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Dielectric Confinement Effect on Calculating the Band Gap of PbSe Quantum Dots

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Considering the dielectric confinement effect on excitonics of PbSe quantum dots (QDs), a correction factor in the wave function was introduced to propose a new band gap calculation model for QDs. The modified model showed great consistency with the experimental data, especially in small size range. According to the variation of confined barrier, the band gap calculation model of PbSe QDs was analyzed in different solvents. The calculating results showed that the modified model was almost solvent-independent, which was consistent with our experimental results and related reports.

Key words: Dielectric confinement effect, PbSe, Band gap

I. INTRODUCTION

PbSe quantum dots (QDs) is a kind of semiconductor materials with a narrow band gap (the bulk band gap is only 0.28 eV) [1], large Bohr radius ($a_B=46$ nm) [2, 3], and small effective mass ($m_c=0.07m_0$, $m_h=0.068m_0$, m_0 is the electron static mass). Its excellent size-dependent optical property due to strong quantum confinement can span the near-infrared range of 0.9–2.5 μm [2, 3]. Those characteristics render it highly promising in a variety of applications in different fields such as optoelectronics [1, 4, 5], biophysics [1, 4, 6], solar cells [3, 7, 8], and electronic communications [4, 9].

In order to calculate the size-dependent band gap of QDs, several theoretical models have been proposed, including effective mass approximation (EMA) [10], tight binding approach (TB) [11], effective bond orbital model (EBOM) [12], empirical pseudopotential method (EPM) [13], and finite barrier version of the EMA (FEMA) [14, 15]. Because the traditional EMA model is based on infinite potential well, the overestimated exciton confinement energy [10] induces that the theoretical data of the band gap are always much larger than the experiment ones in small size range. With regard for the incomplete confinement of solvent for QDs, the FEMA model was proposed as the modified model of EMA, which shows the reasonable results [15]. Pellegrini *et al.* have investigated the band gap calculation of several wide band gap QDs (CdS, CdSe,

CdTe) and narrow band gap QDs (PbSe, PbS, InAs) using FEMA model [14]. Compared with experimental data, FEMA model is accurate for wide band gap QDs (such as CdSe), but the calculating result shows a big tolerance for narrow band gap QDs (such as PbSe). The possible reason may be the dielectric confinement effect on excitonics, which restricts the electrons and holes in PbSe QDs deeply.

In view of dielectric confinement effect on excitonics [16, 17], we revised the FEMA model and calculated the band gap of colloid PbSe QDs with different particle sizes. Comparing the theoretical calculating results with the experimental data in several work [2, 3, 14], we introduced a appropriate correction factor in the wave function, and the results show a good consistent with the experimental data.

II. EXPERIMENTS

PbSe QDs were prepared in our experiment via a synthetic route reported by Yu *et al.* [18]. Typically, PbO (0.892 g, 4.00 mmol), OA (oleic acid, 2.260 g, 8.00 mmol), and ODE (1-octadecene, 12.848 g) were loaded into a three-neck flask and heated to 170 $^\circ\text{C}$. After PbO powder completely dissolved under a nitrogen flow, 6.400 g of TOP-Se (trioctylphosphine-Se) solution containing 0.640 g of Se (prepared in a glovebox) was swiftly injected into the vigorously stirred solution. Subsequently, the temperature was kept at 140 $^\circ\text{C}$ for the nanocrystal growth. At different reaction intervals, aliquots were taken out for transmission electron microscope (TEM) and absorption spectra measurement. Figure 1 is the high definition TEM images which legibly show that the PbSe nanocrystals have intact lattice

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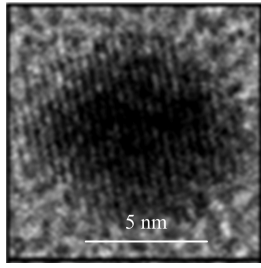


FIG. 1 High definition TEM images legibly show that the PbSe nanocrystals have intact lattice structures.

