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Total Energy and Electronic States of CdSe Nanoparticles

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ARTICLE INFO	ABSTRACT
	The authors fulfilled calculations of the total energy and electronic states of Cd_nSe_n nanoparticle:"wurtzite", "sphalerite" and "rock-salt" types of the structure. It was shown that at $n \leq 72$ the "rock-salt" type is the most favorable energetically. However the extrapolation of the behavior of the energy per Cd-Se atomic pair shows that for $n > 130$ (corresponding to a size of about 2 nm), particles with a "wurtzite" structure can be more advantageous. Particles of the "wurtzite" and "rock-salt" types have an electronic structure with an energy gap. For particles with the "wurtzite" structure, the gap width decreases with increasing particle size: from 3.3 eV to 2.2 eV as the particle increases from 0.5 nm to 1.5 nm. For particles of the "rock-salt" type, the gap width grows slightly, remaining about 3 eV. "Sphalerite"-type particles have a metal-like electronic structure.

1. Introduction

Cadmium selenide is interesting as a material with a band gap comparable to the photon energy of visible light (1.7-1.8 eV). There are a large number of works, which describe the electronic properties of quantum dots based on CdSe nanoparticles, which can be used as elements of high-resolution optical systems [1-16]. In particular, X-ray diffraction analysis indicates [15] 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. Vitaly

Proshchenko and Yuri Dahnovsky theoretically studied [14] the electronic structure of CdSe particles 0.5 nm to 2 nm in size with structures of the "rock-salt" and "wurtzite" types and obtained values of E_{gap} in the range of 1.7 eV-3.7 eV, depending on the approximation used for the exchange-correlation interaction and on the size particles. At the same time, they reported that for "wurtzite" type particles, the gap width decreases with increasing particle size, while for particles of the "rock-salt" type, it increases. The authors compare the total energies of $Cd_{32}Se_{32}$ particles with the "wurtzite" and "rock-salt" structures. According to their calculations, the "wurtzite" structure is favorable,

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but the energy difference is so small (0.01 eV per Cd-Se atom pair) that the authors themselves doubt the reliability of their results. Thus, the question of what is the structure of small CdSe nanoparticles ("wurtzite" or "rock-salt") remains open. In addition, it is of interest to find out how the atomic structure of these particles changes and how these changes affect their electronic structure. Our work is dedicated to these tasks.

2. Modeling Technique

Cadmium selenide in the crystalline state has two stable structures: hexagonal "wurtzite" (w-CdSe) and cubic "sphalerite" (s-CdSe), and at high pressures it can also exist with a "rock-salt" type structure. Since changes in energy preferences are possible at the nanoscale level, we studied nanoparticles of all three structural modifications.

The simulation was carried out using the FHI96md package [17] based on the density functional theory [18] and the pseudopotential approach. Pseudopotentials were generated using the FHI98pp package [19] and tested on calculations of w-CdSe and s-CdSe crystals to obtain the lattice parameters and band gap close to the experimental values. We compared the results obtained in the local density approximation (LDA) [20,21] and the generalized gradient approximation (GGA) [22], and also compared the efficiency of pseudopotentials obtained by the Hamman [23] and Troullier-Martins (TM) [24] schemes, and concluded that for this material, the best results were obtained in the LDA-TM combination.

Particular attention was paid to the choice of the pseudopotential for the Cd atoms. The fact is that the cadmium atom has a filled d-shell (10 electrons), on top of which (in the energy sense) there are 2 s-electrons. Usually, for d-elements (for example, for Cu, Ag, Au), researches use pseudopotentials obtained by including d-electrons in the number of valence ones. However, in our case, it turned out that the electronic structure of CdSe nanoparticles is better described by the cadmium pseudopotential formed for two valence s-electrons (d-electrons remain in the core and contribute to the pseudopotential). Looking ahead, we note that for particles of the same size, the 2-electron pseudopotential gives an energy gap that is wider (i.e., closer to reality) than the 12-electron pseudopotential. In addition, the exclusion of d-electrons from consideration makes it possible to use a lower cutoff energy for a set of plane waves (20 rydbergs instead of 40), which significantly speeds up calculations and allows us to study larger particles, so we opted for the Cd pseudopotential with 2 valence electrons. The 12-electron pseudopotential is used in some cases only for comparison.

