



# Tight-binding Calculations of Ellipsoidal In As Nanocrystals

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## ABSTRACT

The  $sp^3s^*$  empirical tight-binding calculations of electron and hole states for ellipsoidal InAs nanocrystals passivated by hydrogen atoms are presented. The electronic structure is numerically calculated for various shapes within keeping a constant volume of nanocrystals. The significant impact of the shape for the nanocrystals on the electronic structure and the emission spectra along the x, y and z polarized direction is fruitfully observed. The results demonstrate that by changing the ellipsoidal aspect ratios the electronic structure and optical signatures are different.

**Keywords:** tight-binding calculations, nanocrystal

## 1. INTRODUCTION

The electronic and optical properties of semiconductor nanocrystals have been attracted considerable attention in recent years due to their possible applications in quantum dot lasers, light-emitting diode, photovoltaic devices, solar cell, etc. because of the significant effect of the low dimensionality [1, 2, 3, 4, 5, 6]. Nanocrystals are also particularly attractive systems because their physical properties can be tailored by controlling their shapes and sizes [7, 8, 9]. The sizes and shapes of the nanocrystals can be experimentally manipulated by the external parameters such as growth time, temperature, concentration and material [10, 11, 12]. In this paper, the electronic structure and optical properties of

InAs nanocrystals are mainly considered because III-V semiconductor nanocrystals have been the subject of intensive desired topics during the last two decades owing to the existing commercial products such as heterostructure bipolar transistors, diodes, lasers, light emitting diodes, etc [13].

In order to lucratively comprehend the electronic structure and optical properties, various theoretical approaches were utilized to study the nanocrystals, ranging from first-principle calculations to empirical models [14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26]. Owing to the regularly high computational demand of the first-principle calculations, empirical models are widely considered to study the electronic structure

and optical properties of nanoclusters [17, 21]. Recently there are three primary empirical models, (i) multi-band effective-mass approximation (EMA), (ii) pseudopotential model and (iii) tight-binding model. The effective-mass approximation (EMA) tends to describe a nanocrystal by means of continuum system [16], while the pseudopotential model and the tight-binding model mainly treat a nanocrystal within the atomistic description. In case of the tight-binding calculations [17, 18, 19, 20, 21, 22, 23, 24], the atomistic wave functions are limited to a small basis set. While in case of the pseudopotential calculations [25, 26], the atomistic wave functions are described with a large basis set. Therefore the tight-binding model is computationally less expensive than the pseudopotential model. Because of this reason, the tight-binding model is a good candidate for studying the electronic structure and optical properties of nanocrystals.

The shape dependence of nanocrystals is recognized to play an important role in determining their electronic structure and optical properties [27, 28]. Lin-Wang Wang and Alex Zunger [26] established that the gap variation with cluster sizes was almost identical for spheres, rectangular boxes, and cubes. J. Hu et al. [29] stated that elongated CdSe nanorods could produce differently polarized emission spectra as compared to spherical nanocrystal. Jingbo Li and Lin-Wang Wang [30] demonstrated that the band gap energy of CdSe spherical nanocrystal had the smallest value when compared to other elongated shapes of nanoclusters within similar volumes. V. Albe et al. [7, 8] reported that the exact shape of nanocrystals had some influence on the confinement energies. The results confirmed that shape was used to modify the features of the optical spectra. W. S. Ferreira et al. [31] declared that the

shape control of quantum dots was important for a fine tuning of their optical emission, which had important applications in the field of biological markers. Cantele *et al.* [32, 33] analyzed the optical anisotropy of ellipsoidal quantum dots as a function of the dot aspect ratios. They concluded that the optical processes significantly depended on the radiation polarization in contrast to non-polarized processes observed for spherical quantum dots. F. Trani et al. [34] studied the effects persuaded by the shape on the lowest unoccupied molecular orbitals (LUMO) electronic structure of ellipsoidal silicon nanocrystals by tight-binding method. The minimum confinement energy was obtained for an ellipsoid with aspect ratio  $X = 0.05$  within a structure containing the constant volume. Recently, quantum ellipsoids have been widely synthesized [9, 29, 35]. The main factor to characterize the physical shape of the ellipsoidal nanocrystal is the aspect ratio. The aspect ratios are defined as the fraction of the semi-axes along the perpendicular and parallel direction with respect to the symmetry axes. By varying the aspect ratios, the physical properties are considerably changed [31, 32, 33, 34, 35, 36]. Therefore it is the main objective of this paper to apprehend the dependence of aspect ratios for InAs ellipsoidal nanocrystals on the electronic structure and optical properties within a theoretical framework. The  $sp^3s^*$  empirical tight-binding calculations are implemented for the calculated purpose.

