Lattice contraction in free-standing CdSe nanocrystals

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Colloidal CdSe nanocrystals (NCs) with high photoluminescent quantum yield are fabricated by a method adopting a large initial Se: Cd ratio of the precursors in the solution. X-ray diffraction and Raman measurements confirm that there exists lattice contraction in the free-standing wurtzite CdSe NCs. The lattice contraction indicates the occurrence of surface optimization/reconstruction during the growth, which results in the high quantum yield of the obtained CdSe NCs. © 2002 American Institute of Physics. [DOI: 10.1063/1.1507613]

Colloidal II–VI semiconductor nanocrystals (NCs) are of increasing interest because of their applications as optoelectronic, photochemical, and nonlinear optical materials. An important feature of these NCs is the very large surface-to-volume ratio. For example, CdSe nanocrystals have 10%–50% of their total atoms exposed on the surfaces. Therefore, various passivation ligands have to be used during synthesizing the colloidal NCs to neutralize the surface dangling bonds and to sterically prevent the nanocrystals from touching each other and permanently fusing together. The surface of the resulting NCs might then be considered as an ensemble of dangling and terminated bonds and various point defects. As a result, the complex surfaces of the obtained colloidal semiconductor NCs play an important role in the photoluminescence (PL) quantum yield (QY) and the stability of the emission. An organometallic approach using dimethylcadmium as the cadmium precursor has been well developed during the past ten years to fabricate CdSe NCs. Traditionally, the initial Se: Cd ratio of the precursors in the solution is set close to unity. The best PL QY reported for the as-grown NCs is around 20% in the wavelength range between 520 and 600 nm, and the PL QY can be boosted to 50% with some inorganic/organic surface passivations. Recently, an alternative route with safe and inexpensive cadmium precursors has been introduced, which adopts a large initial Se: Cd ratio of the precursors (in the range of 5–10). The resulting CdSe NCs have high PL QY values (as high as 80% in the orange–red range) and long stability period upon aging at least for several months. Previous work proposed that the high PL efficiency is not only from surface passivation by ligands, but also from surface optimization/reconstruction during growth. In the letter, we further explore and experimentally confirm such surface optimization/reconstruction by taking Raman and x-ray diffraction (XRD) measurements of these newly synthesized NCs.

The fabrication of the colloidal CdSe NCs was described with detail in previous publications. The initial Se: Cd ratio was selected to be 10 to fabricate these CdSe NCs used in this letter. A series of samples was taken from the solution during growth and washed to remove excess surfactants. The size of the NCs, which was controlled by the growth time, ranged between 2.5–6 nm. Transmission electron microscopy (TEM) images indicated that these obtained NC dots are spherical. The PL, absorption, and PL excitation (PLE) measurements were taken for these NCs in toluene solution, but the Raman and XRD measurements were done with these NCs on silicon wafers. The PL QY values were obtained by comparing the integrated PL intensities of the NCs to the well-characterized dye (Rh6G). Figure 1 shows the dependence of PL QY on the size of the NCs. With the increase of the size of the NCs (R), i.e., the growth time, the PL QY increases to a maximum value at R around 4 nm and then decreases. The point was defined as the PL bright point in the previous article. The typical PL, absorption, and PLE spectra are also shown in Fig. 1 (inset). The narrow PL spectral band and the fine features shown in both the absorption and PLE spectra indicate that the obtained CdSe NCs have a narrow size distribution. The size distribution, as determined by measuring TEM images of more than 500 particles for each sample, was about 5%–10%. Hexadecylamine (HDA) was used as the surface ligand for the NCs used in the ex-

FIG. 1. The dependence of PL QY on the size of the CdSe nanocrystals. Three samples used for XRD and Raman measurements are labeled as S1, S2, and S3. The inset shows the typical PL (dashed), absorption (solid), and PLE (dotted) spectra.
perimeter, but the Fourier-transform infrared spectra measurements show that the position and width of vibrational modes related to HDA exhibit no detectable variations among the series of NCs. This indicates that the coordination arrangement between HDA and the surface atoms does not vary via the increase in the size of the NCs. The dependence of PL QY on the size of the NCs shown in Fig. 1 indicates that factors other than the passivation of the ligand might play a vital role in the high PL QY of these NCs fabricated with a large excess of the selenium precursor.

