Quantum size effects on exctions properties of CdSe/ZnS core/shell quantum dots

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The electronic and optical properties of CdSe/ZnS core/shell quantum dots are investigated systematically based on effective-mass approximation theory. The Coulomb interaction between the electron and hole is also taken into account. The calculated results shown that the electron and hole can be mainly localized in the core area for the CdSe/ZnS type-Ⅰ heterostructure. The electron and hole wavefunctions are almost completely localized in the core area and remain a large overlap for the CdSe/ZnS quantum dots. The quantum confinement plays an important role in the transition energies and overlap integral of the carriers. The changing of the shell thickness alone does not provide signficant spectral tunability of the emission wavelength. It can be efficient to tune the range of spectrum by controlling core size.

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1. Introduction

Research on core/shell quantum dots (QDs) has recently received much attention due to its fascinating optical and electronic properties and potential application in optoelectronic devices and with low cost and high performances. There has been growing interest in the physics of core/shell QDs in recent years [1-3] because of the rapid development of fabrication technology. The carriers confined in all spatial dimensions in the QDs can remarkably modify the physical properties of materials, which exhibit a richer variety of physical phenomena than quantum wells. The effective mass and confinement potential energy play critical roles in the carriers 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. The different structures designed can be achieved the separating of the carriers spatial distribution [3].

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 [4]. Chang *et al*. pointed out that the spatially separated characteristic of electron and hole can be enhanced significantly in QDQW with the two wells [5]. 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 [6]. More recently, Jia *et al*. invesitigated that the QDs with a ternary semiconductor compound core can produce a new degree of freedom for tailoring the band structure. The electronic structures core/shell structure QDs have been investigated by effective-mass approximation method with taking into the Coulomb interaction account. The heterostructure type of QDs can be tuned from the type-I to type-II by changing the molar fraction in the core layer and the corresponding "spatially indirect" energy gap formed [7]. Therefore, it is essential to theoretically analyze the excitons distribution in the CdS/ZnS core/shell structure to understand the physics for improving the QDs performance.

The optical properties of core/shell structure QDs have attracted an enormous interest in recent years [8-10]. These results show that the optical properties in core/shell QDs can be tunned by changing the composition and structure parameters of QDs. In this work, we will devote our calculations to electron and hole wave function behaviors in CdSe/ZnS core/shell structure QDs with the changing of the core radius and the shell thickness. The mechanism of the excitons spatial distribution is discussed, in which the main reason is attributed to the effect of valence band offset on carrier quantum confinement for different structure QDs. To the best of our knowledge, this problem has not been studied extensively in the literature. The variation of the shell and core radius will allow us to gain more insight into its optical properties.

2. Theory

In the type-I structure QDs, both the condutction and the valence band edges of the core are located within the energy gap of the shell semiconductor. We consider the core/shell structure QDs, which consisted of ZnS shell and CdSe core materials. When the space-dependent effective mass of carriers is taken into account, the Schrodinger equation of carriers in the framework of the effective mass approximation in the QDs region is given by

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

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:

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

$R_{nl}(r)$ 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:

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

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

where $k_{i/i+1}=\left[\frac{2m_i(E-V)}{\hbar^2}\right]^{1/2}$ are the wave vectors in the core and the 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 CdSe and ZnS, respectively. For simplicity, we assume that the QDs was placed in a infinite potential well. 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 [3,7]

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

As for the schematic energy diagram of the CdSe/ZnS core/shell under investigation, ZnS has the higher valence and conduction bands than CdSe, which corresponds to the classic Type-I semiconductor heterostructure. In our calculations we take the material parameters are illustrated in Table 1.

Table 1. Material parameters for cdse and ZnS.

Material	m_e/m_0	m_h/m_0	Dielectric constants	Band gap (eV)
CdSe	0.2	0.7	5.5	2.5
ZnS	0.28	0.410	8.10	3.10

3. Results and discussion

Fig. 1 shows the variation of the Coulomb interaction energy versus the shell thickness (H) with the core diameter fixed. The Coulomb interaction energy is decreasing with increasing the core radius (R) due to the quantum confinement effect. It can be seen that the Coulomb interaction energy strongly depends on the shell, which can be attributed to the confinement of carriers enhanced for the thin shell thickness due to the influence of the outer infinite potential. 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.

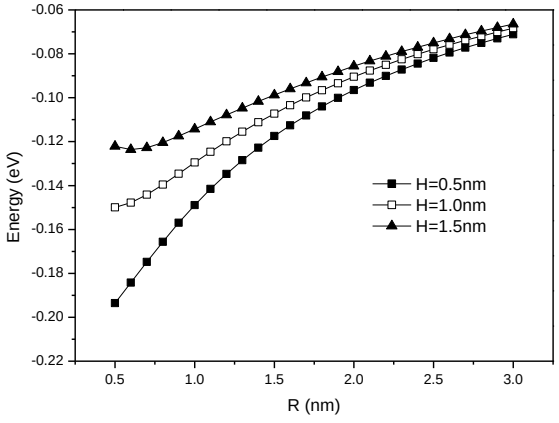

Fig. 1. The Coulomb interaction energy as a function of the core diameter with the different shell size.

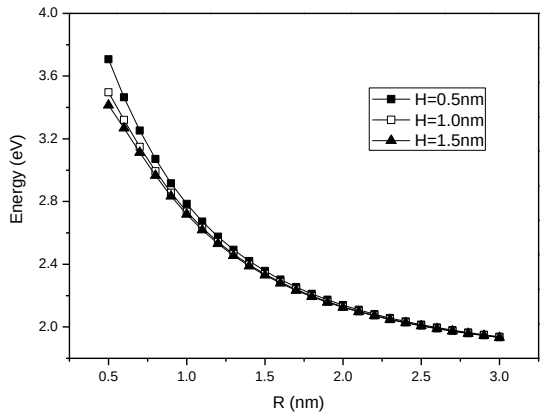

Fig. 2. The calculation of the 1s-1s transition energy as a function of the shell size with the core diameter fixed (r=3nm).

