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Experimental Observation of Quantum Confinement in the Conduction Band of CdSe Quantum Dots

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X-ray absorption spectroscopy has been used to characterize the evolution in the conduction band (CB) density of states of CdSe quantum dots (QDs) as a function of particle size. We have unambiguously witnessed the CdSe QD CB minimum (CBM) shift to higher energy with decreasing particle size, consistent with quantum confinement effects, and have directly compared our results with recent theoretical calculations. At the smallest particle size, evidence for a pinning of the CBM is presented. Our observations can be explained by considering a size-dependent change in the angular-momentum-resolved states at the CBM.

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Semiconductor quantum dots (QDs) are known to exhibit size-dependent optical and electronic properties and, as a consequence, offer considerable potential for a diverse range of technological applications. In contrast to many binary semiconductor quantum dots, CdSe QDs are readily synthesized with narrow size distributions and possess excellent photochemical stability when passivated properly [1,2]. In addition, they demonstrate size-dependent photoluminescence that encompasses the visible region of the electromagnetic spectrum [3]. Hence, CdSe represents an archetypal system for numerous QD applications and an ideal model for the study of quantum confinement effects. Although extensive research has been devoted to characterization of the electronic structure in CdSe QDs [4,5], the size-dependent evolution of the valence band (VB) and conduction band density of states (CBDOS) remain unresolved from one another via experimental study. It has been demonstrated that theoretical calculations provide a means for the deconvolution and isolated study of the VB and conduction band (CB) [6–11]. Nonetheless, the results reported for CdSe exhibit strong model dependence, which is illustrated by predicted scaling laws ranging between $E_c \propto R^{-0.8}$ [11] and R^{-2} [8] for size-dependent energy shifts in the bottom of the CBDOS. As such, identification of the most representative theory is paramount.

Several experimental techniques have been used to address the development of the band gap in nanocrystalline CdSe [3,4,12,13] (particularly uv-visible absorption spectroscopy because it also provides a diagnostic of QD particle size and size dispersion), but the band gap represents only the convolution of the VB and CB and does not allow for an independent treatment of these edges. The application of alternative methods is essential, therefore, for successful mapping of the electronic structure in CdSe QDs. In previous publications, we have shown that x-ray absorption spectroscopy (XAS) offers the ideal technique with which to probe quantum confinement induced shifts in the lowest unoccupied states (CB) of nanocrystalline materials [14,15]. In this manuscript, we have additionally shown that XAS can be a powerful tool to elucidate the angular-momentum-resolved quantum shifts as only $\Delta l = \pm 1$ transitions are allowed. Because of this angular momentum specificity, selection of the appropriate absorption edge allows one to focus upon the bottom of the CB. The projected DOS obtained from theory demonstrates that the bottom of the CB is composed of Cd $5s$ states [see Fig. 1(a)]. Hence, the Cd L_3 edge should be ideal for probing any size-dependent effects in this region because transitions between the $2p$ initial state and unoccupied s states are dipole allowed. If the bottom of the CdSe CB moves by some energy, ΔE_c, then the L_3 absorption edge should shift by a corresponding amount representing the quantum confinement induced shift in the CB. In principle, the Cd M_2 and M_3 edges, which are composed of a $3p$ initial state, could also be used to probe the bottom of the CB. The M edges, however, suffer from weak signals and a large background which limits the usefulness of using these edges for quantitative information.

CdSe quantum dots (QD) with a mean radius ranging from 9–19 Å and coated with the ligand trioctylphosphine oxide (TOPO) were synthesized using a known method [1]. QD size and size dispersion were derived using uv-visible absorption spectroscopy [4]. Because of the difficulties in producing very small colloidal QDs, a cluster sample of the form $\mathrm{Cd_{10}Se_4(SC_6H_5)_{16}^{4-}}$ ($\mathrm{Cd_{10}}$) was prepared using an established technique [16]. This allowed the investigation of very small particle sizes without being limited by colloidal chemistry techniques. It should be noted that the $\mathrm{Cd_{10}}$ cluster has a radius of 7 Å [17] and is not coated with TOPO but with thiophenol. While the change in surface structure could have an impact on these experiments, we defer to previous measurements on the electronic structure of CdSe QD while changing surface chemistry which show

