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Evidence for the chemical nature of capping in CdSe nanoparticles prepared by thermolysis in tri-n-octylphosphine oxide from P-edge EXAFS spectroscopy

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The nature of the capping agent on the surface of CdSe quantum dots has been investigated using P-edge EXAFS spectroscopy. Two samples prepared by different synthetic routes were compared and the results show similar capping in which tri-n-octylphosphine oxide and tri-n-octylphosphine selenide are bound to the surface of the dots.

Introduction

Nanoparticles of semiconductor materials, often referred to as quantum dots, have attracted great interest as a result of their novel electronic, catalytic and optical properties. The electronic properties arise from their small size; the electronic structure of the materials is changed and the continuous band structure breaks down to give discrete bonding and anti-bonding levels.[1,2] The unusual properties of these materials are due to both their large surface area to volume ratio and the above quantum mechanical effects. Various methods of synthesising nanoparticular materials can be employed: colloidal chemistry,[3,4] deposition from various organometallic compounds[5,6] and particle surface passivation.[7–9] In this work, nanoparticular CdSe has been prepared by the surface passivation of CdSe particles produced by the thermolysis of a single-source precursor in the capping agent, tri-n-octylphosphine oxide (TOPO), and as the product of the reaction of dimethylcadmium with tri-n-octylphosphine selenide (TOPSe). Both synthetic routes are well established and the particles produced have sizes of the order of a few nanometers. However, the exact nature of the capping on the surface of these compounds is not clear. In this work, extended X-ray absorption fine structure (EXAFS) spectroscopy is used to study the local environment of phosphorus in the capping agent on the surface of CdSe quantum dots, the way the capping agent binds on to the surface and any differences in the capping agents on the material produced from the two synthetic routes.

Experimental

Syntheses of nanocrystalline CdSe

Sample 1 was prepared by the route previously described by Bawendi *et al.*[7] Standard air-sensitive laboratory practice was followed throughout the synthetic stages. A solution of tri-n-octylphosphine selenide in tri-n-octylphosphine (1 M, 6 cm^3, 6 mmol) was added to dimethylcadmium (1.5 g, 10.5 mmol) under a nitrogen atmosphere. The mixture was injected into a reaction vessel containing tri-n-octylphosphine oxide (15.08 g, 39 mmol) at 250 °C and stirred at this temperature for 30 min. The reaction mixture then was allowed to cool down to 60 °C and methanol (30 cm^3, 23.73 mol) was added. The precipitate formed was centrifuged and the solid isolated was dispersed in toluene.

Sample 2 was prepared by a method similar to the Bawendi route using the single source precursor bis[methyl(n-hexyl)diselenocarbamato]cadmium, $Cd[Se_2CN(CH_3)C_6H_{13}]_2$.[8,9] The precursor (1 g, 1.46 mmol) was dissolved in tri-n-octylphosphine (15 cm^3, 33.6 mmol). The solution was then injected into hot tri-n-octylphosphine oxide at 200 °C and kept at this temperature for 30–40 min. The resulting solution was cooled to *ca.* 70 °C and an excess of methanol added, resulting in the formation of a flocculent precipitate. The solid was separated by centrifugation and dispersed in toluene.

EXAFS spectroscopy

EXAFS spectra were collected on Station 3.4 at the CLRC Daresbury Synchrotron Radiation Source. The synchrotron operates at an energy of 2 GeV and the current during the scans had an average value of 150 mA. Station 3.4 is suitable for absorption edges in the energy range from 800 to 3500 eV tuned by an element-interchangeable double crystal monchromator. In this work, the energy of the experiments was tuned by a pair of InSb(111) crystals. The experiment was carried out under vacuum and the sample was in the form of a spin coated film on glass. A minimum of four scans were collected and averaged in order to improve the signal-to-noise ratio. Data was analysed in the conventional manner, using the Daresbury suite software, EXCALIB, EXBROOK and EXCURV98.[10] EXCURV98 employs a least squares fitting routine, by which raw data can be fitted to a structural model. Phase shifts are derived from *ab initio* calculations within EXCURV98. Analyses were carried out to yield a best fit by refining the radial distribution (RD), the coordination number (CN), the Debye–Waller ($2\sigma^2$, where σ^2 is the mean square separation in interatomic positions) and the Fermi energy (EF) parameters. Calculations were performed using the small atom theory. Fourier filtering around the first shell and editing routines were used in order to exclude the glitch in the high k region (9–10), which results from sulfur contaminants in the line. The quality of fit to the EXAFS in k-space is defined by:

