]	polymer	2.1	1.95		1.709		1.786	
[45]	solvothermal	2.3	17.5	17.5	0.013	0.013	0.013	0.013

In this research, we tried use precise experimental data from literature, and we report the variation of reduced effective masses in CdSe quantum dots using two theoretical models in Table 1 and the Figs. 3 and 4.
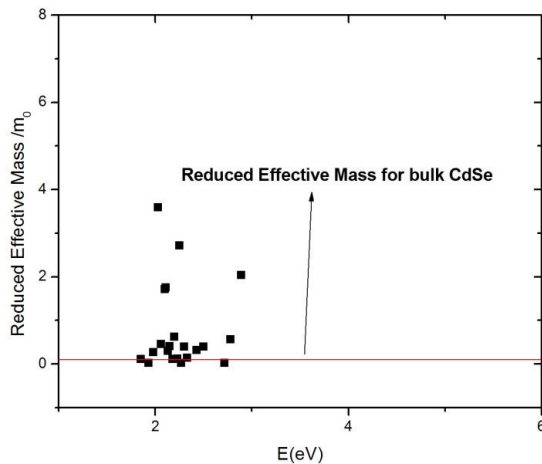

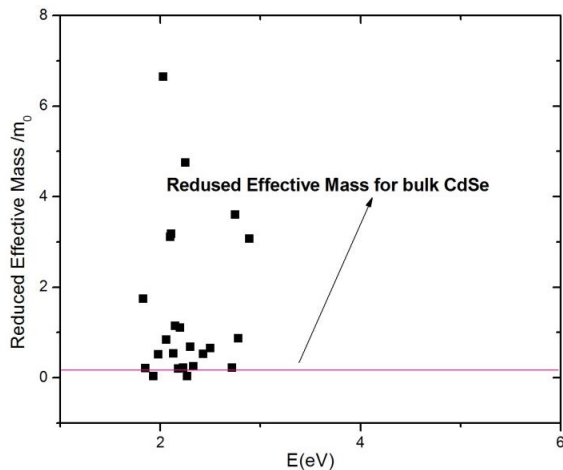*Fig. 3. Plot of reduced effective mass value of CdSe quantum dots versus band gap estimated using EMA.*

Fig. 4. Plot of reduced effective mass value of CdSe quantum dots versus band gap estimated using HBM.

4. Discussion

The values of nanoparticle size, band gap, estimated reduced effective masses for CdSe nanocrystals prepared by different methods are reported in Table 1 and Fig. 3and 4 . In fact talking about the main reasons and physics of this scattered data is not simple, because this process is a very complicated process, and surely the consideration of the precision and also the estimated errors are essential. One of the best ways obtaining certain value is that we analyze more experimental data. From figure 3 and 4, it is clear that, the value of reduced effective masses increased by decreasing the nanoparticle size. We can discuss about this variation the reason of this changes, and also the physics of the different of reduced effective mass of nanostructures generally this changes may be connected with variation of electron potential, defects, capping

material, breaking of boundaries, variation in nanomaterial shape and etc.

5. Conclusion

For the prepared nanocrystals using EMA and HBM, we have estimate the reduced effective masses for charge carriers, for different sizes and energy gaps of CdSe semiconductor nanocrystals. This paper, introduces the relation between simple quantum mechanical models and quantum confinement effect. We also concluded that preparation technology is very important. Also we concluded that the increasing in effective mass value by decreasing nanoparticle sizes, but we cannot find any regular behavior due to the complexity of preparation technology and limited precisions of characterization devices.

Acknowledgements

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