Soft X-ray spectroscopy of single sized CdS nanocrystals: size confinement and electronic structure

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Abstract

Soft X-ray spectroscopy of CdS nanocrystals within their crystalline superlattice allows to relate unambiguously changes of the electronic structure with the particle size and shape which is known from single crystal X-ray diffraction. We find that the valence and conduction band edge shift contribute to the same extent to the total band gap opening of about 2 eV with respect to CdS bulk as the particle size decreases to 10 Å. Taking a finite height of the potential walls into account, we can reproduce these results within an effective mass approximation model.

The development of the electronic band structure of solids from discrete localized atomic states is one of the key points of interest in cluster physics. To investigate size-dependent changes most techniques require macroscopic amounts of samples with a narrow size and shape distribution. These requirements can now be fulfilled by colloid chemistry for several II–VI and III–V semiconductors [1–3]. In certain cases, even crystalline superlattices of single-sized nanoparticles can be synthesized, guaranteeing even a uniform structure of the particles [4–6].

We present here the first detailed spectroscopic investigation of single sized CdS nanocrystals (NC) within their crystalline super-lattices. These particles resemble small units of the bulk lattice, which are covered by thiols (SR, R organic rest). The studied particles are a NC of 40 Å diameter [7], and the more molecule-like NCs Cd_{32}S_{14}(SR)_{36} (17.5 Å) [5] and Cd_{17}S_{4}(SR)_{26} (13.5 Å) [6] whose structures are known from single crystal X-ray diffraction. To extend the size range into a truly molecular regime, we also studied a pure Cadmium thiolate whose single crystal structure consists of Cd_{8}(SR)_{16} units [8].

So far, only optical absorption measurements of these samples have been possible in solution and on thin films after dissolution of the super-lattice. These data reveal the changes in the total optical gap, but the optical properties of the NCs within their super-lattice are still unknown. The optical excitation energies for the dissolved particles (ΔE in Table 1) increase from 2.5 eV for CdS bulk to around 4.7 eV for Cd thiolate [5–8].

The unique combination of properties of photon based soft X-ray spectroscopy techniques (SXS) [9], i.e. bulk sensitivity, element selectivity, and insensitivity to electrostatic sample charging, enables us to study the valence and conduction band electronic structure of the NCs surrounded by their stabilizing ligand shell in the super-lattice crystal. Probing separately the occupied and unoccupied part of the electronic structure, SXS can especially resolve their individual contributions to the total band gap opening [10].

In soft X-ray absorption (SXA) spectroscopy a core electron is excited into the conduction band (CB) (using as convention the terminology of solid state physics even for the more molecular-like particles). The transition probability is to a good approximation proportional to the local...
partial density of states (LPDOS) \[11,12\] of the CB, i.e., the DOS projected onto the site of the atom carrying the core hole (local) and onto the angular momentum symmetry of the core state (partial).

In soft X-ray emission (SXE) spectroscopy the radiative decay of an excited core hole state by a transition of a valence band (VB) electron is observed, and the occupied LPDOS of the VB is mapped by the spectral intensity distribution in SXE spectra \[13\].

The experiments were carried out at the undulator beamline BW3 \[14\] at HASYLAB, Hamburg. S L2,3 SXA spectra were measured with a photon energy resolution of better than 40 meV by monitoring the fluorescence yield using a channeltron, thereby avoiding sample charging problems. Saturation effects were minimized due to a normal-in grazing-out geometry \[15\]. SXE spectra were recorded with a resolution set to 0.7 eV for high spectrometer throughput. The energy scales of the SXA and SXE spectra are referred to each other better than 50 meV using reflection of the monochromatized synchrotron radiation into the spectrometer.

All samples, prepared and characterized as described in Refs. \[5–8\], were pressed as polycrystalline powders into indium foil, including a CdS bulk sample for reference.

