# Size Effect of CdSe Quantum Dots Studied by X-ray Absorption Spectroscopy

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As the size of the nanocrystals is decreased, the atoms on the surface experience broken symmetry and often higher anisotropy, new surface states are formed. For the CdSe quantum dots, a number of interesting optical properties such as band edge luminescence and excitonic radiative decay have been related to the surface state. CdSe nanoparticles are often passivated by capping with TOPO (tri-n-octylphosphine oxide) to avoid aggregation and surface oxidation, it is important to understand the effect of TOPO on the surface atoms and on the measured properties. Thus, Cd K-edge x-ray absorption near-edge structure (XANES) spectra of CdSe with diameter of 2.8, 4.1 and 5.6 nm were measured to study the electronic structure. Extend x-ray absorption fine structure (EXAFS) analysis at Cd K-edge revealed the change in local atomic structure around Cd ion due to the size reduction.

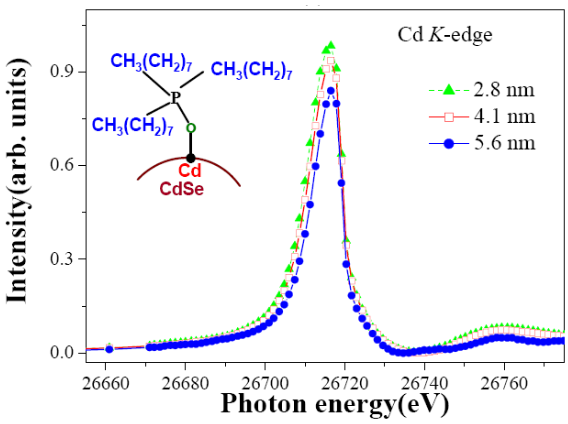

**Figure 1.** Normalized Cd K-edge XANES spectra of CdSe for 2.8nm, 4.1nm and 5.6nm nanoparticles after background subtraction.

Figure 1 presents the Cd K-edge XANES spectra of CdSe for various size of nanoparticles. The spectra were obtained after the background subtraction. The absorption feature measures the number of unoccupied states above the Fermi level. It shows an increase in the peak intensity by the size reduction, which suggests an increase in the number of unoccupied states and an increase of charge loss in occupied state of Cd ion. The electronegativity of Se is larger than that of Cd, consequently, the larger charge transfer from Cd to Se is expected in nanoparticles with smaller diameters. Besides, the interaction between the nanoparticles and surfactant/solvent molecules leads to the charge transfer from nanoparticles to ligand molecules. The oxygen has even larger value of electronegativity than Se. As a result, the charge transfer between Cd and TOPO is also expected.

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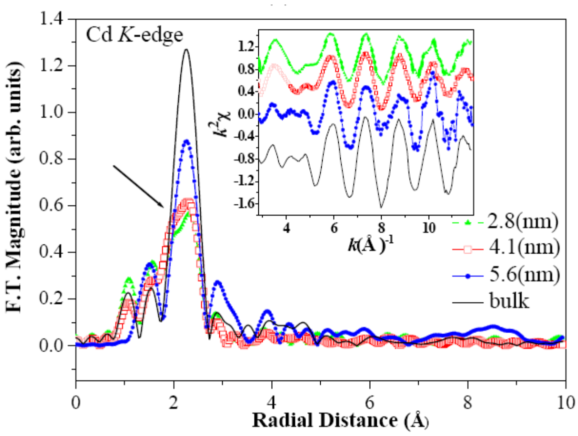

**Figure 2.** Fourier transform amplitutes of the EXAFS $k^2\chi$ data at the Cd K-edge for 2.8nm, 4.1nm and 5.6nm and bulk CdSe. The inset represents . $k^2\chi$ data of the EXAFS oscillations.

Figure 2 displays the Fourier transform (FT) of the EXAFS $k^2\chi$ data at the Cd K-edge, which presents the local atomic structure around the Cd atoms. The inset shows the Cd K-edge $k^2\chi$ data of the EXAFS oscillations. The weaker intensity of the oscillations from the smaller nanoparticles are observed and the oscillation of bulk and 5.6 nm are quite similar which are slightly different from 4.1 nm and 2.8 nm, indicate that the local structure is disordered compared to bulk and the local structure is different when the size is smaller than 5.6 nm. In the FTs, the position of the strong peak ~2.27 Å reflects the Cd-Se bond length. The decrease in the amplitude of the peak relative to bulk CdSe indicates the reduction of coordination number and increase in the local atomic disorder due to the size effect. The bond length of Cd-O is ~0.2 Å shorter than Cd-Se distance. Thus the additional feature shown at the low energy side of the main peak is attributed to the presence of Cd-O bonds in 2.8 nm and 4.1 nm nanoparticles.

The Cd: Se stoichiometry is yielded 1:1 for bulk CdSe. However, the Cd: Se ratio is increasing as the nanocrystal is reducing and thus the nanocrystals CdSe are found to be Cd- rich surface. Our EXAFS analysis, indicating the local atomic disorder and the stronger interaction with the TOPO, supports the assumption that the charge transfer between cadmium and oxygen.