Self-Healing of CdSe Nanocrystals: First-Principles Calculations

Aaron Puzder,* A. J. Williamson,[†] François Gygi, and Giulia Galli

Lawrence Livermore National Laboratory, Livermore, California 94550, USA
(Received 8 September 2003; published 25 May 2004)

Ab initio calculations of the structural, electronic, and optical properties of CdSe nanoparticles are presented. The atomic structures of the clusters are relaxed both in vacuum and in the presence of surfactant ligands. In both cases, we predict significant geometrical rearrangements of the nanoparticle surface while the wurtzite core is maintained. These reconstructions lead to the opening of an optical gap without the aid of passivating ligands, thus "self-healing" the surface electronic structure. Our calculations also predict the existence of a midgap state responsible for recently observed subband emission.

    PACS numbers: 78.67.–n, 68.65.–k, 73.22.–f, 78.55.–m

The ability to routinely synthesize CdSe semiconductor nanocrystals with narrow size distributions [1,2] has made these particles one of the most promising building blocks for new nanoscale materials. The reproducibility of optical absorption and emission properties has contributed to the popularity of CdSe nanocrystals for potential applications such as biosensors [3], displays [4], and quantum dot lasers [5].

In spite of a wealth of experimental data reported for CdSe nanocrystals, many fundamental questions regarding their structural and optoelectronic properties remain unanswered. In particular, although transmission electron microscopy (TEM) indicates that CdSe nanoparticles adopt the wurtzite structure [1,6], resolving their surface geometry and assessing the influence of organic ligands on surface reconstructions is difficult. In contrast to types IV and III-V semiconductors, the size dependence of the optical gap of CdSe nanoparticles is largely independent of the surface termination. The origin of this insensitivity is not well understood. In addition, recent optical measurements indicate the presence of a subband gap state [7–11], with an unknown nature and dependence on the nanoparticle structure.

In this Letter, we present *ab initio* electronic structure calculations of CdSe nanoparticles with diameters up to 1.5 nm. The nanoparticle structures were relaxed both in vacuum and in the presence of representative organic ligands. These calculations predict a substantial structural relaxation of each cluster, especially at the surface, while still maintaining a wurtzite core. These relaxations differ significantly from those used in previous calculations, most of which have assumed either bulk-derived wurtzite structures [12–16], surface reconstructions derived from empirical atomic adjustments [17], or structures built from relaxed fragments [18]. Unlike Si, Ge, and III-V nanoclusters, the predicted CdSe atomic structures are found to be relatively insensitive to the presence of surface passivation. We find that CdSe nanoparticles with ideal wurtzite structures are quasimetallic and that surface relaxations, not passivation by organic ligands, are responsible for opening up the gap in the clusters.

Our *ab initio* calculations were performed using a plane wave implementation [19] of density functional theory (DFT). Supercells were chosen with at least 10 Å between replica to remove spurious periodic interactions. Norm-conserving pseudopotentials [20] were used to represent the ionic cores. All structures were calculated using 18 Cd ($4p^6 4d^{10} 5s^2$) and six Se ($4s^2 4p^4$) valence electrons as this was determined to be the minimum number of valence electrons required to accurately predict the nanoparticle structure [21]. For Cd, the nonlocal pseudopotential energy contribution to the total energy was computed using a quadrature integration technique to avoid possible incorrect solutions produced by, e.g., a Kleinmann-Bylander construction of the pseudopotential. Four representative wurtzite $Cd_x Se_x$ clusters were studied with $x = 6$, 15, 33, and 45. $Cd_6 Se_6$ represents the smallest possible wurtzite cage, and the clusters with $x = 15$, 33, and 45 are 1.0, 1.3, and 1.5 nm in diameter, respectively. Each cluster was initially constructed on a wurtzite lattice with bulk Cd-Se bond lengths and then relaxed using a preconditioned conjugate gradient algorithm to its lowest energy configuration. As this procedure relaxes the structure into a local energy minimum, we repeated the relaxation from a variety of starting points, with and without surface passivation. Each time we find nearly identical structures with subtle changes corresponding to total energy differences significantly smaller than room temperature.

