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Multichannel detection x-ray absorption near edge structures study on the structural characteristics of dendrimer-stabilized CdS quantum dots

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Starburst poly-(amidoamine) dendrimers were used to obtain dendrimer stabilized CdS nanoparticles, or quantum dots (QDs). The average particle size of the QDs was examined by UV-vis absorption spectra and powder x-ray diffraction measurements. The technique of x-ray absorption near edge structure (XANES) near the S *K*-edge was employed to study the structural characteristics of a series of QDs. The use of a multichannel detection scheme in XANES, monitoring total electron yield, x-ray fluorescence yield, and photoluminescence yield simultaneously, was demonstrated to be a powerful tool to evaluate the structure of the QDs from a sulfur perspective. The relationship between the luminescence property and the local structure of sulfur in the QDs was also discussed on the basis of the results of x-ray excited optical luminescence and XANES studies. © 2001 American Institute of Physics. [DOI: 10.1063/1.1394899]

I. INTRODUCTION

The advent of nanoscience and technology has led to increasing demands for structural characterization of materials in nanosize. While measurements through microscopes such as transmission electron microscope (TEM), scanning tunnel microscope (STM), atomic force microscope (AFM), etc., are playing an important role in determining the morphology, the spectroscopic and diffraction techniques such as extended x-ray absorption fine structure (EXAFS), nuclear magnetic resonance (NMR), x-ray diffraction (XRD), etc., are also showing potentials in gaining structural and electronic properties information that cannot be obtained through microscopic measurements.¹ There have been recent reports from Hamad *et al.*,² J. Luning *et al.*,^{3a} and Nowak *et al.*^{3b} on the application of x-ray absorption near edge structure (XANES) and x-ray emission spectroscopy (XES) to the structure and property studies of nanoclusters. Here we demonstrate that the combined use of x-ray absorption near edge structure with multichannel detections (MD-XANES)⁴ can be an efficient method to investigate the structure characteristics of dendrimer-stabilized CdS quantum dots (QDs), which show interesting blue-light emission.⁵ However, the structural and electronic properties of this system are not been fully understood.⁶

II. EXPERIMENT

Reagents used in this work were all purchased from ALDRICH including starburst poly (amidoamine) dendrimer of generation 4 with 64 hydroxyl end groups (G4 PAMAM-OH) and with 64 amine end groups (G4 PAMAM-NH₂) and bulk CdS powder. The synthesis of a series of dendrimer-stabilized QDs reported here was based on a procedure simi-

lar to that reported by Murphy *et al.*,⁶ but modified in some aspects. For instance, QDs (a) was prepared in the following procedure. 6 ml of a 2 mM CdCl₂ methanol solution was added to 20 ml of a 0.05 mM methanol solution of generation 4 poly (amidoamine) dendrimer with hydroxyl surface groups (PAMAM-OH). The dendrimer-stabilized cadmium ion solution was then titrated with 6 ml of a 2 mM Na₂S solution of methanol while stirring. Hence the obtained CdS/dendrimer solution appears colorless but shows strong blue light luminescence under an UV lamp. A series of other QDs with varied synthesis conditions were also prepared for the comparative MD-XANES study. The experimental conditions will be given below.

The UV-vis absorption spectra of the QDs solution were recorded using a CARY 100 Bio UV-vis spectrophotometer. The QDs were then concentrated and transferred to a solid substrate, a Si (100) single crystal wafer for XRD and XANES characterization. The wide angle x-ray powder diffraction patterns were measured with an INEL automatic powder diffractometer using Cu *K*_{α1} radiation and a linear detector. The XANES measurements were made at the double crystal monochromator (DCM) beamline of the Canadian Synchrotron Radiation Facility (CSRF) located at the Synchrotron Radiation Center (SRC), the University of Wisconsin at Madison. In the MD-XANES measurement, three detection channels, total electron yield (TEY), x-ray fluorescence yield (FLY), and photoluminescence (200–850 nm) yield (PLY), were recorded as a function of soft x-ray energy across the S *K*-edge. TEY and FLY spectra were monitored using specimen current and a multichannel plate fluorescence detector, respectively. X-ray excited optical luminescence (XEOL) was detected using a JYH 100 monochromator which equipped a Hamamatsu photomultiplier (PMT). The XEOL technique^{7,8} involves the measurement of the photoluminescence (PL) at a selected excitation photon energy.

