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Atomistic tight-binding computations of excitonic fine structure splitting in CdSe/ZnSe type-I and ZnSe/CdSe invert type-I core/shell nanocrystals

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ABSTRACT

The excitonic fine structure splitting (FSS) in semiconductor core/shell nanocrystals is intrinsically caused by electron-hole exchange interactions. Here, I present the model based on the combination of the atomistic tight-binding theory (TB) and configuration interaction description (CI) that allows determining the band-edge excitonic fine structure. Using this atomistic model, I highlight the operation of the excitonic fine structure splitting by engineering the type of the band alignments and the thickness of the growth shell in CdSe/ZnSe type-I and ZnSe/CdSe invert type-I core/shell nanocrystals, indicating to control the location of the carrier confinement in these nanostructures. To theoretically examine the atomistic behaviors of excitonic fine structure splitting, the single-particle spectra, optical band gaps, ground-state wave function overlaps, ground-state coulomb energies, ground-state exchange energies, dark-bright (DB) excitonic splitting and bright-bright (BB) excitonic splitting are computed. I discover that ZnSe/CdSe invert type-I core/shell nanocrystals provide a sturdily reduced energies of DB and DB excitonic splitting as described by a diminished electron-hole exchange interaction. Besides, the energies of DB and DB excitonic splitting are decreased with the increasing dimensions of the growth shell. This deeper insight is much important for the theoretical understanding and practical control by type of the band alignments and sizes in growth shell with the aim to generate the entanglement of the polarized photon source in the application of the quantum information processing.

1. Introduction

Colloidal semiconductor core/shell nanocrystals have confirmed to be a very multipurpose class of quantum optics, sensors and quantum information. Interestingly, they have also appealed a curiosity as the single photon sources for quantum information processing. To generate the polarized entangled photon pair, the biexciton (XX)-exciton (X)-ground state (0) cascade process [1] is recognized in the conjunction with the highly desirable degenerate excitonic states. However, involved bright excitonic states are realistically not degenerate with the discrepant energy of several tens of micro electronvolts (eV). This discrepancy, explicitly fine structure splitting (FSS), is naturally induced by the so-called electron-hole exchange interaction. Therefore, polarized entangled photon pair is destroyed by the excitonic fine structure splitting. Hence, the dynamical control of excitonic fine structure splitting is significant for the entanglement of photon pair. Over the past two decades, significant efforts have been spent to reduce the excitonic fine structure splitting of semiconductor core/shell nanocrystals, thus leading to the motivation to implement colloidal semiconductor core/shell nanocrystals to the application of the quantum information processing. Brovelli et al. [2] successfully reduced the electron-hole exchange interaction in CdSe/CdS core/shell nanocrystals by enlarging the growth shell thickness as described by the overlaps of the electron and hole wave functions. Iwan Moreels et al. [3] reported that the excitonic fine structure splitting of CdSe/ZnS core/shell nanocrystals was not sensitive with the geometric structures, while it mainly depended on the structural shape. Raino et al. [4] demonstrated that CdSe/CdS core/shell nanorods with small core and/or thick rod diameters provided a strongly condensed fine structure splitting. Vezzoli et al. [5] presented the first time method to determine the band-edge exciton fine structure of CdSe/CdS dot-in-rods core/shell nanocrystals based on the emission polarization of single particles at room temperature. The effect of the relevant geometrical parameters, core size, shell thickness and length, on the emission polarization and the excitonic fine structure was clearly elucidated. Biadala et al. [6] reported a time-resolved study of the photoluminescence of CdSe/CdS dot-in-rod core/shell nanocrystals with various

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geometries. They found that the stoke shift quadratically scaling with the rod width provided a control of the fine structure levels. According to the literature review, several experimental researches have been carried out to describe the impact of dimensions and structural shapes on the excitonic fine structure in semiconductor core/shell nanostructures. However, less attention is concerned on type of the band profiles in spite of the modern advances in the chemical growth methods. Therefore, the atomistic elucidation of band alignments induced by type of the coated shells is essentially curious to be delivered. This is what I purpose to do here.

To identify the impact of the type of the band profiles and also growth shell thickness on the excitonic fine structure splitting (FSS), I consider CdSe/ZnSe type-I and ZnSe/CdSe invert type-I core/shell nanocrystals as the computational candidates. Electron and hole are confined in core regime of CdSe/ZnSe type-I core/shell nanocrystals, while those are localized in shell regime of ZnSe/CdSe invert type-I core/shell nanocrystals, thus allowing determining the carrier localization in the desired nanostructures. I theoretically clarify and understand the excitonic fine structure splitting using atomistic model. The atomistic empirical tight-binding theory with sp^3s^* orbitals [7], the first nearest-neighboring interaction, spin-orbital coupling and strain effect is theoretically implemented with the reason to keep an accurate and realistic description of core/shell nanocrystals. The accurate calculations [8–12] of the excitonic fine structure splitting in semiconductor nanostructures based on atomistic tight-binding theory are successfully demonstrated. On the basis of my model, I compute the single-particle spectra, optical band gaps, ground-state wave function overlaps, ground-state coulomb energies, ground-state exchange energies, dark-bright (DB) excitonic splitting and bright-bright (BB) excitonic splitting of CdSe/ZnSe type-I and ZnSe/CdSe invert type-I core/shell nanocrystals as a function of the growth shell thicknesses.