This paper is organized as follows. In Sec. 2, the brief descriptions of the tight-binding model and optical spectra are provided. In Sec. 3, the electronic structure and optical spectra as a function of the aspect ratios are discussed. Finally, Sec. 4 is devoted to the conclusions.

## 2. MATERIALS AND METHODS

### 2.1 Empirical Tight-Binding Method

The empirical tight-binding method [18, 19, 20, 21, 22, 23] is utilized to study the nanocrystals. The tight-binding method is represented in terms of an orthogonal basis set of atomic-like orbitals. In this model, the interaction is restricted to the on-site and the first nearest-neighbors. The tight-binding wave function can be explained as a linear combination of the atomic orbitals  $\varphi_\alpha(\vec{r}-\vec{R})$  given by.

$$\psi(\vec{r}) = \sum_{\vec{R}} \sum_{\alpha} C_{R\alpha} \varphi_\alpha(\vec{r}-\vec{R})$$

Here  $\vec{R}$  denotes the atomic position and  $\alpha$  also represents to the atomic orbitals ( $s, p_x, p_y, p_z, s^*$ ). The coefficients  $C_{R\alpha}$  determining the single-particle states and the corresponding single-particle energies are calculated by diagonalizing the  $sp^3s^*$  empirical tight-binding Hamiltonian.

$$H_{TB} = \sum_{\vec{R}} \sum_{\alpha} \epsilon_{R\alpha} c_{R\alpha} c_{R\alpha} + \sum_{\vec{R}} \sum_{\alpha} \lambda_{R\alpha\alpha'} c_{R\alpha} c_{R\alpha'} + \sum_{\vec{R}} \sum_{\vec{R}'} \sum_{\alpha} \sum_{\alpha'} t_{R\alpha R'\alpha'} c_{R\alpha} c_{R'\alpha'}$$

In which the operator  $c_{R\alpha}(c_{R\alpha}^\dagger)$  creates (annihilates) the particle on the atomic orbital  $\alpha$  of atom  $\vec{R}$ . The Hamiltonian is parameterized by the on-site orbital energies  $\epsilon_{R\alpha}$ , the spin-orbit coupling constant  $\lambda_{R\alpha\alpha'}$  and the hopping matrix elements  $t_{R\alpha R'\alpha'}$  connecting different orbitals sited at neighboring atoms. The parameter set used in this work is defined in Reference 36. In addition, The InAs nanoclusters are terminated by dangling with hydrogen atoms. For simplicity, there is no hydrogen-hydrogen interaction. The on-site energy of the Hydrogen atom, the In-H and As-H orbital interaction parameters are taken from Y. M. Niquet's paper [20].

### 2.2 Optical Spectra

Having established the  $sp^3s^*$  empirical tight-binding method to calculate the electronic structure of nanocrystals, the optical properties are then computed. The optical spectra between the conduction and valence levels by means of Fermi's Golden Rule are defined as.

$$I(E) = \frac{2\pi}{\hbar} \sum_{c,v} | \langle \psi_v(\vec{r}) | \vec{e} \cdot \vec{r} | \psi_c(\vec{r}) \rangle |^2 \delta(E_c - E_v - E)$$

$$\text{where } \delta(E_c - E_v - E) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(E_c - E_v - E)^2}{2\sigma^2}}$$

