Optik 155 (2018) 242–250

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Original research article

Effect of size and shape on electronic and optical properties of CdSe quantum dots

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ARTICLE INFO

Article history:
Received 20 August 2017
Accepted 27 October 2017

Keywords:
8-Band $k \cdot p$ method
CdSe quantum dots

ABSTRACT

In this paper, we used the 8-band $\boldsymbol{k} \cdot \boldsymbol{p}$ model with valence force field considerations to investigate the effect of size and shape on electronic and optical properties of cadmium selenide quantum dots. Major factors related to their properties including band mixing probabilities, spatial charge distributions, transition matrix elements and Fermi factors were studied. Volumetrically larger CdSe dots were found to have smaller band-gaps but higher transition matrix elements and Fermi factors. The maximum optical gain for dots was observed to have an initially positive and then negative correlation with their real-space size as a result of combined effects of various factors. For the shape effects, cubic dots were found to have smaller band-gaps, Fermi factors and transition matrix elements than spherical dots due to higher level of asymmetry and different surface effects. Consequently, cubic dots have lower emission energy, smaller amplification. The occurrence of near E1–H1 transition broadens the gain spectrum of cubic dots. Cubic and spherical dots are both proven to be promising candidates for optical devices under visible range. We have demonstrated that size and shape change could both effectively alter the properties of quantum dots and therefore recommend consideration of both when optimizing the performance for any desired application.

1. Introduction

Cadmium selenide (CdSe) quantum dots have gained vast amount of research attention over the recent years. As II–VI semiconductors, their innate large band-gap allows their great potential in optoelectronic industries, such as laser and light-emitting devices (LEDs) under the visible spectrum range [1]. CdSe quantum dots have been found to possess significantly improved performance compared to conventional bulk semiconductor, including higher tunability [2], energetic efficiency [3] and optical amplification [4] due to their three-dimensional quantum confinement effects. Recent advancements in nanocrystal synthesis have demonstrated the feasibility of accurate size [5] and shape [6] control of CdSe quantum dots using colloidal synthesis. The size and shape changes were expected to profoundly affect the properties of CdSe dots. However, at the current stage, despite that the effect of size on quantum dots has been studied thoroughly [7], the research work done on the shape effect is still limited.

Optoelectronic properties of CdSe quantum dots heavily depend on their band structure and band-mixing probabilities, which are sensitive towards size and shape changes. A few methods have been developed to determine their electronic

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https://doi.org/10.1016/j.ijleo.2017.10.165
0030-4026/

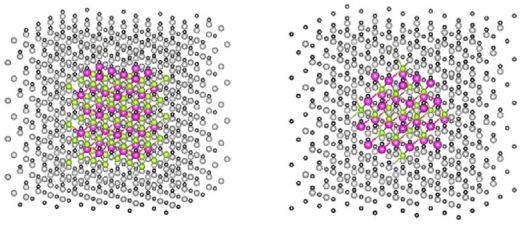

Fig. 1. A 3D atom-by-atom model of cubic and spherical CdSe quantum dot.

structures, including empirical pseudo-potential theory [8], effective mass approach [9] and multi-band $\boldsymbol{k}\cdot\boldsymbol{p}$ methods [10]. All three methods generally predict similar qualitative features. However, persisting minor difference exist for each energy level calculated for a particular quantum dot morphology. The $\boldsymbol{k}\cdot\boldsymbol{p}$ method is most popular as it automatically considers the piezoelectric effect of lattice strain [11]. In this study, we used the 8-band $\boldsymbol{k}\cdot\boldsymbol{p}$ method to compute the electronic properties of CdSe quantum dots. The subsequent computation of optical properties took into account of transition matrix element [12], carrier density [13], Fermi factor [14] and homogeneous broadening [15] which were determined to have profound influence over optical gain spectrum. The findings of this study could provide insights to use shape control during quantum dots synthesis as an alternative, instead of solely relying on the size change, to alter the properties of CdSe quantum dots for various industrial purposes.

