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Excitons properties in CdSe/$Cd_xZn_{1-x}S$ core/shell quantum dots

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Using the effective-mass approximation method, the electronic structures of CdSe/$Cd_xZn_{1-x}S$ core/shell quantum dots are investigated systematically. The Coulomb interaction between the electron and hole is also taken into account. The calculated results shown that the electron and hole can be strongly confined in the core for the CdSe/$Cd_xZn_{1-x}S$ type-Iheterostructure, which can mainly be ascribed to the large valence and conduction band offset between CdSe and $Cd_xZn_{1-x}S$. The lattice mismatch between core and shell layer can easily be implemented by adjusting the molar ratio of Cd in the shell layer. The transition energies can be widely tuned by the changing the structure parameters.

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1. Introduction

Core/shell structure quantum dots have recently attracted a great deal of attention due to its potential application in light-emitting devices[1], biological tagging materials [2], and solar cell [3]. One of the most interesting research of semiconductor composite structures is the high photoluminescence efficiency.[4-7] The emission quantum yields can be improved by combining different materials to forming the core/shell structure QDs. II–VI semiconductor composite structures, especially CdSe/ZnS QDs, have been widely studied because the emission spectrum spans most of the visible spectrum from blue through red at room temperature [8]. Meanwhile, defects can be formed at the interface of two different materials with a large mismatch between the core and shell. As for CdSe/ZnS QDs, mismatches in the a and c lattice parameters of ZnS to those of CdSe are 11.14% and 10.74%, respectively. The fluorescence efficiency can be reduced due to the lattice mismatch [9].

The effective mass and confinement potential energy play critical roles in the carrier's distribution in the core/shell QDs. The confinement potential energies of carriers mainly depend on the core radius, shell size and ratio between core and shell layer. The different structures designed can be achieved the high emission efficiency. Currently, more theoretical study have showed the effective mass approximation (EMA) is an important method to theoretically research the quantum confinement effect, and can be applied to the core/shell QDs to quantify the energy levels [10]. The EMA can be applied to calculate the electronic structure of the core/shell QDs, the electron and hole wave functions, the transition energy, and the overlap of the wave functions [10-13]. Haus *et al*. applied the effective mass approximation to calculate the electronic structure of Quantum-dot quantum well (QDQW). They systematically investigated the electron and hole wave functions, the 1*s* transition energy, and the overlap of the wave functions [10]. Schooss *et al*. further take into account the Coulomb interaction between electron and hole, the results showed that the probabilities of the carriers can present in the different layers in the QDQW CdS/HgS/CdS structure [11]. Chang *et al*. pointed out that the spatially separated characteristic of electron and hole can be enhanced significantly in QDQW with the two wells [12]. More recently, Nizamoglu *et al*. presented that the multi-color spontaneous emission can be obtained by the exciton localization in distinct layers in the onion-like QDQW structure [13]. It is therefore of great interest and importance to engineer spatial distributions wave function of electron and hole in nano-particles [6].

To date, several II-IV semiconductor alloy nanocrystals have been synthesized via organometallic routes: CdS_xSe_{1-x}, $Cd_xZn_{1-x}S$, $Cd_xZn_{1-x}Se$, $CdSe_xTe_{1-x}$, and $HgSe_xS_{1-x}$.5. [14] More recently, water-soluble $Cd_xZn_{1-x}Te$ alloyed QDs with glutathione (GSH) as the stabilizer was prepared through a one-step aqueous route [15]. Ternary semiconductor compounds provides greater tuning range of lattice constant and energy levels than the binary compounds. The lattice parameters of ternary semiconductor compounds can easily be changed by controlling the components ratio. The knowledge of the electronic structure properties is the key to expand ternary semiconductor compounds in the application of core-shell structure.

In this letter, the EMA model was used to study the

CdSe/Cd$_x$Zn$_{1-x}$S core/shell QDs with taking into the Coulomb interaction account. The electron and hole wave function behaviors in CdSe/Cd$_x$Zn$_{1-x}$S core/shell structure nanocrystals were investigated with the changing of the structure parameters and the component ratio of Cd$_x$Zn$_{1-x}$S. The electron and hole wave functions, the 1*s* transition energy, and the overlap of the wave functions is analyzed.

