

# PHONON CONFINEMENT AND SURFACE PHONON MODES IN CdSe-CdS CORE-SHELL NANOCRYSTALS

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**Abstract.** The main aim of this article is to demonstrate the unique characteristics of the nanocrystals, such as confinement of optical phonons and the appearance of surface phonons in CdSe-CdS core-shell particles. Including the optical phonon confinement in core and shell components of the particles separately, we have estimated the diameter of the particle and the shell thickness, which have been further matched with the measured values of the same from transmission electron microscopy. Making use of the dielectric continuum model, we have matched the experimental and theoretical values of the frequencies of the surface phonon modes.

## 1. INTRODUCTION

The current direction of research in understanding the physical properties of semiconductor nanoparticles, due to quantum confinement effects, includes modification of size-quantized semiconductor particles by means of surface chemistry. In core-shell nanoparticles, the surface of the particles is passivated by inorganic shell component. As the band gap of the capping material is higher than that of the core material, the non-radiative decay channels through surface states are not accessible to photo-excited electrons, generated within the core [1]. Thus, core-shell structures show higher luminescence quantum yield.

The phonons are also confined in nanocrystals. In bulk materials, Raman modes obey the fundamental selection rule  $\bar{q}=0$ , where  $\bar{q}$  is the wavevector of the scattered phonon. In finite domain, this selection rule is relaxed. All phonon modes with  $\Delta q \cong 2\pi/d$ , where  $d$  is the dimension of the crystallite domain, contribute to the Raman intensity [2]. Another important observation from nanocrystals is the appearance of surface phonon (SP) modes. In the frequency range between bulk longitudinal optical (LO) phonon frequency,  $\omega_{LO}$ , and transverse optical (TO) mode frequency,  $\omega_{TO}$ , a new mode, known as surface phonon mode, appears in nanocrystals, which is absent in corresponding bulk materials [3].

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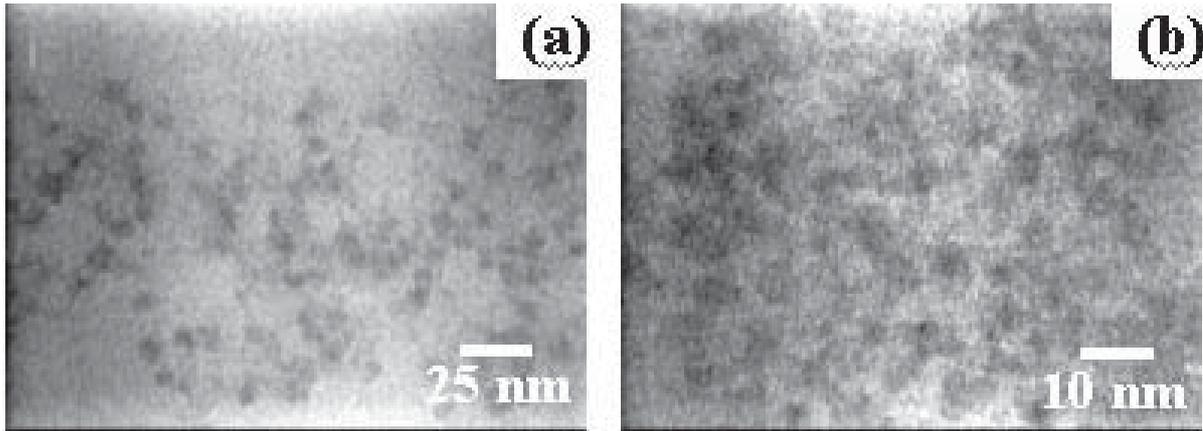


Fig. 1. Transmission electron micrographs of (a) Sample A and (b) Sample B.

The inorganic capping of CdSe core by CdS results better surface passivation and high photostability [4-7]. In this report, we have quantitatively compared the asymmetric Raman line shape in CdSe-CdS core-shell particles and CdSe bare particles including both confined optic modes and surface phonon modes. The observed frequencies of SP modes in these systems have been compared with the calculation based on the dielectric continuum model.

