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Investigation of the radiative lifetime in core–shell CdSe/ZnS and CdSe/ZnSe quantum dots

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ABSTRACT

Using the one band effective mass approximation model we computed the optical properties of the spherical shaped CdSe/ZnS and Cdse/ZnSe core–shell quantum dot (CSQD). For each structure we calculated the charge carrier energies and corresponding wave functions. We investigated the dependence of the carrier energies on various parameters of the CSQD, including its size. Then we calculated the radiative recombination lifetime for the two types of CSQDs nanocrystals. We found that as the size of the dot is increased the optical gap of CSQD is reduced, resulting in a reduction in electron energies and an increase in hole energies. We have shown that the radiative recombination lifetime in the CdSe/ZnS and CdSe/ZnSe CSQDs decreased by increasing the shell thickness around the core of the QD. We also showed that the radiative lifetime in the CdSe/ZnS is less than that in the CdSe/ZnSe CSQDs and is sensitive to the size and nature of shell of the semiconductor's material.

1. Introduction

Recent progress on the synthetic chemistry of semiconductor nanocrystals has made it possible to access high quality semiconductor nanocrystals with controlled size, shape and optical properties. The low-dimensional semiconductor structures, such as quantum wells (QWs), quantum wires (QWRs) and quantum dots (QDs), have been applied in several areas.

In the semiconductor quantum dots, the electrons and holes are confined within the width of semiconductor layer of low energy gap which is surrounded by another semiconductor with a higher band gap and is generally lattice matched with the former [1]. The confinement of electrons and holes gives rise to novel optical and electronic properties. These nanostructures are popularly known as core–shell quantum dots (CSQDs). It has been experimentally observed that such CSQDs exhibit improved photoluminescence (PL) efficiency over that of the bare quantum dots and the thickness of the shell provides further control on optical and electronic properties of these QDs [2]. Application of these quantum dots are found in the optical domain such as QD Lasers [3], displays [4], optical communication and other light-emitting devices [5,6] and for several biological purposes [7].

Due to their ease of preparation, high quantum yields and tunable emissions in the visible range, CdSe QDs are undoubtedly among the most promising materials used for the fabrication of fluorescent thin films. Moreover, for better confined carriers in CdSe QDs, the potential barrier and the band gap of passivation material should be greater than those of CdSe. To this end, ZnS and ZnSe are good candidates [8]. Thus we propose to investigate and compare the optical properties of CdSe/ZnS and CdSe/ZnSe CSQDs.

The electronic structure calculations of excitons are the key to understanding the resulting optical properties and designing functional nanodevices. Subsequently, numerous studies have been reported using different methods and approximations [9,10]. In this paper, the description of the quantum confinement is based on the framework of the effective mass approximation (EMA). In strong confinement regimes (dot radius $R_{dot} \ll$ exciton Bohr radius a_{exc}), EMA has been shown to be sufficient for understanding the electronic structure of these low-dimensional systems [11–13]. Using the EMA model allowed calculating energies of electrons and holes in CSQDs, these energies have been used to obtain the optical gap, optical wavelengths and radiative recombination lifetime for CdSe/ZnS and CdSe/ZnSe CSQDs.

In this paper, we have calculated the confinement energies of electrons and holes and simulated the exciton ground state energy spectrum. Particularly, we have studied the quantum size dependent optical properties. We investigated the influence of shell thickness on optical properties. In addition, we evaluated the radiative recombination lifetime in the two types of CSQDs (CdSe/ZnS and CdSe/ZnSe) and examined the core and shell size variations. The theoretical results have been compared and discussed.

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2. Theory and calculation

In this work, we have considered the system of an electron confined in an isolated CdSe/ZnS and CdSe/ZnSe CSQD with inner radius R_1 and outer radius R_2 shown in Fig. 1.

The effective mass approximation is used to model the CSQD, which is assumed to be perfectly spherical. The core's potential is chosen to be reference zero point energy and the band gap of ZnS or ZnSe is wider than that of CdSe, thus $V_c > 0$ [14]. In strong confinement regimes, EMA has been sufficient for understanding the electronic structure of these low-dimensional systems [15]. In most studies especially in the strong confinement regime [i.e., dot radius $R_{dot} \ll$ exciton Bohr radius a_{exc}], the Coulomb term is completely ignored on comparing with the kinetic energy of the electron and hole in the calculation [16]. In some cases, although the Coulomb term is considered as a perturbation and the first order energy modification is performed, the wave function is not modified [17]. In our study the Coulomb term has been neglected and within this approximation method (EMA), the Schrödinger equation for electron (hole) can be written as

$$\left[-\frac{\hbar^2}{2m^*_{ie(h)}r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\right.$$

$$\left.+V_{i,e(h)}(r)\right]\psi^{e(h)}_{nlm}(r,\theta,\varphi)=E_{e(h)}\psi^{e(h)}_{nlm}(r,\theta,\varphi)$$

Here $\hbar$ is reduced Planck constant, $E_{e(h)}$ the energy eigenvalue and $\psi^{e(h)}_{nlm}(r,\theta,\varphi)$ the electron (hole) eigenfunction, n is the principal quantum number, and l and m are the angular momentum quantum numbers. $m^*_{ie(h)}$ is the effective mass of electron (hole) in the ith region and $V_{i,e(h)}(r)$ is the confining potential of electron and hole. The effective mass and potential for electron and hole are expressed as

$$m^*_{i(e,h)}=\begin{cases} m^*_{1(e,h)}, & r\le R_1 \\ m^*_{2(e,h)}, & R_1<r\le R_2 \end{cases}$$