Figure 1 compares our calculated relaxed atomic geometries with the corresponding ideal wurtzite structures. A substantial structural relaxation is observed on the surface of each cluster, although the wurtzite core is maintained as seen along the c axis. The $Cd_{45} Se_{45}$ nanoparticle, for example, features a relaxation of the core atoms corresponding to a 1% decrease in bond lengths and a 6° rms deviation in angles from the ideal wurtzite structure. The observed contraction in bond lengths for this 1.5 nm particle is consistent with recent experimental measurements [22]. In contrast to the relatively small relaxation of the nanoparticle core, the surface atoms reconstruct significantly with rms deviations in bond
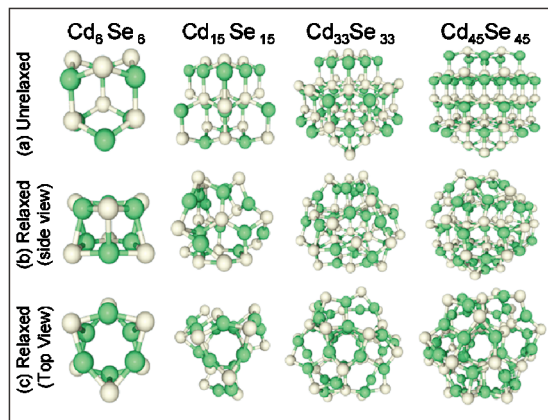
FIG. 1 (color). Unrelaxed (a) and relaxed (b),(c) wurtzite structures of Cd_xSe_x, $x = 6$, 15, 33, and 45. The Cd is green and the Se is yellow in the ball and stick models. The side (top) view is parallel (along) the c axis.

lengths and angles of 25% and 25°, respectively. The observed structural relaxation reduces the total energy of the clusters by ~0.8, 0.7, and 0.6 eV per CdSe pair in $Cd_{15}Se_{15}$, $Cd_{33}Se_{33}$, and $Cd_{45}Se_{45}$, respectively. We note that these significant structural relaxations occur even at zero temperature, i.e., the ideal wurtzite structure is unstable.

The observed relaxations of the polar (0001) surfaces are similar to the relaxations predicted [23,24] and observed experimentally [1,25] for bulk CdSe (0001) surfaces, in particular, the pulling in of surface Cd atoms and the puckering out of Se atoms. On the nonpolar (1010) surfaces, recent scanning tunneling microscopy measurements [26] predict a modest 1×1 reconstruction of the bulk surface. Our simulations predict a larger reconstruction of these CdSe nanoparticle facets, including a Cd-Se dimer rotation into the surface. Therefore, when considering interactions between CdSe nanoparticles and organic ligands, it is important to use the reconstructed structures of the nanoparticle, rather than the bulk surface structure.

To compare these relaxed structures with previous studies of CdSe nanoparticles, we consider two size regimes: molecules containing <10 Cd atoms and 1–5 nm quantum dots. For small molecules, DFT calculations [18,27] that have been used to determine the lowest energy structures agree closely with our structure. For larger, 1–5 nm quantum dots, we are aware of four approaches for predicting atomic geometries; Rabani [28] used a classical molecular dynamics simulation to relax the atomic geometry, Pokrant *et al.* [17] applied empirical changes to the structure at the surface based on observations of bulk surface relaxations, Deglmann *et al.* [18] constructed clusters from optimized fragments of bulk layers, and Kasuya *et al.* [29] predicted a cage structure similar to boron nitride. With the exception of these works, previous theoretical investigations [12,14–

16] assumed bulk-derived wurtzite clusters without geometric optimization.

To investigate the effect of organic ligands on the relaxed atomic geometry of the CdSe nanoclusters, structural relaxations were repeated with short chain versions (single C atom in the alkyl group) of trioctyl phospine oxide (TOPO) and hexyl-phosphonic acid bound to the surfaces. Upon geometry optimization of the nanoparticle-ligand composite systems, we observe that globally, the CdSe structure is similar to that of unpassivated relaxed structures, although small changes occur locally due to the weak bonds formed between surface atoms and the ligands. In particular, we observe that ligand oxygen atoms attract surface Cd atoms on the Cd-rich surface, displacing them by ≈ 0.15 Å.

In summary, we find that passivating ligands do not "lock in" the ideal wurtzite structure as previously suggested [17] and that *globally*, the relaxed structures are qualitatively the same, whether relaxed in the presence of ligands or not. *Locally*, the active oxygen in a ligand attracts the Cd to the surface, moving out the closest Cd by 0.1 to 0.2 Å slightly counterbalancing the 0.7 Å it had already relaxed inward in the absence of surfactants.