$$R_{\text{EXAFS}} = \sum\nolimits_i^n \left\{ \sigma_i \left| \chi_i^{\text{Experimental}}(k) - \chi_i^{\text{Theoretical}}(k) \right| \right\}^{-1} \times 100\%$$

where,

$$\left(\frac{1}{\sigma_i}\right) = \frac{k(i)^n}{\sum_j k(j)^n |\exp(j)|}$$

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Table 1 Fitted EXAFS data for the surface-derivatised CdSe quantum dots, sample 1

Shell	CN	R/Å	Error/Å	$2\sigma^2$/Å^2	Error/Å^2
C	3	1.49	0.010	0.007	0.001
O	1	1.67	0.028	0.016	0.010
Se	1	2.03	0.012	0.015	0.003
Cd	1	2.17	0.020	0.018	0.004
EF = 10.98 (±1.54)		R = 19.77%			

Table 2 Fitted EXAFS data for the surface-derivatised CdSe quantum dots, sample 2

Shell	CN	R/Å	Error/Å	$2\sigma^2$/Å^2	Error/Å^2
C	3	1.47	0.008	0.007	0.002
O	1	1.60	0.040	0.021	0.015
Se	1	2.02	0.016	0.017	0.004
Cd	1	2.15	0.016	0.015	0.003
EF = 10.37 (±1.62)		R = 26.05%			

Results

The P-edge EXAFS results are summarised in terms of CN, Debye–Waller and EF parameters (Table 1 and 2). The EXAFS $\chi(k)$ oscillations for both experiments are weighted by k^3 (Fig. 1 and 3) and the Fourier transformation of the EXAFS oscillation (Fig. 2 and 4) results in an average radial distribution of atoms in terms of their type, abundance and distance (Å) from the phosphorus centre. The values are given with their statistical experimental errors for each parameter, although these are not an estimate in the actual value of the error in each parameter, as they do not include errors in the theory, the experimental errors in the original data or those made in creating the EXAFS file. The solid lines in the plots represent the experimental data as collected and the dashed lines the best fitted EXAFS spectrum and Fourier transformation.

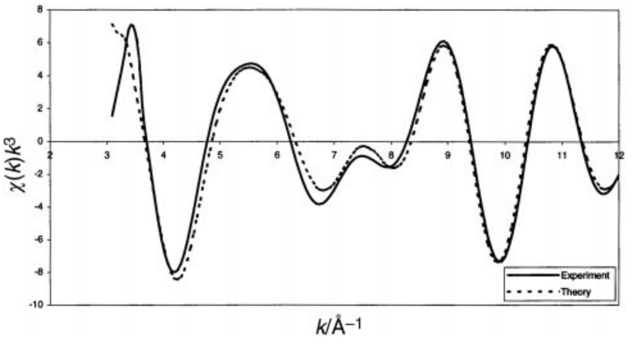

Fig. 1 P-edge EXAFS spectrum of derivatised CdSe quantum dots, sample 1.

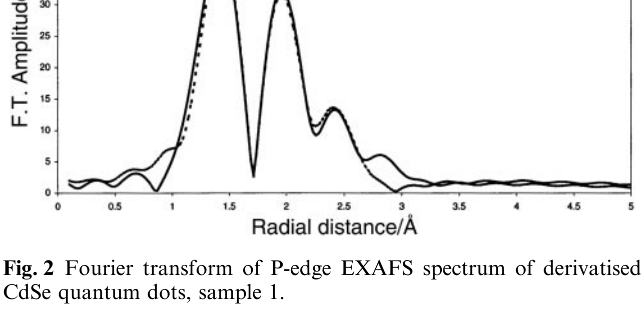

Fig. 2 Fourier transform of P-edge EXAFS spectrum of derivatised CdSe quantum dots, sample 1.