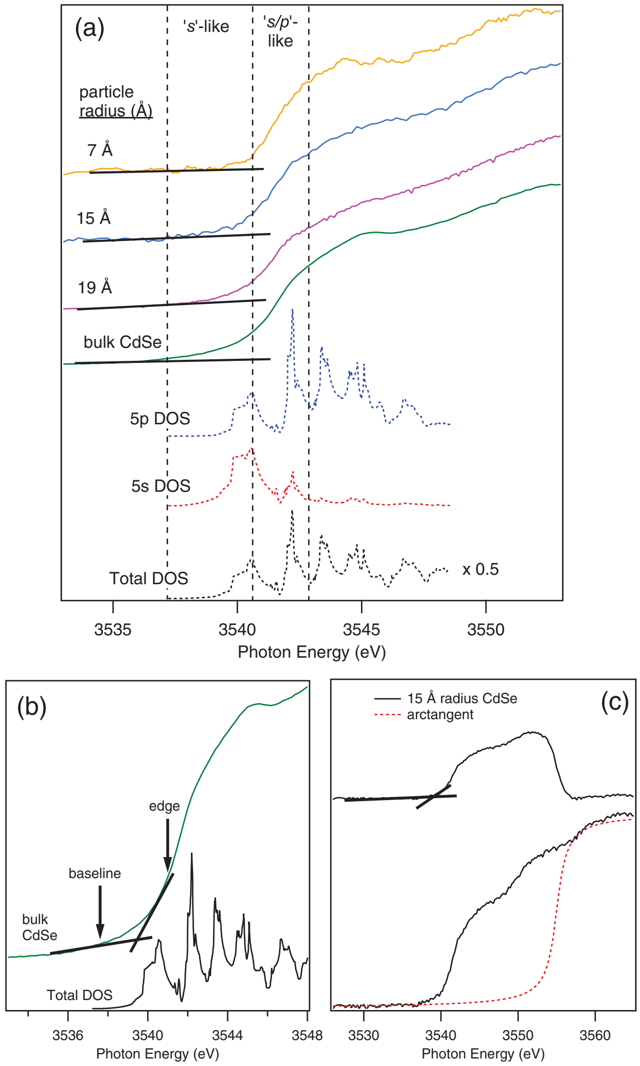

FIG. 1 (color). (a) Experimental Cd L_3-edge XAS spectra (top four traces) and calculated conduction band (CB) density of states (DOS) for bulk CdSe (bottom three traces); (b) extrapolation method to derive CB shifts as described in the text; (c) arctangent method to derive CB shifts as described in the text.

very small changes in the band edges with surface termination [3]. For the 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 beam line 9.3.1 at the Advanced Light Source, 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 a aluminized Mylar grid, I_o, 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.

Figure 1(a) plots selected XAS spectra at the Cd L_3 edge for CdSe QDs of different sizes and the corresponding bulk spectrum. For comparison with the experimental CBDOS features, we show the calculated CBDOS for bulk CdSe as a dotted line in Fig. 1. The calculated projected CBDOS were obtained using a full-potential linear muffin-tin orbital method [18–20]. The angular-momentum-resolved projected CBDOS were generated on the basis of a Mulliken decomposition and by projecting out against the atom-centered numerical basis functions obtained from the self-consistent calculations [20–22].

The bulk CdSe L_3-edge spectrum shows a sharp absorption onset with a distinct foot [Fig. 1(a)] and additional absorption features ca. 4, 7, and 14 eV above the onset. A noticeable difference in the spectral features between bulk CdSe and the QD samples is a reduction of intensity in the foot of the absorption onset. The calculated CBDOS indicate that the foot in the absorption spectrum is due only to Cd 5*s* states and composes the CB minimum. Therefore, it is necessary to look at this region of the spectrum in order to identify any shifts in the bottom of the CB that may arise from quantum confinement effects. The presence of significant DOS features near the baseline, however, causes some difficulty in obtaining an absolute measure of the absorption onset. The energy of the absorption onset is obtained by extrapolation of the linear region of the baseline and the linear region of the absorption edge above the threshold and identifying the point at which they intersect. A specific protocol was followed to determine where the extrapolated lines are drawn on the spectrum to warrant self-consistent results (and error). The baseline is extrapolated from the linear component of the preedge region and is defined to delineate from the experimental data at the energy for which the calculated CBDOS is nonzero. In other words, the baseline of the experimental spectrum ends at the point where DOS features begin and is $\sim 2\sigma$ above baseline noise. Allowing the DOS features to be defined by points $\sim 2\sigma$ about baseline noise establishes a lower limit on the experimental error in our measurements (~0.15 eV). The line on the absorption edge begins at the median y value between the baseline and step edge and from this point, a tangent is drawn to the edge [see Fig. 1(b)]. Using this protocol, values of the extrapolation onset can be obtained with minimal contribution from biased error. A second and alternative protocol was introduced which sharpens the DOS features present near the baseline. An arctangent function [Fig. 1(c)] was subtracted from the experimental data which allows a more straightforward analysis of the absorption edge [23]. The arctangent function represents transitions between the $2p$ initial state → continuum or free electron states. The values obtained from both data analysis protocols are closely comparable and indicate that the shifts reported in this Letter represent an accurate measure of the evolution of the CB minimum with particle size.