2. Theory

We consider the core/shell structure QDs, which consisted of ZnS shell and CdS core materials. When the space-dependent effective mass of carriers is taken into account, the Schrodinger equation of carriers in the framework of the single-band effective mass approximation in the QDs region is as follows:

$$\left(-\frac{\hbar^2}{2}\nabla\frac{1}{m_i}\nabla - V\left(r\right)\right)\Psi(r) = E\Psi(r) \qquad (1)$$

where $\hbar$ is Planck's constant divided by 2π, m_i and $V(r)$ the particle mass and a potential depending on the position in the QDs, E the energy eigenvalue, and $\psi(r)$ the corresponding eigenfunction. Here, we consider QDs with spherically symmetric structure and homogeneous potentials, which leads to separate the wave functions into the radial and angular parts as follows:

$$\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi) \qquad (2)$$

$R_{nl}(r)$ is the radial wave function, and $Y_{lm}(\theta,\phi)$ a spherical harmonic. n is the principal quantum number, and l and m are the angular momentum numbers. We shall restrict the calculations to 1*s* states for $n=1$, $l=m=0$. We obtain the solutions for QDs by solving the continuity relations of the carriers wave functions and the probability currents at the boundaries:

$$R_{nl,i}(k_i r_i) = R_{nl,i+1}(k_{i+1} r_i) \qquad (3)$$

$$\frac{1}{m_i}\frac{dR_{nl,i}(k_i r_i)}{dr}\bigg|_{r=r_i} = \frac{1}{m_{i+1}}\frac{dR_{nl,i+1}(k_{i+1} r_i)}{dr}\bigg|_{r=r_i} \qquad (4)$$

where $k_{i/i+1} = \left[\frac{2m_i(E-V)}{\hbar^2}\right]^{1/2}$ is the wave vectors in core and shell, repectively, $R_{nl,i}(r_i)$ and $R_{nl,i+1}(r_i)$ are the radial wave functions for the carriers (electron or hole) in the core and shell, respectively, m_i and m_{i+1} are the carrier effective masses in the CdS and ZnS, respectively. For simplicity, we assume that the QDs was placed in a infinite potential well. That is to say, no wave functions tunnel from the QDs to the outside of QDs with taking into account the complete confinement. Thus, at the outer boundary of the QDs, the nontrivial solution can be obtained to determine the general energy eigenvalues by letting the determinant of the coefficients of the wavefunction at the interface as zero.

The Coulomb interaction energy between electron and hole pair can be treated as a heliumlike perturbation according to the first-order perturbation approximation. After expanding of $1/|r_e - r_h|$ in spherical harmonics form and integrating the angular coordinates, the Coulomb interaction energy can be expressed as[11,13]

$$E_c = -\frac{e^2}{4\pi\varepsilon_0}\iint dr_e dr_h r_e^2 r_h^2 \frac{|R_e(r_e)|^2 |R_h(r_h)|^2}{\max(r_e,r_h)\bar{\varepsilon}(r_e,r_h)} \qquad (5)$$

For ternary semiconductor compound, the optical band-gap was given using bowing parameters:

$$E_g = xE_{gap}^{AB} + (1-x)E_{gap}^{AC} - b_{bow}x(1-x)$$

where E_{AC} and E_{AB} are the band gaps of compounds AC and AB, respectively, and b_{bow} the bowing parameter. Tit *et al.* studied the origins of bandgap bowing in coumpound-semiconductor common-cation ternary alloys based on the sp3s* tight-binding method, which can replied that the mismatch in electro-negativity would play a role in the bandgap bowing of alloys[17]. This can result in the velence band states lowing in energy with the increasing of Cd molar fraction in the ternary alloy, while the cation Zn are contributors to the conduction band of the alloy. Here, it can be a very reasonable conjecture as follows: the conduction band edge was approximated by linear interpolation between that the constituent binary compounds, then the valence band edge was calculated by $E_V = E_C - E_g$. As far as the core/shell structure QDs is concerned, the strain plays a key role in the transition energy levels. The lattice-mismatch between core and shell can further decrease with Cd molar fraction increasing in the ternary alloy shell. The lattice mismatch between core and shell layer can easily be implemented by adjusting the molar ratio of Cd in the shell layer, as shown in the Fig.1.

3. Results and discussion

In the following we present the numerical results for the parameters appropriate to a CdSe/$Cd_xZn_{1-x}S$ core/shell QD. The values of the physical parameters used in our calculations are given in Table 1. To investigate the influence of structure parameters (core radius r and shell thicknesses R) on spatial distributions of carriers, we performed the radial probabilities of the carriers in the lowest energy 1*s* eigenstates for CdSe/$Cd_xZn_{1-x}S$ core/shell QDs. Fig. 2 shows the radial probabilities of electron and hole with different Cd^{2+} ion molar ratio in the shell layer. It can be seen that the wave function of the electron can slightly spread out the CdSe core layer with the increasing of Cd^{2+} ion molar ratio. It was also found that Cd^{2+} ion molar ratio weakly affected the probability of hole at the core of the QDs. Both of the electron and hole are completely localized at the range of core, which can be ascribed to the large energy band offset in valence band and conduction band.