## 2. SAMPLE PREPARATION

### A. Preparation of mercaptoacetic acid stabilized CdSe nanocrystals: Sample A

Following Liu *et al.* [8], 150 ml of  $\text{Cd}(\text{ClO}_4)_2$  ( $2 \cdot 10^{-4}$  M) and 150 ml of  $\text{HS-CH}_2\text{-COOH}$  ( $2 \cdot 10^{-4}$  M) were mixed and stirred vigorously for about 5 min. Subsequently, 0.5 ml of  $\text{Na}_2\text{SeSO}_3$  was added drop wise to the solution and boiled again for about half an hour under stirring condition. The solution turned orange in color indicating the formation of CdSe particles.

### B. Preparation of mercaptoacetic acid stabilized CdSe-CdS core-shell nanocrystals: Sample B

For the preparation of coated CdSe-CdS particle, the above CdSe solution was cooled to 50 °C and 20  $\mu\text{l}$  of  $\text{Cd}(\text{ClO}_4)_2$  (0.1M) and 20  $\mu\text{l}$  of  $\text{Na}_2\text{S}$  (0.1M) were added drop wise alternatively under stirring condition in  $\text{N}_2$  atmosphere. After 30 min of stirring the

solution turned orange-red in color due to formation of CdSe-CdS core-shell particles.

## 3. AVERAGE PARTICLE SIZE AND SIZE DISTRIBUTION: HRTEM

Transmission Electron Microscopy (TEM) images have been used to determine the particle size in afore-mentioned nanocrystals. TEM micrographs for Sample A and Sample B are shown in Figs. 1a and 1b, respectively. The average particle sizes for Sample A and Sample B are estimated to be 5.2 and 5.4 nm, respectively.

## 4. CONFINEMENT OF OPTIC PHONON AND SURFACE PHONON MODES: RAMAN SCATTERING

Raman spectra are obtained using 1200 g/mm holographic grating, a holographic supernotch filter, and a Peltier cooled CCD detector. Spectra are taken using a 488 nm Argon ion laser as an excitation source. The slit width of the spectrometer during the experiment was 50  $\mu\text{m}$ . The first order Raman spectra for the samples are shown in Fig. 2. Using the phonon confinement model of Campbell and Fauchet, the first order Raman intensity  $I_c^j(\omega)$  is given by [2]

$$I_c^j(\omega) = A \int_0^{q_{\max}} \frac{|C(0, \mathbf{q})|^2 d^3 \mathbf{q}}{[\omega - \omega(\mathbf{q})]^2 + (\Gamma_{0j} / 2)^2}, \quad (1)$$

where  $\omega(\mathbf{q})$  and  $\Gamma_{0j}$  are the phonon dispersion curve and the natural line width (FWHM) of the corresponding bulk materials,  $C(0; \mathbf{q})$  is the Fourier coefficient

of the phonon confinement function.  $A$  is an arbitrary constant.  $j=1$  for CdS and  $j=2$  for CdSe. For nanoparticles, it has been shown that the phonon confinement function, which fits the experimental

data best, is  $W(r, \bar{d}_z) = \exp\left(\frac{-8\pi^2 r^2}{\bar{d}_z^2}\right)$ , the square of the Fourier coefficient of which is given by

$|C(0, \mathbf{q})|^2 \equiv \exp\left(-\frac{q_2^2 \bar{d}_z^2}{16\pi^2}\right)$ . Here,  $\bar{d}_1$  is the average size of the spherical nanocrystals in Sample A and  $d_2$  is the average diameter of the core in Sample B. For the shell component of the core-shell particles, we have used an additional confinement function, suitable for layers, given by [2]

$$|C(0, \mathbf{q})|^2 \equiv \exp\left(-\frac{q_1^2 t^2}{16\pi^2}\right) \left[1 - \operatorname{erf}\left(\frac{q_1 t}{\sqrt{32\pi}}\right)\right]^2, \quad (2)$$

where  $t$  is the average shell thickness for the particles. The average phonon dispersion in the bulk CdSe and CdS crystal for the LO phonon modes are taken as [10,11]

