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Raman analysis of CdSe/CdS core–shell quantum dots with different CdS shell thickness

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Abstract

We report the first-order and high-order Raman scattering from core–shell CdSe/CdS nanocrystals and investigate the evolution of the longitudinal mode of CdSe (LO1) and CdS (LO2), and the surface mode of CdSe (SO1) and CdS (SO2) with increasing shell thickness (0–5.5 ML (monolayer)). We find that the shift of the LO2 peak from 268 to 291 cm^{-1} agrees well with the theoretical values based on the phonon confinement model. The variation of the dielectric environment of the CdSe core with increasing CdS shell thickness is modified according to the shift of SO1 from 198 to 185 cm^{-1} . The SO2 modes at 267 and 275 cm^{-1} , corresponding to the shell thickness 3.5 and 5.5 ML in CdSe/CdS nanocrystals, respectively, are also obtained for the first time in our experiment. Moreover, they agree well with the theoretical values of the dielectric corresponding function model. Besides, a new Raman peak at 482 cm^{-1} is observed, and it remains at that value with shell growth, the new peak is supposed to be caused by the alloying at the core–shell interface. Therefore, Raman spectroscopy can be used to determine the shell thickness and other surface and interface parameters of CdSe/CdS core–shell nanocrystals.

1. Introduction

It is well known that nanocrystals (NCs) have a high surface to volume ratio, and many of their optoelectronic characteristics are related to the nature of the surface [1, 2]. Surface atoms act like defect sites unless they are passivated [2]. A CdSe core capped by an inorganic shell CdS has been suggested as a good example for surface passivation in order to improve the photoluminescence quantum efficiency [3–5]. Recently, core–shell NCs have

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mostly been analyzed through x-ray diffraction (XRD), photoluminescence spectroscopy (PL), optical absorption spectroscopy (OAS), and high-resolution transmission electron microscopy (HRTEM). However, the XRD analysis shows a clear contribution from the CdS shell only for samples with high CdS coverage [3, 5], and the internal structure of the shell and the interface between core and shell is not discernible by HRTEM due to lack of resolution [5]. If the core size is unknown, even the thickness of the shell cannot be distinguished. Besides, although the core size can be obtained through optical measurement, it is difficult to determine the shell thickness of core-shell NCs [6]. On the other hand, Raman spectroscopy is a fast and non-destructive technique for the estimation of the composition and size of NCs, as well as obtaining some additional information, such as disorder, compressive stress, size distribution, and so on [7–9]. It has been successfully used for the analysis of glass-embedded $\text{CdS}_x\text{Se}_{1-x}$ NCs, which shows a two-mode behavior simultaneously with the CdS-like and CdSe-like modes [10, 11]. There exist a few studies on the Raman spectra of core-shell CdSe/CdS [12, 13], and CdSe/ZnS [14] NCs. Roy [12] compared the Raman spectra of core-shell CdSe/CdS NCs with shell thickness 0.6 nm with bare-core CdSe NCs. Dzhagan [13] reported the Raman spectra of core-shell CdSe/CdS and CdSe/ZnS NCs synthesized in aqueous solutions at different excitation wavelength. However, the evolution of the longitudinal mode (LO) frequency for CdSe and CdS, and the surface mode (SO) for CdSe and CdS with different shell thickness has not been studied as far as we know. In this paper, we report the first-order and high-order Raman scattering from bare-core CdSe NCs and core-shell CdSe/CdS NCs with different shell thickness. A reliable method to determine the shell thickness of CdSe/CdS core-shell NCs by Raman measurement is also proposed.

2. Experimental details

The bare-core CdSe NCs and core-shell CdSe/CdS NCs were prepared by an organometallic synthetic approach in two steps [3, 15]. Five samples with the same core size (3.3 nm) and CdS shell thickness 0, 1, 2.3, 3.5 and 5.5 ML were used for spectroscopic measurements; the shell thicknesses were confirmed by HRTEM. The average thickness of one monolayer of CdS is 0.35 nm.

