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Atomistic tight-binding calculations of near infrared emitting $Cd_xHg_{1-x}Te$ nanocrystals

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ABSTRACT

I present the structural and optical calculations for $Cd_xHg_{1-x}Te$ zinc-blende nanocrystals with the experimentally synthesized Cd compositions (x) in the framework of atomistic tight-binding model (TB) and configuration interaction description (CI). This atomistic tight-binding model incorporates the sp^3s^* orbital and the first neighbouring interaction, in addition to the non-linear dependence of compositions on the band gaps the bowing factor is involved into this model through the extended virtual crystal approximation (VCA). The information of DOS highlights that the contribution of the conduction and valence bands is subjected by cation and anion atoms, respectively. The improvement of the optical band gaps in $Cd_xHg_{1-x}Te$ nanocrystals is presented with the increasing Cd compositions. The optical band gaps can be used to tune their optical properties across a technologically useful range from 688 nm to 2755 nm which can be implemented for the near infrared emitting devices. In addition, the enhancement of the optical property is reported with the increasing Cd contents. With the increasing Cd compositions, the atomistic electron-hole Coulomb interaction is mainly increased, whereas the atomistic electron-hole exchange interaction is reduced. The Stokes shift and fine structure splitting are progressively reduced with the increasing compositions and diameters. The application of fine structure splitting is utilized to implement as a source of entangled photon pairs in the quantum information. Finally, the comprehensive computations of alloy $Cd_xHg_{1-x}Te$ nanocrystals effectively determine the composition- and size-dependent structural and optical properties which render these nanocrystals promising candidates as the near infrared emitting devices and optical amplifiers.

1. Introduction

Semiconductor nanocrystals with near infrared (NIR) emission in the spectral region of 700–2500 nm have fascinated much interest in the active applications of biological tissue imaging [1–3], solar cells [4–7] and telecommunication [8,9]. Mercury telluride (HgTe) is particularly well-suited for use in the near infrared applications because of its almost zero bulk band gap, thus introducing the HgTe nanocrystals with the tunable sizes throughout the near infrared region [10]. However, the range of the near infrared emission is quite narrow due to the limitations of the sizes. In addition, HgTe nanocrystals have poor optical performance. To expand the near infrared window with a better optical property, alloying composition with cadmium (Cd) to produce $Cd_xHg_{1-x}Te$ is considered for the flexible manipulation [11,12]. $Cd_xHg_{1-x}Te$ is also one of the most important mercury compounds due to the wide range of tunable optical, electronic and magnetic properties, obtained through compositional tuning (x) of this material. Therefore, it is still very imperative to exploit the systematic studies to deliver and explain the detailed information as demonstrating in the succeeding. Lesnyak et al. [12] synthesized the alloy $Cd_{1-x}Hg_xTe$ nanocrystals by an efficient one-pot aqueous method. The $Cd_{1-x}Hg_xTe$ nanocrystals with an emission tunable in the near infrared (NIR) spectral regions ranging from 640 to 1600 nm were obtained with high optical property. Cai et al. [10] synthesized the high quality $Cd_xHg_{1-x}Te$ nanocrystals via the one-step method. The highest quantum yield ~80% was gained through the variance of the prepared conditions. Gupta et al. [11] reported the Cd compositional control of $Cd_xHg_{1-x}Te$ nanocrystals with diameter of 2.3 nm by exchange of Hg^{2+} in place of Cd^{2+} ions. The optical emission was tuned across the technologically useful wave lengths from 500 nm to almost 1200 nm. In addition, the sub-nanosecond exciton dynamics of $Cd_xHg_{1-x}Te$ alloy nanocrystals were studied using an ultrafast transient absorption spectroscopy by Leontiadou et al. [13]. Leubner et al. [14] reported the surface chemistry on the composition and optical properties of $Cd_{1-x}Hg_xTe$ nanocrystals with three different thiol ligands, thioglycolic acid (TGA), 3-mercaptopropionic acid (MPA) and glutathione (GSH). With MPA,