$$\omega(\mathbf{q}) = \omega_0^j - \Delta\omega^j(q_j^2), \quad (3)$$

which fits the experimental curve well in the direction of  $\Gamma$ -M upto  $q_{\max} = 0.4$ .  $\omega_0^j$  is the corresponding bulk LO phonon frequency:  $\omega_0^1 = 302 \text{ cm}^{-1}$  and  $\omega_0^2 = 213 \text{ cm}^{-1}$ .  $\Delta\omega^j$  is the band width of bulk LO phonon branch:  $\Delta\omega^1 = 102 \text{ cm}^{-1}$ ,  $\Delta\omega^2 = 118 \text{ cm}^{-1}$ . We have taken  $a_1 = 5.82 \text{ \AA}$  and  $a_2 = 6.08 \text{ \AA}$  [12]. The expressions for  $d\mathbf{q}^3$  in Eq. (1) are taken to be  $4\pi q^2 dq$  for the core component and  $dq$  for the shell component.

In the low frequency region of the LO phonon peak, we have observed an additional feature in the spectra for Sample A and Sample B. Keeping in mind the presence of SP modes between longitudinal and transverse optical phonon modes, together with the confined optical phonon, we have fitted this additional peak with the Lorentzian function

$$I_{SP}^j(\omega) = \frac{B\Gamma_{SP}}{(\omega - \omega_{SP})^2 + \Gamma_{SP}^2}, \quad (4)$$

where  $\omega_{SP}$  and  $\Gamma_{SP}$  are the peak position and the HWHM, respectively, for the SP mode. We fit the full spectrum for Sample A and B by a combined line shape  $I(\omega) = I_c^j(\omega) + I_{SP}^j(\omega)$ . The best fit obtained for both the samples are shown by the solid lines in Fig. 2. The phonon confinement components

are shown by dashed lines and the surface phonon components are shown by dotted lines in Fig. 2. In the fitting procedure, we have kept  $\bar{d}_z$ ,  $t$ ,  $\omega_{SP}$ ,  $\Gamma_{SP}$ ,  $A$  and  $B$  as fitting parameters. From the non-linear least square fit, the average particle size ( $\bar{d}_1$ ) for Sample A is obtained as 4.7 nm. The core diameter ( $\bar{d}_2$ ) and shell (film) thickness,  $t$ , for Sample B are obtained as 4.0 nm and 1.25 nm. The diameters of the particles in Sample A and B thus measured are very close to the same estimated from TEM measurements. We have observed that the SP modes for Sample A at  $183 \text{ cm}^{-1}$  and for CdSe and CdS-like modes in Sample B at  $180 \text{ cm}^{-1}$  and  $244 \text{ cm}^{-1}$ , respectively.

Surface phonons in core-shell structure (in host medium) have been studied by dielectric continuum approach [13], in which one takes into account the polar optical vibrations of each component in the core-shell-medium structure. In this model, the surface phonon dispersion relation is given by

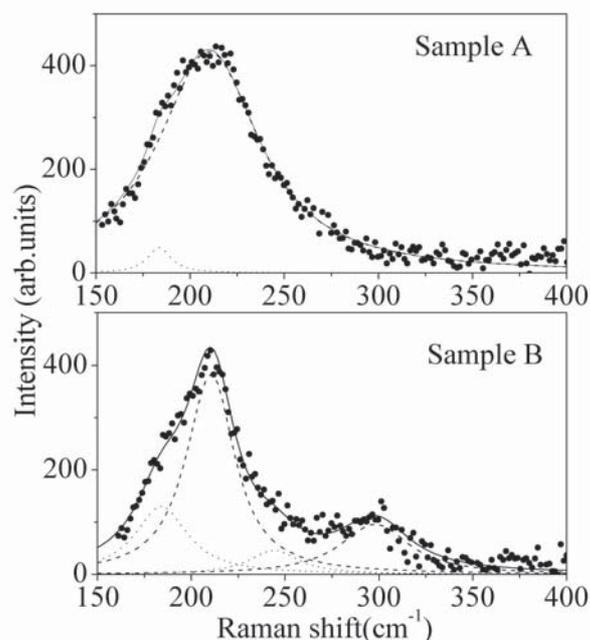
$$\frac{\epsilon_2(\omega)}{\epsilon_m} = \frac{[\gamma^{2l+1} - 1] \epsilon_1(\omega) + [1 + \gamma^{2l+1}(l+1)/l] \epsilon_2(\omega)}{[\gamma^{2l+1} - 1] \epsilon_2(\omega) + [1 + \gamma^{2l+1}l/(l+1)] \epsilon_1(\omega)} \quad (5)$$

