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ARTICLE

# Electronic Structure of CdS Nanoparticles and CdSe/CdS Nanosystems

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ABSTRACT

The electronic states of "wurtzite" CdS nanoparticles and CdSe/CdS nanosystems with up to 80 pairs of Cd-Se or CdS atoms were calculated. The results for CdS particles were compared with the results obtained earlier for CdSe particles of the same size and with published calculations of other authors. The calculated gap values in the range of 2.84 eV ~ 3.78 eV are typical for CdS particles of studied sizes in accordance with results of published data. The CdSe/CdS nanosystems were considered as layered ones and as quantum dots. The layered CdSe/CdS systems with two-layer CdS coverings can be interpreted in terms of combinations of two semiconductors with different energy band gaps (2.6 eV and 3.3 eV), while analogous systems with single-layer CdS coverings do not demonstrate a two-gap electron structure. Simulation of a CdSe/CdS quantum dot shows that the single-layer CdS shell demonstrates a tendency for the formation of the electronic structure with two energy gaps: approximately of 2.5 eV and 3.0 eV.

## 1. Introduction

Cadmium selenides and cadmium sulfides (CdSe and CdS), semiconductors with band gaps of about 1.8 eV and 2.4 eV, respectively are promising materials for optoelectronic devices [1-15]. X-ray diffraction analysis indicates that the structure of CdSe nanoparticles with sizes of 2.8 nm, 4.1 nm and 5.6 nm is wurtzite-like, and the energy gaps $E_{gap}$ for these particles are 2.5 eV, 2.2 eV, and 2.0 eV, respectively [6]. Our calculations [16] confirm this conclusion. As for CdS nanoparticles they can have both sphalerite and wurtzite structures, depending on what sulphur source are used [8,10]. However, the wurtzite structure is energetically more favorable [17]. One main application of these substancies is their using in the core/shell CdSe/CdS quantum dots [18-22], in which an improved luminescence quantum yield is achieved, the fluorescence lifetime is reduced and the desired band gap is achieved, that is, a

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given wavelength of light radiation is provided.

Elecronic structure of CdS nanoparticles was studied in some works using the density functional theory (DFT) calculations. Mahesh M. Kamble et al. [8] obtained the energy gap of 2.38 eV ~ 2.65 eV for the wurtzite type particles; Soltani et al. [10] demostrated the gap close to 2.6 eV for the both wurtzite and sphalerite structure; Favero et al. [15] claimed that sphalrite nanoparticles were unstable but the wurtzite ones were stable with the energy gap of 1.8 eV.

The ab initio calculations for CdSe/CdS quantum dots were described in two works [21,22] the both works used a wurtzite structure. Romanova and Galyametdinov [21] studied the layered CdSe/CdS quantum dots in the frame of DFT; the CdSe/CdS monolayers ratio was taken as 3/7; the calculated two-band structure was found with gaps of 2.5 eV and 13 eV. Ying Luo and Lin-Wang Wang [22] investigated CdSe/CdS core/shell nanorods with 3063 atoms included the surface passivation pseudo-hydrogen atoms. They obtained the band gaps for CdS and CdSe are 2.079 eV and 1.414 eV, respectively.

In our recent work, we studied in detail the energy and electronic structure of CdSe nanoparticles [16] and found that, at small sizes (less than 2 nm), particles with a "rock-salt"-type structure are energetically favorable, however for larger nanoparticles, a "wurtzite"-type structure is preferable. The dependences of the energy gap width near the Fermi level on the particle size were also studied. In this work, we calculate the electronic structure of CdS nanoparticles in comparison with the results obtained for CdSe particles and study the electronic structure of CdSe/CdS layered nanosystems and quantum dots.

## 2. Modeling Technique

As in the previous work [16], the simulation was carried out using the FHI96md package [23] based on the DFT [24] and the pseudopotential approach; the calculation procedure was also similar. In particular, for Cd atoms, we used a 2-electron pseudopotential acting on two s-electrons, considering them to be valence, and referring ten d-electrons to be in the atomic core. It was shown [16] that this pseudopotential, in contrast to the 12-electron one, leads to correct values of the energy gap for nanoparticles. Pseudopotentials were generated using the FHI98pp package [25] with the local density approximation (LDA) [26,27] in the framework of the Troullier-Martins (TM) [28] scheme, as it was made studying the CdSe nanoparticles [16].

## 3. Results and Discussion

### 3.1 CdS Nanoparticles: Comparison with CdSe

Since the "wurtzite" phase (w-CdS) is the most stable one for cadmium sulfide [17], we studied CdS nanoparticles with this structure, taking them in the same form in which we took w-CdSe particles [16]. Atomic schemes of studied particles are shown in Figure 1.