Absorption spectra were measured on an HP 8453 diode array spectrophotometer. PL spectra were measured with a HITACHI F-2500 fluorescence spectrophotometer. HRTEM images were taken using a JEOL 2000 FX microscope with an acceleration voltage of 200 kV. XRD patterns were obtained using a Philips PW1830 x-ray diffractometer. The Raman spectra were recorded with the 514.5 nm line of an Ar⁺ laser as the excitation source in a back-scattering configuration at room temperature. The spectral resolution of the spectrometer was about 1 cm^{-1} . The power of the laser was kept at about 0.5 mW and the accumulation time was only 5 s to prevent heating CdSe NCs and reduce the PL background. In addition, it was essential to remove excess organic ligands to obtain meaningful Raman peaks. The NCs were precipitated by adding acetone into the chloroform solution and isolated by centrifugation and decantation twice to remove excess reaction materials. Finally, the NCs were deposited on a glass substrate from their chloroform solution for Raman measurement.

3. Results and discussion

3.1. Optical and structural characterization

The optical properties of the bare-core CdSe NCs and the core-shell CdSe/CdS NCs with the shell thickness 1, 2.3, 3.5 and 5.5 ML are presented in figure 1. The growth of the CdS shell

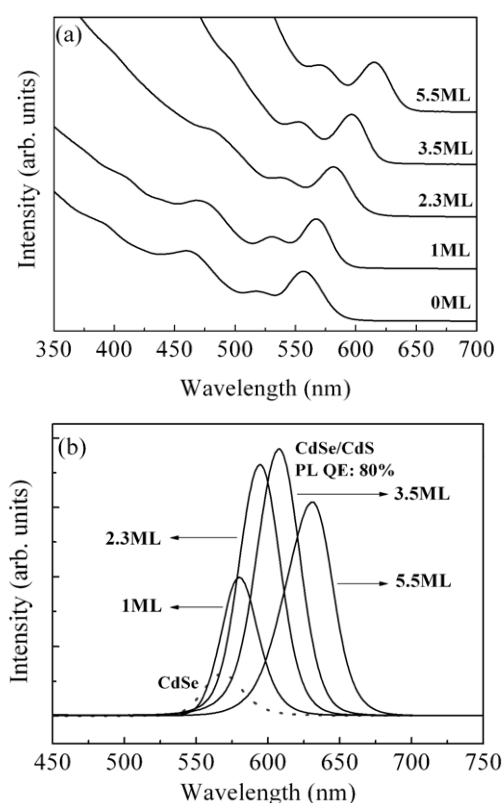


Figure 1. (a) Absorption and (b) emission spectra for bare-core CdSe NCs and core-shell CdSe/CdS NCs with different shell thickness.

results in a considerable shift of the emission peak from 568 nm (bare-core NCs) to 630 nm (core-shell NCs, 5.5 ML), and a corresponding shift of the first exciton absorption peak from 556 to 615 nm. Similar shifts induced by the partial leakage of the exciton into the shell have previously been reported for CdSe/CdS [3, 4] and CdSe/ZnS [6]. In addition, with the shell growth, the emission intensity first increases progressively because of the increasing passivation of the core surface, then decreases greatly as the shell grows to 5.5 ML, presumably as a result of the higher concentration of structural defects created within the thicker deposited shell [4, 5]. In addition, when the shell thickness grows from 0 to 3.5 ML, the full widths at half maximum (FWHMs) of the emission peaks are almost the same (30 nm). The similar FWHMs of the emission peaks and sharp feature absorption peaks suggest that CdSe/CdS core-shell NCs have similar size distribution below 10% [5]. With the shell thickness grows to 5.5 ML, the FWHM of the emission peak broadens to 35 nm, which indicates the size distribution deterioration.

Figure 2 shows the powder XRD patterns from bare-core CdSe NCs, and from core-shell CdSe/CdS NCs with shell thickness 3.5 ML. They reveal a wurtzite structure. The lattice parameters of bare-core CdSe calculated from the (110) and (112) peaks are $a = 4.295 \text{ \AA}$ and $c = 7.007 \text{ \AA}$. Compared to the bare-core CdSe NCs, the diffraction peaks of core-shell NCs become broader and shift to higher diffraction angles, towards those of the wurtzite bulk CdS. In fact, when the shell thickness is less than 2 ML, the diffraction peaks do not show obvious difference from those of the bare-core CdSe NCs [5].

