First principles study of CdSe quantum dots: Stability, surface unsaturations, and experimental validation

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Ab initio computational studies were performed for CdSe nanocrystals over a wide range of sizes and topologies. Substantial relaxations and coordination of surface atoms were found to play a crucial role in determining the nanocrystal stability and optical properties. While optimally (threefold) coordinated surface atoms resulted in stable closed-shell structures with large optical gaps, suboptimal coordination gave rise to lower stability and negligible optical gaps. These computations are in qualitative agreement with recent chemical etching experiments suggesting that closed-shell nanocrystals contribute strongly to photoluminescence quantum yield while clusters with nonoptimal surface coordination do not. © *2006 American Institute of Physics.*
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The size, shape, and surface passivation of semiconductor CdSe nanocrystals (NCs) have been a topic of intense theoretical and experimental investigations, in light of their effect on the NCs' optical and electronic properties.[1,2] The NCs' tunable emission, enhanced photo-oxidation stability, and electron transporting nature render them ideal candidates for applications on biological labels,[3,4] laser media,[5] light emitting diodes,[1,2] nonlinear optics,[6,7] and photovoltaics.[8] Although considerable understanding has been achieved in terms of quantum confinement, much less is known about the state of bonding and disorder at NC surfaces.[1,2] The size discrepancy between effective sizes obtained from small angle x-ray diffraction and transmission electron microscopic (TEM) results[9] has been attributed to the lack of order of the outermost surface layer. This layer, together with the variety of passivating agents, is deemed essential for cladding these NCs to achieve high photoluminescence (PL) efficiency (i.e., as high as 50%).[10] If, however, various asperities (such as vacancies, incomplete coverage, and dangling bonds) are present at the outermost surface layer, NC PL efficiency is severely reduced.[1,2]

This study intends to provide a more comprehensive understanding of the influence of surface imperfections on the electronic properties of CdSe NCs. In particular, first principles computational methods have been employed over a large range of smoothly varying cluster sizes with different topologies to determine the local structure at the NC surface in relation to their contribution to the NC density of states (DOS), which ultimately controls optical properties. CdSe nanoclusters with diameters up to 2 nm (150 atoms or 75 CdSe pairs) were investigated as a function of number of CdSe pairs to emulate close- and open-shelled structures. Our findings are in qualitative agreement with the cyclic modulations of PL quantum efficiencies with respect to the

average NC diameter seen experimentally.[11–13]

Prior computational studies of CdSe clusters fall in two broad classes: (1) efforts based on classical molecular dynamics, and first principles techniques without self-consistency or geometry optimization, involving a wide range of cluster sizes,[14–18] and (2) sophisticated self-consistent *ab initio* calculations that treat only small or limited cluster sizes.[19–21] Owing to an inadequate treatment of the electronic or structural degrees of freedom, the former type of calculations may lead to erroneous conclusions concerning the impact of surface relaxations on optical properties, as pointed out recently.[19] The second class of calculations referred to above provide very accurate information concerning the stability, structure, and optical properties of small semiconductor clusters.[19–21] However, we are not aware of a systematic study of trends in such properties over a wide range of experimentally relevant cluster sizes and topologies at a high level of theory. We believe that our study fills this void while maintaining a close connection with prior experimental work.

All calculations reported here were performed using the local density approximation (LDA) within density functional theory[22] (DFT) as implemented in the local orbital SIESTA code.[23] Norm-conserving nonlocal pseudopotentials of the Troullier-Martins type[24] were used to describe all the elements, with Cd and Se at the $[Kr]5s^24d^{10}$ and $[Ar3d^{10}]4s^24p^4$ atomic configurations, respectively. A double-zeta plus polarization (DZP) basis set was used for all calculations. The equilibrium positions of the atoms were determined by requiring the forces on each atom to be smaller than 0.04 eV/Å.

As a test of the pseudopotentials and computational method, bulk CdSe calculations in the zinc blende and wurtzite phases were performed. The calculated lattice constant for the zinc blende phase was 6.15 Å, and those for the wurtzite phase were 4.31 and 6.84 Å. These calculated values compare well with the experimental values[25,26] of 6.05 Å

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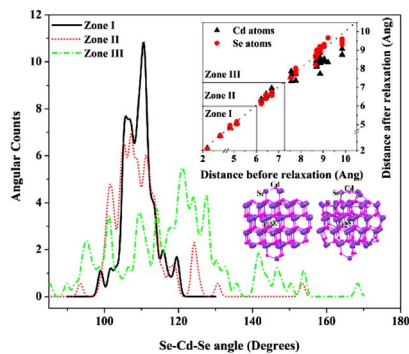
FIG. 1. (Color online) Angular and radial (top inset) relaxations for the 144 atom CdSe cluster whose structures before (bottom left inset) and after (bottom right inset) geometry optimization are also shown. Points that fall on the dotted line in the top inset correspond to atoms that have not relaxed radially.
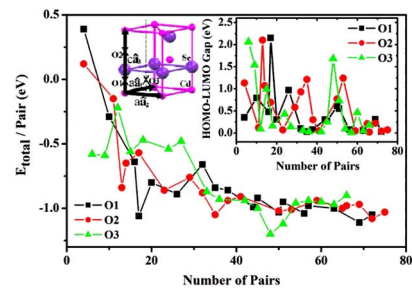