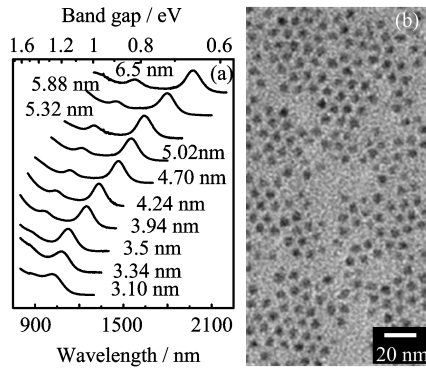


FIG. 2 (a) The evaluation of absorption spectra versus particle size. (b) The TEM of 4.8 nm PbSe QDs.

structures. TEM images of nanoparticles with different sizes were taken by a JEOL FasTEM-2010 TEM. The TEM of 4.8 nm PbSe QDs is shown in Fig.2(b). A Perkin-Elmer Lambda 9 UV-Vis-NIR spectrometer was employed to record the absorption spectra of PbSe QDs samples. The evaluation of absorption spectra versus particle size is shown in Fig.2(a).

III. CALCULATION AND DISCUSSION

A. Modified FEMA model

According to the dielectric confinement effect-based FEMA model, the Hamiltonian for electron-hole system can be written as

$$H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 + V_e + V_h + V_{\text{pol}} - \frac{e^2}{4\pi\epsilon_0\epsilon r_{eh}} \quad (1)$$

where m_e (m_h) is the effective electron (hole) mass, V_{pol} is the additional potential energy induced by the dielectric confinement effect, V_e (V_h) is confining potential energy for electron (hole), which is determined by the following formula

$$V_e + V_h = E_g^M - E_g^S \quad (2)$$

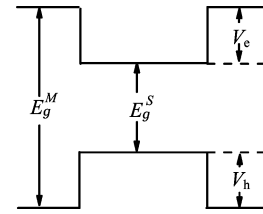


FIG. 3 Potentials V_{0e} and V_{0h} for a semiconductor material in a matrix.

where E_g^S is the band gap of bulk PbSe, and E_g^M is the band gap of the solvent, Fig.3 shows potentials (V_e and V_h) for a semiconductor material in a matrix. Thus the confining potential energy is given by

$$V_0 = \begin{cases} 0, & r < R \\ V_{e(h)}, & r > R \end{cases} \quad (3)$$

where r is the radial coordinates, R is the radius of quantum dot. If the Coulomb interaction between electron and hole is treated in the frame of first-order perturbation theory, by adopting the Hylleraas coordinate system, the Hamiltonian for the $l=0$ ground state are [15]

$$H = -\frac{\hbar^2}{2m_e} \left[\frac{\partial^2}{\partial^2 r_e} + \frac{2}{r_e} \frac{\partial}{\partial r_e} \right] - \frac{\hbar^2}{2m_h} \left[\frac{\partial^2}{\partial^2 r_h} + \frac{2}{r_h} \frac{\partial}{\partial r_h} \right] - \frac{\hbar^2}{2m_r} \left[\frac{\partial^2}{\partial^2 r_{eh}} + \frac{2}{r_{eh}} \frac{\partial}{\partial r_{eh}} \right] + V_{\text{pol}}, \quad r \leq R \quad (4)$$

$$H = -\frac{\hbar^2}{2m_e} \left[\frac{\partial^2}{\partial^2 r_e} + \frac{2}{r_e} \frac{\partial}{\partial r_e} \right] - \frac{\hbar^2}{2m_h} \left[\frac{\partial^2}{\partial^2 r_h} + \frac{2}{r_h} \frac{\partial}{\partial r_h} \right] - \frac{\hbar^2}{2m_r} \left[\frac{\partial^2}{\partial^2 r_{eh}} + \frac{2}{r_{eh}} \frac{\partial}{\partial r_{eh}} \right] + V_e + V_h, \quad r > R \quad (5)$$