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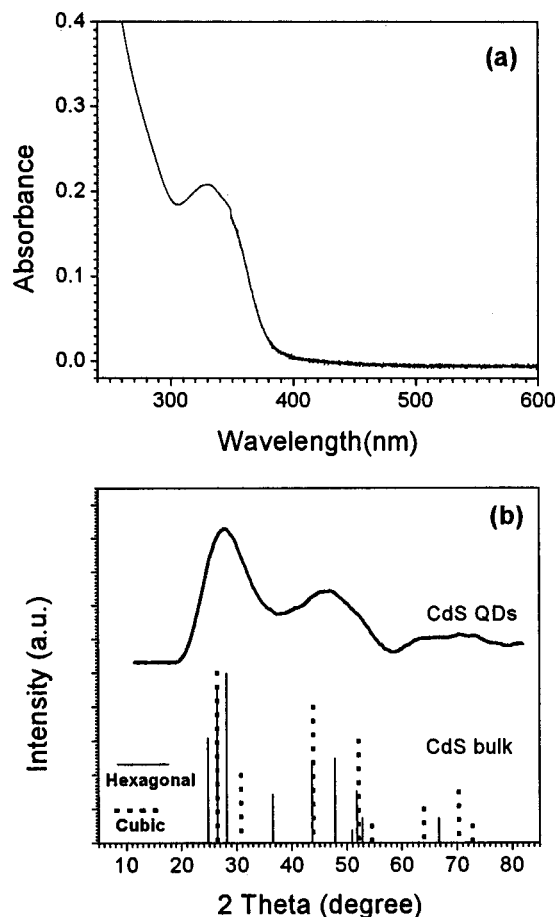


FIG. 1. (a) UV-visible absorption spectrum of the CdS/dendrimer, QDs(a), in methanol. The concentration of cadmium is $\sim 10^{-4}$ M. (b) X-ray powder diffraction patterns of QDs(a). The other two sets of diffraction patterns shown at the bottom were from Ref. 11.

The photoluminescence yield (PLY) in turn can be used to monitor the absorption across the edge.

III. RESULTS AND DISCUSSION

It has been recognized that direct size measurement of the individual QDs by transmission electron microscopy (TEM) could hardly be realized because of the aggregation behavior of dendrimer.^{6,9} However, UV-vis absorption spectra and x-ray powder diffraction (XRD) pattern can still allow us to obtain the average size of the QDs. Figure 1(a) shows the UV-vis absorption of a CdS/dendrimer [QDs (a)] solution. The absorption edge was found to be located at about 380 nm. Comparing with the band gap value of bulk CdS, 2.6 eV (477 nm), there is an obvious blueshift in the absorption edge, which is evidence for the effect of quantum confinement (opening up the band gap) in nanoparticles. Furthermore, the first excitonic absorption feature is found to be around 330 nm. According to the Brus' formula,¹⁰ this feature corresponds to an average diameter of ~ 2 nm for the QDs. This can be regarded as the upper limit of the nanoparticle size since Brus' formula tends to overestimate the size in the strong quantum confinement region.¹ The strong line broadening observed in XRD pattern in Fig. 1(b) is another strong evidence for the formation of the QDs. The measured