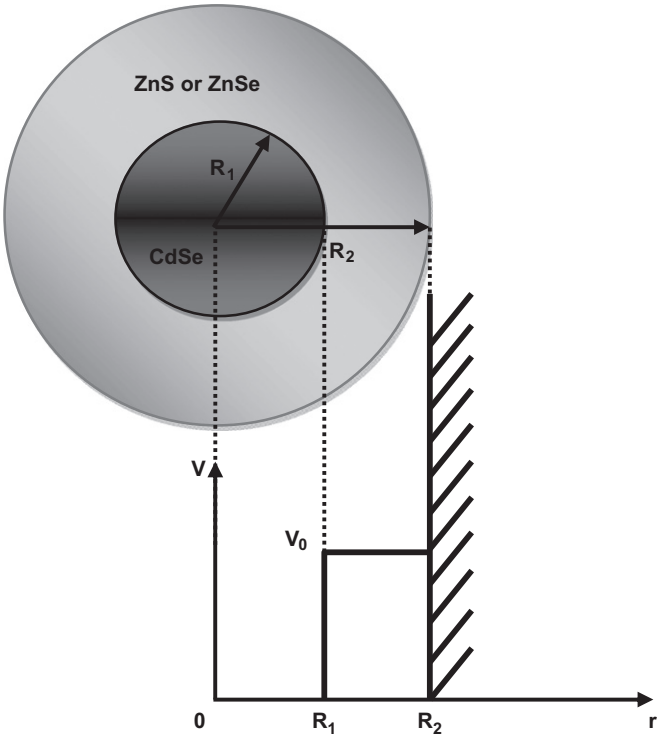

Fig. 1. Core shell QD model and its schematic diagram of potential.

$$V_{i(e,h)}(r)=\begin{cases} 0, & 0<r\le R_1 \\ V_{c(e,h)}, & R1<r\le R_2 \\ \infty, & r>R_2 \end{cases}$$

For spherically symmetric potential $V(r)$ the separation of radial and angular coordinates leads to

$$\psi_{n,l,m}(r,\theta,\varphi)=R_{n,l}(r)Y_{l,m}(\theta,\varphi)$$

$R_{n,l}(r)$ is the radial wave function, and $Y_{l,m}(\theta,\varphi)$is the spherical harmonics. For the spherical potential consists of three parts, the radial eigenfunction $R_{n,l}(r)$ consists of three parts too, according to the position of the electron in the model. Consequently, to calculate$R_{n,l}(r)$, two cases must be considered. In the region where $E > V_{c(e,h)}$, the solution of radial wave function $R_{n,l}(r)$is a linear combination of spherical Bessel function J_l (x) and Newmann function$\eta_l(x)$ and is written as [17]

$$R_{n,l}(r)=\begin{cases} AJ_l(k_{nl,1}r)+B\eta_l(k_{nl,1}r) & r\le R_1 \\ CJ_l(k_{nl,2}r)+D\eta_l(k_{nl,2}r) & R_1<r\le R_2 \\ 0, & r>R_2 \end{cases}$$

where A, B, C and D are normalized constants, and $k_{nl,1}=\sqrt{(2m^*_1E_{e(h)})/\hbar^2}$, $k_{nl,2}=\sqrt{(2m^*_2(E_{e(h)}-V_{c(e,h)}))/\hbar^2}$.

As the wave function is limited when $R\to 0$, $B=0$ because of the divergence of Newmann function η_l when R vanishes. At the same time the wave function has to vanish rapidly when $r\to\infty$, namely: $R_{nl,2}(R2)=0$.

The two boundary conditions [18,19] that we will use, in combination with previous results, leading to different results of our research are

$$R_{nl,1}(R_1)=R_{nl,2}(R_1)$$

$$\frac{1}{m^*_1}\frac{dR_{nl,1}(r)}{dr}\bigg|_{(r=R_1)}=\frac{1}{m^*_2}\frac{dR_{nl,2}(r)}{dr}\bigg|_{(r=R_2)}$$

Normalization constants A–D can be found by normalizing the wave function, which allows us to calculate the wave function and eigenenergy.

Table 1
Material parameters used in the calculations [20,21].

Materials	m^*_e	m^*_h	E_g(eV)	χ^a
CdSe	$0.13m_0$	$0.45m_0$	1.75	4.95
ZnS	$0.28m_0$	$0.49m_0$	3.75	3.9
ZnSe	$0.21m_0$	$0.6m_0$	2.8215	4.09

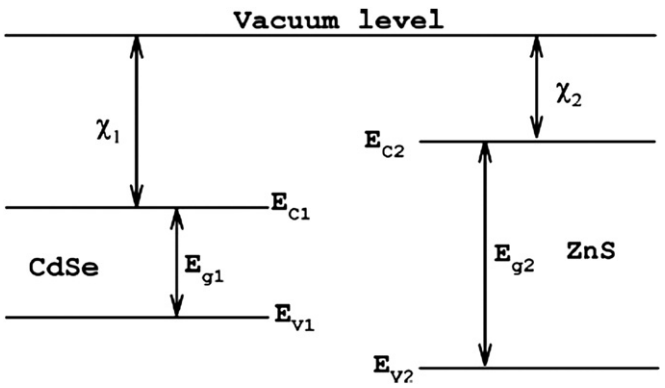

Fig. 2. Schematic energy band representation of CdSe/ZnS.