Table 1. Material parameters for CdSe , CdS, and ZnS.

Material	m_e/m_0	m_h/m_0	Dielectric constants	Band gap (eV)
CdSe [16]	0.13	0.45	10.2	1.74
ZnS [10]	0.28	0.49	8.9	3.9
CdS [10]	0.2	0.7	5.5	2.5

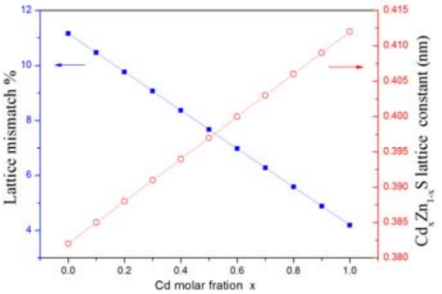

Fig. 1. Variation of the lattice constant of $Cd_xZn_{1-x}S$ and lattice mismatch between the core CdSe and $Cd_xZn_{1-x}S$ shell layer with Cd molar fraction in shell layer.

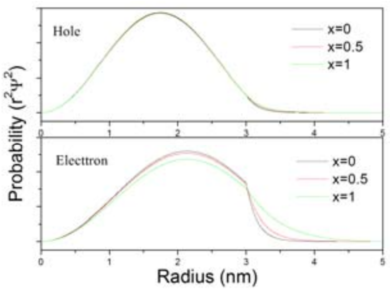

Fig. 2. The probability of the presence of electron and holes in the lowest energy 1s eigenstates in CdSe/$Cd_xZn_{1-x}S$ QDs structure with the different Se molar fraction in the ternary semiconductor core and keeping the core radius and shell size constant r=3nm and R=3nm, respectively.

Fig. 3 shows the variation of the energies of electron and hole levels in the ternary CdSe/$Cd_xZn_{1-x}S$ core/shell QDs as a function of the core radius for different Cd molar fraction, i.e., x=0, 0.5 and 1, respectively. It can be seen that the hole energies was changed weakly with variation of the Cd molar fraction, which implied the slight effect of the confinement potential on the transition energy with the increasing of the Cd molar fraction. From Fig. 2 we find that the dependence of energies of electron level on Cd molar fraction is more obvious than those of the hole level. It is readily seen that the changing of the electron energies level of strong-confinement QDs (with small core radius) is much larger than that of weak-confinement QDs (with large core radius) in the same Cd molar fractions. The carriers should appear in the region of core or shell, which mainly depend on the competition between the kinetic energy and the potential energy in the heterostrucuture QDs.[5]

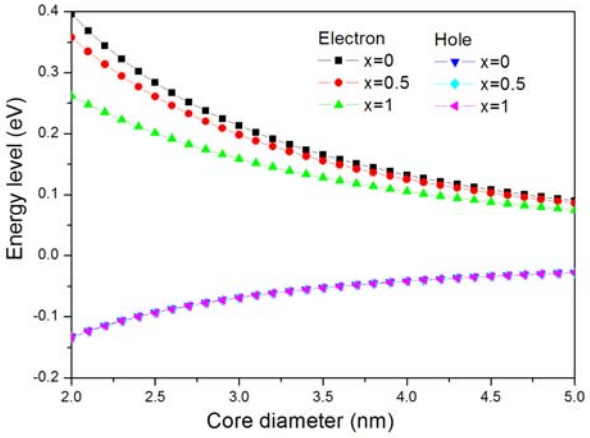

Fig. 3. The energies of the electron and hole in the lowest energy 1s eigenstates as a function of the core radius in CdSe/$Cd_xZn_{1-x}S$ QDs structure with the different Cd molar fraction.

Fig. 4 shows the band gap energy of the ground state for the ternary CdSe/$Cd_xZn_{1-x}S$ core/shell as a function of the core radius for the five different Cd molar fraction x=0, 0.5, and 1, respectively. From the figure, it can be clearly seen that the band edge transition energy in the structure with low Cd molar fraction is larger than the energy gap for the CdS shell layer. This shows that the Cd molar fraction in the ternary $Cd_xZn_{1-x}S$ core is the weak influence on the QDs energy levels. The changing of molar fraction in the ternary $Cd_xZn_{1-x}S$ core results in the variation of the effective masses of electron and hole, and the band offset between the core and shell changed. In addition, the valence band bows in the ternary semiconductor compound can also slightly influence the energy level. It can be very import to design the high efficiency QDs with small strain between core and shell layer.