2. Methodology

CdSe quantum dots considered in this study are assumed to have the zincblende lattice structure and be colloidally synthesized. We studied the cubic quantum dots with length from 4 to 12 units of lattice constants (corresponding volume: 14–383 nm^3) and spherical dots of the same volume. The temperature is assumed to be 300 K (room temperature), as electronic and optical properties of quantum dots are temperature-sensitive. Fig. 1 shows an atom-by-atom model of typical CdSe quantum dots under infinite potential well studied in this project. For each quantum dot geometry, we applied an effective mass envelope wavefunction theory approach based on 8-band $\boldsymbol{k}\cdot\boldsymbol{p}$ methods with the consideration of orbit-splitting effects to obtain the bandstructure near the Γ-point of the Brillouin zone. The 8-band Hamiltonian is represented in the Bloch function basis of $|S\rangle\uparrow$, $|P_x\rangle\uparrow$, $|P_y\rangle\uparrow$, $|P_z\rangle\uparrow$, $|S\rangle\downarrow$, $|P_x\rangle\downarrow$, $|P_y\rangle\downarrow$, $|P_z\rangle\downarrow$ as [16]

$$H_{=}\begin{pmatrix} h_{11} & \frac{ip_0(k'_x+ik'_y)}{\sqrt{2}} & ip_0k'_z & \frac{ip_0(k'x-ik'_y)}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ \frac{ip_0(k'_x+ik'_y)}{\sqrt{2}} & h_{22} & h_{23} & h_{24} & 0 & 0 & 0 & 0 \\ -ip_0k'_z & h_{23} & h_{33} & h_{34} & 0 & 0 & 0 & 0 \\ \frac{ip_0(k'x-ik'_y)}{\sqrt{2}} & h_{24} & h_{34} & h_{44} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & h_{55} & \frac{ip_0(k'_x+ik'_y)}{\sqrt{2}} & ip_0k'_z & \frac{ip_0(k'x-ik'_y)}{\sqrt{2}} \\ 0 & 0 & 0 & 0 & \frac{ip_0(k'_x+ik'_y)}{\sqrt{2}} & h_{66} & h_{67} & h_{68} \\ 0 & 0 & 0 & 0 & -ip_0k'_z & h_{76} & h_{77} & h_{78} \\ 0 & 0 & 0 & 0 & \frac{ip_0(k'x-ik'_y)}{\sqrt{2}} & h_{86} & h_{87} & h_{88} \end{pmatrix} + H_{so} + V_0 \tag{1}$$

where H_{so} is the Hamiltonian for orbit-splitting, E_p is the matrix element of Kane's theory and $p_0 = \sqrt{E_p/2m_e}$. Each element of the Hamiltonian matrix is given below

$$h_{11} = h_{55} = E_g - \frac{\hbar^2}{2m_0}\gamma_c(k_x^2+k_y^2+k_z^2) + a_c[tr(\varepsilon)] \tag{2}$$

$$h_{22} = h_{44} = h_{66} = h_{88} = -\frac{\hbar^2}{2m_0}\left[\frac{L'+M'}{2}(k_x^2+k_y^2)+M'k_z^2\right] + a_v[tr(\varepsilon)] + \frac{b}{2}[tr(\varepsilon) - 2\epsilon_{zz}\Big] \tag{3}$$

$$h_{23} = h_{34} = h_{67} = h_{78} = -\frac{\hbar^2}{2m_0}\left[\frac{N'(k_x-ik_y)}{\sqrt{2}}\right] + \sqrt{6}d(\varepsilon_{xz}-i\varepsilon_{yz}) \tag{4}$$

$$h_{24} = h_{86} = -\frac{\hbar^2}{2m_0}[\frac{L'-M'}{2}(k_x^2-k_y^2) - iN'k_xk_y] + \frac{3b}{2}(\varepsilon_{xx}-\varepsilon_{yy}) - i\sqrt{12}d\varepsilon_{xy} \tag{5}$$