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# Studies on the electronic and vibrational states of colloidal CdSe/ZnS quantum dots under high pressures

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## Abstract

The electronic and vibrational states of colloidal core/shell CdSe/ZnS quantum dots are studied at room temperature by using high pressure optical measurements. Pressure-induced quadratic variations of lattice constants can be observed clearly from both photoluminescence (PL) and Raman spectra up to  $\sim 7$  GPa. This quadratic relationship is consistent with the theoretical prediction. The pressure coefficients of linear and quadratic terms are  $32 \text{ meV GPa}^{-1}$ ,  $-1 \text{ meV GPa}^{-2}$  for PL and  $4.2 \text{ cm}^{-1} \text{ GPa}^{-1}$ ,  $-0.1 \text{ cm}^{-1} \text{ GPa}^{-2}$  for Raman measurements, respectively.

## 1. Introduction

Colloidal quantum dots (QDs), or semiconductor nanocrystals have attracted much attention for potential applications in biological labels [1, 2]. Due to strong confinements in all spatial directions, the emission colours can be tuned to cover the whole visible range by changing the size instead of the chemical composition [3]. On the other hand, the high pressure technique is another approach to vary the electronic levels of crystalline materials. Incorporation of colloidal QDs under a high pressure environment can provide valuable information to study the electronic and vibrational states of nanometre size materials. Previous reports have demonstrated that colloidal QDs exhibit distinct properties from bulk materials. For example, structure transformation of CdSe bulks from wurtzite (WZ) to rock salt (RS) occurred at 2.9 GPa [4]. In contrast to bulk CdSe, the structures of nanocrystals are stable at pressures above 5 GPa [5, 6]. For both nanocrystals and bulk materials, the pressure-induced lattice constant variations are all a linear

relationship which can be reflected in the pressure-dependent optical measurements [4–6]. However, from the theoretical predictions [7], the lattice constant variations under high pressures should follow a quadratic relationship since the bulk modulus is a function of pressure. Surprisingly, this quadratic relationship was not observed explicitly in previous reports. One possible reason is that the limitation of structure phase transformation occurred before entering the quadratic regime. To confirm this, it is necessary to delay the transformation pressure of samples. The elevation of transformation pressure can be achieved by the capping of ZnS.

The effect of ZnS capping on the delay of transformation pressure of CdSe nanocrystals can be illustrated by the thermodynamic arguments proposed by Tolbert and Alivisatos to explain the WZ to RS structure transformation of uncapped CdSe nanocrystals [8]. Surface energy, which depends on the inverse of the radius squared, was accounted for in the size-dependent WZ to RS structure transition. The surface atoms, which have dangling bonds, are more energetic and unstable than those atoms inside the nanocrystal. As the

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external pressure was applied, the surface atoms play the role of nucleation sites for structure transformation. The nucleation sites decrease with the decreasing nanocrystal radius. As a result, the WZ to RS transformation pressure varies inversely with the square of the CdSe nanocrystal radius and can be fitted by the thermodynamic model [8]. Although the capping of ZnS increases the strain energy due to lattice mismatch between ZnS and CdSe, more importantly, it greatly reduces the surface nucleation sites for the WZ to RS phase transition. In the case of SiO<sub>2</sub> coated Si nanocrystals, the semiconductor diamond structure to the metallic  $\beta$ -Sn structure transformation can be elevated from 11 GPa of bulk Si to 22 GPa [9]. In addition, the WZ to RS transformation pressure of ZnS is 17.4 GPa [10] and is much higher than that of bulk CdSe of 2.9 GPa [4]. Therefore, the delay of WZ to RS transformation pressure can be accomplished by the capping of ZnS. The crystal structure of capped CdSe nanocrystals is more stable than that of the uncapped CdSe nanocrystals of the same size. Furthermore, the ZnS capped CdSe nanocrystals are optically more stable [11].