FIG. 2. (Color online) Calculated total energies per pair of the fully relaxed CdSe nanoclusters and the HOMO-LUMO gaps (right inset) as a function of the nanocluster size (number of CdSe pairs) for three different choices, O1, O2, and O3, of origin (left inset). Note the correlation between high stability and large HOMO-LUMO gaps, especially for smaller clusters containing 60 or less pairs.

for zinc blende and 4.30 and 7.01 Å for the wurtzite phase. Thus the structural parameters for the infinite crystalline materials were well reproduced.

Stoichiometric CdSe clusters based on an underlying wurtzite crystal structure with an approximately spherical shape were considered in all calculations. The wurtzite structure is the hexagonal analog of the (cubic) zinc blende structure and has hexagonal $\cdots ABAB \cdots$ packing, with a two-atom basis. In CdSe, a Cd and a Se atom form the basis and one of their (nearest neighbor) bonds is directed along the c axis, perpendicular to A or B planes. Spherical clusters, based on the wurtzite structure, could be generated using one of several choices for the cluster center or origin (resulting in different topologies for the same cluster size). The choice of the center and the radius will determine the (chemical) type of the atoms that occupy the surface region. In this work, we have considered three choices of the center, O1, O2, and O3, defined as follows: (1) the midpoint of a nearest neighbor Cd–Se bond along the $\hat{a}_3$ direction, i.e., $O1 \equiv (0,0,u/2)$, (2) the point at a distance $c/2$ from O1 along the $\hat{a}_3$ direction, i.e., $O2 \equiv [0,0,(c+u)/2]$, and (3) $O3 \equiv (a/3, a/3, u/2)$. Here $u(=0.37c)$ denotes the nearest neighbor Cd–Se distance (i.e., Cd–Se bond length) in bulk wurtzite CdSe, while a and c are the lattice parameters in the standard notation. Our choice of wurtzite being the underlying crystal structure of all CdSe clusters studied computationally was guided by our prior high resolution transmission electron microscopy (HR-TEM) measurements of synthesized CdSe nanocrystals.

For each of the three choices of the center of the clusters, a wide variety of sizes ranging from 8 to 150 atoms was considered. The electronic and geometric structures were optimized for all these clusters, resulting in equilibrium physical structures, total energies, DOS, and highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps, which form the basis of all our conclusions. First, we discuss the calculated structural relaxations for a particular CdSe cluster, namely, the 144 atom cluster (with center at O2). Figure 1 (inset) illustrates the calculated (radial) structural relaxations of this cluster from its initial starting geometry [which was based on an ideal wurtzite structure]. The dotted line represents the situation with no radial relaxations. For clarity, we have divided the regions occupied by the atoms of the nanocluster into three mutually exclusive zones. In zone I, extending from the origin to 6 Å, atoms undergo negligible radial relaxations; this zone is thus the "core region" which is well screened from the surface atoms.

In zone II, Cd and Se atoms show small but perceptible relaxations. In zone III, which consists mainly of surface atoms, Cd atoms prefer to move radially inward while some Se atoms move radially outward. This inward relaxation of Cd atoms has been observed in other self-consistent calculations.[19]

Figure 1 also shows the angular distribution of Se–Cd–Se bond angles of the same 144 atom cluster. In the core region (zone I), most of the Se–Cd–Se angles are within a few percent of the tetrahedral (109.5°) angle, indicating predominantly sp^3 bonding. The corresponding angles in zones II and III show progressively more dispersion, indicating that sp^3-like bonds between Cd and its four neighboring Se atoms are not the dominant ones (especially in zone III, where angles in the neighborhood of 120° dominate, characteristic of sp^2 bonding).

The total energies and HOMO-LUMO gaps calculated for clusters up to 75 CdSe pairs (150 atoms) are shown in Fig. 2 (inset). Several interesting trends can be observed. Firstly, the total energy per CdSe pair, E_{pair}, converges steadily with increasing cluster size. However, E_{pair} shows local minima, reminiscent of the so-called "magic sizes,"[27–29] with clusters composed of 13, 17, 26, 35, 48, 69, and 72 pairs displaying the maximum relative stability. Some of these clusters have already been identified by Kasuya *et al.* as having high stability based on their time-of-flight experiments.[21] Secondly, the stability is strongly a function of the choice of origins, especially for the small clusters. Thirdly, while the HOMO-LUMO (or optical) gaps generally decrease for increasing cluster sizes, occasional large gaps can be seen that correlate with a low E_{pair} (or high stability); i.e., the magic size clusters show relatively large, and locally largest, gaps.