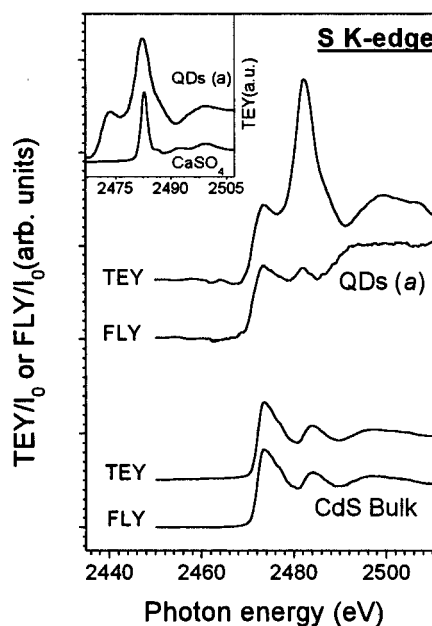


FIG. 2. S *K*-edge XANES of bulk CdS powder and CdS/dendrimer QDs(a) in TEY and FLY. Inset: TEY-XANES of QDs(a) and bulk CaSO_4 .

XRD pattern does not allow us to unambiguously assign the crystallographic structure, since the very broad peaks represent the convolution of several diffraction patterns. However, by comparing the data of bulk CdS shown in Fig. 1(b), our x-ray data seem to be more consistent with a distorted sphalerite cubic crystalline phase. An average diameter of ~ 2 nm is obtained by fitting the line broadening of the XRD peaks,¹² which is basically consistent with the calculated result from UV-vis absorption. Based on the results of size measurements, it is deduced that the QDs are outside of and encapsulated by the dendrimer molecules, since the holes inside of a G4 PAMAM dendrimer is ~ 1 nm.

Figure 2 shows the TEY and FLY XANES, taken at the S *K*-edge, of a CdS QDs specimen [QDs(a)] and a bulk CdS sample. A couple of important features from Fig. 2 are noted. First, in both TEY spectra, two similar edge jumps, known as the *K*-edge jump of sulfide (S^{2-}) species, occur at ~ 2472 eV, but followed by quite different spectral response in the higher energy region, i.e., 2476–2486 eV. While the bulk TEY spectrum shows a relatively weak feature at ~ 2484 eV, usually assigned to electron transition of sulfide from *1s* to empty *p*-like (probably *4p*) orbitals,¹³ a very intense resonance at ~ 2482 eV appears in the QDs TEY spectrum. Second, bulk CdS displays identical XANES in TEY and FLY whereas the QDs show very different features in the region of 2476–2486 eV in the two yields. That is, that the very intense feature at ~ 2482 eV found in the QDs TEY spectrum is dramatically reduced in FLY. By comparing the XANES data of both reference sample CaSO_4 (see inset of Fig. 2) and literature,¹⁴ the feature at ~ 2482 eV in QDs XANES can be attributed to the absorption of sulfur in the form of sulfate (SO_4^{2-}). Given that the probing depths for TEY and FLY are around several and a hundred nanometers, respectively,^{4,15} it has been well established that the TEY spectrum is more surface sensitive whereas FLY more bulk sensitive. This ob-

servation therefore suggests that some surface sulfate layer of several nm or less exists in the CdS QDs sample. Since the SO_4^{2-} species is mainly the surface component, it can be easily understood that the oxide feature only appears as a weak resonance in the more bulk-sensitive FLY spectrum. The question then arising is where the oxide layer of the QDs sample is, on the surface of each individual QD or elsewhere? The suggestion that SO_4^{2-} exists on the surface of each QD is unacceptable if we consider the average diameter of the QDs of ~ 2 nm as obtained from Fig. 1. For such a small size, the contribution of surface component from each QD will hardly be distinguishable from the difference between TEY and FLY spectra. However, based on the aggregation behavior of dendrimers and hence the CdS/dendrimer nanocomposites observed by TEM and dynamic light scattering (they form aggregates of $\sim 10^2$ nm),⁶ we propose that the sulfate is on the surface of the outer layer of the larger dendrimer aggregates. The QDs in the core of the aggregates, unlike those near the aggregates surface that are relatively exposed, are stabilized by intense interaction with the dendrimer branches. Thus they are less susceptible to oxidation, giving little contribution to the ~ 2482 eV feature in the FLY spectrum. It is also possible that the sulfate comes from the oxidation of the unreacted S^{2-} in the system since CdS tends to have a Cd-rich surface even with a 1:1 Cd/S ratio in the reaction. We will return to this below.