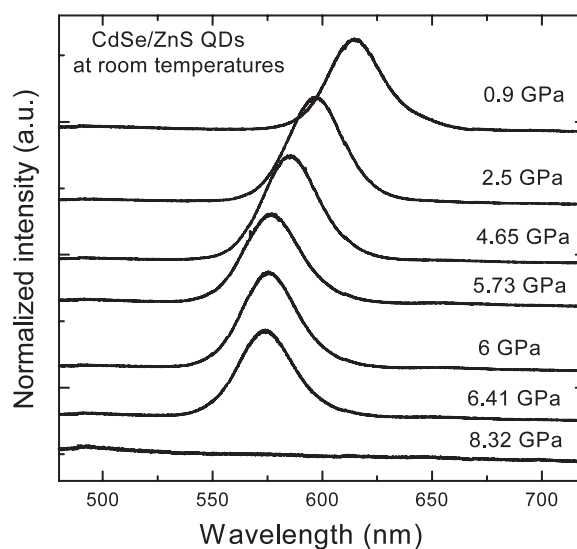
To observe the pressure-induced quadratic variations of lattice constants, the colloidal CdSe QDs with ZnS thin capping layers were investigated under high pressures with de-ionized water as the pressure transmission medium. PL and Raman scattering measurements have been performed under various pressures up to  $\sim 7$  GPa at room temperatures. Pressure-induced quadratic variations of lattice constants are observed explicitly from both PL and Raman measurements. The pressure coefficients of linear and quadratic terms are  $32 \text{ meV GPa}^{-1}$ ,  $-1 \text{ meV GPa}^{-2}$  for PL, and  $4.2 \text{ cm}^{-1} \text{ GPa}^{-1}$  and  $-0.1 \text{ cm}^{-1} \text{ GPa}^{-2}$  for Raman measurements, respectively.

## 2. Experiment

For room temperature PL measurements, the incident beam from a Ti:sapphire laser was guided through the doubly BBO crystals as the excitation sources. The emitted light was dispersed by a spectrometer and detected by a liquid-nitrogen-cooled charge coupled device. Raman spectra were recorded by collecting the scattering line in backscattering configuration. The incident beam from an argon ion laser with 514.5 nm wavelength was focused on a sample through a microscope objective. A notch filter was utilized to reject the unnecessary incident laser line. Hydrostatic high pressure surroundings were created within a 0.2 mm hole at the centre of steel gaskets embedded in two diamond cells. Colloidal CdSe/ZnS QDs were dissolved in de-ionized water, which is used as a pressure transmission medium under relative high pressure [12]. The applied high pressures were determined by monitoring the Raman shift of the ruby R1 line. Colloidal CdSe/ZnS QDs were wet chemical synthesized by conventional methods [11] and transferred into a water pressure medium by replacing the original hydrophobic trioctylphosphine oxide (TOPO) with mercaptopropionic acid (MPA) hydrophilic surface ligands.

## 3. Results and discussion

Selected pressure-dependent PL spectra are shown in figure 1 and the corresponding high pressure values are marked in



**Figure 1.** Pressure-dependent PL spectra of colloidal core/shell CdSe/ZnS QDs at room temperatures.

the figure. The main peaks are attributed to band edge emission of the QDs. The typical blue shift of PL peak positions can be observed with increasing pressures below  $\sim 7$  GPa. However, as the pressure was applied above 7 GPa, the PL signal disappeared. It is ascribed to the semiconductor WZ to metallic RS transition occurring at 7 GPa. The pressure-induced metallization was also observed in the resistance measurement of zinc-blende (ZB) ZnSe at high pressure. As the semiconductor ZB ZnSe transforms to the RS structure at 13.5 GPa, its resistance drops 15 orders of magnitude and it becomes metal [13]. In our previous paper, we found that, when semiconductor ZB ZnSe transforms to metallic RS structure, the longitudinal optical (LO) phonon peak disappears suddenly [14]. Bulk CdSe also undergoes a phase transformation from semiconductor WZ to metallic RS structures at 2.9 GPa [4]. In the case of core/shell CdSe/ZnS nanocrystals of 4 nm, the phase transformation occurs at 7 GPa. Above 7 GPa, nanocrystals become metal. The nanocrystal clusters transform from transparency (bright) to opaque (dark). As a result, the excitation of PL and lattice vibration by laser becomes impossible. No PL, 1LO and 2LO phonon peaks can be detected. It is a reversible process, i.e. when the pressure was released, the PL and LO phonon signals recovered but exhibited hysteresis. The RS to WZ transformation during the down-stroke process occurs at lower pressure than that of the up-stroke WZ to RS structure transformation. Tolbert and Alivisatos [8] found that zinc-blende (ZB) is structure-isoenergetic to the WZ phase. Both ZB and WZ phases were observed during the down-stroke process.

