Ligand-Mediated Modification of the Electronic Structure of CdSe Quantum Dots

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Ⓢ Supporting Information

ABSTRACT: X-ray absorption spectroscopy and ab initio modeling of the experimental spectra have been used to investigate the effects of surface passivation on the unoccupied electronic states of CdSe quantum dots (QDs). Significant differences are observed in the unoccupied electronic structure of the CdSe QDs, which are shown to arise from variations in specific ligand-surface bonding interactions.
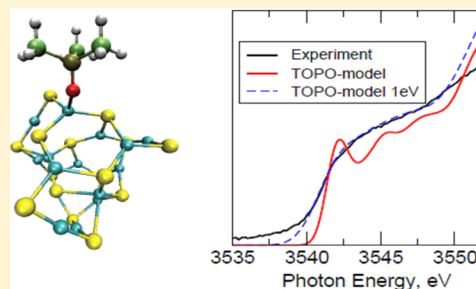
KEYWORDS: X-ray absorption spectroscopy, quantum dot, electronic structure, ab initio modeling, surface passivation, CdSe

The organic molecules used to passivate the surface of quantum dots (QDs) can exert considerable influence over their physical properties.[1] As such, addressing the means by which these surface ligands govern the behavior of nanomaterials is important, particularly for the development of QD-based materials with tailored properties. CdSe QDs are known to exhibit a range of ligand-dependent behavior and, therefore, provide an ideal system for investigating the underlying mechanisms: for example, the choice of organic molecule used to overcoat QDs in CdSe-based photovoltaic devices is reported to have a substantial impact upon their photo energy conversion.[2] Meanwhile, ligand-mediated changes have been observed in the photoluminescence[3] (including blinking phenomena[4]), electronic structural dynamics[5] and even magnetic properties[6] of nanocrystalline CdSe. In this study, X-ray absorption spectroscopy (XAS) and ab initio calculations are used to examine the effects of surface passivation on the electronic structure of CdSe QDs. XAS is a well-established technique for investigation of the unoccupied electronic structure of nanocrystalline materials but has an important drawback in that it is difficult to distinguish between spectral changes induced by ligand-surface interactions versus alternative sources, such as quantum confinement effects. Our combined experiment/theoretical approach proposes to resolve

this long-standing problem by definitively measuring ligand-mediated changes in the electronic structure and relating them to theoretical models. We demonstrate that overcoating CdSe QDs with ligands of distinct end group functionalities brings about specific changes in the electronic structure, particularly near the bottom of the conduction band (CB), and that the combination of XAS experiments and ab initio calculations at the Cd L_3-edge offers an ideal means with which to identify and characterize ligand-mediated changes in the unoccupied electronic structure of these materials.

CdSe QDs with a mean radius, R, ranging from 14 to 25 Å and coated with a passivating layer of either trioctylphosphine oxide (TOPO) or hexadecylamine (HDA) ligands were synthesized using established techniques.[7,8] The QD size and size dispersion were derived using UV–visible absorption spectroscopy. Ligand exchange at the surface of the TOPO or HDA passivated QDs for alternative ligands (specifically dodecanonitrile (DDN), HDA, or TOPO) was conducted via established protocols described in the literature.[6,9,10] Initially, the sample of interest was immersed in an excess of substituting

ligand, which was either in the form of a pure liquid, or a saturated solution in methyl benzene. The mixture was then sonicated under gentle heating (40−65 °C) for between 6 and 24 h to aid in driving the ligand exchange. Following sonication, any QDs that had resisted ligand exchange were removed as a solid residue following centrifugation of the mixture and extraction of the supernatant. The addition of methanol/methyl benzene served to precipitate the ligand-exchanged QDs from the extracted supernatant solution. Separation of the precipitate and solution was then achieved via centrifugation. Samples for analysis with nuclear magnetic resonance (NMR) were subsequently dried to a powder under vacuum. Significantly, attempts at ligand exchange for the smallest QDs ($R < 14$ Å) were largely unsuccessful and any yield was insufficient for the purposes of XAS analysis.

