Research Article

Atomistic Tight-Binding Theory of Electron-Hole Exchange Interaction in Morphological Evolution of CdSe/ZnS Core/Shell Nanodisk to CdSe/ZnS Core/Shell Nanorod

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Based on the atomistic tight-binding theory (TB) and a configuration interaction (CI) description, the electron-hole exchange interaction in the morphological transformation of CdSe/ZnS core/shell nanodisk to CdSe/ZnS core/shell nanorod is described with the aim of understanding the impact of the structural shapes on the change of the electron-hole exchange interaction. Normally, the ground hole states confined in typical CdSe/ZnS core/shell nanocrystals are of heavy hole-like character. However, the atomistic tight-binding theory shows that a transition of the ground hole states from heavy hole-like to light hole-like contribution with the increasing aspect ratios of the CdSe/ZnS core/shell nanostructures is recognized. According to the change in the ground-state hole characters, the electron-hole exchange interaction is also significantly altered. To do so, optical band gaps, ground-state electron character, ground-state hole character, oscillation strengths, ground-state coulomb energies, ground-state exchange energies, and dark-bright (DB) excitonic splitting (stoke shift) are numerically demonstrated. These atomistic computations obviously show the sensitivity with the aspect ratios. Finally, the alteration in the hole character has a prominent effect on dark-bright (DB) excitonic splitting.

1. Introduction

Because of the wealth in the improved photoluminescence quantum yields, high photostability, and size-tunable emission properties, core/shell semiconductor nanocrystals are exceptionally fascinating in the extensive applications such as light-emitting diodes [1, 2], solar cells [3–6], lasers [7], and biological imaging [8–11]. Indeed, they have already demonstrated an excellent material system for the single photon sources in quantum information processing. However, the strong confinement of the charge carriers localized in nanostructures essentially induces the intrinsic electron-hole exchange interaction resulting in a complicated excitonic band-edge fine structure that can destroy the polarization entanglement of photon source. There are several reports being concentrated on the electron-hole exchange interaction of size-dependent II–VI semiconductor nanocrystals [12–15]. Brovelli et al. [16] demonstrated that the electron-hole exchange energies could be tuned by increasing CdS shell thickness in CdSe/CdS core/shell nanocrystals. Bryant et al. [17] implemented a nanomechanical strain to theoretically engineer the fine structure splitting of quantum dots for quantum processing using the tight-binding theory. Welander and Burkard [18] theoretically reported that a finite applied electric field was used to suppress the fine structure splitting in nonparabolic quantum dots. Sinito et al. [19] demonstrated that it was possible to manipulate the fine structure splitting using an external magnetic field which could be used to tailor the properties of entangled photon sources. Apart from the literature review, an innovative improvement in chemical synthesis of the nanostructures allows control of the material compositions and structural shapes and the realization of high-quality heterostructures in the atomic scale. Thus, Rainò et al. [20] informed about the manipulation and the tunability of the excitonic fine structure splitting in a core/shell nanorod consisting of a CdSe spherical core and an asymmetric rod-like CdS shell. A core/shell nanorod with small core and/or thick rod
diameters could robustly decrease the fine structure splitting. Exclusively, disk-type and rod-type core/shell nanostructures attracted the significant attention because they can provide the new prospects for tailoring the structural and optical properties. In the present study, the atomistic tight-binding theory is implemented to theoretically analyze the electron-hole exchange interaction in morphological evolution of CdSe/ZnS core/shell nanodisk to CdSe/ZnS core/shell nanorod with the aim of offering a deep insight into the knowledge of the shape. Undoubtedly, the atomistic tight-binding model is proficient in affording quite accurately the excitonic fine structure splitting in nanostructures [21–23]. The empirical tight-binding theory in the conjunction with sp\(^3\)\(^*\) orbitals [24], the first nearest-neighboring interaction, spin-orbital interaction, and strain distribution is theoretically utilized as the computational tool. The strained atomic positions of CdSe/ZnS disk-type and rod-type core/shell nanostructures are optimized using the valence force field theory [25, 26]. To obtain the excitonic states near the band edges, the configuration interaction (CI) approach together with 12 lowest electron and 12 highest hole states considering the spin component is numerically implemented.

To study the electron-hole exchange interaction in morphological transformation of CdSe/ZnS core/shell nanodisk to CdSe/ZnS core/shell nanorod, the present paper is organized as follows. In Section 2, theory and methodology are briefly described. In Section 3, the computations corresponding to morphological evolution of CdSe/ZnS core/shell nanodisk to CdSe/ZnS core/shell nanorod are discussed with the aim of addressing the pronounced effect of the change in hole states on the structural and optical properties and electron-hole exchange interaction. To finish the task, Section 4 demonstrates the core conclusion.