$\sigma$  represents the spectral line broadening.  $\psi_c(\vec{r})$  and  $\psi_v(\vec{r})$  are the tight-binding wave functions of the conduction and valence states with energies  $E_c$  and  $E_v$ , respectively.  $\vec{e}$  symbolizes for the polarized vector.  $\langle \psi_v(\vec{r}) | \vec{e} \cdot \vec{r} | \psi_c(\vec{r}) \rangle$  is defined by:

$$\langle \psi_v(\vec{r}) | \vec{e} \cdot \vec{r} | \psi_c(\vec{r}) \rangle = \frac{\sum_{\vec{R}-\vec{R}\alpha-\beta} \sum_{\alpha} c_{R\alpha}^* c_{R'\beta} \vec{e} \cdot \vec{R} + \sum_{\vec{R}-\vec{R}\alpha-\beta} \sum_{\alpha} \sum_{\alpha'} c_{R\alpha}^* c_{R'\beta} \vec{e} \cdot \vec{d}_{\alpha\beta}}{\sum_{\vec{R}-\vec{R}\alpha-\beta} \sum_{\alpha} \sum_{\alpha'} c_{R\alpha}^* c_{R'\beta} \vec{e} \cdot \vec{d}_{\alpha\beta}}$$

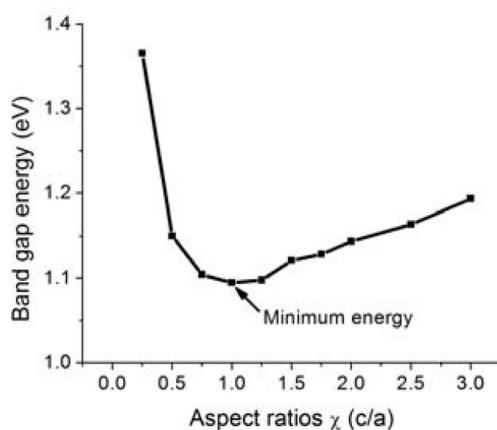
The first term indicates the global effect.  $\vec{d}_{\alpha\beta}$  in the second term stands for the dipole matrix element generally defined by  $\langle \varphi_\alpha(\vec{r}-\vec{R}) | \vec{e} \cdot \vec{r} | \varphi_\beta(\vec{r}-\vec{R}) \rangle$ . The dipole matrix elements are considered between different atomic orbitals on the same site taken from this reference [37].

## 3. RESULTS AND DISCUSSIONS

The studied shape of the nanocrystals is ellipsoidal. The core consists of In As material. The entire surface of the core is terminated with Hydrogen atoms to avoid the formation of dangling bonds because these bonds may generate the gap states that will interfere in these calculations [38]. The nanocrystal structure is considered to find all the atomic positions represented as the ellipsoid of equation  $\frac{(x^2 + y^2)}{a^2} + \frac{z^2}{c^2} = 1$  and

$X = c/a$  is a symbol for the structural aspect ratio. Here,  $a$  and  $c$  are the semi-axes along the parallel and the perpendicular direction with respect to the symmetry axes, respectively. The structures of nanocrystals within the condition that have been constructed to obtain a constant volume are theoretically examined. It means that the number of the atoms is approximately constant.

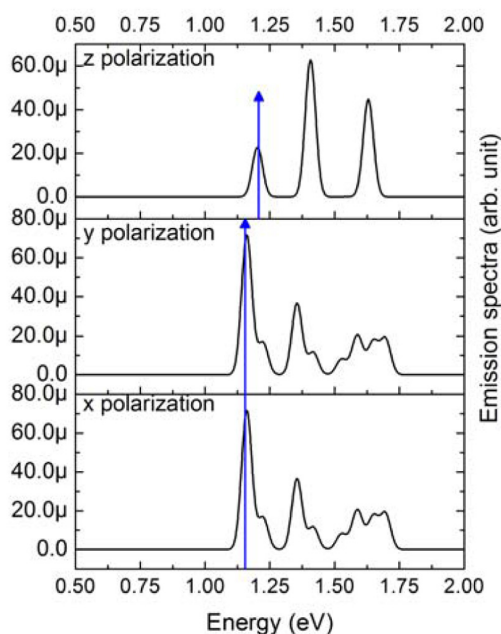
The calculations are initially argued with the electronic structure of nanocrystals passivated by hydrogen atoms. The considered volume has been taken to be that of a sphere with a radius 2.4 nm. This choice was suggested by the fact that there was the experimental data, a series of nanocrystal sizes ranging from 34 to 60 Å in diameter [39]. The band gap energy is termed as the difference between the lowest electron and highest valence state. The band gap energies as a function of the aspect ratios ( $X$ ) going from oblate  $X < 1$  to prolate  $X > 1$  ellipsoids are depicted in Figure 1. The calculations illustrate that as increasing the aspect ratios ( $X$ ) the band gap energies mainly decline until the aspect ratio (sphere) the minimum band gap energy is obtained. Conversely, as the shapes become prolate, the band gap energies gradually increase. According to these calculations, there is an agreement with the previous results performed Jingbo Li and Lin-Wang Wang [30] and G. Cantele et al. [32]. They established that the spherical nanocrystal had the smallest band gap energy compared to other elongated ones within similar volumes. On the other hand, F. Trani et al. [34] found that the minimum band gap was achieved for an ellipsoidal Si nanocrystal with aspect ratio within a structure containing the constant volume.