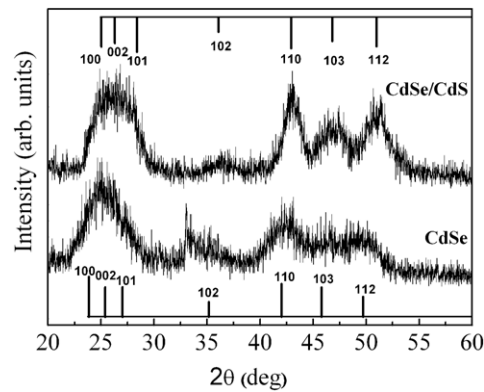


Figure 2. X-ray diffraction patterns from bare-core CdSe NCs and core-shell CdSe/CdS NCs with shell thickness 3.5 ML. Note: the diffraction angle 33° in CdSe NCs belongs to substrate Si(211).

In figure 3, HRTEM micrographs of the bare-core CdSe and core-shell CdSe/CdS NCs are presented. The NCs are almost spherical. The average diameter of bare-core CdSe NCs and core-shell CdSe/CdS NCs is 3.3 nm and 5.8 nm, respectively. Since the CdSe/CdS NCs were prepared by adding shell precursors on the same batch of the CdSe NCs, it is reasonable to assume the same core size in the CdSe/CdS as in the bare-core CdSe.

3.2. Analysis of Raman spectroscopy

3.2.1. Raman line shape: first-order and high-order Raman scattering. The Raman spectra of bare-core CdSe NCs and CdSe/CdS core-shell NCs with different shell thickness are presented in figure 4. The outstanding peak in the Raman spectrum of bare-core CdSe NCs is attributed to the scattering of CdSe longitudinal optic phonons; the peak at 201.9 cm^{-1} is marked as LO1. With the bare-core CdSe NCs capped by a 1 ML CdS shell, a new peak appears at 268 cm^{-1} on the right of the LO1 peak; moreover, it shifts to higher frequency (291 cm^{-1}) gradually with the shell growth along with showing increasing intensity. The new peak is caused by the scattering of longitudinal optic phonons of CdS shell and is marked as LO2. This provides evidence for the Raman response from the shell in CdSe/CdS NCs, even through the shell thickness is only 1 ML. In addition to the first-order Raman line, the high-order Raman peaks are also observed showing a difference mode: 2LO1 , the second-order phonon frequency of CdSe located at 407 cm^{-1} , 2LO2 at 585 cm^{-1} , and another mode at 482 cm^{-1} . To explain the 482 cm^{-1} mode, let us look at the case of the ternary alloy $\text{CdS}_x\text{Se}_{1-x}$: the peak between 480 and 500 cm^{-1} is the combination mode of $\text{LO1} + \text{LO2}$ (the sum of a CdSe-like LO mode and a CdS-like LO mode) and it shifts with the varying composition x [7]. However, in the core-shell CdSe/CdS NCs system, as shown in figure 4, when the shell thickness grows to 2.3 ML, the new peak appears at 482 cm^{-1} , which is almost the sum of $\omega_{\text{LO1}} = 201.9$ and $\omega_{\text{LO2}} = 279.1\text{ cm}^{-1}$. As the shell thickness further increases, it remains at 482 cm^{-1} , while the LO2 peak shifts to high energy. In addition, a peak at 482 cm^{-1} was also observed at the core-shell CdSe/ZnS NCs [13]. Consequently, it is supposed to be caused by the alloy $\text{CdS}_x\text{Se}_{1-x}$ in the interface of core-shell NCs. We also note here that the peaks of the LO1 and LO2 modes show an asymmetric line shape towards the lower-frequency side as observed in mixed semiconductors such as $\text{CdS}_x\text{Se}_{1-x}$ [16–18], $\text{Al}_x\text{Ga}_{1-x}\text{As}$ [19, 20], and $\text{CdZn}_x\text{Te}_{1-x}$ [21]. With further shell growth, this asymmetry becomes so prominent that the shoulders, marked by the arrows in figure 4, on the left of the main peaks LO1 and LO2 can be clearly observed. This has been