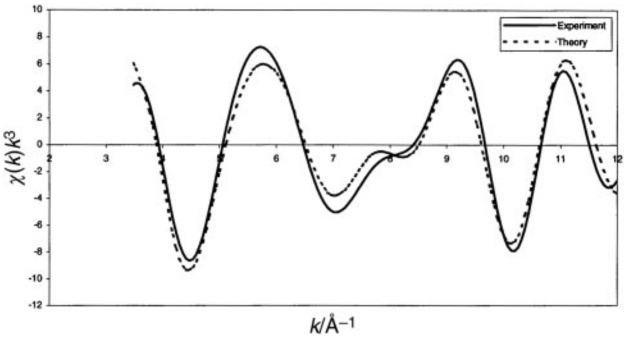

Fig. 3 P-edge EXAFS spectrum of derivatised CdSe quantum dots, sample 2.

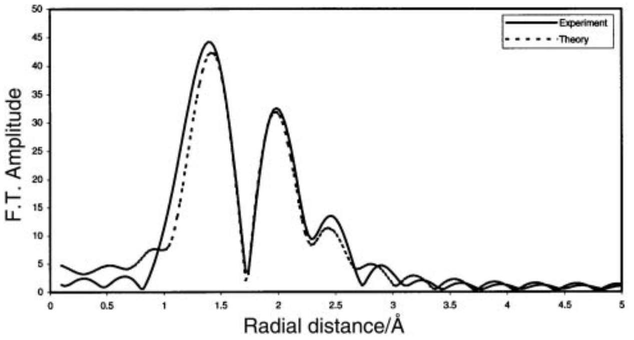

Fig. 4 Fourier transform of P-edge EXAFS spectrum of derivatised CdSe quantum dots, sample 2.

Discussion

Both samples show similar results for the local environment of phosphorus in the capping agent, as shown in a comparison plot of the raw EXAFS data prior to the analysis (Fig. 5). The EXAFS results clearly show that two phosphorus environments exist on the surface of CdSe for both sample 1 and sample 2. The averaged environments for tri-n-octylphosphine oxide (Fig. 6A) and tri-n-octylphosphine selenide (Fig. 6B) bound to the surface of CdSe through the oxygen or the selenium atoms, respectively, give a complex phosphorus EXAFS model. The relative coordination numbers of oxygen and selenium do not indicate the relative concentrations of tri-n-octylphosphine oxide or selenide present on the surface of both samples due to the high degree of disorder in the system. Contour maps of the coordination number of both selenium and oxygen against their Debye–Waller factors indicated a wide variation in their minima.

Tri-n-octylphosphine oxide binds on the surface through the

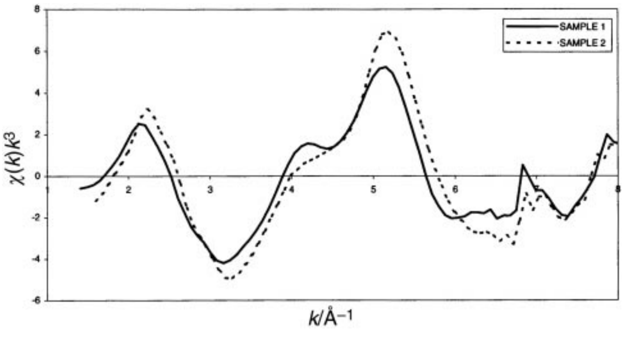

Fig. 5 Comparison of the raw EXAFS data for samples 1 and 2.