The trial wave function is chosen as [15–17]

$$\psi(r_e, r_h) = \varphi(r_e)\varphi(r_h) \quad (6)$$

According to Eqs. (4) and (5), the wave functions of electron (hole) inside and outside the QDs can be expressed as

$$\varphi_{\text{in}}(r) = A_i \frac{\sin(K_i r_i)}{r_i} e^{-\chi_i r_i / R}, \quad (i = e, h, \quad r < R) \quad (7)$$

$$\varphi_{\text{out}}(r_i) = B_i \frac{e^{-N_i r_i}}{r_i}, \quad (i = e, h, \quad r > R) \quad (8)$$

$$K_i = \sqrt{\frac{2m_i E_i}{\hbar^2}}, \quad N_i = \sqrt{\frac{2m_0(V_0 - E_i)}{\hbar^2}} \quad (9)$$

m_i stands for the effective mass, E_i includes quantum size-confinement energy and quantum dielectric-confinement energy of electron or hole, respectively. χ_i

is attenuation factor which is dependent on the polarization energy V_{pol} induced by surface dielectric effects, and it can be calibrated using experimental data.

Both size effect and dielectric confinement effect are important to calculate the band gap of QDs. Several factors may induce the variation of excitonic state, the atom stress on the surface is different from the one inside, which will induce the change of the lattice constant on the surface; the different bond mode of the surface atom results in the surface reconstruction; there is adsorption layer on the QDs surface. Surface state is the electronic energy state on the interface of QDs and solvent and will generally induce the decay of wave function.

The wave function must meet the Barstard conditions [19] are the wave function continuity condition and the mass flow conservation condition in the boundary

$$\begin{cases} \varphi_{\text{in}}(R) = \varphi_{\text{out}}(R) \\ \left. \frac{1}{m} \frac{\partial \varphi_{\text{in}}}{\partial r} \right|_{r=R} = \left. \frac{1}{m_0} \frac{\partial \varphi_{\text{out}}}{\partial r} \right|_{r=R} \end{cases} \quad (10)$$

By substituting Eq.(7) and Eq.(8) into Eq.(10), we get the

$$\tan(KR) = \frac{KR}{(1 + \chi) - m(NR + 1)/m_0} \quad (11)$$

Assuming that

$$\beta = \frac{m}{m_0}, \quad X_0^2 = \frac{2m_0 V_0 R^2}{\hbar^2}, \quad KR = X_0 \xi \quad (12)$$

Eq.(11) can be replaced by

$$\tan(X_0 \xi) = \frac{X_0 \xi}{(1 + \chi) - \beta - \beta X_0 \sqrt{1 - \xi^2/\beta}} \quad (13)$$

$$\xi^2 = \left(\frac{KR}{X_0} \right)^2 = \beta \frac{E}{V_0} \quad (14)$$

$$E = \frac{\xi^2 V_0}{\beta} = \frac{\hbar^2 X_0^2 \xi^2}{2mR^2} \quad (15)$$

Then the energy eigenvalues E_e and E_h can be obtained by Eq.(13).

Utilizing the first-order perturbation theory, the Coulomb energy can be calculated by

$$\begin{aligned} E_{e-h} &= \left\langle \varphi(r_e), \varphi(r_h) \left| \frac{e^2}{4\pi\epsilon_0\epsilon(\bar{r}_0)|r_e - r_h|} \right| \varphi(r_e), \varphi(r_h) \right\rangle \\ &= -\frac{2e^2}{4\pi\epsilon_0\epsilon(\bar{r}_0)} \int_0^R \varphi^2(r_h) 4\pi r_h dr_h \cdot \\ &\quad \int_0^{r_h} \varphi^2(r_e) 4\pi r_e^2 dr_e \end{aligned} \quad (16)$$

here $\varphi(r_e)$ and $\varphi(r_h)$ are the internal wave functions for electron and hole, respectively. $\epsilon(\bar{r}_{eh})$ is the dielectric constant varying with the mean electron-hole distance