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the intensely fluorescent $Cd_{1-x}Hg_xTe$ nanoparticles were obtained with quantum yields as high as 45%. Hatami et al. [15] underlined that a new near-infrared/infrared integrating setup was designed for the wavelength region of 600–1600 nm using the $Cd_{1-x}Hg_xTe$ and PbS semiconductor nanocrystals. Size and temperature dependence of the photoluminescence properties was additionally studied in near-infrared emitting ternary alloyed mercury cadmium telluride (CdHgTe) nanocrystals by Jagtap et al. [16] CdHgTe nanocrystals with sizes in the range of 2.5–4.2 nm were synthesized with NIR wave lengths of 650–855 nm. Besides, Shen et al. [17] systematically presented the one-pot aqueous synthesis of CdHgTe nanocrystals using Na_2TeO_3 as an alternative Te source. The crystalline nature of CdHgTe nanocrystals was successfully characterized. In spite of the interesting applications of $Cd_xHg_{1-x}Te$ nanocrystals, there are a number of physical properties that have not been well clarified. Therefore, an understanding of the electronic structures and optical properties is a fundamental point. Recently, there are extensive experimental studies, while there is no theoretical investigation. In the present study, the structural and optical properties of $Cd_xHg_{1-x}Te$ nanocrystals with the experimentally synthesized compositions (x) are numerically investigated by the atomistic simulation tool.

For the purpose, the atomistic tight-binding theory is theoretically utilized to describe the electronic structures and optical properties of $Cd_xHg_{1-x}Te$ nanocrystals. In the present study, five orbitals sp^3s^* per atom and spin component are used to generate the empirical tight-binding Hamiltonian in the conjunction with the Slater and Koster parameters and the first nearest neighbouring interaction [18]. To include alloy Cd compositions into $Cd_xHg_{1-x}Te$ nanocrystals, the extended version of the virtual crystal approximation is modified by introducing the empirical bowing factors to compensate the non-linear dependence of compositions on the band gaps [19,20]. To analyze the structural and optical properties of $Cd_xHg_{1-x}Te$ nanocrystals with the realistic condition, the experimentally synthesized concentrations and geometric structures from Cai et al. [10] are modeled. To do so, the single-particle spectra, density of states (DOS), charge densities, optical band gaps, ground electron-hole wave function overlaps, oscillation strengths, radiative lifetimes, atomistic electron-hole interactions, Stokes shift and fine structure splitting are numerically computed as a function of diameters and Cd concentrations (x) in $Cd_xHg_{1-x}Te$ nanocrystals. It is expected that the atomistic calculations of $Cd_xHg_{1-x}Te$ nanocrystals can be used to provide the guideline for the near infrared optoelectronic components.

In the present manuscript, the computations of $Cd_xHg_{1-x}Te$ nanocrystals using the atomistic tight-binding theory (TB) and configuration interaction description (CI) are demonstrated as follows. Section 2 describes the theoretical methodology utilizing to construct the atomistic model. Using the home-made model, Section 3 highlights that the structural and optical properties of $Cd_xHg_{1-x}Te$ nanocrystals are principally sensitive with Cd compositions (x) and sizes. It is expected that the inclusive information of $Cd_xHg_{1-x}Te$ nanocrystals is used to elucidate the composition- and size-dependent structural and optical properties which solidify these nanocrystals the auspicious candidates as the near infrared emitting devices and optical amplifiers. In addition, $Cd_xHg_{1-x}Te$ Cd-rich nanocrystal with a large size may be a good choice to be a source of entangled photon pairs in the application of quantum information. In the end, I summarize the resultant calculations in Section 4.