In preparation of samples for XAS measurements, the QDs were deposited from toluene onto a Si(111) wafer and the solvent was allowed to slowly evaporate. Multiple depositions were performed to ensure a sufficiently thick CdSe film was obtained. XAS experiments were performed on the bend magnet beamline 9.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The measurements were taken in both total electron and total photon yield without any noticeable differences between the two detection methods. The current from an aluminized Mylar grid, I_0, located upstream of the experimental sample was used to normalize the XAS spectra. Although the experimental resolution in these experiments was ~0.2 eV with lifetime broadening of ~1.0 eV, the accuracy in measurement of the absorption onset energy is considerably better. Each of the spectra was also normalized to the magnitude of the edge step, which was measured between the pre-edge (3525 eV) and postedge (3600 eV) regions. We note that preliminary measurements at the Cd M_3-edge were performed on beamline 8.0.1 at the ALS.

To calculate XAS spectra, we utilize density functional theory (DFT) with a planewave basis as implemented in the Quantum ESPRESSO code.[11] The final state effects of the exciton interaction are included via the eXcited electron Core Hole (XCH) method.[12] We note that L-edge spectra can be impossible to reproduce with the XCH approach, particularly for early 3d transition elements where Bethe-Salpeter solutions including multiplet effects are required.[13] However, in the case of Cd with a nominally filled d-shell and well-separated L_2 edge (by 200 eV) we expect reasonably accurate predictions for the L_3 edge spectra measured in this work. Measured XAS comprises a convolution of signals from all absorbing atoms in the sample. Calculating a spectrum for comparison with experiment therefore requires information on the relevant bonding geometries for a sample and the relative proportions of different bonding geometries. The QDs measured in the XAS experiments contain ~3000 atoms, making direct DFT studies impractical. We therefore develop a structural model for the 15 Å QDs based on experimental data, a previous molecular dynamics study, and a comparison of our computed spectra to experimental data. We utilize the computed spectra for Cd atoms in smaller QDs (specifically $Cd_{15}Se_{15}$ and $Cd_{33}Se_{33}$, which have radii of ~5 and 7 Å, respectively) which exhibit a range of Cd coordination geometries representative of bulk and surface atoms in CdSe QDs.

Figure 1a displays XAS spectra recorded at the Cd L_3-edge for CdSe QDs of several sizes prepared in HDA and a bulk CdSe reference. Significantly, time-of-flight secondary ion mass spectrometry measurements of the CdSe QDs indicate that
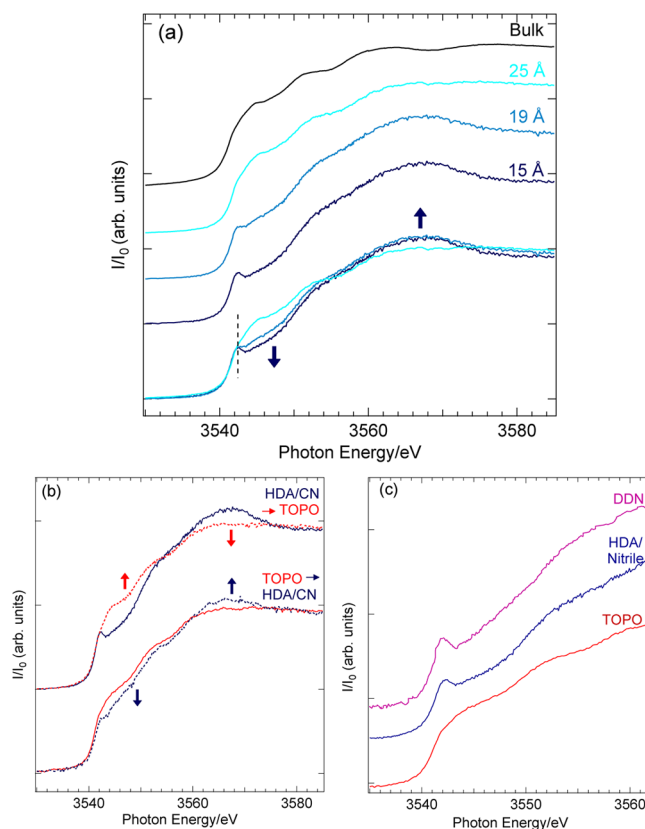
Figure 1. Cd L_3-edge XAS spectra for (a) CdSe-HDA/CN QDs of various sizes vs bulk CdSe, (b) as prepared CdSe-HDA/CN and CdSe-TOPO QDs following ligand exchange with TOPO and 90% HDA (including nitrile contaminants), respectively, and (c) 15 Å CdSe-TOPO QDs following ligand exchange with DDN (vs reference 15 Å CdSe-TOPO and CdSe-HDA/CN QD spectra).