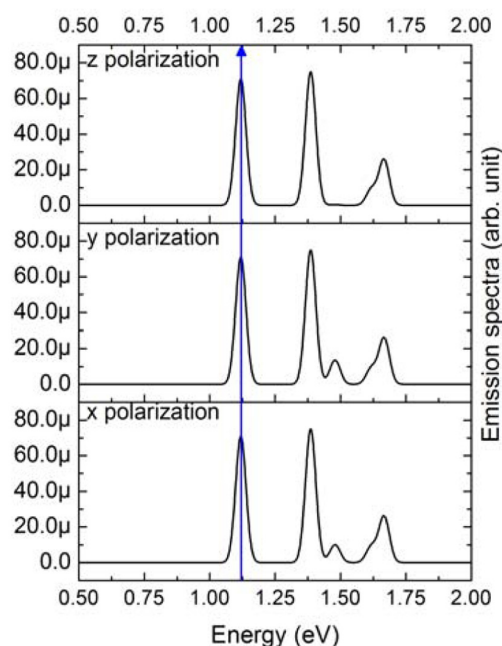
**Figure 1.** The band gap energies as a function of the aspect ratios within a constant volume.

Apart from scrutinizing the shape influence on the band gap energies, the optical spectra of ellipsoidal nanocrystals are also figured. In the calculations,  $s$  (20 meV used here) represents the spectral line broadening and the number of electron and valence bands is 10 each. The optical spectra are calculated along the polarized vectors ( $e$ ) in  $x$ ,  $y$  and  $z$  axes. The emission spectra of oblate  $X = 0.50$  ellipsoidal, spherical  $X = 1.00$  and prolate  $X = 1.50$  ellipsoidal nanocrystal are selected to be plotted in Figure 2, 3 and 4, respectively. For oblate and prolate ellipsoidal nanocrystal, the emission spectra along  $x$  and  $y$  polarization are identical while one along the  $z$  polarization is dissimilar with the others. In case of oblate ellipsoidal nanocrystal, the amplitudes of the peaks for the emission spectra along the  $x$  and  $y$  axes become larger than one along the  $z$  axes because the alignments of the electron and hole states for nanocrystals are mainly confined in the  $xy$  plane. While for the prolate ellipsoidal nanocrystal, the amplitudes of the peaks for the emission spectra along the  $x$  and  $y$  axes are smaller than one along the  $z$  axes due to the strong

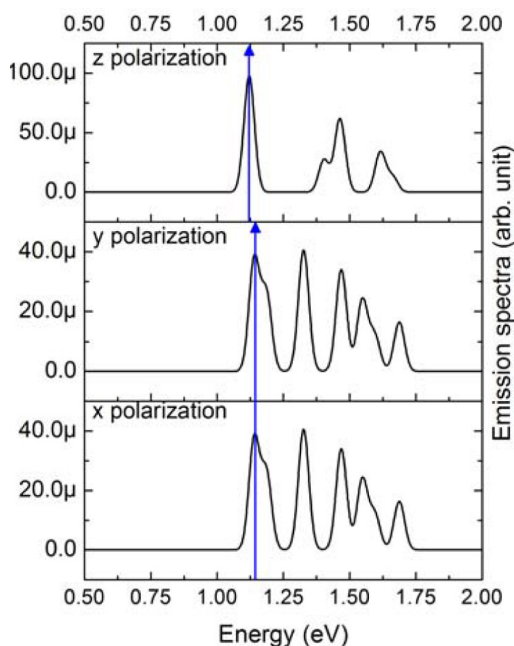
localizations of the electron and hole states in the  $z$  axes. In case of spherical nanocrystal, the optical spectra along the  $x$ ,  $y$  and  $z$  axes are approximately identical even though there is slightly different at the peaks due the anisotropic alignments of the hole wave functions. The amplitudes of the peaks for the emission spectra along the  $x$ ,  $y$  and  $z$  polarization are equivalent owing to the spherical symmetry. According to the calculations, these results mainly validate that the ellipsoidal nanocrystals display differently polarized emission spectra judged against the spherical nanocrystals. The numerical data is consistent with the previous calculations [7, 29, 31].