To further examine the surface characteristics of the dendrimer stabilized QDs, we next compare the XANES measurements of a series of samples prepared under various conditions. Sample QDs(a) is the CdS nanoparticles with stoichiometry Cd:S = 1:1 stabilized by G4 PAMAM-OH dendrimer (CdS/PAMAM-OH). For QDs (b), (c) and (d), only one aspect of the synthesis conditions is different from QDs (a) while other conditions are the same. They are QDs(b)—ZnS/PAMAM-OH; QDs(c)—CdS/PAMAM-NH₂, and QDs(d)—Cd_{1.5}S/PAMAM-OH. Figure 3 shows the TEY spectra of QDs(a)—(d) together with bulk CdS. The FLY detection results are not shown here, since all the FLY spectra of the QDs are similar to that of bulk CdS, i.e., the strong sulfate resonance does not appear in them. The TEY spectra of QDs(b) and QDs(c) in Fig. 3 are both similar to that of QDs(a) in that the intense sulfate features appear in all of them. The XANES of QDs(d), however, are more like that of bulk CdS, since the strong sulfate resonance cannot be found in both. These observations indicate that the oxide layers are still formed when we change the type of either the metal ions ($\text{Cd}^{2+} \rightarrow \text{Zn}^{2+}$) or the dendrimer end groups ($-\text{OH} \rightarrow -\text{NH}_2$) relative to QDs(a). However, excess Cd^{2+} can dramatically reduce the oxidization of the sulfur in the surface of the QDs aggregates. A closer examination in Fig. 3 about the relative intensity of sulfate feature in QDs(a)—(c) reveals that more sulfate species exist in QDs(a) than QDs(b) and QDs(b) than QDs(c) because the intensity of the ~ 2482 eV feature decreases in the order of QDs(a) > QDs(b) > QDs(c). The difference in the intensity of sulfate features between (a) and (b) may be caused by the difference in counter ions of sulfate, i.e., Cd^{2+} vs Zn^{2+} , which is supported by the slight redshift in their sulfate peaks. The considerably less intense oxide peak in QDs(c) relative to

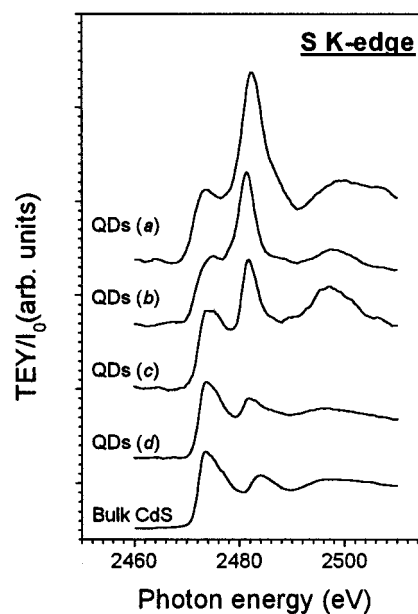


FIG. 3. TEY-XANES at the S K edge of four QDs samples prepared under various conditions together with that of bulk CdS. QDs(a)—CdS/PAMAM-OH, QDs(b)—ZnS/PAMAM-OH, QDs(c)—CdS/PAMAM-NH₂, QDs(d)—Cd_{1.5}S/PAMAM-OH.