On the right hand side of Fig. 1 we show the S L2,3 SXA spectra of bulk CdS (which agrees with Refs. \[16,17\]), of the CdS NCs, and of Cd thiolate. As the S 2p level is spin–orbit split, only the first 1.1 eV above the absorption onsets belong uniquely to S L3 absorption, while for higher photon energies the SXA spectra are a superposition of S L3 and S L2 absorption. The pronounced structures in the CdS bulk SXA spectrum above 163 eV result from various maxima in the unoccupied DOS, and can be assigned to high-symmetry points \[16,18\].

Comparing all SXA spectra one notices that with decreasing particle size the first shoulder of the bulk spectrum separates increasingly from the remaining absorption spectrum and becomes a discrete peak. In addition, the energy of the absorption onset is nearly identical for all samples (core level binding energy shifts, which affect absorption energies are discussed below). This indicates that the first peak does not result from quantization of the unoccupied DOS due to the restricted particle size. Otherwise, one would expect a

### Table 1

Optical excitation energies for the dissolved particles. The sizes are taken from Refs. \[5–8\], $\Delta E_{\text{opt}}$ (eV) values denote the increase of the optical excitation energies relative to the bulk value of 2.5 eV as measured on dissolved nanoparticles. Note, that it is known from $^{111}$Cd-NMR \[24\] spectroscopy that the Cd$_{32}$S$_{14}$ (SR)$_{36}$ (Cd$_{32}$) and the Cd$_{17}$S$_{4}$ (SR)$_{26}$ (Cd$_{17}$) NC, and the Cd thiolate Cd$_8$ (SR)$_{16}$ (Cd$_8$). The dotted lines show the separation into excitonic and LPDOS excitation. Left part: top part of the smoothed S L3 SXE spectra (crosses show the non-smoothed data) mapping the local S(s + d) symmetric DOS of the upper VB. The width of the upper VB is quantified by the arrows indicating the full width at half maximum of the upper VB.

<table>
<thead>
<tr>
<th>Size (Å)</th>
<th>CdS$_{40}$</th>
<th>CdS$_{17}$</th>
<th>CdS$_{12}$</th>
<th>CdS$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ$E_{\text{opt}}$ (eV)</td>
<td>0.5</td>
<td>1.2</td>
<td>1.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Δ$E_{\text{SXE}}$ (eV)</td>
<td>-0.50</td>
<td>-0.76</td>
<td>-1.24</td>
<td>-1.50</td>
</tr>
<tr>
<td>Δ$E_{\text{SXA}}$ (eV)</td>
<td>0.24</td>
<td>0.40</td>
<td>0.55</td>
<td>0.65</td>
</tr>
<tr>
<td>Δ$E_{\text{gap}}$ (eV)</td>
<td>0.7</td>
<td>1.2</td>
<td>1.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Δ$E_{\text{L3}}$ (eV)</td>
<td>0.13</td>
<td>0.31</td>
<td>0.33</td>
<td>0.46</td>
</tr>
<tr>
<td>BW (eV)</td>
<td>4.6</td>
<td>4.3</td>
<td>4.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

1. This DOS interpretation (e.g. Ref. \[11\]) is valid for systems like CdS where electron correlation effects are negligible.
2. For correlation effects in SXS see, e.g. Ref. \[12\].
3. The applicability of the underlying ‘two-step approximation’ is discussed in, e.g. Ref. \[13\].
significant shift of the absorption onset as the effective mass approximation (EMA), using infinitely high potential walls [19], predicts for CdS that the band gap opening (of the order of \(2\) eV for the smaller particles) is mainly due to a shift of the CB minimum (CBM).

The observed spectral changes are, however, consistent with an assignment of the peak to a \(S\ L_3\) core exciton. Since no distinct structure is observable in the bulk SXA spectrum, the \(S\ L_3\) core exciton is weakly bound, i.e. the bulk exciton radius is of the order of several \(10\) Å [20]. In particles with a size comparable to the exciton radius, the core exciton binding energy thus increases with decreasing particle size due to confinement [19], increasing the separation between the exciton and the remaining absorption features in line with the observation in Fig. 1. So, the apparent absorption onset appears to be size independent while the unoccupied states shift to higher binding energies.