**Figure 2.** Emission spectra of oblate  $X = 0.50$  ellipsoidal nanocrystal along the  $x$ ,  $y$ ,  $z$  axes.



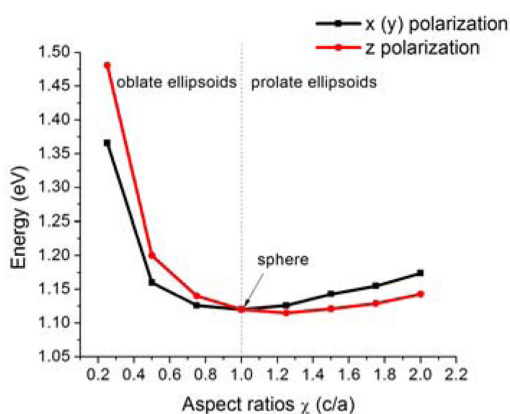
**Figure 3.** Emission spectra of spherical  $X = 1.00$  nanocrystal along the  $x$ ,  $y$ ,  $z$  axes.



**Figure 4.** Emission spectra of oblate  $X = 1.50$  ellipsoidal nanocrystal along the  $x$ ,  $y$ ,  $z$  axes.

In addition, the dependence of the aspect ratios on the first transition energies (the 1<sup>st</sup> peak in optical spectra) is studied. The first transition energies along the x, y and z direction as a function of the aspect ratios  $X$  going from oblate  $x < 1$  to prolate  $x > 1$  ellipsoids are plotted in Figure 5. For oblate ellipsoidal nanocrystals, the first transition energies along the x and y polarization are lesser than one along the z polarization. While in case of prolate ellipsoidal nanocrystals, the first transition energies along the x and y axes are greater than one along the z axes. The first transition energies along the x, y and z axes are equal for the spherical nanocrystal. Finally the calculations are theoretically confirmed that the optical anisotropy is associated to the morphological changes of nanocrystals [7, 8, 27, 28] as illustrated by the first transition energies and emission spectra along the x, y and z polarized axes.

Apart from these calculations, the degree of linear polarization (DOP) and excitonic states are the other physical challenges required to be investigated further in order to understand the mechanism in ellipsoidal InAs nanocrystals. The degree of linear polarization [32] presents the change of the emission spectra with decreasing the quantum confinement along one direction which obviously realizes how to manipulate the polarization in nanocrystals. Also, excitonic states [18, 21] are the bound state of an electron and hole confined in the nanocrystal by the Coulomb interaction. Hence, it is essentially interesting to study further the dependence of the ellipsoidal shape on degree of linear polarization and excitonic states.



**Figure 5.** The first transition energies along the x, y and z axes as a function of the aspect ratios within a constant volume.

## 5. CONCLUSIONS

In this paper, the behavior mainly induced by the shape on the electronic structure and optical properties of ellipsoidal InAs nanocrystals passivated by Hydrogen atoms is theoretically carried out. The tight-binding calculations conclude that the band gap energies remarkably depend on the ellipsoidal aspect ratios. The minimum band gap energy is gained for the spherical shape  $x = 1$  which is consistent with the simple geometrical argument that suggests the incidence of the minimum for a spherical shape. Besides, the optical signatures of oblate  $x < 1$  ellipsoidal, spherical  $x = 1$  and prolate  $x > 1$  ellipsoidal nanocrystals along the x, y and z axes of polarization are numerically verified. The results indicate that the emission signatures are mainly sensitive with the structural aspect ratios. Finally the effects of the aspect ratio are shown to modify the features of the optical spectra and the first transition energies along the x, y and z polarized axes.

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