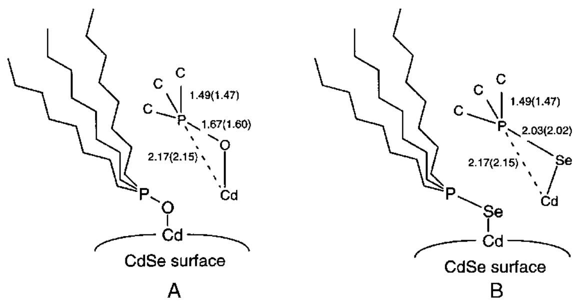

Fig. 6 The proposed models for the two capping agents arising from the EXAFS analysis. Data for sample 2 are given in parentheses.

oxygen, located 1.67 and 1.60 Å from the phosphorus for samples 1 and 2, respectively, whereas tri-n-octylphosphine selenide binds to the surface through the selenium atom which is 2.03 and 2.02 Å from the phosphorus for samples 1 and 2, respectively. The cadmium site located 2.17 and 2.15 Å from the phosphorus for samples 1 and 2, respectively is part of the CdSe surface. Hence, it is hard to assign which of the two bonding regimes dominates. All the bond distances are reasonable. The P–C distances for the three ends of the alkyl chains in both tri-n-octylphosphine oxide and selenide are 1.49 Å for sample 1 and 1.46 Å for sample 2, with no spatial inhomogeneity as a result of the different electronegativities of the oxygen and selenium atoms in the two capping agents being resolved for these bonds.

The P–O distance is slightly longer than that of free tri-alkylphosphine oxides, which usually contain P–O bond lengths of the order of 1.45 Å as a result of the strong interaction of the oxygen p-orbitals and the relatively low energy empty d-orbitals of the phosphorus.[11] The elongation of the P–O bond in this case is due to the interaction between the cadmium on the CdSe surface and the oxygen atom. Infrared studies[12] have shown a decrease in the P–O stretching frequency upon coordination to zinc and cadmium halides. Also, ^{31}P MAS NMR studies of tri-n-octylphosphine oxide and selenide on CdSe quantum dots have shown a 25 ppm increase in shielding of the capping species relative to free tri-n-octylphosphine oxide and selenide, indicating a weakening of the P–O and P–Se bonds upon coordination to the surface.[13]

The relatively short P–Cd distance gives a clear indication of a non-linear P–X–Cd (X = O, Se) angle. Both P–O–M and P–Se–M can vary from 113 to 180°[11,14] and 96 to 120°,[14–16] respectively. Further support for the non-linearity of the P–X–Cd angle and the short P–Cd bond arises from the ^{31}P MAS NMR data of other researchers who studied the chemical shift anisotropies of tri-n-octylphosphine oxide in the free state and coordinated on CdSe quantum dots using rotational side-band intensities and shift tensor parameters. It was suggested that the threefold or higher symmetry of free tri-n-octylphosphine oxide, as indicated by the axially symmetric chemical shift tensor, is not present on the coordinated species and results in the loss of axial symmetry on the phosphorus site.[13]

The presence of tri-n-octylphosphine selenide as a capping agent is clearly indicated by the P–Se distances of 2.03 and 2.02 Å for samples 1 and 2, respectively. Typically, $R_3P{=}Se$ distances lie within the range 2.094–2.136 Å.[17–20] X-Ray studies have shown the unidentate and bridging character of the Y_3P–S group.[14,16] Hence, none of the tri-n-octylphosphine present in the reaction mixture binds at the selenium sites that are part of the surface as this would force the P–Se group into an unfavourable tridentate system.

Conclusions

There have been earlier studies of quantum dots by related methods.[21–24] The majority of these papers are concerned with the determination of the structure within individual quantum dots, the studies often using Cd or Se edges; the use of the phosphorus edge allowed us to focus on the surface of the material. EXAFS analysis indicates the presence of both tri-n-octylphosphine oxide and selenide on the surface of CdSe quantum dots as prepared by two different methods. Both synthetic routes yield nanoparticles with the same type of capping agent on the surface. This observation probably reflects the lability of TOPO, giving rise to TOPSe *in situ* which binds at the surface. Hence, in all cases, $^{n}Oct_3P{=}Se$ can occur at the surface.The non-linear character of the P–X–Cd (X = O, Se) vector is clearly indicated by the short P–Cd distance. As tri-n-octylphosphine cannot bind directly on to the surface selenium sites, the selenium fitted in the EXAFS data arises purely from tri-n-octylphosphine selenide.

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