3. Results and Discussion

3.1 Energetics of Nanoparticles

To find out what type of structure is most beneficial for small nanoparticles, we compared the energy values of stoichiometric particles with different structures ("wurtzite", "sphalerite", and "rock-salt") and with different numbers of atoms, calculated taking into account the relaxation of atomic configurations. It turned out that relaxation slightly changes the structure of "rock-salt" type particles, and the energy value per Cd-Se atom pair is uniquely determined by the particle size (number of atoms), and the particles themselves are fragments of a cubic crystal. The structure of "wurtzite"-type particles changes significantly during relaxation, and these changes depend not only on the number of atoms entering the particle, but also on its initial configuration. Therefore, we considered three options for configurations of wurtzite-like particles, the schemes of which are shown in Figure 1. Particles of the "sphalerite" type were also considered (for completeness of the study), although their electronic structure does not have an energy gap and they are of no interest from the point of view of semiconductor electronics.

Figure 1 shows that the atomic structure of w-CdSe 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 gap between the Se layers. In addition, noticeable displacements of atoms in the lateral direction also occur. We also note that as a result of relaxation, the interatomic distances generally decrease, which agrees with the results of X-ray diffraction studies of w-CdSe nanoparticles [15].

Figure 2 shows the results of calculating the energy of CdSe nanoparticles with "wurtzite", "sphalerite", and "rock-salt" structures.

Figure 2 shows that at small sizes particles with the "rock-salt" structure are energetically favorable. However, the dependences of the particle energy on their size are such that, at a certain critical size, particles of the "wurtzite" type turn out to be more advantageous. Unfortunately, we did not have the technical ability to perform calculations for particles with more than 72 pairs, so we extrapolated our results using exponential functions, the course of which is also shown in Figure 2. The intersection of these functions shows that wurtzite-like nanoparticles become energetically favorable when the number of Cd-Se atom pairs is about 130, which corresponds to a size of about 2 nm (depending on the shape). This agrees with the fact that particles with a "wurtzite" type structure with sizes of 2.8 nm and larger were observed [15]. Note that the case n
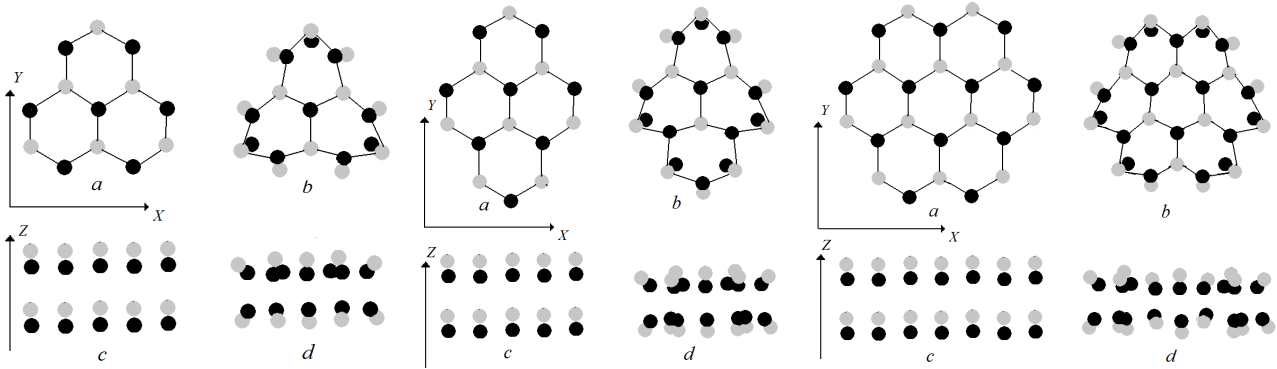
Figure 1. Schemes of the structure of the studied Cd_nSe_n particles with the "wurtzite" structure. Schemes of particles of minimum sizes are shown: left panel (variant 1) is $Cd_{13}Se_{13}$; central panel (variant 2) is $Cd_{16}Se_{16}$; right panel (variant 3) $Cd_{24}Se_{24}$. The remaining particles 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). The variant 1 corresponds to particles with n = 13, 26, 39, 52. The variant 2 is particles with n = 16, 32, 48, 64. The variant 3 is particles with n = 24, 48, 72. Black spheres represent Cd atoms, gray spheres represent Se 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.
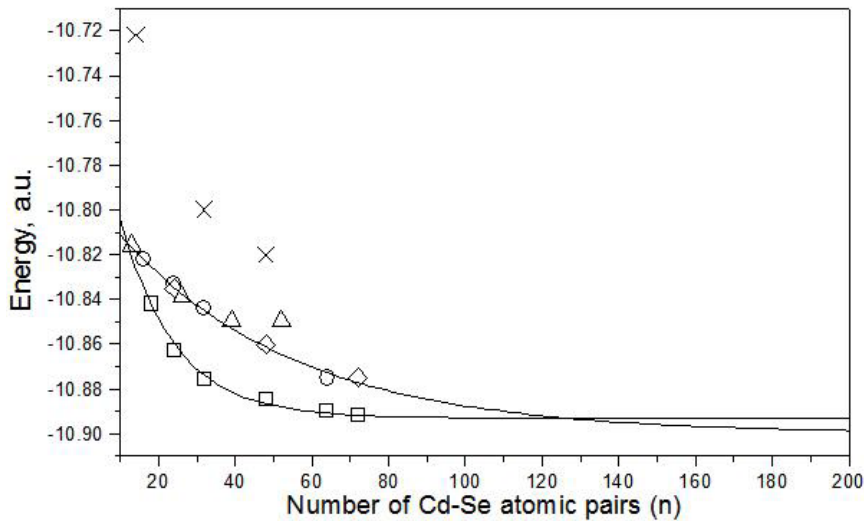