The relative insensitivity of the global structure of CdSe nanoparticles to surface passivation can be understood in terms of the weak binding of these surfactants to the surfaces. This insensitivity also provides an explanation for the robustness of some CdSe nanocluster properties to changes in surfactants and supports a "self-healing" mechanism for obtaining optical gaps.

Comparing the *ab initio* derived structures shown in Fig. 1 with classical or empirically derived models is informative. A recent classical molecular dynamics study [28] predicted significantly different structures to those described here. In this classical model, the surface Cd and Se atoms in successive layers were electrostatically attracted to each other leading to a "pinching" of the layers. Whereas classical models such as this tend to overemphasize the Coulomb attraction between cations and anions resulting in this pinching, *ab initio* models include charge transfer and screening effects which counterbalance this ionic attraction.

A recent tight-binding calculation utilized information from observed surface calculations to empirically reconstruct the CdSe surface [17]. The Se atoms in this study were moved out from the surface by 1 Å, similar to our calculated 0.7 Å relaxation. The Cd atoms in this study were left unrelaxed on the assumption that bonding surface ligands would prevent their movement. Our calculations show that the Cd relax vertically *into* the surface by 0.7 Å, and this relaxation is only weakly counterbalanced (0.1 to 0.2 Å) by the ligands.

Finally, an empirically derived structure taken by stacking DFT relaxed fragments [18] demonstrates the same qualitative movement as here; however, the surface relaxation in that work is not nearly as pronounced. This

discrepancy suggests that a different combination of relaxed fragments may be required as building blocks for these >1 nm structures.

We note that orbital hybridization effects are significant in CdSe nanoparticles, exhibiting similar behavior to bulk CdSe surfaces [24]. The surface cations (Cd) show a preference to form sp^2-like bonds with their three nearest anion (Se) neighbors. In Cd_6Se_6, this is the most dominant effect, resulting in two parallel Cd_3Se_3 planes. In the larger nanoparticles, the hybridization strongly affects the Cd-rich surface [bottom layer in Fig. 1(b)] leading to a planar surface.

Figure 2 compares the electronic density of states (DOS) of the CdSe nanocrystals with ideal wurtzite structure to those with relaxed geometries. For each of the CdSe nanoclusters studied here, the ideal wurtzite structures are quasimetallic, i.e., the spectra of states are continuous with no clear gap at the Fermi level. As the gap is close to zero, we used the ensemble DFT formalism [30] to optimize the occupation of the electronic states in these calculations. In each case we found that fractional occupations are necessary to yield the correct ground state.

This quasimetallic, behavior arises from the multiple chemically active bonds present at the surface. While previous calculations have attempted to remove these states by either "projecting them out" (discarding them) [13], or by passivating the active sites on the surface with artificial potentials designed to reproduce the effects of hydrogen atoms [15] or oxygen terminated ligands [17], we have found that structural relaxation alone is sufficient to open up a gap in CdSe nanoparticles.

The DOS of the CdSe clusters after structural relaxation is shown in Fig. 2(b). For each cluster, structural
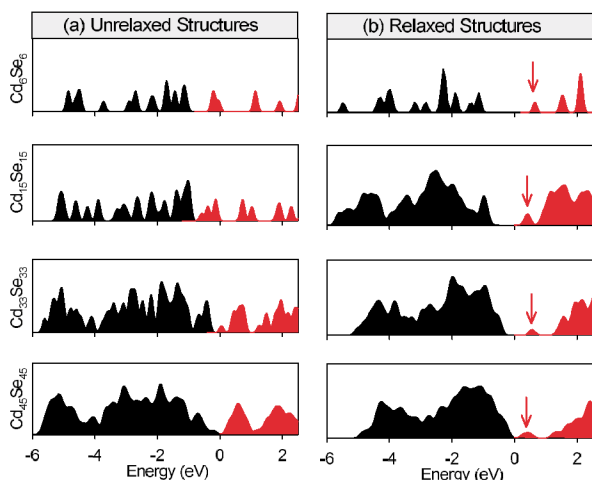

FIG. 2 (color).   Electronic density of states (DOS) of (a) bulk wurtzite CdSe clusters and (b) relaxed CdSe clusters. The black (red) curves show valence (conduction) DOS. The states have been Gaussian broadened by 0.05 eV. The zero of energy is aligned with the top of the valence band.