To theoretically investigate the excitonic fine structure splitting (FSS) in CdSe/ZnSe type-I and ZnSe/CdSe invert type-I core/shell nanocrystals with different growth shell thicknesses, the present paper is organized in the following. Section 2 describes the key process for the computations of excitonic fine structure splitting in semiconductor core/shell nanocrystals. In Section 3, I present the resulting calculations to devise the dependence of the coated shell thickness and type of band alignments on the behaviors of the excitonic fine structure splitting. The results presented here have important consequences for the fundamental understanding of the excitonic fine structure splitting in core/shell nanocrystals. It is expected that the atomistic calculations can confirm the opportunity to generate entangled photon pairs based on the studied core/shell nanocrystals. Finally, the central conclusions are offered in Section 4.

2. Theory and methodology

The computations of excitonic fine structure splitting (FSS) in semiconductor core/shell nanocrystals consist of three important stages. In the first stage, CdSe/ZnSe type-I and ZnSe/CdSe invert type-I core/shell nanocrystals with wurtzite structure are used as the simulated candidates. Because of the lattice difference between CdSe and ZnSe, the strain field and valence band offset are additionally recognized. To optimize the atomic positions, the atomistic valence force field (VFF) method is utilized as described in more information in Refs. [13–15]. Besides, the valence-band offset of +0.13 eV [16] between CdSe and ZnSe is performed in the computations. In the second stage, the single-particle spectra are calculated using the atomistic tight-binding theory. It is well known that the atomistic tight-binding theory has been effectively practical to study the structural and optical properties of semiconductor core/shell nanocrystals [15,17–21]. The empirical tight-binding theory with the combination of sp^3s^* hybrid, spin-orbit interaction and the first nearest neighboring interaction is generated as the computational tool. The single-particle states are expanded as a linear combination of atomistic orbitals α localized on each atom R under the total number of atoms N_{at} as defined by:

$$\Psi = \sum_{R=1}^{N_{at}} \sum_{\alpha=1}^{10} C_{R,\alpha}\varphi_{\alpha}(\vec{r} - \vec{R})$$

The parameterization of CdSe and ZnSe semiconductor which is tailored to reproduce the experimental bulk band structure, determined bulk transition energies and effective masses is obtained from Akinci et al. [22] and Olguin el al. [23], respectively. The parameterization applied to this work is delivered in Table 1. As induced by lattice mismatch, the strain field computationally scales the hopping matrix elements as defined by:

$$V_{ac}^{'} = V_{ac}\left(\frac{d_0}{d}\right)^n$$

V_{ac} and V_{ac}' are the ideal and strained hopping matrix elements, respectively. The bond lengths of the unstrained and strained binary materials are d_0 and d, correspondingly. n of 2.0 is utilized as identified in Harrison's d^{-2} rule [24]. In the third stage, I implement the configuration interaction technique (CI) [10–12] to compute the excitonic fine structure splitting. Using the single-particle states and energies obtained via the atomistic tight-binding method, the single excitonic Hamiltonian is demonstrated in the second quantization as:

$$H = \sum_i E_i e_i^{\dagger} e_i + \sum_j E_j h_j^{\dagger} h_j - \sum_{ijkl} V_{ijkl}^{eh,\,coul} h_i^{\dagger} e_j^{\dagger} e_k h_l + \sum_{ijkl} V_{ijkl}^{eh,exch} h_i^{\dagger} e_j^{\dagger} e_k h_l$$

The first two terms are the tight-binding single-particle energies of electron and hole states, respectively. The third and fourth term present the electron-hole coulomb and exchange interaction, respectively. The coulomb ($V_{ijkl}^{eh,\,coul}$) and exchange ($V_{ijkl}^{eh,exch}$) matrix elements are numerically calculated using the tight-binding single-particle states as described in Ref. [25].

Table 1
Empirical tight-binding parameters of CdSe [22] and ZnSe [23] material. a and c mean anion and cation. The subscripts s, p and s* stand for s, p and s* orbital, respectively. x and y are briefly called for p_x and p_y orbital.

Parameters	CdSe (eV)	ZnSe (eV)
E_s^a	−9.63	−12.42728
E_p^a	1.326	1.78236
E_s^c	0.03	0.04728
E_p^c	4.73	5.52031
E_{s*}^a	7.53	7.84986
E_{s*}^c	5.72	8.52031
V_{ss}	−4.64	−6.50203
V_{xx}	2.64	3.30861
V_{xy}	5.36	5.41204
$V_{sa,pc}$	4.57	1.13681
$V_{sc,pa}$	5.54	5.80232
$V_{s*a,pc}$	3.05	3.26633
$V_{pa,s*c}$	2.49	1.86997
Δ_a	0.42	0.5812
Δ_c	0.18	0.05811

3. Results and discussions

To get the deeper insight into the atomistic impact of the band