Figure 2. Energy per Cd-Se atom pair in Cd_nSe_n nanoparticles as a function of the number of atom pairs n. The squares are the results for particles of the "rock-salt" type. The crosses are the results for "sphalerite"-type particles. The remaining data correspond to particles with the "wurtzite" structure: triangles is variant 1, circles is variant 2, rhombuses is variant 3. Solid curves is extrapolation using exponential functions.

= 52 falls out of the general sequence of the variant 1: the energy does not decrease in comparison with the particle of the previous size. This is a sign that too elongated particles of this kind are energetically unfavorable.

3.2 Electronic Structure of Nanoparticles

Calculations have shown that the electronic structure of cadmium selenide nanoparticles of different types ("wurtzite", "sphalerite" and "rock-salt") are very different from each other. As an example, Figure 3 shows the electronic spectra of $Cd_{32}Se_{32}$ particles of all three types,

constructed by smearing the energy levels with Gaussian functions centered on them. The main difference is that the spectrum of electronic states of a "sphalerite"-type particle has a metal-like character, with a high density of states at the Fermi level, while particles with the "wurtzite" and "rock-salt" structures have semiconductor properties with energy gaps of about 2.7 eV. The spectra of particles of the "wurtzite" and "rock-salt" types, in turn, differ from each other by the position and intensity of the peaks of occupied and free states. Further, we will be interested in the electronic structure of particles of only these two types, since it is they that have semiconductor properties.
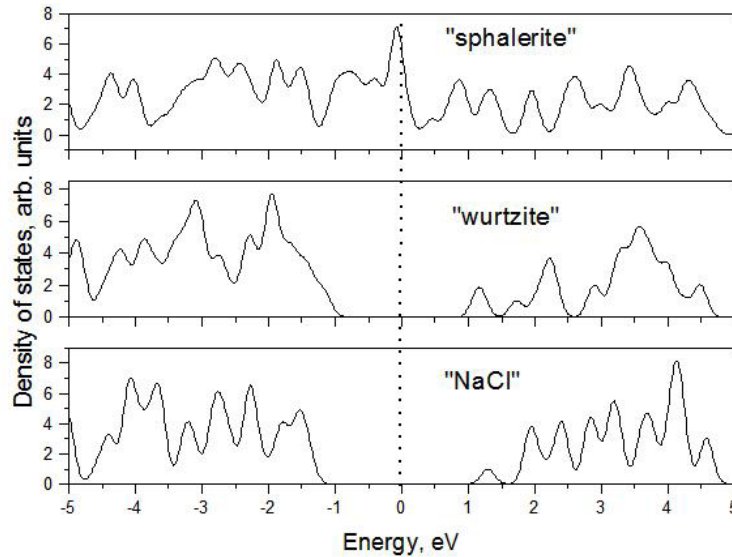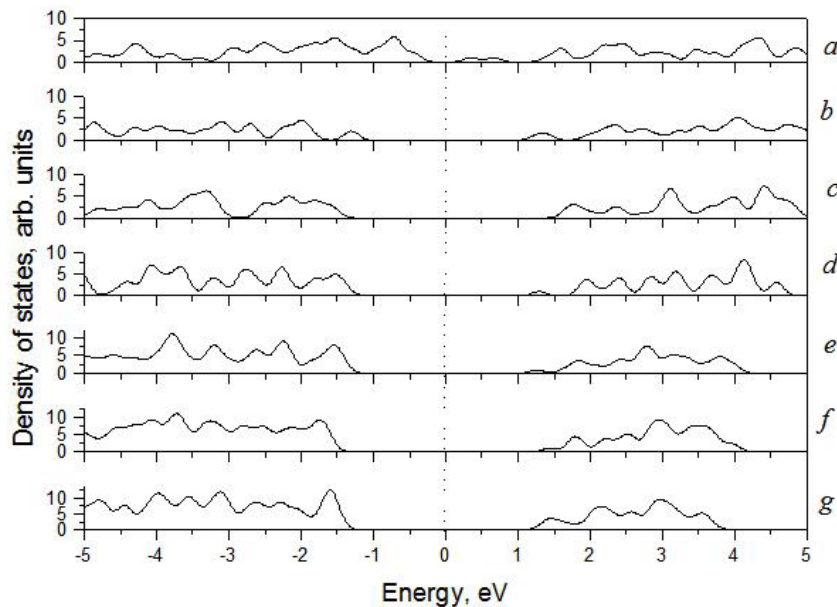
Figure 3. Electronic structure of $Cd_{32}Se_{32}$ particles of three types of structure. The vertical dotted line is the Fermi level.

Particles of the "Rock-salt" Type