nitrile impurities present in the HDA bind to the surface of the CdSe QDs during synthesis, leading to a mixed HDA/nitrile surfactant coating.[6] Solid-state $^1H-^{13}C$ cross-polarization magic angle spinning nuclear magnetic resonance measurements conducted as a component of this study provide supporting evidence for this assignment (Supporting Information) and, therefore, QDs synthesized in HDA are referred to as CdSe-HDA/CN in the remainder of the paper. Because of the constraints of the $\Delta l = \pm 1$ dipole selection rule, the Cd L_3-edge XAS spectra formally correspond to electron transitions from a Cd 2p core state into the unoccupied states in the CB of Cd s and d character. Quantitative analysis of the absorption edge onset was conducted according to protocols established in the investigation of CdSe QDs prepared in TOPO[14] and indicates that the energy of the absorption threshold is equal to within experimental error for CdSe-HDA/CN and CdSe-TOPO QDs of equal size. As such, the shift in the energy onset, E_c, with R is largely unaffected by the variation in surface passivation and follows an equivalent scaling law ($E_c \propto R^{-0.6}$) in the two systems. Although no ligand-dependent shifts are observed in the absorption onset, there are considerable variations in the XAS spectral features as a function of size. The spectra for bulk CdSe and the 25 Å CdSe-HDA/CN QDs are closely comparable but increasingly pronounced changes in the absorbance are evident beyond the absorption edge as the QD radius decreases. Most notably, there is a reduction in the absorbance between ~3 to 15 eV above the absorption onset for the 19 and 15 Å radius QDs and an increase at energies >15

eV above the onset. The dependence of the XAS data on size provides a strong indication that these spectral variations are surface-related because the reduction in QD radius is accompanied by a substantial increase in the proportion of surface Cd atoms and by extension a greater surface contribution to the overall signal. In principle, two distinct surface effects could contribute to the observed behavior: (1) the electronic and/or geometrical structure of the surface Cd atoms is intrinsically different to those in the core (a ligand independent effect) and (2) the organic ligands modify the electronic and/or geometrical structure of the surface Cd atoms (a ligand dependent effect). To determine the greater contributor to the observed spectral changes, the CdSe-HDA/CN XAS spectra were compared with those recorded for CdSe-TOPO QDs over the same size regime.[14] The CdSe-TOPO spectra do not exhibit the reduction in absorbance observed in the near-edge region for the CdSe-HDA/CN QDs but instead retain a comparable shape to the spectrum for bulk CdSe, which suggests that the surface ligands are primarily responsible for the differences in appearance of the XAS spectra.