relaxation opens the gap without the aid of passivation or projecting out states. Instead, the clusters self-heal by opening the gaps to values that range between 0.7 to 2.0 eV when calculated within the local density approximation (LDA). Although these predicted gaps are still smaller than those observed experimentally, (≈ 3 eV for a 1.5 nm cluster), the change of the gap compared with that of unrelaxed clusters is significant. Furthermore, the LDA underestimate of the band gap in CdSe is greater than in types IV and III-V semiconductors due to the artificial pushing up of the valence CdSe states by the Cd d states. Therefore, the calculated 1 to 2 eV LDA gaps without *any* surface passivation are reasonably consistent with 3 eV experimental gaps. This shows that passivating ligands do not affect the optical gaps of CdSe nanoparticles in any significant manner, although they may well affect their growth rate, coagulating effects, and perhaps the quantum yield.

An additional intriguing feature of the DOS of these relaxed clusters is the presence of a midgap state, i.e., the lowest unoccupied state (LUMO) is an orbital positioned in energy in the middle of the gap between the highest occupied orbital (HOMO) and the LUMO + 1 [see arrows in Fig. 2(b)]. Experimentally, a midgap state has been observed to be as much as 0.6 eV below the strong absorption peak in 3 to 4 nm clusters by several groups and has been interpreted through a variety of mechanisms [7–9,11,31]. This state is rarely observed in absorption measurements but is often seen in emission, with a variable lifetime, which is always comparable to an excitonic lifetime of standard band edge emission. In distinction from the core confined band edge states, the intrinsically different midgap state is assumed to be a surface or dangling bond state [31,32]. This state is also assumed to have weak oscillator strength [9–11]. Our computed dipole matrix elements show that this state is optically active in each cluster, but has only 1/3 to 1/4 the oscillator strength of the next highest transition (corresponding to an order of magnitude slower exciton lifetime), in agreement with the only available measured exciton lifetime [10]. The dipole matrix elements are also found to be an order of magnitude stronger perpendicular to the c axis, suggesting that absorption into this state would be strongly polarized.

The nature of the HOMO and LUMO in CdSe nanoparticles has been extensively discussed in the literature [17,25,32,33], but a consensus has not been reached. Common interpretations include the facts that both states are Se dangling bond states or that the LUMO is a Cd localized state. In the latter interpretation, the efficiency of TOPO passivating CdSe surfaces has been explained by the TOPO pushing the LUMO higher in energy opening a gap [25]. This picture is consistent with the empirical observations that photoluminescence is enhanced in crystals with core/shell structures [33].
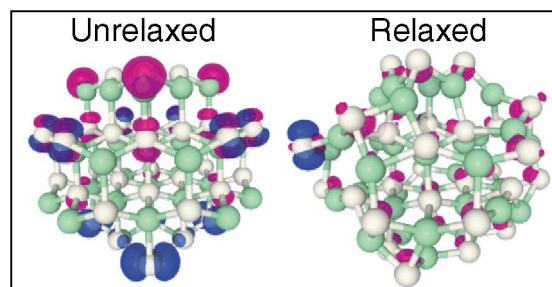
FIG. 3 (color). Probability density of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for wurtzite and relaxed $Cd_{33}Se_{33}$ clusters. The blue (magenta) isosurface includes 50% (25%) of the HOMO (LUMO) density. The Cd atoms are green and the Se atoms are yellow in the ball and stick models.

Figure 3 shows the probability density of the HOMO (blue) and LUMO (magenta) of the relaxed and unrelaxed $Cd_{33}Se_{33}$ structures. In the unrelaxed structure, the HOMO is localized on the Se atoms, predominantly those with two free bonds, consistent with tight-binding predictions [17] and DFT calculations for unrelaxed clusters [27]. The LUMO is predominantly localized on Cd atoms, in agreement with the DFT calculations of Deglmann *et al.* [18], but in contrast to tight-binding [17] and other DFT [27] calculations. Upon surface relaxation, the HOMO is still localized on Se dangling bonds, but the LUMO is primarily a Se state.