Figure 1 shows that the atomic structure of w-CdS particles undergoes a significant change in the process of relaxation. The arrangement of cadmium atoms changes most significantly: the outer Cd atoms are shifted into the space between the S layers. The same conclusion was made by Favero et al. [15] who marked that the relaxated CdS nanoparticles are S-terminated. In addition, noticeable displacements of atoms in the lateral directions also occur.

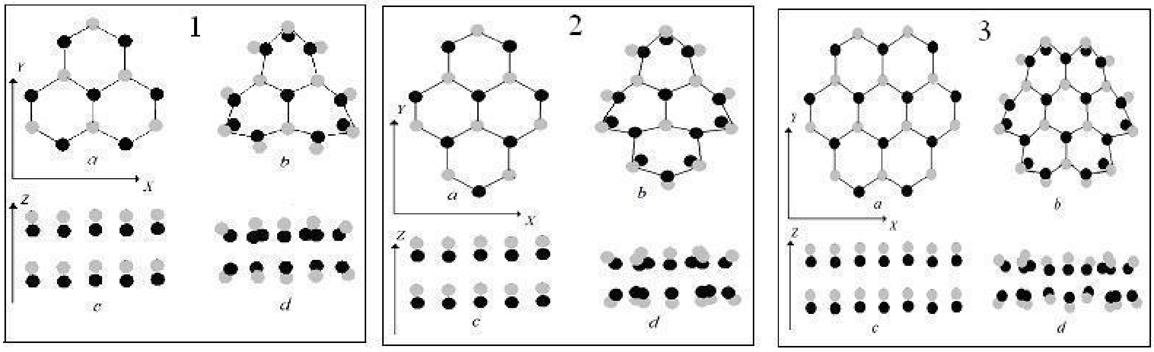

**Figure 1.** The structure schemes of the studied $(CdS)_n$ particles with the "wurtzite" structure

The numbers 1, 2, and 3 are the numbers of options. Schemes of particles of minimum sizes are shown: $(CdS)_{13}$ for option 1; $(CdS)_{16}$ for option 2); $(CdS)_{24}$ for option 3. The remaining particles are obtained by adding the appropriate number of layers along the Z axis. The letters indicate: a and b are views "from above" (in the XY plane); c and d are "side views" (along the Z axis). Option 1 corresponds to particles with n = 13, 26, 39, 52. Option 2 means particles with n = 16, 32, 48, 64, 80. Option 3 means particles with n = 24, 48, 72. Black spheres represent Cd atoms, gray spheres represent S atoms. In each panel, the left figures show the starting configurations, the right ones show the changed arrangement of atoms as a result of relaxation.

Calculations showed that, in accordance with the experimental data [12-14], the energy gap $E_{gap}$ for w-CdS particles decreases with increasing particle size, similarly to how it occurs in the case of w-CdSe particles [16]. Table 1 demonstrates our calculation results in comparing with previous results for w-CdSe particles [16].

It can be seen from this Table that, in general, in each option, the gap width decreases with increasing particle size, however, an increase in the size in the lateral direction can lead to an increase in the gap width with the same number of atoms (the case: n = 48, options 2 and 3). In all cases, as expected, the gap is wider for cadmium sulfide particles than for cadmium selenide ones of the same size and shape. We also note that our values of the gap (from 2.84 eV up to 3.78 eV) are typical for CdS particles of such sizes [6,13], therefore, we can trust our calculation methodology.

## 3.2 Electronic Structure of CdSe/CdS Layered Nanosystems

To study the electronic structure of the layered CdSe/CdS nanosystems, we took CdSe particles from all three options presented in Figure 1 as a basis and added CdS layers to them as covering. The constructed particles are as follows: A) two $Cd_{13}Se_{13}$ layers between two single layers $Cd_{13}S_{13}$ (option 1, N=104); B) four $Cd_8Se_8$ layers between two single $Cd_8S_8$ layers (option 2, N=96); C) four $Cd_8Se_8$ layers between two double $Cd_{16}S_{16}$ layers (option 2, N=128); D) two $Cd_{12}Se_{12}$ layers between two double $Cd_{24}S_{24}$ layers (option 3, N=144). The calculated values of the energy gap are collected in Table 2.

From this Table, we see that for the same number of atoms N, the value of $E_{gap}$ increases when CdSe surface layers are replaced by CdS layers. However, since these systems are compounds of two materials with different band gaps, the question arises: Is a certain common electronic structure established in the entire CdSe/CdS nanosystem or is it formed differently in layers of different compositions?

To answer this question, we studied the local (layer-by-layer) electronic structure, using as examples the cases of a single-layer coating (B) and a doble-layer coating (C) and plotted the local densities of electronic states (LDOS) in Figure 2 in comparison with the total densities of electronic states (DOS).