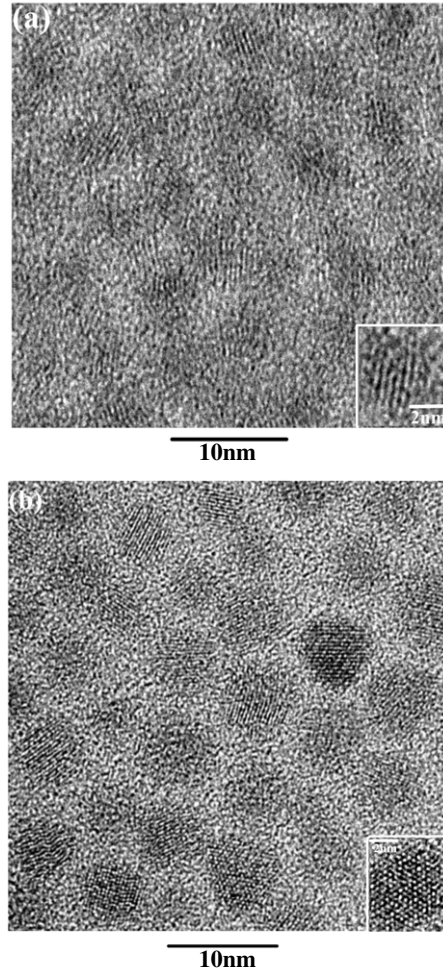


Figure 3. HRTEM images of (a) CdSe bare-core NCs and (b) CdSe/CdS NCs with 3.5 ML shell thickness.

explained by the increasing role of surface phonons [10, 17, 18] as well as by confinement-induced scattering from phonons with non-zero wavevectors [22, 23]. We attempted to fit the observed line shape with a combined line shape $I^j(\omega) = I_c^j(\omega) + I_{sp}^j(\omega)$, where $I_{sp}^j(\omega)$, $I_c^j(\omega)$ are taken to be a Lorentzian function $I_{sp}^j(\omega) = \frac{B^j \Gamma_{sp}^j}{(\omega - \omega_{sp}^j)^2 + (\Gamma_{sp}^j)^2}$, $I_c^j(\omega) = \frac{A^j \Gamma_c^j}{(\omega - \omega_c^j)^2 + (\Gamma_c^j)^2}$, where $j = 1$ is for the CdSe mode, and $j = 2$ is for the CdS mode; ω_{sp}^j and Γ_{sp}^j are the peak position and the FWHM for the surface mode (SO), and ω_c^j and Γ_c^j are the peak position and the FWHM for the confinement phonon mode (LO), respectively. We fit the spectrum from 100 to 340 cm^{-1} for all samples. The best fits obtained for all samples are shown in figure 5. The peak position and FWHM given by the fits are presented in table 1.

3.2.2. Confinement optical phonon. Compared to the LO phonon frequency of the bulk CdSe 210 cm^{-1} [18], the LO1 frequency 201.9 cm^{-1} of bare-core CdSe shifts to lower energy by 8.1 cm^{-1} . The shift originates mainly from the phonon confinement effect [24]. Actually, the

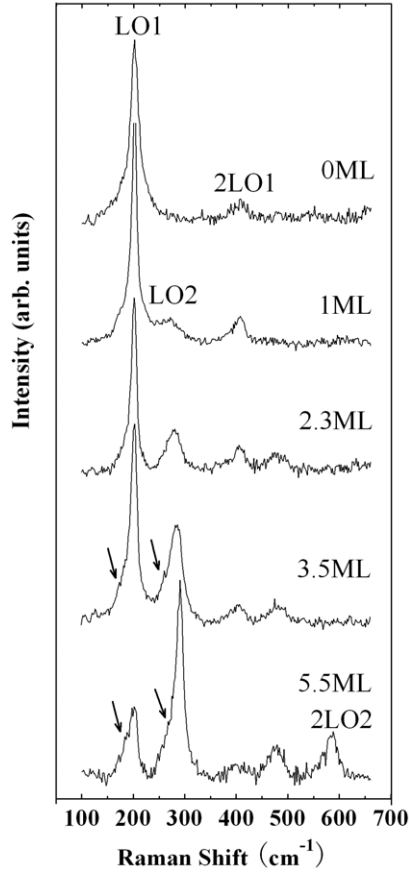


Figure 4. Optical Raman spectra for bare-core CdSe NCs and core-shell CdSe/CdS NCs with different shell thickness.

Table 1. The values ω_{sp}^j , Γ_{sp}^j , ω_c^j and Γ_c^j obtained from Lorentzian fit in figure 5. $j = 1$ is for the CdSe mode, and $j = 2$ is for the CdS mode.