The contrasting appearance of the CdSe-TOPO and CdSe-HDA/CN QD data alone does not, however, provide conclusive evidence for surfactant-mediated changes in the electronic structure of the QDs because the samples were prepared under different synthetic conditions, which could lead to the formation of materials with equal size but distinct physical properties (e.g., surface structures) and associated changes in the absorption spectra. To address this possibility, the ligands on the as prepared CdSe-TOPO and CdSe-HDA/CN QDs were exchanged for the alternative surfactant, HDA/CN and TOPO respectively, and Cd L_3-edge XAS spectra were collected and compared for the resulting samples. Significantly, the ligand exchange results in profound changes to the XAS data: replacing the ligands on the as prepared CdSe-HDA/CN QDs with TOPO results in the XAS spectrum adopting the characteristic form for as prepared CdSe-TOPO QDs and vice versa, as demonstrated for 15 Å CdSe QDs in Figure 1b. The ability to "switch" the appearance of the XAS spectrum by exchanging the passivating ligand provides a clear demonstration that the electronic structure of the CdSe QDs is dependent upon the identity/functionality of the passivating molecules and the nature of the ligand-surface interactions. This result alone is extremely important as it indicates that the varying chemical methods used to prepare CdSe QDs do not affect the electronic structure and suggests that future applications-oriented research on these materials should focus on modification of the passivating layer. It is noteworthy that the ligand exchange of CdSe-TOPO QDs with HDA/CN does not lead to a complete conversion of the XAS spectrum to the form observed for the as prepared CdSe-HDA/CN, which is consistent with the reported resistance of CdSe-TOPO to complete substitution for all of the original ligands[15] and also consistent with the large and comparable binding energies reported by our calculations below.

Given that the changes observed in the XAS appear to arise from surfactant-driven events, it is essential to determine which ligand functionalities are responsible for the purposes of studying the surface chemistry and, ultimately, controlling the electronic structure of the QDs. To this end, we performed an additional series of XAS measurements to determine whether the variations in the spectral features exhibited by the CdSe-HDA/CN QDs arise from interactions between the QD surface

and the HDA ligands, the nitrile ligands or both. Figure 1c displays Cd L_3-edge XAS spectra recorded for 15 Å CdSe-TOPO QDs following ligand substitution with DDN to yield CdSe-DDN QDs. The resulting XAS data for the CdSe-DDN QDs exhibits a comparable appearance to the spectrum for the as prepared CdSe-HDA/CN QDs but, importantly, with more pronounced variations in absorbance relative to the CdSe-TOPO samples. In particular, ligand substitution by DDN is accompanied by a reduction in total absorbance between ~3−15 eV above the absorption onset with respect to CdSe-HDA/CN QDs of the same size. Equivalent effects were observed for CdSe-DDN QDs prepared via ligand substitution of the larger (19 Å) CdSe-TOPO QDs and the CdSe-HDA/CN QDs. As such, the XAS spectra demonstrate more pronounced variations in total absorbance as the proportion of nitrile-terminated ligands increases and provide a strong indication that the associated changes in unoccupied electronic structure arise due to interactions between the nitrile moieties and surface Cd atoms.

While these experiments illustrate that variation of the ligands produces obvious differences in the CB electronic structure of CdSe QDs, the data do not give a direct indication of what features produce these effects. In order to understand how changes in the surface geometry and chemistry produce the observed changes in the Cd XAS, we examine the XAS using ab initio calculations. We computed spectra for the methyl-substituted analogues of TOPO, HDA, and DDN. Previous studies have shown that the length of the alkyl chain does not affect observed properties of the QDs,[16] so the methyl species was chosen here for the sake of computational efficiency. The calculated spectra for a single Cd atom at the surface of the 5 Å cluster are shown in Figure 2a along with the spectrum of bulk CdSe. A corresponding structural diagram for the 5 Å cluster is displayed in Figure 3a. In comparing the spectra of the bulk (black, dotted) and the unpassivated surface Cd atom (black, dashed) displayed in Figure 2a, we see that the presence of a dangling bond and the associated surface reconstruction yield a decrease in the intensity in the region between about 3−7 eV above the absorption onset. Passivation of this surface atom with a single ligand does not fully restore the tetrahedral geometry. When the surface Cd atom is passivated with either TOPO, for which a structural diagram is presented in Figure 3b, or HDA analogues the spectra regain some intensity in this region but notable differences remain. The spectrum of the atom passivated with the DDN analogue differs significantly from the other two ligands. The bonding geometries around the surface atom are almost identical for all three ligands. We therefore attribute the changes in the spectra with respect to surface termination to differences in chemistry. In examining the spectra of this single surface atom, we already find correlation with the experimentally measured spectra, namely that the DDN passivated QD spectra show reduced intensity with respect to the spectra of TOPO passivated QDs. We note that the strong similarity between the spectra calculated for CdSe coated with TOPO and HDA is consistent with the conclusion that the changes in absorbance observed experimentally between the CdSe-TOPO and CdSe-HDA/CN QDs arise primarily from the effects of the nitrile-terminated ligands rather than the HDA.