In Fig. 2, we plot the 1s-1s transition energy (the lowest energy state) as a function of the core radius with the shell thickness fixed. It is worth noting that the emission wavelength can be tuned during a very wide range. The core size variation can be considerably more effective in tuning the emission wavelength than the changing of the shell thickness. As shown from this figure, when $R < 1.5$ nm, the transition energy is monotonic function of the core diameters and decreases rapidly with an increasing R. When $R > 1.5$ nm, the transition energy is weak dependent on the core size.

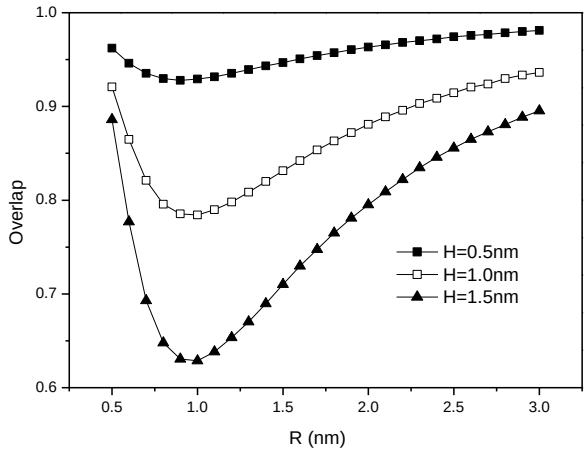

Fig. 3. The overlap integral as a function of the shell size with the core diameter fixed (r=3nm).

The carrier recombination time is an important parameter for the core/shell QDs systems, which can be calculated from overlap integral of the electron and hole wave functions. A relatively larger lifetime can be expected in QDs due to the spatial separation of the carriers. In addition, the strength of the ground state interband optical transition maily depend on the overlap integral. Generally, the overlap integral between electron and hole wavefunctions is defined as

$$\Theta = \left| \int_0^{R+H} r^2 \Re^e(r) \Re^h(r) dr \right|^2 \tag{6}$$

where r is the radial coordinate with the origin at the core center and $\Re^{e(h)}(r)$ is the radial part of the electron (hole) envelope wavefunction. In order to study the effect of structure on the overlap integral between electron and hole wavefunctions in the core/shell QDs, a numerical calculation has been performed for the overlap integral as a function of the core radius in the range from 0.5 to 3 nm for three different shell thickness, i.e., H=0.5, 1.0, and 1.5 nm, respectively. Fig. 3 shows the variations of the overlap integral as a function of the QDs radius. The overlap integral, at the beginning, decreases with an increasing R, but it reaches a minimum value at around 1 nm, as R is increased further, it begins to increase. It is readily seen that the variation of the overlap integral in weak-confinement QDs is much obviouser than that in strong-confinement QDs in the same core radius.The reducing the electron-hole wave function overlap can degrade the optical property of the sample. Interestingly, when *H*=0.5nm, the overlap integral increases with the shell size increasing slightly, indicating the carriers are localized in the area of core with the increasing of core size. The core size is main factor to influence the wavefunction distribution in the QDs. As the shell thickness increases, the confinement of carriers is increased. It is well known that the carriers are localized in the shell or core region, determined by the effective masses and the energy band offsets between the core and shell materials. For thick ZnS shells (*H*=1.5 nm), the energy band offsets play an important role in confining the carriers in the core region, the distribution of wavefunction can mianly determinated to the confinement energy.

4. Conclusions

In general, we study the electronic structures of CdSe/ZnS 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, while weakly on the shell size. The quantum confinement plays an important role in the transition energies and overlap integral of the carriers. The overlap integral in weak-confinement QDs is much obviouser than that in strong-confinement QDs in the same core radius.

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References

[1] S. Y. Ryu, B. H. Hwang, K. W. Park, H. S. Hwang, J. Sung, H. K. Baik, C. H. Lee, S. Y. Song, J. Y. Lee, Nanotechnology, **20**(6), 065204 (2010).
[2] G. Z. Jia, X. N. Fei, J. Wang, Chalcogenide Letters, **7**(3), 181 (2010).
[3] G. Z. Jia, Y. F. Wang, J. H. Yao, Optoelectron. Adv. Mater.-Rapid Commun., **4**(12), 2080 (2010).
[4] J. W. Haus, H. S. Zhou, I. Honma, H. Komiyama, Physical Review B, **47**(3), 1359 (1993).
[5] K. Chang, J. B. Xia, Physical Review B, **57**(16), 10780 (1998).
[6] S. Nizamoglu, H. V. Demir, Optics Express, **16**(6), 3515 (2008).
[7] G. Z. Jia, Y. F. Wang, L. Gong, J. H. Yao, Digest Journal of Nanomaterials and Biostructures, **6**(1), 43 (2011).
[8] L. P. Balet, S. A. Ivanov, A. Piryatinski, M. Achermann, V. I. Klimov, Nano Letters, **4**(8), 1485 (2004).
[9] S. Kim, B. Fisher, H. J. Eisler, M. Bawendi, Journal of the American Chemical Society, **125**(38), 11466 (2003).
[10] D. Schooss, A. Mews, A. Eychmuller, H. Weller, Physical Review B, **410**(24), 17072 (1994).

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