The crystal lattice of the "rock-salt" type has a cubic structure, so its fragments (nanoparticles) look like either cubes or rectangular parallelepipeds. We studied Cd_nSe_n particles with n = 18, 24, 32, 48, 64, 72. Of these, only the particle with n =32 has the shape of a cube, all the rest are parallelepipeds. For the case of n = 18, for comparison, we also performed a calculation using a pseudopotential with 12 valence electrons.

It can be seen from Figure 4 that the electronic structure of all studied particles of the "rock-salt" type has an energy gap near the Fermi level, while the gap width depends nonmonotonically on the particle size and ranges from 2.6 eV to 3.3 eV. The calculation for $Cd_{18}Se_{18}$, carried out using the 12-valent pseudopotential for the Cd atom, gave an energy gap of 0.8 eV wide (panel *a*), which is significantly less than 2.6 eV obtained with the 2-valent pseudopotential (panel *b*). It should be noted that the configurations of the particles do not undergo strong

Figure 4. Electronic structure of Cd_nSe_n nanoparticles with a "rock-salt" type structure. By layers: *a*) n = 18 (12 valence electrons); *b*) n = 18 (2 valence electrons); *c*) n = 24; *d*) n = 32; *e*) n = 48; *f*) n = 64; *g*) n = 72. The vertical dotted line shows the position of the Fermi level.

changes during the relaxation of the structure. Only the surface atoms shift by 0.1-0.2 Å.

It was noted above that the energy of "wurtzite"-type nanoparticles essentially depends on the shape of the particle. The same can be said about their electronic structure. Figures 5, 6, 7 show the spectra of electronic states for three variants for constructing Cd_nSe_n particles of the "wurtzite" type.

It can be seen from these figures that all studied particles of the "wurtzite" type are characterized by a semiconductor electronic structure with a gap width of 2-3 eV. Figure 4 shows that the calculation using the 12-valent pseudopotential for the Cd atom gives an electronic structure for the $Cd_{13}Se_{13}$ particle similar to that obtained using the 2-valent pseudopotential, but the energy gap is much smaller: 1.8 instead of 3.3 eV.