Sample (ML)	LO1		SO1		LO2		SO2	
	ω_c^1 (cm ⁻¹)	Γ_c^1 (cm ⁻¹)	ω_s^1 (cm ⁻¹)	Γ_s^1 (cm ⁻¹)	ω_c^2 (cm ⁻¹)	Γ_c^2 (cm ⁻¹)	ω_s^2 (cm ⁻¹)	Γ_s^2 (cm ⁻¹)
0	201.9	18	198.3	60				
1	201.9	10	195.0	44	268.2	56		
2.3	201.9	10	191.4	19	279.1	26		
3.5	201.9	13	184.8	23	285.4	24	267.2	32
5.5	201.9	16	185.0	26	291.5	16	275.2	25

phonon frequency has a small blue shift due to the lattice contraction given by the formula [25] $\Delta\omega_c = \omega_L[(1 + 3\frac{\Delta c}{c})^{-\gamma} - 1]$, where ω_L is the LO phonon frequency of the bulk CdSe, $\frac{\Delta c}{c}$ is the lattice contraction, and γ is the Grüneisen parameter. The bare-core CdSe in our experiment is wurtzite with the lattice parameters $a = 4.295 \text{ \AA}$ and $c = 7.007 \text{ \AA}$. If $\omega_L = 210 \text{ cm}^{-1}$ [18], $\gamma = 1.1$ [25] and $\Delta c/c = 0.04\%$, the calculated blue-shift value is only 0.3 cm^{-1} , which

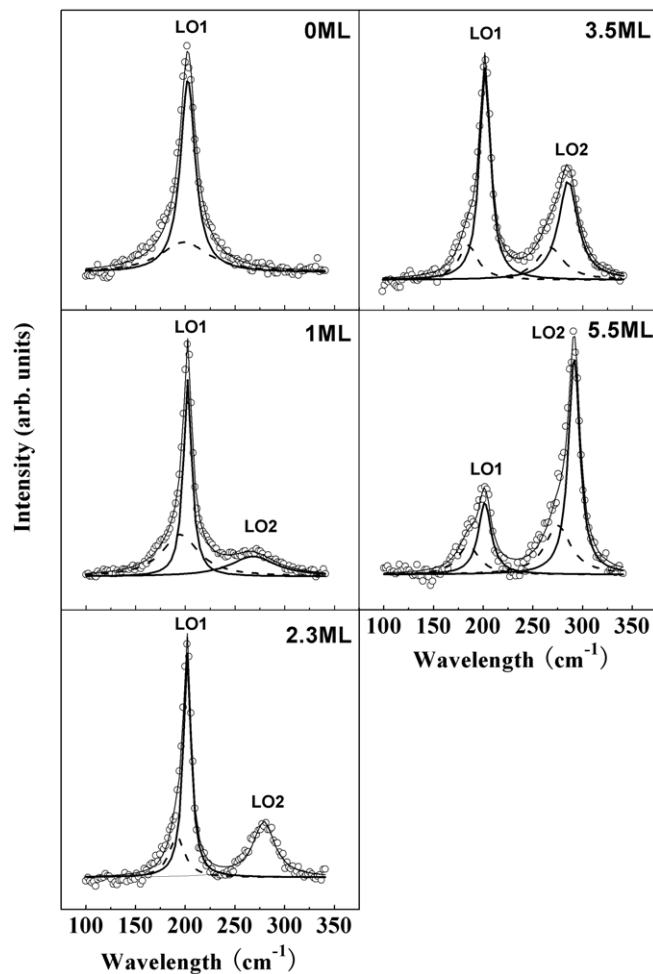


Figure 5. First-order Raman spectra for bare-core CdSe NCs and core-shell CdSe/CdS NCs with different shell thickness. The solid curves are the first-order mode and the dashed curves are the surface mode.

can be neglected. With the shell growth on the bare-core CdSe NCs, we expected that a stress would occur at the interface of the core-shell NCs, which will induce a LO1 peak shift to high energy by almost $1\text{--}2\text{ cm}^{-1}$, as observed in CdSe/ZnS [24, 14]. However, the LO1 peak remains at 201.9 cm^{-1} as the shell grows from 1 to 5.5 ML. This indicates that the stress across the interface of CdSe/CdS NCs is less than the case of CdSe/ZnS NCs; this may be due to the fact that the lattice mismatch of CdSe and CdS is only 3.9%, less than that of CdSe and ZnS, 12% [4]. Consequently, the stress induced by the CdS shell layer is too small to be detected through Raman spectroscopy. With the bare-core CdSe NCs capped by 1 ML CdS shell, the FWHM of the LO1 peak reduces greatly from 18 to 10 cm^{-1} . This can be explained by the fact that most of the surface defects of CdSe NCs, such as dangling bonds and unsaturated bonds, have been passivated by the CdS shell layer. However, as the shell thickness grows to 5.5 ML, the FWHM of the LO1 peak becomes broader (up to 16 cm^{-1}), which is related to disorder effects that may originate from the deterioration of the size distribution [10].