Rutherford back scattering (RBS) measurements of CdSe nanomaterials have shown that approximately 70% of surface Cd atoms are passivated by organic ligands.[17] Our surface model therefore incorporates 70% contribution from a single
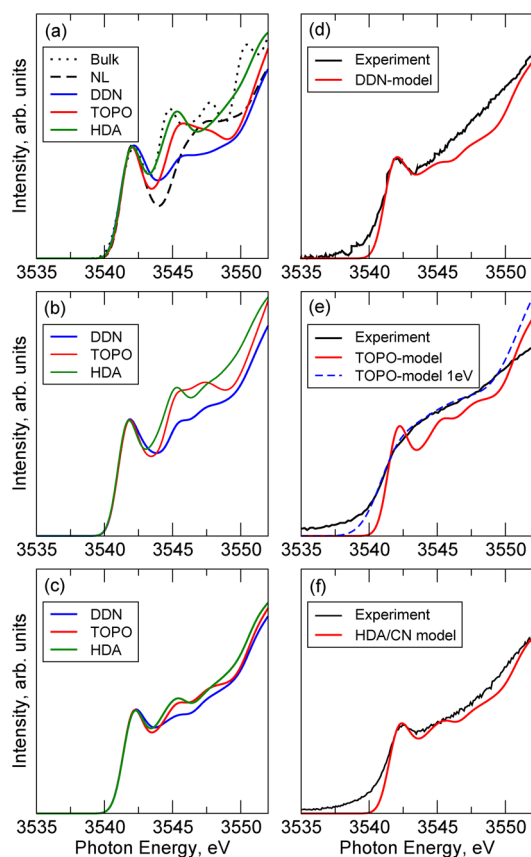
Figure 2. (a) Comparison of computed spectra for the Cd L$_3$-edge of spectrum for bulk (wurtzite) CdSe and the computed spectra for a single surface atom in a 5 Å cluster. Model of the surface contribution to the QD spectrum for each of the three ligands are shown in (b) and the total model spectra are shown in (c). Plots (d−f) show comparisons of the computed model spectra to the experimental measurements. Solid red lines are computed spectra broadened using a uniform Gaussian broadening of 0.5 eV. The dashed blue line in (e) is plotted with a Gaussian broadening of 1.0 eV.

nanomaterials[19] or to an excess of Cd atoms at the QD surface. The computed spectra assuming passivation by a single species are shown in Figure 2c, and the same spectra for DDN and TOPO passivated QDs are compared with the experiment in Figure 2d,e. In order to incorporate the effects of the presence of π-conjugated nitrogen on the measured HDA spectra, we also computed a spectrum with a 50−50 mix of HDA and DDN passivation (Figure 2f).
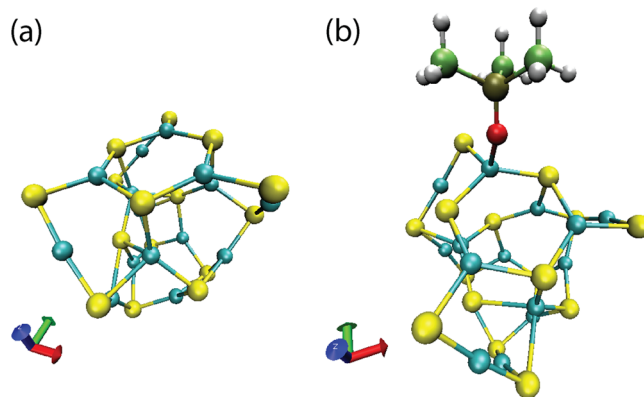
Figure 3. Optimized ground state structures for (a) the Cd$_{15}$Se$_{15}$ (5 Å) cluster and (b) the same cluster with a TOPO-analogue ligand attached to a single surface Cd atom. The specific Cd atom passivated by the TOPO-analogue ligand in (b) provides the basis for the calculated spectra displayed in Figure 2a. Individual elements are distinguished by color as follows: Cd, light blue; Se, yellow; O, red; P, brown; C, green; and H, white. Orthogonal axes are also displayed for reference.

