

Room-temperature Ferromagnetism in Capped CdSe Quantum Dots

CdSe nanoparticles are of great interest due to their potential used in nonlinear optical materials and their photochemical properties. Its application in optical devices originates from the oscillator strength, relaxation properties and the tunable band gap as a function of particle size. We report the observation of RTFM in CdSe quantum dots (QD) capped with TOPO (tri-n-octylphosphine oxide). This RTFM is labeled as ex-nihilo since the RTFM is due to the marriage of two diamagnetic materials viz. CdSe and TOPO, possibly resulting from charge transfer from Cd d-band to the oxygen atoms of TOPO. We further show that the RTFM varies inversely with the size of the QD, in agreement with our calculations.

The evolution of physical properties with nanosized materials is particularly interesting since extreme small nanoparticles behave like molecules, which are in contrast to the materials with larger size behave more like bulk properties. In addition, as the dimension approach to the nanosized scales, quantum and surface effects start to play an important role, giving rise to drastic changes in physical properties. CdSe nanoparticles are of great interest due to their potential used in nonlinear optical materials^[1] and their photochemical properties^[2]. Its application in optical devices originates from the oscillator strength, relaxation properties and the tunable band gap as a function of particle size. We report the study of the effect of reduced size on electronic and magnetic properties of CdSe nanoparticles capped by TOPO (tri-n-octylphosphine oxide).

Important size effect of CdSe nanoparticles are observed and presented in Fig. 1. The increase in magnetic susceptibility χ with decreasing the particles size is seen. The inset illustrates that χ is dominated by the size and

◎ Beamlines

01C and 17C EXAFS

◎ Authors

Y. Y. Chen and C. L. Dong

Academia Sinica, Taipei, Taiwan

C. L. Chang

Tamkang University, Taipei, Taiwan

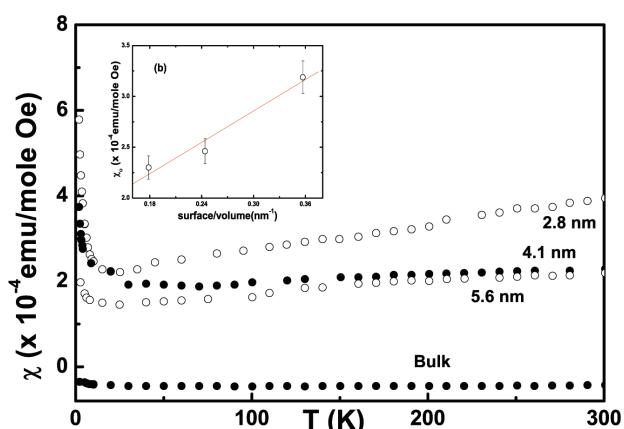


Fig. 1: Magnetic susceptibility as function of temperature for bulk and quantum dots of different size.

surface effect as evidenced by the linear dependent of χ versus $1/d$ (surface-to-bulk ratio). The surface is likely to be disorder and more free charge carriers on the surface.

Figure 2 plots Cd K-edge X-ray absorption near-edge structure (XANES) spectra for CdSe nanoparticles of various size. The absorption feature measures the number of unoccupied states above the Fermi level. It is noted that intensity is sensitive to the particle size (inset). The peak intensity increases as the size decreases, which suggests that an increase in the number of unoccupied states and an increase of charge loss in occupied state of Cd ion as the size is decreased. Two possible facts come to this consequence. The detail was reported in literature^[3]. The lattice constant of CdSe is decreased as reducing the particle size^[4]. The electronegativity of Se (2.55) is larger than that of Cd (1.69), consequently, the larger charge transfer from Cd to Se is expected in nanoparticles with smaller diameters. Besides, it has been found that the interaction between the nanoparticles and surfactant/solvent molecules leading to the charge transfer from nanoparticles to ligand molecules^[5]. The oxygen has even larger value of electronegativity (3.44) than Se. As a result, the charge transfer between Cd and TOPO is also expected.

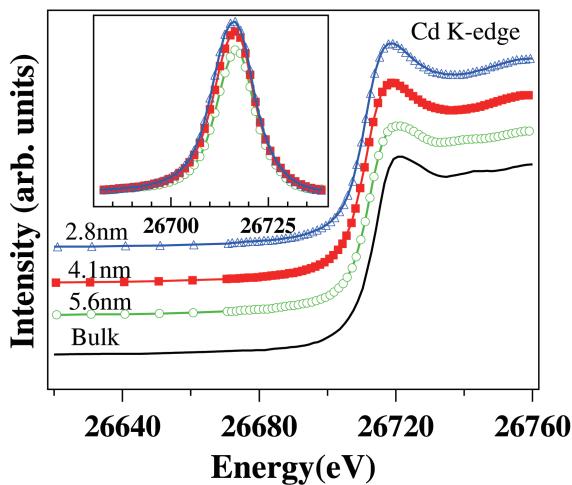


Fig. 2: Cd K-edge spectra for quantum dots of different size. The inset compares the absorption intensity for samples of different size.

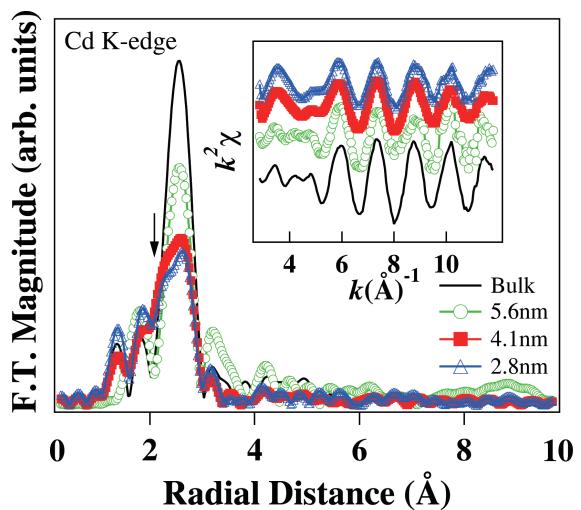


Fig. 3: Fourier transform amplitudes of the EXAFS $k^2 \chi$ data at the Cd K-edge for quantum dots of different size. The inset plots the $k^2 \chi$ data of the Cd K-edge EXAFS oscillations.

Figure 3 displays the Fourier transform (FT) of the extended X-ray absorption fine structure (EXAFS) $k^2 \chi$ data of 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. In FTs the position of the strong peak $\sim 2.27 \text{ \AA}$ 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. It has been reported that the bond length of Cd-O is $\sim 0.2 \text{ \AA}$ shorter than Cd-Se distance^[6]. Thus the additional feature shown at the low energy side (as indicated by an arrow) 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^[7]. Our EXAFS analysis, indicating the local atomic disorder and the stronger interaction with the TOPO, strongly supports the assumption that the charge transfer between cadmium and oxygen.

The observed size-dependent ferromagnetism in TOPO-capped CdSe QDs reported here is convincingly intrinsic. Arguments have been presented that this ferromagnetism is due to d-holes on the Cd site bonded to TOPO created by experimentally observed charge transfer from Cd to TOPO. Experiments using different capping agents and direct observation of spin polarization at the Cd site using X-ray magnetic circular dichroism would provide additional support for the mechanism of size-dependent ferromagnetism suggested in this work.◆

◎ Experimental Station

Gas-ionization chamber and Lytle detector

◎ Publications

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◎ Contact E-mail

Cheny2@phys.sinica.edu.tw