2. Theory

To analyze how the electronic structures and optical properties of $Cd_xHg_{1-x}Te$ zinc-blende nanocrystals are manipulated under the impact of alloy contents and sizes, the atomistic tight-binding theory (TB) is proposed to be implemented. The atomistic tight-binding model is the homemade code written in FORTRAN. To obtain the atomic positions of $Cd_xHg_{1-x}Te$ nanocrystals, the spherical shape with the desired diameter is assembled from a bulk semiconductor supercell without any surface relaxation effects, thus leading to the unstrained nanocrystals [21]. The dangling bonds on the surface of $Cd_xHg_{1-x}Te$ nanocrystals are encapsulated by the energy shift to avoid the gap states as numerically demonstrated by Lee et al. [22] To generate the tight-binding wave functions, the five orbital basis α per spin component σ, namely one s orbital, three p orbitals (p_x, p_y and p_z) and one s^* orbital, localized on the sites R in the total number of atoms N_{at} of $Cd_xHg_{1-x}Te$ nanocrystals are built up as defined by.

$$\Psi = \sum_{R=1}^{N_{at}}\sum_{\alpha=1}^{5}\sum_{\sigma} C_{R,\alpha,\sigma}\varphi_{\alpha,\sigma}(\vec{r}-\vec{R})$$

The empirical tight-binding Hamiltonian (H) [23] is defined by the creating (annihilating) operator $c^{\dagger}_{R\alpha}(c_{R\alpha})$ of the particle on the orbital α of atom R.

$$H = \sum_{R=1}^{N_{at}}\sum_{\alpha=1}^{10}\varepsilon_{R\alpha}c^{\dagger}_{R\alpha}c_{R\alpha} + \sum_{R=1}^{N_{at}}\sum_{\alpha=1}^{10}\sum_{\alpha'=1}^{10}\lambda_{R\alpha\alpha'}c^{\dagger}_{R\alpha}c_{R\alpha'} + \sum_{R=1}^{N_{at}}\sum_{R'=1}^{N_{at}}\sum_{\alpha=1}^{10}\sum_{\alpha'=1}^{10}t_{R\alpha,R'\alpha'}c^{\dagger}_{R\alpha}c_{R'\alpha'}$$

Here, $\varepsilon_{R\alpha}$, $\lambda_{R\alpha\alpha'}$ and $t_{R\alpha,R'\alpha'}$ are the on-site empirical parameters, the spin-orbit coupling constant and the off-site empirical parameters, respectively. In the present study, I use the parameterization from Olguin et al. [20] due to the accuracy of the bulk band structures and the bulk band gaps. From the empirical tight-binding calculations, the valence-band edges of bulk CdTe and HgTe semiconductor are set to be the energy of 0.00 eV. To integrate alloy Cd compositions into $Cd_xHg_{1-x}Te$ nanocrystals, I utilize the virtual crystal approximation (VCA). The matrix elements of the tight-binding Hamiltonian become.

$$H_{Cd_xHg_{1-x}Te} = (1-x)H_{HgTe} + xH_{CdTe}$$

where $H_{HgTe(CdTe)}$ are either on-site or off-site HgTe(CdTe) tight-binding matrix elements. However, due to the non-linear dependence of compositions on the band gaps, the extended version of the virtual crystal approximation is modified by introducing the empirical bowing factors (b) to compensate this effect through the correction of the s orbital on-site tight-binding matrix elements [19,20]. Therefore, the on-site matrix elements of s orbital are rewritten as.

$$E^{s}_{Cd_xHg_{1-x}Te} = (1-x)E^{s}_{HgTe} + xE^{s}_{CdTe} + b_v x(1-x)$$

Here, v denote cation (c) or anion (a) atom. b_a of 0.00 eV and b_c of 0.0180 eV [20] for alloy $Cd_xHg_{1-x}Te$ semiconductor are computationally used. After diagonalizing the empirical tight-binding Hamiltonian (H), the energies and tight-binding wave functions of electron and hole states are obtained. To observe the localization of electron and hole states, the charge densities at atomic position $\vec{R}$ in $Cd_xHg_{1-x}Te$ nanocrystals are defined as.

$$\sum_{\alpha=1}^{5}\sum_{\sigma}|C_{\alpha,\sigma}|^2$$

The oscillation strengths (f_{ij}) of the inter-band transitions between electron (i) and hole (j) states are formulated as $f_{ij} = \frac{2m_0}{\hbar^2}\left|\hat{e}\cdot\vec{D}_{ij}\right|^2 \times (E_i - E_j)$. For the demonstration, m_0 is the free-electron mass. E_i and E_j symbolize the single-particle energies of