passivated Cd atom and 30% contribution from our unpassivated spectra. Figure 2b shows a comparison of spectra for surface atoms in our model; here, we have assumed passivation by a single species. In order to develop a model for comparison to experiment, some contribution from atoms in the core of the QD must be included. A previous MD study showed that ∼70% of Cd atoms in a spherical QD of similar size to those studied here have 4-fold coordination to Se atoms.[18] Some RBS experiments have shown evidence that CdSe QDs in this size regime are nonstoichiometric with an approximate excess of Cd atoms up to 20%.[17] However, more recent NMR measurements of TOP-Se passivated QDs indicate ratios of Cd/Se ranging from 1.11:1 to 1:1.08, depending on the size of the QD.[19] Assuming that the Cd/Se ratio is indicative of an excess of one type of atom at the surface of the QD, this quantity should relate to the percentage of Cd atoms with dangling bonds at the surface.

We therefore examined the dependence of the spectra on the assumed contribution from surface atoms as the contribution was varied from 30 up to 50%. We find the best agreement between the model spectra and our measurements when the contribution from the surface is 50%. The large contribution from trigonal planar bonding geometry, could either be related to the large extent of reconstruction present in 3.0 nm CdSe

We find good agreement between theory and experiment for each of the three cases we computed. The differences that arise are likely due to broadening in the experiment, which results from lifetime broadening and from thermal sources. The calculated spectra shown here have been artificially broadened by convolution with a Gaussian of width 0.5 eV. If we perform the convolution with a Gaussian of larger width (∼1 eV, dashed line in Figure 2e), the spectrum for our model of the TOPO passivated QD shows much better agreement with the experimental measurement. However, the sharp feature near the onset that appears in the case of the DDN and HDA/CN passivated QDs is then washed out. It appears that the measured spectra for TOPO QDs are subject to a more substantial source of broadening than the other cases. This could be due to the stronger binding of TOPO to the surface compared to the nitrile ligand (0.66 eV for the TOPO analog compared to 0.35 eV for nitrile).

Beyond providing a satisfactory model for the experimentally observed ligand dependence, our first-principles approach enables closer examination of why specific features arise in the spectra of a CdSe QD for a given ligand. We find that the spectral changes arise from local variations in the unoccupied density of states (DOS) due to distinct geometries and chemistry at the QD surface and that changes in chemistry account for the ligand dependence observed experimentally. The surface atoms exhibit a decrease in the spectrally active DOS in the region just beyond the absorption edge. Passivation partially restores the spectrally active DOS in this region, but the degree of restoration is dependent on the identity of the passivating ligand.

These changes have potential significance when selecting the organic passivant used in devices based upon nanocrystalline CdSe. Previous studies have shown that surface ligands can have large effects on the charge transfer efficiency of CdSe nanomaterials, yet changes in surface morphology due to ligand exchange can produce behavior that limits their use.[20] We have demonstrated that the XAS is extremely sensitive to the detailed surface structure of the QDs studied here, and that those changes can be understood through ab initio calculations. Further insight into the origin of ligand-induced differences in the experimental data is obtained by calculating two separate spectra for transitions to states with only s or d character respectively. These calculated spectra indicate that the differences in absorbance associated with changes in surface geometry and chemistry arise primarily due to variations in the unoccupied surface states with d character, which could explain the ligand-induced magnetic behavior observed for CdSe.[6] Even so, care should be exercised when inferring ground state properties from XAS measurements due to the strong effects of the core-hole on the measured DOS.