An analysis of Figure 2 (B panels) shows that, when applying a single-layer coating, a different energy gap is not formed in the CdS layer, it is the same as in the CdSe layers (2.6 eV). We see that all LDOS's near the gap are very similar to each other and to those of the total DOS. On the other hand, panels C show that, in the case of the two-layer coating, a special energy gap of 3.3 eV is formed in the CdS layers (panels C2 and C3), and it is wider than the gap of 2.6 eV in the CdSe layers (panels C4 and C5) and in the total DOS spectrum (panel C1). One can see that the spectra in panels C2 and C3 lack the peaks of occupied states, which are marked by arrows in panels C1, C4, and C5. In other words, we see that this system is actually a combination of two semiconductors with two different band gaps.

## 3.3 Simulation of a CdSe/CdS Quantum Dot

To model a CdSe/CdS quantum dot we took the $Cd_{72}Se_{72}$ particle (option 3) and replaced surface Se atoms with S atoms. As a first step we constructed the $Cd_{48}Se_{48}+2\cdot Cd_{12}S_{12}$ system where only the topest and lowest Se atoms were replaced with S ones. Secondly, we made the $Cd_{24}Se_{24}+Cd_{48}S_{48}$ system, in which the $Cd_{24}Se_{24}$ core was completely capped by the $Cd_{48}S_{48}$ single-layer shell from all sides. We calculated the local densities of states and plotted results in Figure 3.

**Table 1.** Energy gap widths (in eV) for $(CdSe)_n$ and $(CdS)_n$ particles with the "wurtzite" structure for different particle shapes (options).

| | Option 1 | | | | Option 2 | | | | Option 3 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| n | 13 | 26 | 39 | 52 | 16 | 32 | 48 | 64 | 24 | 48 | 72 |
| $(CdSe)_n$ | 3.26 | 2.96 | 2.55 | 1.87 | 3.25 | 2.72 | 2.35 | 2.15 | 3.00 | 2.96 | 2.36 |
| $(CdS)_n$ | 3.57 | 3.32 | 3.16 | 2.84 | 3.78 | 3.54 | 3.25 | 3.01 | 3.74 | 3.54 | 3.39 |

**Table 2.** The energy gap widths (in eV) calculated for CdSe/CdS layered nanosystems. For comparison, the results for the $Cd_nSe_n$ particles of the same size (with the same total number of atoms: 2n=N) are given.

| N=104 | | N=96 | | N=128 | | N=144 | |
|---|---|---|---|---|---|---|---|
| A | $Cd_{52}Se_{52}$ | B | $Cd_{48}Se_{48}$ | C | $Cd_{64}Se_{64}$ | D | $Cd_{72}Se_{72}$ |
| 2.18 | 1.87 | 2.75 | 2.48 | 2.80 | 2.15 | 2.62 | 2.36 |