This assignment of the first structure in the NC SXA spectra implies that the shoulder in the bulk SXA spectrum of CdS bulk is due to \(S\ L_3\) core exciton excitation, in contrast to previous interpretations [16,17].

For a quantitative analysis of the first \(2\) eV of the SXA spectra we make a two-Gaussian fit representing excitation into excitonic and unoccupied states. The description of the latter part by a single Gaussian assumes that the vibrational broadening of around \(700\) meV, as found for the core exciton excitation, masks the fine structure of the CB LPDOS close to the CBM.

All fits give the same energy position of the core exciton of \(162.7\) eV within their accuracy, and a similar full width at half maximum (FWHM) around \(700\) meV. Subtracting the Gaussian representing the core exciton from the SXA spectra we obtain the parts of the SXA spectra which we relate to the LPDOS (dotted lines in Fig. 1). Comparing the LPDOS absorption onset sets one observes the expected shift to higher energies with decreasing particle size which we quantify by linear extrapolation (gray bars in Fig. 1, \(\Delta E_{\text{SXA}}\) in Table 1). Note, that due to broadening these onsets do not necessarily indicate the position of the CBM itself. We further note that this interpretation of the absorption spectra ignores any core hole influence on the unoccupied states which may lead us to underestimate the shift for the smaller particles.

The upper part of the photon excited \(S\ L_3\) SXE spectra is shown on the left hand side of Fig. 1. The spectra map the local \(S(s + d)\) symmetric DOS of the upper VB, as only \(S\ L_3\) core hole states contribute to the spectra due to the selected photon excitation energy of \(162.9\) eV (bandwidth \(100\) meV) just below the \(S\ L_3\) threshold. Note that only due to hybridization the states of the upper VB, derived mainly from the \(S\ 3p\) and Cd \(5s\) states, have local \(s\) and/or \(d\) symmetric character at the S sites.

The influence of the size restriction on the VB structure of the nanoparticles can clearly be seen in Fig. 1. As expected in a quantum confinement framework the high-energy cutoff shifts to lower emission energies with decreasing size. This is accompanied by a decrease of the intensity in the top part of the upper VB reflecting changes in the shape of the local \(S(s + d)\) symmetric DOS.

By linear extrapolation we determine the shift of the high-energy cut-off in the nanoparticle SXE spectra relative to the bulk case (\(\Delta E_{\text{SXE}}\) in Table 1) which we take as a measure for the shift of the VB maximum (VBM) position [21].

Adding the SXS shifts of VBM and CBM one obtains the total band gap opening (\(\Delta E_{\text{gap}}\) in Table 1) for the nanoparticles in their crystalline environment relative to the bulk material. Within the experimental uncertainties we find these values to be in agreement with the optical excitation energies recorded after dissolution of the super-lattice (note, that the present uncertainty exceeds the estimated optical exciton binding energies by which the optical excitation energies are smaller than the band gaps).

The quantum confinement effects are not restricted to the bandgap region alone, but one notices a general decrease of the upper VB width. We quantify this by measuring the FWHM as indicated by the arrows in Fig. 1 (BW in Table 1). This shows that due to the size restriction the width decrease from \(4.8\) eV for CdS bulk to only \(3.5\) eV for the Cd thiolate. We further report that the lower VB (compare Ref. [17]), which is derived from the more localized \(S\ 3s\) and Cd \(4d\) states, is nearly unaffected by the size restriction.