where  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  are given by

$$\epsilon^j(\omega) = \epsilon_\infty^j \left[ 1 + \frac{\omega_{LOj}^2 - \omega_{TOj}^2}{\omega_{TOj}^2 - \omega^2} \right] \quad (6)$$

and  $\epsilon_\infty$  is the high frequency dielectric constant of the crystal.  $\gamma$  is the ratio of diameter of shell and core for  $l = 1; 2; 3 \dots$ . Here, we have  $\gamma = \bar{d}/(\bar{d} - 2t)$ , where  $t$  is the CdS shell thickness, as taken earlier.  $\omega_{LOj}$  and  $\omega_{TOj}$  are longitudinal and transverse mode phonon frequencies for CdS and CdSe.  $\epsilon_m$  is the dielectric constant of the medium, mercaptoacetic acid in our case. Substituting Eq. (6) in Eq. (5) for both CdS and CdSe like modes we obtain surface phonon branches for both CdS-shell and CdSe core materials. As before, we have taken the values of  $\omega_{LO1}$  and  $\omega_{LO2}$  as  $302 \text{ cm}^{-1}$  and  $213 \text{ cm}^{-1}$  and the values of  $\omega_{TO1}$  and  $\omega_{TO2}$  as  $238 \text{ cm}^{-1}$  and  $168 \text{ cm}^{-1}$ , respectively. The values of other parameters are  $\epsilon_m = 14.3$ ,  $\epsilon_\infty^1 = 5.5$  and  $\epsilon_\infty^2 = 8.9$  [14]. The average value of  $t$  is known from HRTEM and Raman measurements to be 1.2 nm.

Using Eq. (6), we have calculated the SP mode for pure CdSe particles to be  $182 \text{ cm}^{-1}$ , which is very close to the measured value of  $\omega_{SP}$  ( $183$



**Fig. 2.** Raman spectra for Sample A and Sample B are shown by filled circles. Phonon confinement components and surface phonon components are given by dashed and dotted lines, respectively. Solid lines correspond to the best fit to the experimental data using combined Raman line shapes.

$\text{cm}^{-1}$ ) for Sample A. It is interesting to note that the observed CdS-like SP frequency ( $244 \text{ cm}^{-1}$ ) from the shell component of the Sample B is away from the frequency ( $252 \text{ cm}^{-1}$ ) of the same for pure CdS particles, estimated directly from Eq. (6). However, it is close to the value,  $245 \text{ cm}^{-1}$ , obtained from the combined Eqs. (5) and (6) using dielectric continuum model. The corresponding CdSe-like mode in Sample B is expected to appear at  $180 \text{ cm}^{-1}$ , same as observed in our experiment. The SP frequencies for the CdS-like and CdSe-like modes in Sample A and B as obtained from the experiments and above calculations are tabulated in Table 1. The observed values of CdS-like and CdSe-like SP frequencies in Sample B correspond to  $l = 1$  in Eq. (5).

**Table 1.** Calculated and experimental CdS and CdSe- like SP frequencies in Sample A and B.

Sample	$\omega_{\text{SP}}$ CdSe(calc)	$\omega_{\text{SP}}$ CdSe(expt)	$\omega_{\text{SP}}$ CdS(calc)	$\omega_{\text{SP}}$ CdS(expt)
Sample A	182	183	–	–
Sample B	180	180	245	244

The unit for above frequencies are in  $\text{cm}^{-1}$ .

## 5. CONCLUSION

Our goal in this article was to show phonon confinement and surface phonon modes in the CdSe-CdS core-shell nanostructure. The first order Raman line shape of the CdSe-CdS nanocrystals is quantitatively explained by taking into account both confined phonon modes and SP modes. The frequencies of SP modes are shown to match well with their calculated values as obtained from the dielectric continuum model. It is interesting to note that the SP frequency of core-shell particles is different from that of bare particles. In summary, we have presented a technique, which can be used to confirm the core-shell structure in this type of semiconductor nanostructure.

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