2. Theory and Methodology

The atomistic simulations consist of several major steps. Firstly, a designation of wurtzite crystal structure with the anion (Se) being in the center of CdSe/ZnS core/shell nanostructures is declared. Secondly, because of the strain distribution induced by the lattice mismatch between CdSe and ZnS, the atomistic valence force field (VFF) method is used to optimize the strained atomic positions as described with more information in [25, 26] and also in my previous papers [27, 28]. Subsequently, the atomic positions of the optimized nanostructures are integrated into the empirical tight-binding model. The single-particle states of the atomistic tight-binding theory are expanded in terms of a linear combination of atomistic orbitals localized on each atom given by

\[ \Psi = \sum_{R=1}^{N} \sum_{\alpha=1}^{10} C_{R,\alpha} \varphi_{\alpha}(\vec{r} - \vec{R}) \]  

(1)

\( \varphi_{\alpha} \) are the localized atomic orbitals on atom \( R \) with the position variable \( \vec{r} \) and the total number of atoms \( N \) in the system. sp\(^3\)\(^*\) empirical tight-binding theory with the spin-orbit interaction and the first nearest neighboring interaction is utilized for the computations in the conjunction with the parameterization [29] which is fitted to reproduce the experimental bulk band structure, band gaps, and effective masses. In addition, the valence-band offset of \( E_{\text{VBO}} = +0.60 \) eV [30] between CdSe and ZnS is incorporated into the tight-binding calculations.

Finally, to theoretically investigate the electron-hole exchange interaction in CdSe/ZnS core/shell nanostructures, a configuration interaction technique (CI) [21–23, 31, 32] is computationally applied. The two-body Hamiltonian of single excitonic states constructed from the single-particle states is given by

\[ H = \sum_{i} E_{i} \epsilon_{i}^{\dagger} \epsilon_{i} + \sum_{j} E_{j} h_{j}^{\dagger} h_{j} - \sum_{ijkl} V_{ijkl}^{\text{eh, coul}} \epsilon_{i}^{\dagger} \epsilon_{j}^{\dagger} h_{k} h_{l} + \sum_{ijkl} V_{ijkl}^{\text{exch}} h_{i}^{\dagger} \epsilon_{j}^{\dagger} \epsilon_{k} h_{l}. \]  

(2)

The first two terms are the single-particle energies of electron and hole states, respectively. The third term describes the electron-hole coulomb interactions. The final term presents the electron-hole exchange interactions. The detailed calculations are numerically provided in the following.

3. Results and Discussions

To study the behavior of electron-hole exchange interaction localized in the morphological transformation of CdSe/ZnS disk-type to rod-type core/shell nanostructures, the structural parameters are assumed in the following. The CdSe diameter is 4.30 nm with the hexagonal base in the \( xy \) plane. The shape evolution from disk to rod is generated in the growth direction (z) defined as \( z = \sigma D \) where the aspect ratios \( \sigma \) represent \( L/D \) with \( L \) and \( D \) being the lengths and diameters of CdSe core, respectively. For all cases of the calculations, ZnS shell thickness is kept fixed to be 0.765 nm. Using these structural parameters, the atomistic tight-binding model (TB) and the configuration interaction method (CI) theoretically analyzed the impact of aspect ratios (\( \sigma \)) on the electron-hole exchange interaction. The evolution of single-particle and excitonic gaps in CdSe/ZnS disk-type to rod-type core/shell nanostructures as a function of the aspect ratios is illustrated in Figure 1. The single-particle and excitonic gaps are decreased with the increasing aspect ratios because of the quantum confinement [33]. Next, the atomistic characters of the first electron and hole states are discussed with the aim of understanding the shape dependence on orbital localization in CdSe/ZnS disk-type to rod-type core/shell nanostructures. In Figure 2, the ground electron states display s-like character. The contribution of the ground electron states is not perturbed by the sizes of the aspect ratios. The ground-state hole character in Figure 3 varies from heavy hole-like (HH) to light hole-like (LH) state with the increasing aspect ratios. In the beginning, the ground hole states are heavy hole-like (HH). At \( \sigma \approx 1.40 \), the level crossing ensues. The ground hole states become light hole-like (LH) character. This analogous crossover has been theoretically reported in InAs/InP nanowire [33] and also my previous paper [34].
The first-electron (e\(_1\)) character (%)

\[
\begin{array}{cccccc}
\sigma(L/D) & 0 & 0.4 & 0.8 & 1.2 & 1.6 & 2.0 \\
\hline
\text{HH} & 100 & 90 & 80 & 70 & 60 & 50 \\
\text{LH} & 0 & 10 & 20 & 30 & 40 & 50 \\
\end{array}
\]

Figure 3: The first-hole character as a function of aspect ratios (\(\sigma\)). HH and LH mean heavy hole-like and light hole-like contribution, respectively.