A comparison of the results from the two methods is provided by Fig. 2, which displays the CB shifts for the

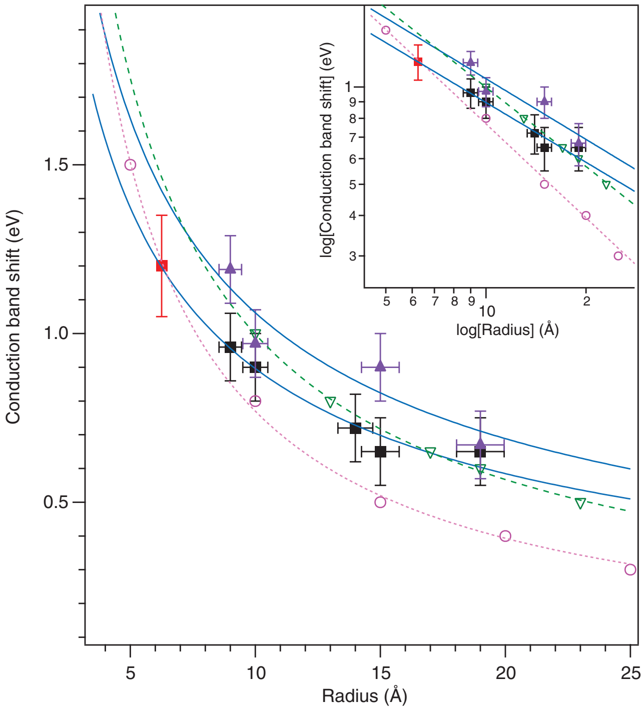

FIG. 2 (color). Size-dependent values for the CdSe conduction band states. The ■ and ▲ represent the CdSe QD experimental data points using the extrapolation and arctangent subtraction data analysis methods, respectively, as described in the text, while the ▽ (CP theory; Ref. [11]) and ○ (TB theory; Ref. [6]) represent theoretical values. The lines through the data points represent a least squares fitting of the data. Inset: Same as A, but plotted on a log-log scale for better distinction between data points.

series of CdSe QD samples studied in this Letter. For the purposes of direct comparison, reported theoretical values [6,11] have been plotted alongside the data. The reduction of the DOS features in the absorption onset in the QD samples with respect to the bulk CdSe sample is most likely due to quantum confinement induced shifts in the bottom of the CB edge. As seen from Fig. 2, the L_3 edges of the QD samples are shifted to higher energies relative to bulk CdSe. For example, shifts of 0.65 to 1.2 eV are observed for the 19 and 7 Å radius CdSe QD samples, respectively, which are consistent with the quantum confinement model. The agreement between experiment and both theories is close, but better agreement is seen with the charge patching (CP) theory [11] at larger particle sizes than with the tight-binding (TB) theory [6]. The CP method, which uses the charge density rather than the local potentials to generate the electronic structure, better represents the experimental system for three reasons: (1) The CP theory is a first-principles theory based on the local density approximation (LDA). In the CP approach, the electronic structure is calculated for a small system (i.e., 10–100 atoms) using LDA. The charge density is then generated for the small system and "patched" (added) together in order to produce the charge densities for larger systems. It has been shown that the CP method, when compared to LDA, is accurate on the order of 50 meV error [9] which is smaller than the experimental error. (2) Within the TB theory, a basis set of sp^3s^* was used, which indicates that the calculated conduction band states are composed of mainly s states with some p state contribution. Although it is believed that shifts will occur from s related states, this basis set gives a relatively crude description of the conduction band. (3) The CP theory includes a hydrogenlike passivation. Although not ideal, it provides a semirealistic model of the surface.

Consolidation of the plot shown in Fig. 2 into a scaling law introduces a means of describing the relevant QD physics in a simple mathematical expression, which is readily compared with theoretical values. For instance, more simplistic theories like the effective mass approximation indicate that the CB shift scaling law should be $E_c \propto R^{-2}$. More sophisticated theories like the TB method indicate the CB shift to be $E_c \propto R^{-1.0}$. Experimentally, we observe a CB shift of $E_c \propto R^{-0.6}$ with an error of ± 0.04 and ± 0.1 for values obtained via the extrapolation and arctangent subtraction, respectively. The scaling law obtained via the CP theory is $E_c \propto R^{-0.8}$ (see Fig. 2). The low error associated with the scaling laws allows the assertion that the experiment demonstrates better agreement with the CP theory than with the TB theory. Despite the close agreement observed in the CB scaling obtained from experiment and CP theory, the small discrepancy between the scaling laws (even with error considered) suggests new physics may occur at small sizes which slows down the shift of the CB. Therefore, we suggest that smaller exponents observed in the scaling laws are observed experimentally because a regime is entered at small sizes in which the CB minimum (CBM) does not shift with size.