Inspection of the physical structure of the clusters indicates that the non-magic-size clusters have surface atoms with a high degree of unsaturation (two or more dangling bonds). These surface atoms give rise to electronic states, resulting in an apparent reduction in the HOMO-LUMO gap. It thus appears that, in contrast to previous beliefs,[19] structural relaxation alone cannot open up the HOMO-LUMO gaps, especially in non-magic-size clusters. This expectation is further confirmed by explicit analysis of the DOS and its decomposition in terms of the contributions from various atomic basis functions (the partial density of states or PDOS). Figure 3(a), for instance, shows a large HOMO-LUMO gap in a DOS plot for the 17-pair magic cluster with origin at O1. For such a cluster, all surface atoms have three
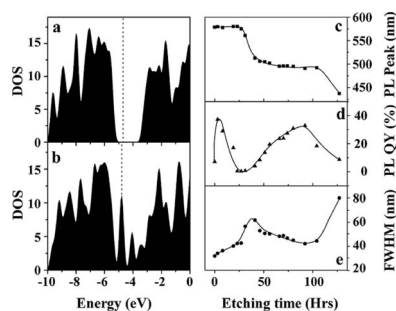
FIG. 3. Calculated density of states (DOS) for a nanocluster with 17 CdSe pairs with center at (a) O1 and at (b) O2. The Fermi level is indicated by the vertical dotted lines. (c) Measured photoluminescence (PL) peak positions, (d) quantum yield (QY), and (e) PL full width at half maximum as a function of nanocluster etching time. The plateaus that develop with etching time in (c) indicate the relative stability of nanoparticles with closed-shell structures.

bonds with their nearest neighbor atoms. On the other hand, by changing the origin to O2, a similar 17-pair cluster has four Cd and four Se surface atoms bonded to only two as opposed to three nearest neighbor atoms. This results in a much smaller HOMO-LUMO gap as shown in Fig. 3(b). Analysis of the PDOS for the 17-pair cluster with center at O2 in fact demonstrates that the origin of the smaller gap is due to states created by the surface atoms with missing or dangling bonds. Upon closer inspection of all simulated clusters, those which have surface atoms missing one or more bonds show uniformly smaller non-well-defined gaps.

The current results shed considerable light on a number of experimental studies alleging optimum performance on CdSe NCs with closed-shell structures.[11–13] In particular, controlled chemical etching has been used to investigate the evolution of UV-vis and PL properties of CdSe quantum dots as a function of NC size.[11,12] Figures 3(c)–3(e) illustrate the PL peak position, quantum yield (QY) or efficiency, and the PL full width at half maximum, respectively, as a function of etching time, which is inversely related to their size (from a diameter of 3.4 nm at the beginning to 2.2 nm after 80 h). Each well defined step (plateau region) in PL peak position corresponds to a Cd-terminated closed-shell NC with a specific size.[11,12] Such discrete PL emission along with the peaking of QY in the plateau regions can be explained in terms of the following: (i) more NCs attain closed-shell structures (during etching) that emit strongly and (ii) upon further etching, NC of non-closed-shell structures are created that exhibit little or no luminescence, thereby causing a decrease in the QY. Such non-closed-shell NC structures are expected to contain surface atoms with less than the optimal, threefold coordinated bonding arrangement, causing them to lack well defined optical gaps, as in the case of Fig. 3(b). Surface atoms with lower than the optimum threefold bonding arrangement possess higher chemical reactivity, thereby explaining the relative thermodynamic stability of closed-shell structures against etching. Although the largest cluster studied computationally is still smaller than the smallest cluster investigated experimentally earlier, we note that our computational study includes the largest CdSe clusters studied at a high level of theory, and that the qualitative trends derived from the computational study are expected to be valid for larger clusters as well.

In summary, we have performed self-consistent *ab initio* calculations to understand the stability of CdSe clusters, and the relationship between cluster size and optical properties of CdSe clusters with different topologies and over a wide range of smoothly varying sizes. Our calculations indicate that the nature of the surface atoms in a given cluster crucially determines both the stability of the cluster and its optical gap. When the nanoclusters were allowed to relax from their bulk wurtzite positions, Cd atoms at the surface are observed to move inwards preferentially compared with Se atoms. A coordination number of 3 for all surface atoms resulted in closed-shell structures with high stability and maximum optical gap. One or more suboptimally coordinated surface atoms resulted in clusters with lower stability and smaller to negligible optical gaps. These computations are in qualitative agreement with recent chemical etching experiments suggesting that closed-shell nanocrystal structures contribute strongly to PL quantum yield while clusters with less than optimal surface coordination do not.

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