Superlattices and Microstructures 95 (2016) 71–77

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Atomistic tight-binding computations in structural and optical properties of CdSe/ZnSe/ZnS core/multi-shell nanocrystals

Worasak Sukkabot

Department of Physics, Faculty of Science, Ubon Ratchathani University, 85 Sathollmark Rd., Warinchamrab, Ubon Ratchathani, 34190, Thailand

ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form 24 April 2016
Accepted 26 April 2016
Available online 27 April 2016

Keywords:
Tight-binding theory
CdSe/ZnSe/ZnS
Core/multi-shell nanocrystals
Exciton
Electron-hole interaction

ABSTRACT

In the present paper, I attempt to theoretically describe, analyze and compare the structural and optical properties in the core/multi-shell nanocrystal structure of a cadmium selenide (CdSe) core surrounded by zinc selenide (ZnSe) inner and zinc sulphide (ZnS) external growth shells. The atomistic tight-binding model (TB) and a configuration interaction method (CI) are implemented to calculate the single-particle spectra, optical band gaps, ground-state wave function overlaps, ground-state oscillation strengths, ground-state coulomb energies, ground-state exchange energies and Stokes shift as a function of ZnS external growth shell thicknesses. I underline that these computations are principally sensitive with the ZnS external growth shell thickness. The reduction of the optical band gaps, overlaps of ground electron-hole wave function, electron-hole interactions and Stokes shift is realized with the increasing ZnS external growth shell thickness. The improvement of the optical intensities is mainly achieved by including the ZnS exterior growth shell encapsulation. Importantly, the optical band gaps based on atomistic tight-binding theory are in a good agreement with the experiment. Finally, this emphasizes that the external passivation shell can now be engineered in a defined way, thus leading to manipulate the natural behaviors of nanodevices based on the scrutinized core/multi-shell nanocrystals.

1. Introduction

The potential applications of colloidal semiconductor nanocrystals have been gaining more interest because of their high photostability, good luminescence efficiency, high oscillator strength and large emission tunability. These great abilities enable them as the promising interest for both fundamental studies [1–3] and practical applications such as light-emitting devices [4–6], lasers [7–9] and fluorescent labels [10–12]. Their most interesting peculiarity, which inspires their applications, is the possibility of a precise tuning of their absorption and emission spectra by adjusting their structural sizes. In term of the semiconductor core/shell nanocrystals, the structural and optical properties are controlled by core and shell sizes as described and analyzed in Refs. [13–19]. Growing an external shell of a wide band gap semiconductor on an internal shell allows the atomistic manipulation of the natural behaviors. These low-dimensional nanostructures are widely called core/

E-mail address: w.sukkabot@gmail.com.

http://dx.doi.org/10.1016/j.spmi.2016.04.037
0749-6036/

multi-shell nanocrystals. Therefore, the electronic structures and optical properties are not only manipulated by core and internal shell sizes but also controlled by external shell dimensions. Such core/multi-shell nanoparticles reveal an effective luminescence with stability superior to single and core/shell nanocrystals, thus leading to the technical interest for the optoelectronic nanodevices. Up to now, the most investigated core/multi-shell nanocrystals are made of CdSe core covered with the various growth II-VI shells. Huaipeng Su et al. [20] presented the microwave synthesis of the CdSe nanocrystals terminated with $Cd_{0.5}Zn_{0.5}S/ZnS$ multi-shells. These studied core/multi-shell nanocrystals interestingly provided the high photoluminescence quantum yield up to 80%. Kyungnam Kim et al. [21] experimentally and theoretically scrutinized the natural behaviors of InP/ZnSe/ZnS semiconductor core/multi-shell nanocrystals. The resulting investigations underlined that the optical properties were enhanced in InP/ZnSe/ZnS semiconductor core/multi-shell nanocrystals. Renguo Xie et al. [22] reported on the preparation and structural characterization of $CdS/Zn_{0.5}Cd_{0.5}S/ZnS$ core/multi-shell nanocrystals using the successive ion layer adhesion and reaction (SILAR) technique. The obtained core/multi-shell nanocrystals displayed a high crystallinity with nearly spherical shape. In addition, the novel type of luminescent CdSe/CdS/ZnS and CdSe/ZnSe/ZnS semiconductor core/multi-shell nanocrystals was successfully synthesized by Dmitri V. Talapin et al. [23]. Compared with CdSe/ZnS core/shell nanocrystals, there was nearly defect free in ZnS shell of semiconductor core/multi-shell nanocrystals. In addition, the photoluminescence efficiency and photostability of the semiconductor core/multi-shell nanocrystals were better than those of the CdSe/ZnS core/shell nanocrystals.