Recent results by Puzder, *et al.* [10] suggest that small CdSe QDs (less than 10 Å radius) do not show a size dependence in the CB; rather, a consistent shift of ~1 eV relative to the bulk value is seen for the CBM. Although the differences between the theoretical results presented in this manuscript are difficult to explain, it has been postulated that this is in part due to differences in modeling the nanoparticle surface. We believe that the XAS results can be used to explain these contrary theoretical results in terms of a simple quantum confinement argument. The XAS results indicate that there are energy states in the upper conduction band of CdSe QDs that are inherently unaffected by quantum confinement, unlike the states at the bottom of the CB which are strongly affected. As already stated, the CdSe CBDOS are composed of Cd 5s states at the bottom of the CB, with hybridized 5p/5s state contribution above the CB minimum. In Fig. 1 it is clear that as the particle size is decreased, the s-like states shift to higher energy whereas the states labeled ps do not move. For the smallest particle size, it appears that the s states have shifted to such a degree that the bottom of the conduction band is now dominated by the hybridized p and s-like states. This would explain the contradictions

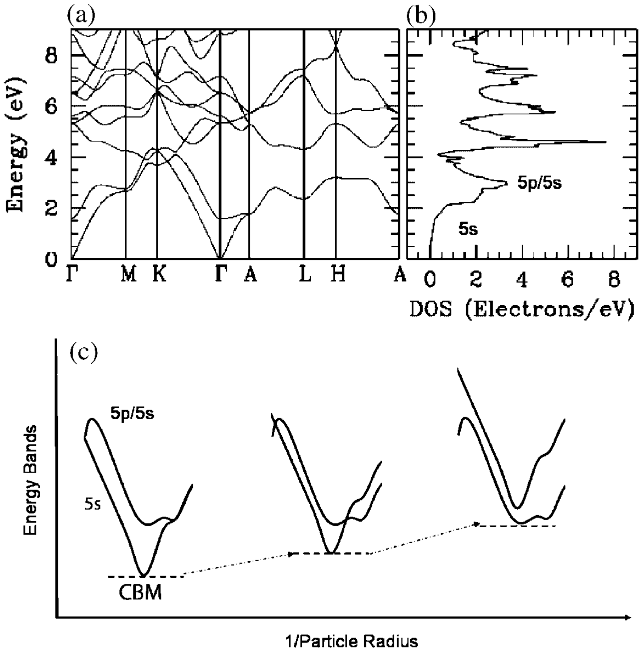

FIG. 3. (a) Calculated bulk CdSe conduction band diagram. (b) Corresponding conduction band density of states (DOS) which emphasizes the correlation of the DOS features with the energy bands. (c) Schematic energy bands depicting movement of the bands as a function of particle size. It must be noted that the *shape* of the bands as a function of particle size is not accurately represented and this illustration is intended only to demonstrate the *shifts* of the bands with particle size.

between theories and suggests that the reason the CB edge no longer shifts in particles below 10 Å is that the CB minimum is now composed of hybridized *p* and *s*-like states. Although Puzder *et al.* argue that surface states are responsible for the pinning of the CBM, our experiments cannot always easily resolve the differences between bulk and surface states so we are only commenting on the partial angular-momentum-resolved DOS, both surface and bulk. It is conceivable, therefore, that the observation of a pinned CB in our measurements may actually be related to surface states as suggested by Puzder *et al.* [10].

Band structure calculations [Figs. 3(a) and 3(b)] show that the Cd 5*s* energy bands are parabolic near the CB minimum and are expected to be highly affected by quantum confinement; the *ps* states are flat and should stay localized irrespective of particle size [Fig. 3(c)] although this has not yet been explored theoretically. We have previously shown that the Cd M_5 edge, which probes *p*-like DOS, does not shift with particle size and only shows a size dependent broadening [5]. In the case of the 5*s* states, the observed shifts are similar to those predicted by CP theory for particles larger than ~10 Å radius. For particles less than 10 Å radius, the weak size dependence of the shifts indicate that the states at the conduction band minimum are most likely the flatband *ps* states.

We conclude that contradictory theories in interpreting the quantum confinement induced shift of the conduction band in CdSe quantum dots can be addressed using x-ray absorption spectroscopy. As the CdSe particle size decreases, *s* states in the bottom of the conduction band shift to higher energy due to quantum confinement while hybridized 5*p*/5*s* states are unaffected by size. A conduction band composed of hybridized *ps* states at small particle sizes is proposed. These results suggest that there exists an upper limit to extent the conduction bands of CdSe can shift with particle size and should have impact on the future fabrication of electronic materials based on CdSe.

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