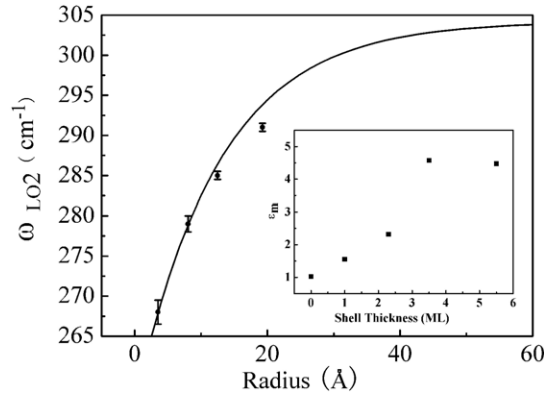


Figure 6. Size-dependent LO phonon frequency of CdS. The theoretical line is from [27], and the square dots represent our experimental LO2 data. The inset picture is the variation of the calculated dielectric constant of the surrounding medium of the CdSe core layer with the increasing shell thickness.

As a result of the phonon confinement effect, the LO2 peak shows a large blue shift from 268.2 to 291.5 cm⁻¹ accompanied with the line width becoming narrowed as the shell grows. The size dependence of the theoretical and the experimental LO2 values is presented in figure 6. The theoretical curve is from [26], which was obtained according to the phonon confinement model proposed initially by Compbell and Faucet [27, 28]. It is clear that the experimental values are in good agreement with the theoretical line. Thus, the Raman spectra can be well used to determine the shell thickness of CdS, which is not available through XRD, PL and HRTEM (in the case of the core size being unknown). Although the LO2 frequency for the sample with 1 ML shell thickness has the same value (268 cm⁻¹) as the observed local mode due to a small S concentration in CdSe [18], the LO2 frequency shifts to 265 cm⁻¹ when the shell thickness is less than 1 ML (not shown here). Therefore, the value 268 cm⁻¹ belongs to the LO2 mode, not to the local mode. The FWHMs of the LO2 peak for all samples are larger than the theoretical values by 3–5 cm⁻¹ [29, 30], which indicates the stronger contribution of disorder-related effects induced by non-homogeneous growth of the CdS shell layer. In addition, the circularity geometry of the shell layer is also responsible for the broad FWHM [27, 28].

3.2.3. Surface phonons. The surface mode of CdSe (SO1) also shows a shift from 198.3 to 185.0 cm⁻¹ as the shell thickness increases from 0 to 5.5 ML, as shown in table 1. This general trend can be explained by the variation of the surrounding dielectric environment. In the case of Fröhlich interaction, the frequency of the surface mode is given by [31] $\omega_{LO}^S = \omega_{TO} \left[\frac{\epsilon_0 l + \epsilon_m (l+1)}{\epsilon_\infty l + \epsilon_m (l+1)} \right]^{1/2}$, where l is the angular momentum, and ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants of the bulk CdSe. ϵ_m is the dielectric constant of the surrounding medium of the CdSe core layer: its value changes from $\epsilon_m = 1$ to 9.1 [32]. Thus, the calculated ω_{LO}^S varies from 198.4 to 178.9 cm⁻¹ by assuming the parameters $l = 1$, $\epsilon_0 = 9.3$ [14], $\epsilon_\infty = 6.1$ [14] and $\omega_{TO} = 168$ cm⁻¹ [18]. Obviously, the experimental values 198.3–185.0 cm⁻¹ are in the range of the theoretical values. However, it is known that the average dielectric constant of NCs would decrease with decreasing radius R of the spherical clusters [33], which indicates that the value $\epsilon_m = 9.1$ should be modified. In addition, the dielectric interface of air and CdS, especially for the considerably thin CdS shell layer, would also affect the dielectric environment of CdSe [34]. Thus, we modify the value ϵ_m by substituting our experimental SO1 values in the equation for the surface mode. The

calculated ε_m ranged from 1.02 to 4.47, as shown in the inset of figure 6. In addition, as the shell grows from 0 to 3.5 ML, SO1 first gradually shifts from 198.3 to 185.0 cm^{-1} , then remains at 185.0 cm^{-1} with the shell growing further to 5.5 ML. This reveals that, when the shell thickness grows to 3.5 ML, the bare-core NCs are supposed to be completely covered by a CdS shell layer. Thus, the optimal shell thickness for CdSe/CdS NCs is 3.5 ML, which is consistent with the result that the PL efficiency of CdSe/CdS NCs with a ~ 3.5 ML thick CdS shell is the most stable under 80 h of UV illumination [5].