In conclusion, using accurate *ab initio* calculations, we have investigated how the surface reconstructions of CdSe nanoparticles affect their electronic and optical properties. We have found that surface reconstructions are remarkably similar in vacuum and in the presence of surface ligands. Surface relaxations in the absence of surfactants lead to the opening of an optical gap, although a midgap state is also observed. The surface geometries predicted by our simulations differ from those found in previous classical and empirical models, indicating that while considerable insight may be gained from studying bulk relaxations and investigating classical models, an *ab initio* approach is required to accurately determine the structure of CdSe nanoparticles.

---

*Current address: Department of Physics, Rutgers University, Piscataway, NJ 08854, USA.
Electronic address: puzder@physics.rutgers.edu

[†]Electronic address: williamson10@llnl.gov
[1] C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).
[2] Z. A. Peng and X. Peng, J. Am. Chem. Soc. **123**, 183 (2001).
[3] W. C. Chan and S. Nie, Science **281**, 2016 (1998).
[4] V. Colvin, M. Schlaub, and A. P. Alivisatos, Nature (London) **370**, 354 (1994).
[5] V. I. Klimov *et al.*, Science **290**, 314 (2000).
[6] J. J. Shiang *et al.*, J. Phys. Chem. **99**, 17 417 (1995).
[7] E. Lifshitz *et al.*, Chem. Phys. Lett. **288**, 188 (1998).
[8] B. Alperson, I. Rubinstein, and G. Hodes, Phys. Rev. B **63**, 081303(R) (2001).
[9] V. N. Soloviev *et al.*, J. Am. Chem. Soc. **123**, 2354 (2001).
[10] C. Landes *et al.*, J. Phys. Chem. B **105**, 2981 (2001).
[11] S. Xu *et al.*, Phys. Rev. B **65**, 045319 (2002).
[12] K. Eichkorn and R. Ahlrichs, Chem. Phys. Lett. **288**, 235 (1998).
[13] C. Troparevsky, L. Kronik, and J. R. Chelikowsky, Phys. Rev. B **65**, 033311 (2002).
[14] P. E. Lippens and M. Lannoo, Phys. Rev. B **41**, 6079 (1990).
[15] L.-W. Wang and A. Zunger, Phys. Rev. B **53**, 9579 (1996).
[16] C. Troparevsky, L. Kronik, and J. R. Chelikowsky, J. Chem. Phys. **119**, 2284 (2003).
[17] S. Pokrant and K. B. Whaley, Eur. Phys. J. D **6**, 255 (1999).
[18] P. Deglmann, R. Ahlrichs, and K. Tsereteli, J. Chem. Phys. **116**, 1585 (2002).
[19] LDA calculations were performed with the GP code version 1.16.0 (F. Gygi, LLNL 1999–2004). A 35 (140) Ry energy cutoff was used for wave functions (charge density). An increase to 50 Ry yielded just 0.03 Å differences in bond lengths with no discernible change to the structure.
[20] D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).
[21] Bond lengths and angles of Cd_6Se_6 calculated using 12 Cd electrons differ by 3.5% from those predicted by an all-electron calculation, while those calculated using 18 Cd electrons agree within 0.5%.
[22] J.-Y. Zhang *et al.*, Appl. Phys. Lett. **81**, 2076 (2002).
[23] Y. R. Wang and C. B. Duke, Phys. Rev. B **37**, 6417 (1988).
[24] D. Vogel, P. Kruger, and J. Pollman, Surf. Sci. **402–404**, 774 (1998).
[25] M. G. Bawendi *et al.*, J. Chem. Phys. **91**, 7282 (1989).
[26] B. Siemens, C. Domke, Ph. Ebert, and K. Urban, Phys. Rev. B **56**, 12 321 (1997).
[27] C. Troparevsky and J. R. Chelikowsky, J. Chem. Phys. **114**, 943 (2001).
[28] E. Rabani, J. Chem. Phys. **115**, 1493 (2001).
[29] A. Kasuya *et al.*, Nat. Mater. **3**, 99 (2004).
[30] N. Marzari, D. Vanderbilt, and M. C. Payne, Phys. Rev. Lett. **79**, 1337 (1997).
[31] M. G. Bawendi *et al.*, J. Chem. Phys. **96**, 946 (1992).
[32] A. C. Carter *et al.*, Phys. Rev. B **55**, 13 822 (1997).
[33] M. A. Hines and P. Guyot-Sionnest, J. Chem. Phys. **100**, 468 (1996).