In order to determine the individual contribution of the VBM and CBM shift to the total band gap opening by comparing the NCs SXS spectra to the CdS bulk spectra, the SXS energy scales have to be corrected for possible shifts of the \(S\ 2p\) core level binding energy. We, therefore, have recorded \(S\ 2p\) photoelectron spectra (XPS) of CdS bulk, the NCs, and the Cd thiolate, which refer the binding energies against each other. These XPS spectra will be thoroughly discussed in a forthcoming publication [18], while here we only report that the nanoparticle spectra show additional intensity on the side of higher binding energies (absolute values) which increases with decreasing particle size. This is related to the increasing relative number of \(S\) atoms at the particle surface which are covalently bound to the C atoms of the thiols. As a consequence, the NC SXA spectra in Fig. 1 are not as structured as the bulk spectrum for higher photon energies, as for higher excitation energies all the \(S\) atoms with different binding energies contribute to the SXA spectra.

For the determination of the VBM and CBM shifts only the \(S\) atoms with the lowest \(S\ 2p\) binding energy (absolute values) are of importance, as these electrons are selectively excited for excitation energies in the vicinity of the absorption threshold. Thus, the determined energies of the LPDOS absorption onsets and the energy scales of the recorded SXE spectra are related to these binding energies. We find that with decreasing particle size the binding energy of this component decreases by the amounts \(\Delta E_{\text{L3}}\) listed in Table

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4. We assume dynamics like energy dissipation (e.g. Ref. [12]) and vibrational relaxation (e.g. Ref. [21]) in the intermediate state to be comparable for the bulk and the nanoparticles.
According to these values, the SXS energy scales of the different samples have to be corrected.

In Fig. 2 the corrected VBM ($\Delta E_{\text{SXE}} + \Delta E_{\text{L}}$) and CBM ($\Delta E_{\text{SXX}} + \Delta E_{\text{L}}$) shifts are compared to theoretical models. The solid line is the EMA calculation for infinitely high potential walls (solid lines, IP-EMA) [19], the EMA taking the finite height of the potential walls into account (dashed lines, FP-EMA) [22], and the tight-binding calculation of Lippens and Lannoo (gray diamonds, TB) [24].

Using an EMA algorithm developed to account for finite potential heights (FP-EMA) in quantum-dot/quantum-well heterostructures [22] we obtain the predictions given by the EMA calculation for infinitely high potential barriers. Apparently, the EMA can be used to estimate the effect of size confinement even in particles of only a few tens of Ångströms, if the finite height of the confining potentials is taken into account.

To summarize, we have investigated size-selected CdS nanoparticles in their crystalline environment using soft X-ray spectroscopy. We observe a strong influence of the size confinement on the electronic structure. The determined opening of the band gap is in agreement with optical data observed for the nanoparticles after dissolution of the superlattice.

The contribution of the occupied and the unoccupied states to the total band gap opening is resolved by combining the SXS data with XPS results for the $S\ 2p$ binding energy in the nanoparticles. We experimentally observe VBM and CBM shifts of comparable size, which we can reproduce within the EMA using finite heights of the confining potential barriers. In contrast, the experimental results show that both, VBM and CBM shifts, contribute about equally to the gap opening.

The FP-EMA results are in general agreement with the results from a tight-binding calculation by Lippens and Lannoo [24] shown by the gray diamonds. For the comparison with our experimental values one has to keep in mind that the structures used in the calculations differ significantly from the actual structures of the NCs investigated. Nevertheless, our results support the theoretical prediction that VBM and CBM shift contribute about equally to the total gap opening.

The importance of the finite height of the confining potential barriers. Apparently, the EMA can be used to estimate the effect of size confinement even in particles of only a few tens of Ångströms, if the finite height of the confining potentials is taken into account.

In addition, we assign the first shoulder in the $S\ L_{2,3}$ SXA spectrum of CdS bulk, which was previously interpreted as a DOS maximum, to the excitation of $S\ L_{3}$ core excitons. In the nanoparticles the binding energy of this core exciton is increased due to size confinement. This demonstrates how a study of the development of the electronic structure with particle size can lead to a better understanding of the properties of the bulk materials.

References