According to the previous studies, there has been no theoretical work on the structural and optical behaviors of core/multi-shell nanocrystals. To acquire the comprehensive knowledge, CdSe/ZnSe/ZnS core/multi-shell nanocrystals are used as the simulated applicants which can aid in the understanding of electronic structures and optical properties of a wider class of core/multi-shell nanocrystals. With the aim to preserve the realistic properties of core/multi-shell nanocrystals, I utilize the atomistic tight-binding model taking account of sp^3s^* orbitals, the first nearest-neighboring interaction, spin-orbital coupling and strain field. To clarify the natural properties in CdSe/ZnSe/ZnS core/multi-shell nanocrystals, I present the computations of the single-particle spectra, optical band gaps, ground-state wave function overlaps, ground-state oscillation strengths, ground-state coulomb energies, ground-state exchange energies and Stokes shift as a function of the ZnS external growth shell thicknesses.

In the present paper, I comprehensively report the simulation of natural properties in CdSe/ZnSe/ZnS core/multi-shell nanocrystals with different ZnS external growth shell thicknesses. To theoretically analyze the structural and optical behaviors of CdSe/ZnSe/ZnS core/multi-shell nanocrystals, the methodology is described in Section 2. In Section 3, the resulting calculations are used to describe the dependence of the ZnS external coated shell thickness on electronic structures and optical properties. These computations are also compared with the experiment in order to approve the theoretical data. Finally, the central conclusions are demonstrated in Section 4.

2. Theory and methodology

To describe, analyze and compare the physical behaviors of core/multi-shell nanocrystals, CdSe core terminated by ZnSe inner and ZnS external shell is the computational candidate with the consideration of three main steps for the simulation. In the beginning, the wurtzite structure for CdSe/ZnSe/ZnS core/multi-shell nanocrystals is defined corresponding to the experimental data of Dmitri V. Talapin et al. [23] To relax the strained atomic positions induced by lattice mismatch, the atomistic valence force field (VFF) method is employed as described in more original perception in Refs. [24,25]. In the second step, the single-particle spectra based on the atomistic tight-binding theory are calculated with the aim to obtain the single-particle states and energies. The linear combination of atomistic orbitals α localized on each atom R under the total number of atoms N is designated as the single-particle states by:

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

In this model, I utilize the atomistic tight-binding theory in the conjunction with sp^3s^* orbitals, spin-orbit coupling and the first nearest neighboring interaction [26]. The parameterization of CdSe [27], ZnSe [27] and ZnS [27] which is fitted to generate the experimental bulk band structures, determined bulk transition energies and effective masses is numerically considered. After obtaining the single-particle spectra, a configuration interaction procedure (CI) [28–30] is computationally implemented to calculate the excitonic states in the final step. To do so, the two-body Hamiltonian constructed from the tight-binding single-particle energies and states is defined by:

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

The single-particle energies of electron and hole states are presented in the first two terms, respectively. The third and fourth term demonstrate the electron-hole coulomb and exchange interaction, respectively. $V_{ijkl}^{eh,\ coul}$ and $V_{ijkl}^{eh,\ exch}$ symbolize the electron-hole coulomb and exchange matrix elements.