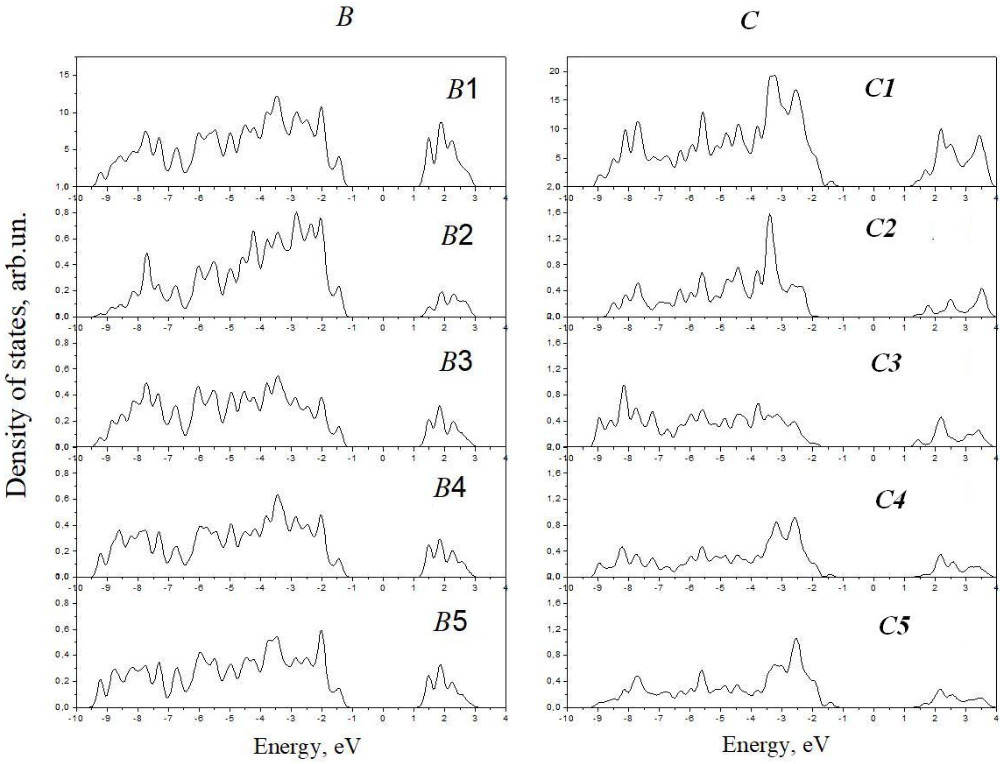

**Figure 2.** Densities of states (DOS) and local densities of states (LDOS) for studied nanosystems.

B: a single-layer coating. B1: the total DOS for the single-layer coating; B2: LDOS for the CdS layer of the a single-layer coating; B3: LDOS for the first CdSe layer in the single-layer coating system; B4: LDOS for the second CdSe layer in the single-layer coating system; B5: LDOS for the third CdSe layer in the single-layer coating system. C: a two-layer coating. C1: the total DOS for the two-layer coating; C2: LDOS for the first CdS layer of the two-layer coating; C3: LDOS for the second CdS layer of the two-layer coating; C4: LDOS for the first CdSe layer in the two-layer coating system; C5: LDOS for the third CdSe layer in the two-layer coating system.

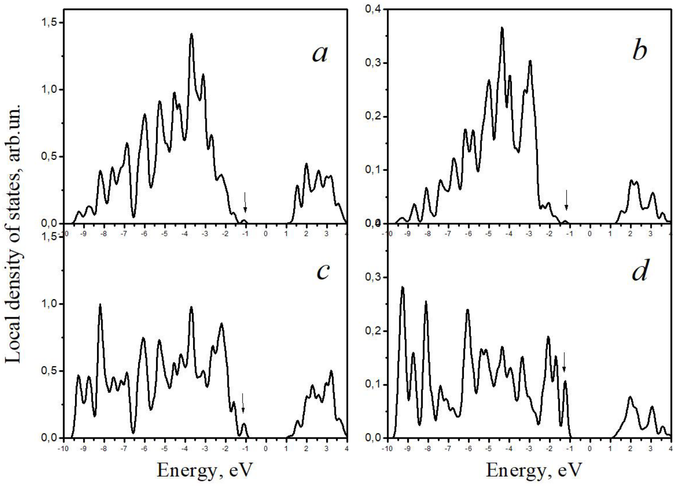

**Figure 3.** Local densities of states for the CdSe/CdS systems

a) the LDOS for the surface CdS layer of the $Cd_{48}Se_{48}+2\cdot Cd_{12}S_{12}$ layered system; b) the LDOS for the CdS shell atoms of the $Cd_{24}Se_{24}+Cd_{48}S_{48}$ quantum dot; c) the LDOS for the middle CdSe layer of the $Cd_{48}Se_{48}+2\cdot Cd_{12}S_{12}$ layered system; d) the LDOS for the CdSe core atoms of the $Cd_{24}Se_{24}+Cd_{48}S_{48}$ quantum dot. Arrows mark peaks of the highest occupied states.

We see in Figure 3 that a peak of the highest occupied states in the LDOS of the CdS cover layer (panel a) has a rather less intensity than an analogous peak in the LDOS of the middle CdSe layer (panel c). This means that in this system there is a tendency to form a wider energy gap. This trend is even more clearly seen in Figure 3 (panels b and d), where results for the $Cd_{24}Se_{24}$+$Cd_{48}S_{48}$ quantum dot with $E_{gap}$ of 2.5 eV are presented. We see that the LDOS of the CdSe core (panel d) has a very intensive peak of the highest occupied states. These results together with ones described in the previous subsection allow us to think that if the CdS shell thickness increases to two layers, a different band gap will be formed in it, and this gap will be wider than that in the CdSe core (approximately up to 3 eV).

## 4. Conclusions

Our density functional pseudopotential study shows that the energy gap width $E_{gap}$ of w-CdS nanoparticles decreases with increasing particle size in agreement with experiments. The calculated width values in the range of 2.84 eV ~ 3.78 eV are typical for particles of studied sizes in accordance with results of published data. In the CdSe/CdS nanosystems $E_{gap}$ increases when the number of sulfur atoms increases. The electronic structures of the layered CdSe/CdS nanosystems with a single-layer CdS covering demonstrate a tendency to form the electron structure with two different energy gaps. The CdSe/CdS systems with two-layer CdS covering can be interpreted in terms of combinations of two semiconductors with different energy band gaps. Simulation of a quantum dot with a single-layer shell showed that the tendency to form two energy gaps in its electronic structure is much more pronounced than in a layered system with a single-layer double-sided coating.

On the whole, as a benefit of this study, our calculations predict that two-layer CdS shells are sufficient for the formation of the electronic structure with two energy gaps in the CdSe/CdS quantum dots. The results obtained can be useful in designing optical systems based on CdSe.

## Conflict of Interest

There is no conflict of interest.

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