QDs(a) [the sulfate resonance in TEY-XANES of QDs(c) is only $\sim 50\%$ intense as that of QDs(a)] is attributed to the better-electron-donation tendency of amine end group in QDs(c) than that of hydroxyl group in QDs(a). If this is true, then it implies that the PAMAM dendrimer branches cannot fully stabilize the QDs prepared at 1:1 Cd:S preparation stoichiometry, at least from the sulfur perspective. In addition, many other factors such as the effect of end groups on the aggregation of dendrimer, should also be taken into account to obtain a more satisfied explanation. The observation that QDs(d) (Cd^{2+} in excess) shows similar TEY spectrum to bulk CdS rather than QDs(a) can be used to deduce the origin of the sulfate species in the QDs. First, it excludes the possibility that the SO_4^{2-} ions come from contamination because QDs(d) were prepared using the same reagents and procedures as QDs(a). Second, it indicates that the reactive surface S(II) species in the QD aggregates are responsible for the existence of SO_4^{2-} ions. Therefore, when Cd^{2+} ions were in excess, the surface S(II) were stabilized by binding to the extra Cd^{2+} ions,¹⁶ resulting in a similar S K-edge XANES to bulk CdS. Another possible origin of the surface oxide layer is, as noted above, related to the oxidation of unreacted S^{2-} , since the preparation of CdS particles typically results in Cd-rich particle surface even if the Cd/S ratio of the starting materials is 1:1. Although both possibilities seem to be supported by the lack of sulfate feature in the XANES of the Cd-in-excess QDs(d), further analysis is required to reach a firm conclusion. It should be noted that the shape of the S^{2-} white line in the four QDs measured in Fig. 3 is slightly different, suggesting that the local structure of S^{2-} in each of them is slightly different. A detailed discussion using EXAFS and XANES will appear elsewhere.¹⁷

Figure 4(a) shows a typical XEOL spectrum excited at 2474 eV of QDs(a). It displays a blue-light maximum emis-