The change in the hole wave-function character has a pronounced effect on the optical spectra. Figure 4 shows the scattering plots of the oscillation strengths for four nominated aspect ratios. The calculations of the oscillation strengths are sensitive with the aspect ratios. The significant change is probed in the level crossing of the ground-hole character. For the disk shape, the transitions between electron and hole states of the in-plane polarization ([110]) are much more pronounced than ones of the out-of-plane direction ([001]). As can be described by the atomistic characters, the dipole moment interactions between s-like ground electron states and heavy hole-like ground hole states in the \(xy\) plane are more prominent than those along the \(z\) direction. With the increasing aspect ratios, the situation changes because of the level crossing in the ground hole states. For the rod shape, the dominant contribution chiefly comes from the out-of-plane polarization ([001]) because the dipole moment interactions between s-like ground electron states and light hole-like ground hole states along \(z\) direction are stronger than those in \(xy\) plane. These atomistic behaviours have been theoretically reported in [33, 34]. Hence, the optical properties are predominantly controlled by the structural shapes of the CdSe/ZnS core/shell nanostructures.

In addition, Figures 5 and 6 show the ground-state coulomb and exchange energies as a function of aspect ratios (\(\sigma\)), respectively. The electron-hole interactions confined in nanostructures are mainly improved by quantum confinement. Therefore, the energies of coulomb and exchange interactions are generally decreased with the increasing aspect ratios. The information of the electron-hole coulomb interaction demonstrates that electron and hole are weakly confined in CdSe/ZnS core/shell nanorods. In case of the electron-hole exchange interaction, the strong reduction of the ground-state exchange energies is probed in CdSe/ZnS core/shell nanorods with the light hole-like character in the ground hole states. It is expected that the atomistic mechanism of electron-hole interactions is achieved by changing the aspect ratios and associated hole characters.

In the last discussions, the dark-bright (DB) excitonic splitting energies of CdSe/ZnS disk-type and rod-type core/shell nanostructures as a function of the aspect ratios are demonstrated in Figure 7. To obtain the excitonic splitting energies, the configuration interaction description (CI) considering coulomb and exchange effect is utilized with inclusion of 12 electron and 12 hole levels each. The dark-bright (DB) excitonic splitting energies, usually called stoke shift, are calculated from the energy difference between
the lowest optically forbidden excitonic state and the lowest optically allowed excitonic state. As can be seen, the reduction of the DB excitonic splitting energies is observed with the increasing aspect ratios. However, when ground-state holes become light hole-like, DB excitonic splitting energies are gradually increased. Therefore, excitonic splitting energies in morphological evolution of CdSe/ZnS core/shell nanodisk to CdSe/ZnS core/shell nanorod are considerably operated by the dimension of aspect ratios in order to grasp the desired hole characters.

4. Summary

The electron-hole exchange interaction in the morphological transformation of CdSe/ZnS core/shell nanodisk to CdSe/ZnS core/shell nanorod is theoretically studied by an atomistic tight-binding theory (TB) and a configuration interaction description (CI). The computations highlight that the variation of the aspect ratios can be used to engineer the structural and optical properties and to switch heavy hole to light hole state. For the disk shape, the interband transitions of the in-plane polarization ([110]) are more promoted than those of the out-of-plane direction ([001]), while, for the rod shape, the central contribution is mostly from the out-of-plane polarization ([001]). In addition, the reduction in the energies of coulomb and exchange interactions is reported with the increasing aspect ratios. Changing from disk to rod, the single-particle and excitonic gaps are decreased because of the quantum confinement. The DB excitonic splitting energies are decreased with the increasing aspect ratios when the ground-state holes are heavy hole-like. Conversely, DB excitonic splitting energies are gradually increased with the...
ground-state holes being light hole-like. Finally, the atomistic computations of the electron-hole exchange interaction can provide the useful recommendation in using a light hole instead of a heavy hole for the quantum information.

**Conflict of Interests**

The author declares that there is no conflict of interests regarding the publication of this paper.

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