Comparison of Figures 5, 6 and 7 shows that the width of the gap for particles with different shapes changes with the increase of the particle in different ways. For a more visual analysis of these dependences, we presented these data in Figure 8 and in the same figure, for comparison, we presented similar dependences for particles of the "rock-salt" type.
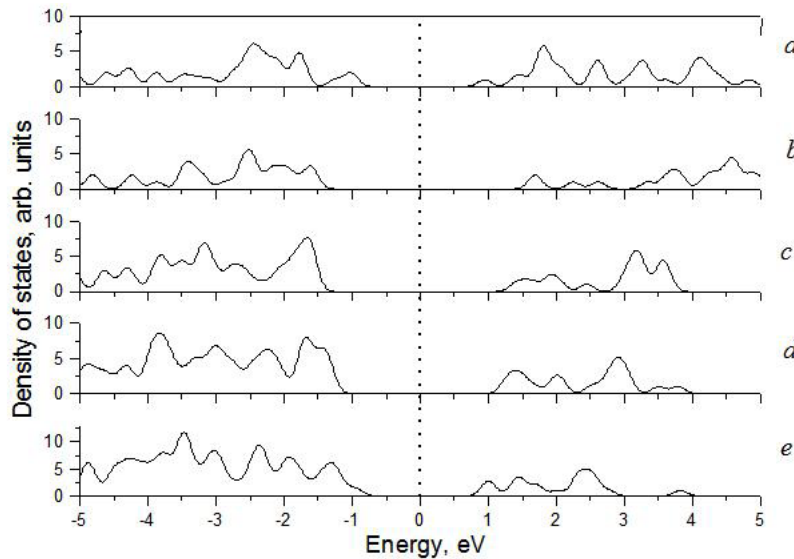

Figure 5. Electronic structure of Cd_nSe_n nanoparticles with a "wurtzite" type structure (variant 1). By layers: *a)* n = 13 (12 valence electrons); *b)* n = 13 (2 valence electrons); *c)* n = 26; *d)* n = 39; *e)* n = 52. The vertical dotted line shows the position of the Fermi level.
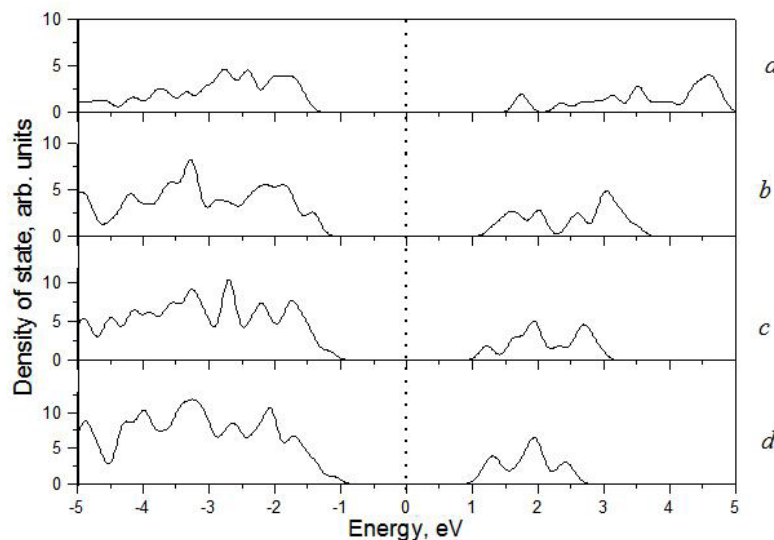
Figure 6. Electronic structure of Cd_nSe_n nanoparticles with a "wurtzite" type structure (variant 2). By layers: *a)* n = 16; *b)* n = 32; *c)* n = 48; *d)* n = 64. The vertical dotted line shows the position of the Fermi level.