Figure 2 shows the powder XRD spectra of 2.8 (S1), 3.9 (S2), and 5.6 nm (S3) CdSe NCs (The XRD spectra were taken by a Philips X'pert dual goniometer). The diffraction peaks become broader with the decrease of the NC's size and for the large NCs (samples S2 and S3), the crystalline domain calculated from Sherrer equation according to the width of the (110) peak is very close to the average size obtained from the statistics of the TEM image. The diffraction pattern of the sample S3 matches well with the hexagonal wurtzite phase of CdSe, and that of sample S2 matches with the hexagonal wurtzite phase also, but the intensities of the diffraction peaks of (102) and (103) planes (2θ around 46° and 35°) are significantly weak compared to the (110) and (112) peaks. The peaks of CdSe NCs are expected to contain at least one stacking fault, which will make the two neighboring planes of atoms on each side appear as zinc blende. The dramatic change in the XRD pattern shown in Fig. 2 is possibly caused by surface reconstruction occurring when the size of the NCs becomes smaller.11

Compared to bulk CdSe, the central positions of XRD peaks exhibit slight shifts to higher scattering angles. Murray et al. proposed that the prolate shape can induce some shifts in XRD peaks of CdSe NCs. Since TEM images of our NCs indicate that these NCs have a spherical shape, we believe that the shifts measured in our samples are not due to a prolate shape, but from the lattice contraction. The lattice parameters calculated from the positions of (110) and (112) peaks are \( a = 4.291 \, \text{Å} \) and \( c = 6.989 \, \text{Å} \) for Sample S1, \( a = 4.292 \, \text{Å} \) and \( c = 6.996 \, \text{Å} \) for Sample S2, and \( a = 4.296 \, \text{Å} \) and \( c = 7.007 \, \text{Å} \) for Sample S3, respectively. Note that the standard lattice parameters of the bulk CdSe are \( a = 4.299 \, \text{Å} \) and \( c = 7.010 \, \text{Å} \). The smaller the NCs, the stronger the lattice contraction. The lattice contraction effect was observed in the experiment on CdSe NCs in glass matrices.12,13 Since our CdSe NCs are free standing, the presence of the lattice contraction must be induced from surface tension due to surface reconstruction.14 Herron et al. reported that free-standing CdS NCs show a bond contraction of \(-0.5\%\) compared to the bulk.11

The Raman spectra were recorded with a backscattering configuration at room temperature with the 514.5 nm line of Ar\(^+\) laser as the excitation source. The power of the laser was kept at about 0.5 mW to prevent CdSe NCs heating. Figure 3 shows the Raman spectra in the range of \( \Gamma_1 \) (longitudinal optical (LO) phonon mode) in the range of 2077–2077 cm\(^{-1}\)).1,15,16 The dotted lines are the best Lorentzian fits.
NCs of 3.9 nm and 5.6 nm, respectively. The experimental results definitively demonstrate the presence of an additional effect competing with the phonon localization in determining the Raman peak positions of our CdSe NCs. The additional effect is proposed to be the lattice contraction, which has been demonstrated by the XRD measurements in Fig. 2. According to Scamarcio, Lugara, and Manno,\textsuperscript{12} the phonon frequency shift due to the lattice contraction \( [\Delta \omega_c(R)] \) is given by

\[
\Delta \omega_c(R) = \omega_L \left[ \left( 1 + \frac{3 \Delta c}{c} \right)^{-\gamma} - 1 \right],
\]

where \( \gamma \) is the Gruneisen parameter, whose value is about 1.1 for CdSe, \( \omega_L \) is the LO phonon frequency of the c axis since CdSe LO phonons are of vibrations along the c axis.\textsuperscript{13} According to \( \Delta \omega_c(R) = \Delta \omega(R) - \Delta \omega_D(R) \),\textsuperscript{12,13} Equation (1) gives the \( \Delta c/c \) of \( \sim 0.23\% \) and \( \sim 0.06\% \) for samples S2 and S3, respectively, which are consistent with the results from the XRD measurements. Both the XRD and Raman measurements indicate the occurrence of the lattice contraction in the free-standing CdSe NCs.

In the following, we will discuss why the NCs exhibit high QY. With the Se precursor initially in large excess, the concentration of the monomer corresponding to Se in the solution can be kept as a constant after the growth reaction proceeds for a short period of time.\textsuperscript{7,8} In virtue of the relatively stable environment, the accomplishment of an optimal surface morphology or surface reconstruction can be possible, as demonstrated by the experiments on compound semiconductor thin films grown by the molecular-beam epitaxy technique.\textsuperscript{16} The impetus of the surface optimization/ reconstruction process is from the surface tension (\( \sigma \)). This surface tension is experimentally manifested by the lattice contraction, which is a function of the size of the NCs: \( \sigma = \sigma_c + b/R \) where \( \sigma_c \) is the value when \( R \to \infty \) and \( b \) is a constant. The smaller the NCs are, the stronger the surface tension will be to drive the surface optimization/ reconstruction process and, thus, to minimize the nonradiative traps originated from the dangling bonds on the surface of the NCs. On the other hand, the smaller NCs possess too few atoms to define a core crystalline and, thus, own higher stacking faults per unit volume. We believe that these two competing factors related to the size of the NCs result in the bright point in the previous experiment.\textsuperscript{8}

In summary, the microstructure of the newly synthesized colloidal CdSe NCs with high QY was studied by using XRD and Raman spectroscopy. Both the Raman and XRD measurements confirm that there exists lattice contraction in the free-standing wurtzite CdSe NCs. Such study will help us to understand the underlying process in the PL bright point.

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