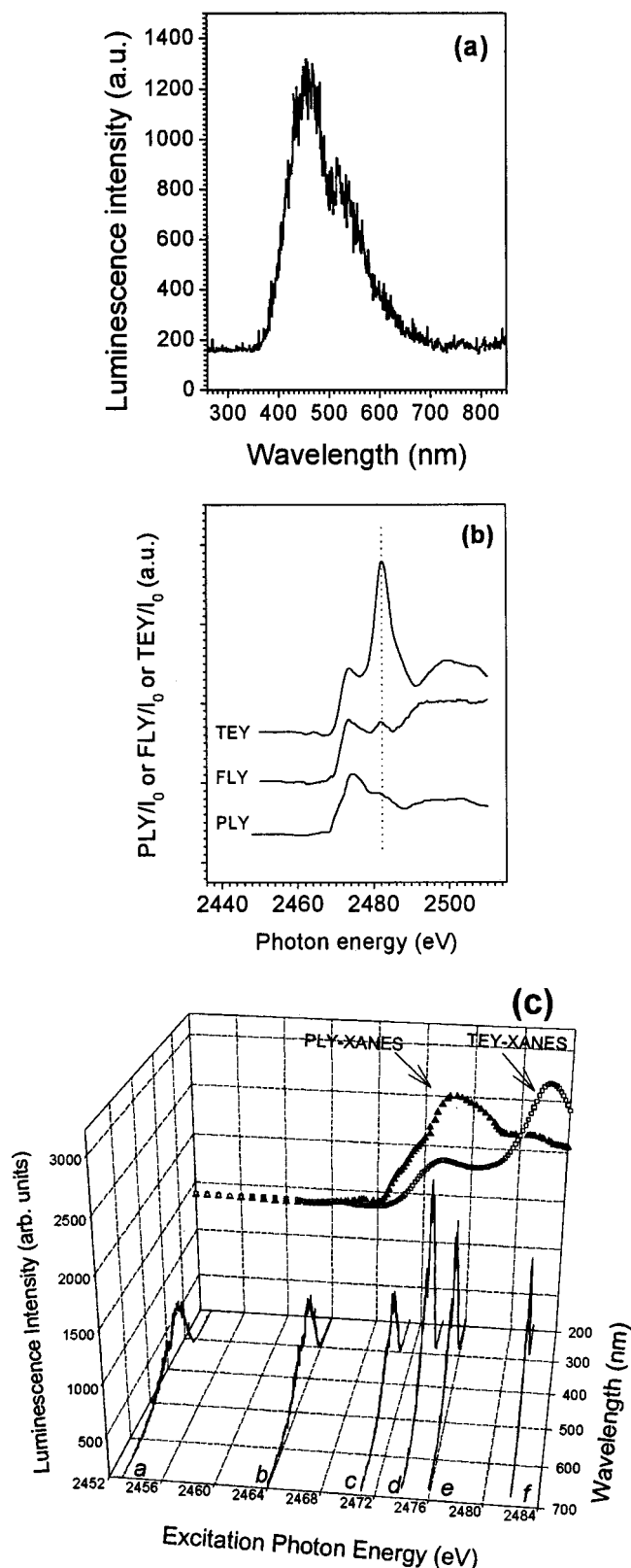


FIG. 4. (a) XEOL spectrum of QDs(a) excited at 2474 eV (the S^{2-} white line); (b) TEY, FLY, and PLY XANES of sample QDs(a). (c) 3D plot of XEOL of QDs(a) with different excitation photon energies near S K edge. XEOL spectra a–f, corresponding to excitation energies of 2453, 2464, 2471, 2474, 2476, and 2482 eV, respectively, basically have similar XEOL band shape. As references, the PLY(zero order) and the TEY XANES are also given and shifted for clarity.

sion at 465 nm followed by a shoulder at ~ 520 nm. It is very similar to the UV-excited spectrum (not shown) because they involve similar radiative decay process, i.e., recombination of holes in the valence band and electrons in the conduction band, regardless of the different excitation process. The blue-light emitting band in XEOL is very stable for more than 2 months in the atmosphere, indicating that each QD is stable in the dendrimer aggregates, not collapsing into bigger CdS whose luminescence band will be redshifted. The optical monochromator of the XEOL was then tuned to zero order (all UV-visible luminescence will be counted) to monitor the PLY XANES across S K edge. Since only sulfur sites that produce photoluminescence efficiently will be responsible for the optical yield, the PLY spectrum should be able to provide information about the local structure of S species contributing to the luminescence of the QDs. In Fig. 4(b), the zero-order PLY spectrum is displayed together with the TEY (more surface sensitive) and FLY (more bulk sensitive). From these multiple-detection-channel XANES, it is evident that the contribution from the SO_4^{2-} species is significant in the more-surface-sensitive yield (TEY), but reduces dramatically in the more-bulk-sensitive yield (FLY) and finally becomes unnoticeable in the luminescence-sites-sensitive yield (PLY). This again confirms our conclusion about the structural characteristics of dendrimer-stabilized CdS QDs in that the QDs are dispersed in the aggregates of dendrimers, that the oxide component is in the form of sulfate existing mainly on the surface of the aggregates outer layer, and that it is the S^{2-} species, not SO_4^{2-} that is responsible for the luminescence behavior of the QDs.

Finally it is shown in Fig. 4(c) a 3D plot of the XEOL excited at several selected photon energies near the S K edge. As references, the PLY and TEY XANES are also shown. The excitation x ray of the XEOL spectra, spectra a to f, were tuned from lower (2453 eV, a) to higher (2482 eV, f) energies. From a to b, there was little change in the XEOL intensity because these two positions are below the K edge. At position c, slightly higher luminescence intensity is observed because the S^{2-} starts to absorb more photons through the sulfur $1s$ core excitation channel (sulfur $1s \rightarrow$ unoccupied states of p character). The luminescence intensity reaches maximum at position d, corresponding to the excitation energy of the white line of S^{2-} species. What is interesting is that when the photon is tuned to the SO_4^{2-} resonance (position f), the corresponding XEOL intensity decreases considerably relative to d, suggesting that sulfate contributes relatively little to the luminescence. The overall variation of the XEOL maximum from position a to f follows the pattern of the zero-order PLY spectrum, supporting the conclusion obtained from Fig. 4(b).

IV. SUMMARY

We have reported the application of MD-XANES to the structural evaluation of dendrimer stabilized CdS QDs. The existence of sulfate species are identified and more importantly, the location of the oxide and hence the configuration

of QDs in the dendrimer aggregates are revealed. A comparison of the XANES results from a series of QDs prepared under varied conditions enables us to study the relationship between the synthetic conditions and the extent of surface stability of the QDs towards oxidation. XEOL and PLY-XANES were also used to analyze the relationship between the luminescence behavior and the structure of the QDs.

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