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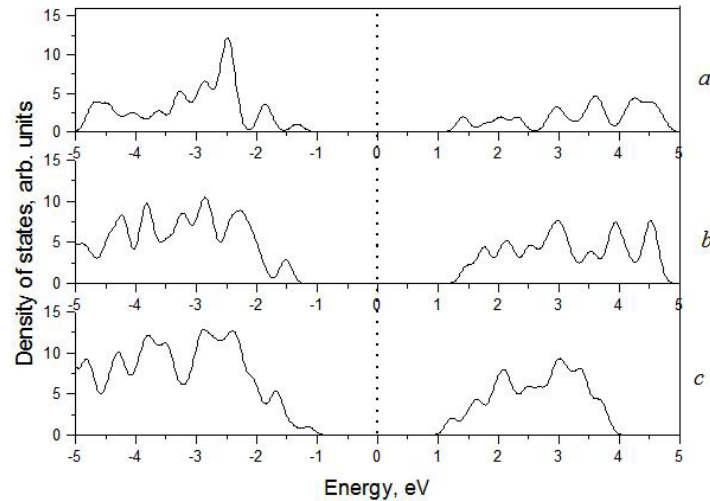
Figure 7. Electronic structure of Cd_nSe_n nanoparticles with a "wurtzite" type structure (variant 3). By layers: *a*) n = 24; *b*) n = 48; *c*) n = 72. The vertical dotted line shows the position of the Fermi level.
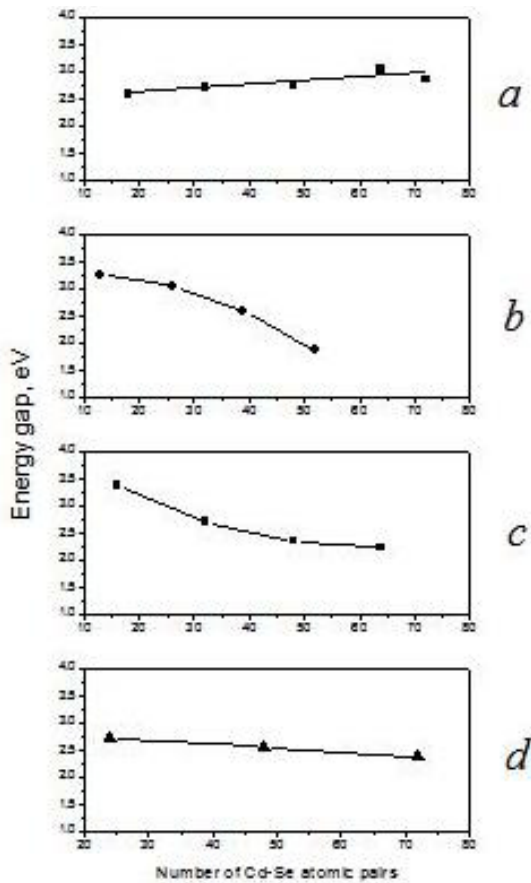
Figure 8. Dependence of the energy gap width on the particle size. By layers: *a*) results for particles of the "rock-salt" type; the rest layers present results for particles of the "wurtzite" type: *b*) variant 1; *c*) variant 2; *d*) variant 3.

It is easy to see that in the case of "wurtzite"-type particles, there is a tendency for the gap width to decrease with increasing particle size. However, for particles of the variant 1 (panel *b*), the gap width decreases steeply, like a falling parabola, for the variant 2 (panel *c*), the size dependence of the gap width can be approximated by a negative exponent, and in the case of the variant 3, the gap width decreases almost linearly. On the other hand, particles of the "rock-salt" type (panel *a*) show a linear increase in the gap width with increasing particle size. Thus, our results are consistent with the conclusion that the gap width of the "wurtzite" particles decreases with increasing particle size, while for particles of the "rock-salt" type it increases [14], however, we present more detailed data on how the value of the gap width is related to the particle shape.

4. Conclusions

Our calculations performed within the framework of the density functional theory show that, at small sizes of CdSe nanoparticles, it is energetically favorable to form a "rock-salt" type structures with an electronic spectrum having an energy gap, the width of which increases linearly with the particle size. Particles with the "wurtzite" structure also have an energy gap, the width of which decreases with increasing particle size: from 3.3 eV to 2.2 eV with increasing particle size from 0.5 nm to 1.2 nm. Extrapolation of the energy values per Cd-Se atom pair shows that when the number of pairs is more than 130 (which corresponds to a size of about 2 nm), particles with a "wurtzite" structure become more energetically favorable than particles with a "rock-salt" structure. Particles with a "sphalerite" type structure are energetically unfavorable and their electronic structure has a metal-like form.

Declaration of Conflict of Interest

The authors declare that they have no individual relationships that could have performed to affected the work reported in this study and have no known conflict of financial interests.

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