This study demonstrates that XAS measurements can be used to investigate the effects of surface termination on the electronic properties of CdSe QDs. A particularly interesting feature of CdSe QDs is that the ligands studied in this Letter primarily affect unoccupied electronic states >3 eV above the absorption edge rather than in the gap, as one might have predicted for surface states. This is consistent with the fact that the optical properties are not affected yet there is a ligand dependent change in the electronic structure, which could be responsible for the novel magnetic properties of the QDs. Significantly, the close agreement between experimental observables and theoretical treatments described indicates that the calculated spectra could provide a predictive capability for other QD systems, which could aid in our understanding of the physics that govern nanocrystal behavior and facilitate the development of optimized ligands for specific technological applications such as photovoltaics.

ASSOCIATED CONTENT

Supporting Information

Additional XAS data and analysis, including shifts in the absorption onset of CdSe-HDA/CN QDs as a function of size, NMR data, and analysis, and extended experimental and modeling details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Owen, J. S.; Park, J.; Trudeau, P.-E.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2008**, *130*, 12279.

(2) Fuke, N.; Hoch, L. B.; Koposov, A. Y.; Manner, V. W.; Werder, D. J.; Fukui, A.; Katayama, H.; Sykora, M. *ACS Nano* **2010**, *4*, 6377−6386.

(3) Kalyuzhny, G.; Murray, R. W. *J. Phys. Chem. B* **2005**, *109*, 7012−7021.

(4) Hohng, S.; Ha, T. *J. Am. Chem. Soc.* **2004**, *126*, 1324−1325.

(5) Kambhampati, P. *J. Am. Chem. Soc.* **2011**, *44*, 1−13.

(6) Meulenberg, R. W.; Lee, J. R. I.; McCall, S. K.; Hanif, K. M.; Haskel, D.; Lang, J. C.; Terminello, L. J.; van Buuren, T. *J. Am. Chem. Soc.* **2009**, *131*, 6888.

(7) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715.

(8) Cumberland, S. L.; Hanif, K. M.; Javier, A.; Khitrov, G. A.; Strouse, G. F.; Woessner, S. M.; Yun, C. S. *Chem. Mater.* **2002**, *14*, 1576−1584.

(9) Becerra, L. R.; Murray, C. B.; Griffin, R. G.; Bawendi, M. G. *J. Chem. Phys.* **1994**, *100*, 3297−3300.

(10) Kuno, M.; Lee, J. K.; Daboussi, O.; Mikulec, F. V.; Bawendi, M. G. *J. Am. Chem. Soc.* **1997**, *106*, 9869−9882.

(11) Giannozzi, P.; et al. *J. Phys.: Condens. Mat.* **2009**, *21*, 395502.

(12) Prendergast, D.; Galli, G. *Phys. Rev. Lett.* **2006**, *96*, 215502.

(13) Laskowski, R.; Blaha, P. *Phys. Rev. B* **2010**, *82*, 205104.

(14) Lee, J. R. I.; Meulenberg, R. W.; Hanif, K. M.; Mattoussi, H.; Klepeis, J. E.; Terminello, L. J.; van Buuren, T. *Phys. Rev. Lett.* **2007**, *98*, 146803.

(15) Katari, J. E. B.; Colvin, V. L.; Alivisatos, A. P. *J. Phys. Chem.* **1994**, *98*, 4109−4117.

(16) Meulenberg, R. W.; Bryan, S.; Sun, C. S.; Strouse, G. F. *J. Phys. Chem. B* **2002**, *106*, 7774−7780.

(17) Rosenthal, S. J.; McBride, J.; Pennycook, S. J.; Feldman, L. *Surf. Sci. Rep.* **2007**, *62*, 111−157.

(18) Grunwald, M.; Rabani, E.; Dellago, C. *Phys. Rev. Lett.* **2006**, *96*, 255701.

(19) Lovingood, D. D.; Oyler, R. E.; Strouse, G. F. *J. Am. Chem. Soc.* **2010**, *130*, 17004−17011.

(20) Lokteva, I.; Radychev, N.; Witt, F.; Borchert, H.; Parisi, J.; Kolny-Olesiak, J. *J. Phys. Chem. C* **2010**, *114*, 12784−12791.