The surface mode of CdS (SO2) in CdSe/CdS NCs is now analyzed. When the shell thickness is 1 or 2.3 ML, there is no obvious surface mode of CdS observed in the Raman spectra (see figure 4). Such a case was also observed for the CdSe NCs [18, 35]. However, the surface mode of CdS becomes prominent at 267 cm^{-1} when the shell thickness grows to 3.5 ML; it shifts to high energy (275 cm^{-1}) as the shell thickness grows to 5.5 ML. The surface phonons in a core-shell structure in a host medium have been studied by the dielectric continuum approach, given by [32]:

$$\frac{\varepsilon_2(\omega)}{\varepsilon_m} = -\frac{[\gamma^{2l+1} - 1]\varepsilon_1(\omega) + [1 + \gamma^{2l+1}(l+1)/l]\varepsilon_2(\omega)}{[\gamma^{2l+1} - 1]\varepsilon_2(\omega) + [1 + \gamma^{2l+1}l/(l+1)]\varepsilon_1(\omega)},$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are $\varepsilon_i(\omega) = \varepsilon_\infty^i \frac{\omega^2 - \omega_{LOi}^2}{\omega^2 - \omega_{TOi}^2}$ ($i = 1, 2$ corresponds to the CdSe core layer and the CdS shell layer, respectively), ω_{LOi} and ω_{TOi} are longitudinal and transverse mode phonon frequencies for the bulk CdSe and CdS, $\gamma = b/a$ is the ratio of the diameter of the core-shell NCs to that of the core, and ε_m is the dielectric constant of the surrounding medium of the nanocrystals. By using the parameters $\varepsilon_m = 1$ (air), $\varepsilon_\infty^1, 6.1$ [14], $\omega_{LO1}, 210 \text{ cm}^{-1}$ [18], $\omega_{TO1} = 168 \text{ cm}^{-1}$ [18], $\varepsilon_\infty^2, 5.5$ [32], $\omega_{LO2}, 302 \text{ cm}^{-1}$ [18], and $\omega_{TO2} = 238 \text{ cm}^{-1}$ [18], the values obtained for SO1 and SO2 are 187 cm^{-1} and 266 cm^{-1} , respectively, when the shell thickness is 3.5 ML ($b = 5.75 \text{ nm}$, $a = 3.3 \text{ nm}$). They are very close to our experimental values 185 cm^{-1} (SO1) and 267 cm^{-1} (SO2). Similarly, when the shell thickness is 5.5 ML, the calculated values are 189 cm^{-1} (SO1) and 269 cm^{-1} (SO2), which deviate from the experimental 185 and 275 cm^{-1} by about 5 cm^{-1} . This may be due to the fact that the core-shell NCs could deviate from being spherical more easily as the shell thickness grows to 5.5 ML. The interface phonon modes strongly depend on the NC geometry [36], which was not considered in the dielectric response function model [32].

4. Conclusions

To summarize, we have reported the Raman scattering from bare-core CdSe and core-shell CdSe/CdS NCs and have shown the evolution of the longitudinal mode frequency of CdSe (LO1) and CdS (LO2), and the surface mode of CdSe (SO1) and CdS (SO2) with the increasing shell thickness from 0 to 5.5 ML. The observed LO1 and LO2 agree well with the theoretical values based on the phonon confinement effect. SO1 and SO2 also agree well with results from the dielectric response function model. With the CdS shell growing from 0 to 5.5 ML, the dielectric constant of the medium surrounding the CdSe core layer varies from 1.02 to 4.47. In addition, the new observed Raman peak at 482 cm^{-1} is supposed to be caused by alloying at the core-shell interface. Therefore, Raman measurements can serve well to determine the shell thickness of CdSe/CdS NCs and to obtain some surface and interface parameters of the NCs.

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