$\bar{r}_{eh} = |r_e - r_h|$, for which an average value of 0.69932R should be used. $\epsilon(\bar{r}_{eh})$ is determined by

$$\frac{1}{\epsilon(\bar{r}_{eh})} = \frac{1}{\epsilon_\infty} - \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \cdot \left[1 - \frac{e^{-\bar{r}_{eh}/\rho_e} + e^{-\bar{r}_{eh}/\rho_h}}{2} \right] \quad (17)$$

ϵ_∞ and ϵ_0 are the optical and static dielectric constants,

$$\rho_{e,h} = \left(\frac{\hbar}{2m_{e,h}\omega_{LO}} \right)^{1/2} \quad (18)$$

where ω_{LO} is the LO phonon frequency. By substituting Eq.(7) and Eq.(8) into Eq.(16), the Coulomb energy is calculated as

$$\begin{aligned} E_{e-h} &= \frac{2e^2 16\pi^2 (A_e A_h)^2}{4\pi\epsilon_0\epsilon(\bar{r}_{eh})} \frac{R}{4\chi_e(\chi_e^2 + K_e^2 R^2)} \cdot \\ &\quad \int_0^R \frac{\sin^2(K_h r_h)}{r_h} e^{-2\chi_h r_h/R} \{ e^{-2\chi_e r_h/R} \cdot \\ &\quad [\chi_e^2 + K_e^2 R^2 - \chi_e^2 \cos(2K_e r_h) + \\ &\quad K_e R \chi_e \sin(2K_e r_h)] - K_e^2 R^2 \} dr_h \end{aligned} \quad (19)$$

where χ_e and χ_h stand for the electron and hole attenuation factors, respectively. The coefficient $A_{e,h}$ is determined by

$$\begin{aligned} A_{e,h} &= \left\{ 4\pi \left[\int_0^R \sin^2(K_{e,h} r) e^{-2\chi_{e,h} r/R} dr + \right. \right. \\ &\quad \left. \left. \frac{\sin^2(K_{e,h} R)}{e^{-2N_{e,h} R}} e^{-2\chi_{e,h}} \int_R^{+\infty} e^{-2N_{e,h} r} dr \right] \right\}^{-1/2} \end{aligned} \quad (20)$$

Summing up, the band gap of QDs can be expressed as

$$E_g = E_e + E_h + E_{e-h} + E_{\text{bulk}} \quad (21)$$

In the absorption spectrum experiment of PbSe QDs, tetrachloride was employed as the solvent. According to Ref.[14], confining potential should be designated as: $V_e=2.97$ eV, $V_h=2.3$ eV. Meanwhile, we used experimental data of 2.21 nm PbSe QDs reported by Wise *et al.* [3] to obtain the correction factor: $\chi_e=0.1519$, $\chi_h=0.3061$.

IV. RESULTS AND DISCUSSION

Figure 4 shows the theoretical values of LUMO and HOMO calculated by the infinite potential well model (EMA), the finite potential well model (FEMA) and the revised FEMA model, respectively. It is obvious that the FEMA model can revise the errors of HOMO and LUMO caused by overestimation of the quantum confinement energy in EMA model compared with experimental HOMO and LUMO data by Wise *et al.* [3],

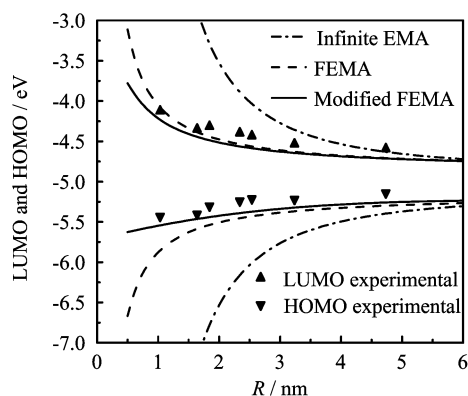


FIG. 4 Comparison between experimental and theoretical results for LUMO and HOMO, experimental values [3].