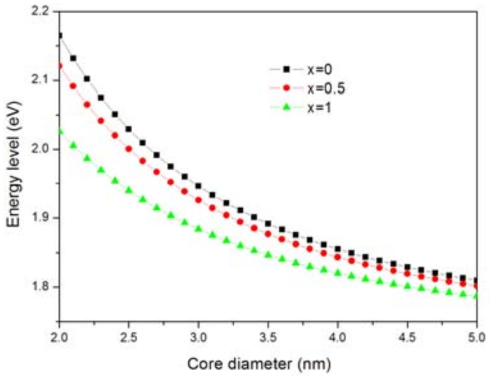

Fig. 4. The lowest energy 1s eigenstates as a function of the core radius in CdSe/Cd$_x$Zn$_{1-x}$S QDs structure with the different Cd molar fraction.

Fig. 5 reveals the Coulomb interaction energy of the ground state for the ternary CdSe/Cd$_x$Zn$_{1-x}$S core/shell as a function of the core radius for the five different Cd molar fraction x=0, 0.5 and 1, respectively. The Coulomb interaction energy strongly depends on the core radius and the type of QDs. The strength of the Coulomb interaction energy decreases as the core radius is increased. According to the expression (5), the overlap integral play an important role in carrier-carrier interaction. Thus, the QDs with large size core, which results in a large overlap integral due to the weak spillover of carriers. It can also been seen that the Coulomb interaction energy increase with the Cd molar fraction in shell layer, which can be ascribed to small overlap integral for the small size core QDs.

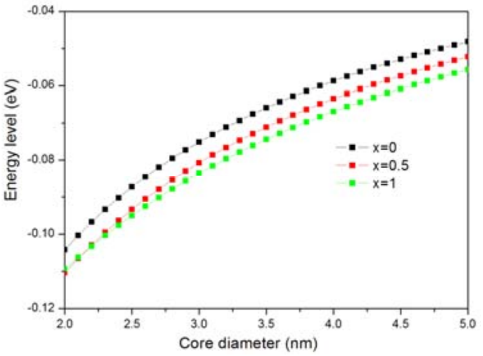

Fig. 5. The Coulomb interaction energy as a function of the core radius in CdSe/Cd$_x$Zn$_{1-x}$S QDs structure with the different Cd molar fraction.

In order to study the effect of Cd molar fraction in the ternary Cd$_x$Zn$_{1-x}$S shell on the spatial distribution of carriers, we analyze the overlap integral between electron and hole functions defined as $\Theta = \left| \int_0^{r+R} H^2 \Re^e(H) \Re^h(H) dH \right|^2$, where H is the radial coordinate with the origin at the core center and $\Re^{e(h)}(H)$ is the radial part of the electron (hole) envelope wavefunction. Fig. 6 shows the overlap integral for fixed values of the shell thickness (R=3nm) as a function of the core radius for the different Cd molar fraction in the ternary Cd$_x$Zn$_{1-x}$S shell. It can be clearly seen that the overlap integral exhibit a perfect type-I structure. It can also been seen that the overlap integral can reduce with decreasing of the core radius for the large Cd molar fraction.

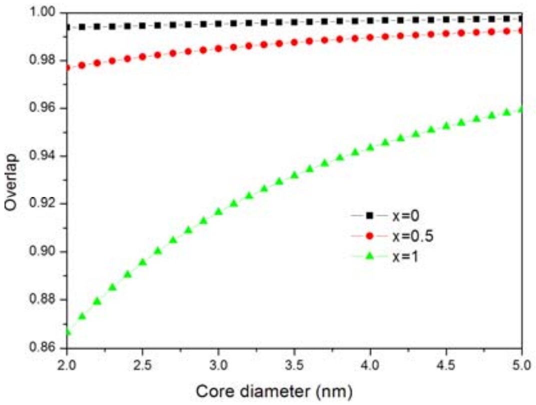

Fig. 6. The calculation of the overlap integral as a function of the core radius with the different Se molar fraction in CdSe/Cd$_x$Zn$_{1-x}$S QDs for the shell size fixed (r=3nm).

4. Conclusions

We have studied the electronic structures of a ternary CdSe/Cd$_x$Zn$_{1-x}$S core/shell structure QDs, including the Coulomb interaction between electron and hole. It is found that the 1*s* transition energies depend sensitively on the core radius of the QDs and weakly on Cd molar fraction in the ternary shell. The spatial separation between electron and hole in QDs can easily be implemented by adjusting Se molar fraction in the core region. The lattice mismatch between core and shell layer can easily be implemented by adjusting the molar ratio of Cd in the shell layer.

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