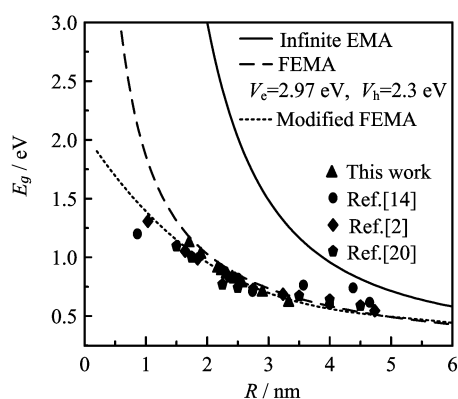


FIG. 5 Comparison between experimental and theoretical results for band gap energy.

but in the small size range, the theoretical slope of E versus R in the FEMA model is quite higher than experimental data. And the calculated curve using revised FEMA model agreed with the experimental data best.

The experimental data from several groups [2, 14, 20] and theoretical values of band gap calculated by the three models are presented in Fig.5. The results of the infinite potential well model are with large error and considerably deviate from the experimental data. The results calculated by the finite potential well model coincide closely with the experimental data in large size range ($R > 2$ nm), but deviate significantly from the experimental data when the radius is less than 2 nm. And the present calculation of revised finite potential well model is much closed to the experimental size-dependent band gap in all size range. This indicates that the surface state effect plays a considerable role as the size of the QDs reduces, which may induce moderate increase of band gap.

In Fig.6 the experimental band gap values of PbSe QDs synthesized in different solvent conditions are from different groups. All these results are consistent very well, which has been reported by related researchers

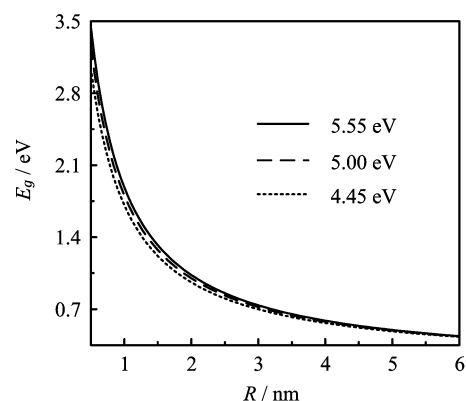


FIG. 6 Band gap calculated using present model with different proportions of V_e and V_h .

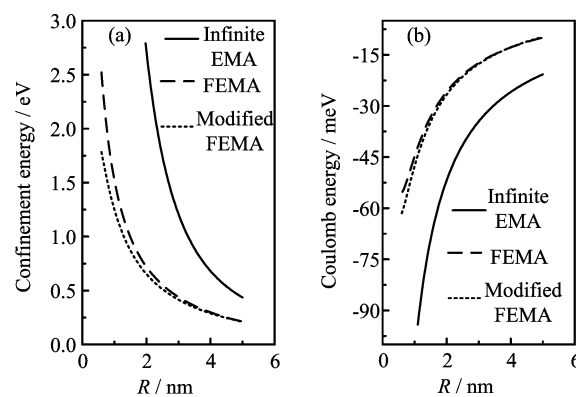


FIG. 7 Comparison between three models for confinement energy (a) and Coulomb energy (b).

[21]. The calculated curves using present model in different proportions of V_e and V_h are shown in Fig.6. Those closed curves indicate that the present model is insensitive to the change of V_e and V_h in different solvents.

The contribution of confinement energy and Coulomb energy in the band gap using three models are shown in Fig.7. It can be seen that the size dependent confinement energy (kinetic energy of electrons and holes) plays the master role in minimizing the total energy. Actually, Coulomb energy is very small and its changes in different models are not notable. Because of the main contribution of confinement energy, the surface effect will increase with the decrease of particle size. Therefore, the increase of surface effect will cause the significant deviation of PbSe QDs band gap with small size according to FEMA model reported by Pellegrini *et al.* [14]. The modified results show a better fit to the experimental results.

V. CONCLUSION

In summary, considering surface effect we introduced the correction factor to the wave function and proposed a new calculation model for band gap of QDs. The results agree well with experimental data. We hope that the present model can provide a new method to study narrow band gap QDs.

VI. ACKNOWLEDGMENTS

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