Figure 2 is a plot of the PL peak positions as a function of applied hydrostatic pressures. The pressure dependence quadratic relationship can be observed, that is, the slope decreases with increasing pressure. It implied that the pressure coefficient is not a constant, but depends on the pressures. The equation  $E(P) = E_0 + \alpha P + \beta P^2$  can be used to fit the overall experimental data. Here,  $\alpha$  and  $\beta$  are pressure coefficients of linear and quadratic terms.  $E_0 = 1.990 \text{ eV}$  is the energy gap at ambient pressure and can be obtained by experiment.

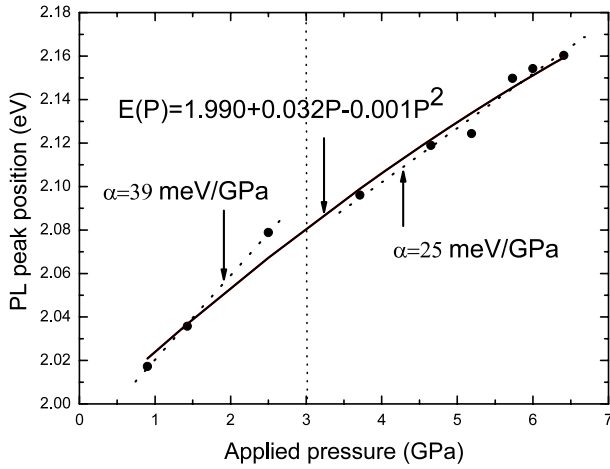


Figure 2. PL peak positions as a function of applied pressures.

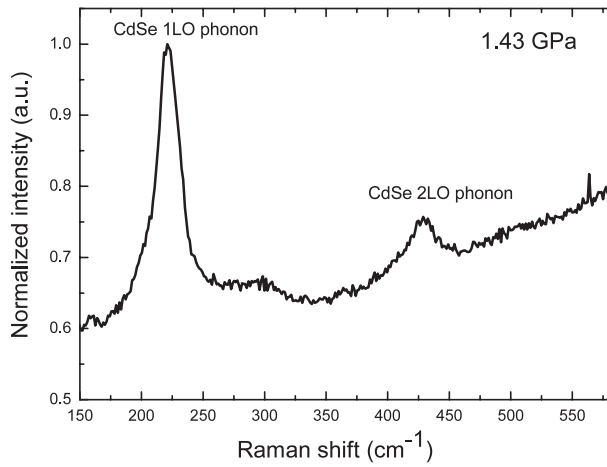


Figure 3. Raman spectrum of colloidal core/shell CdSe/ZnS QDs at the pressure of 1.43 GPa at room temperature.

The fitting parameters for  $\alpha$  and  $\beta$  are  $32 \text{ meV GPa}^{-1}$  and  $-1 \text{ meV GPa}^{-2}$ , respectively. To compare with previous reports [4–6], we divided the overall data into two parts; the relative low and high pressure regimes. The threshold pressure is assigned to 3 GPa due to dramatic change of the slope. This threshold is just close to the transition pressure of CdSe bulk. The linear function  $E(P) = E_0 + \alpha P$  can be used to fit two regimes. The pressure coefficients  $\alpha$  are 39 and  $25 \text{ meV GPa}^{-1}$  for low and high pressure regimes. The former is close to bulk value [15]. In contrast, the latter resembles the value of nanocrystals [5].

According to the above findings, actually, there is a nonlinear factor that influences the relationship between PL peak positions and applied pressures. This effect can be explicitly observed in the relatively high pressure regime. We thus consider the Murnaghan equation of state which describes the relationship between applied pressure and lattice constants,  $P = \frac{B_0}{B'_0} \left[ \left( \frac{a_0}{a_0 + \Delta a} \right)^{3B'_0} - 1 \right]$ , where  $B_0$  and  $B'_0$  are the bulk modulus and its derivative with respect to  $P$ ,  $a_0$  is lattice constant at ambient pressure and  $\Delta a$  is the decrement of the lattice constants induced by the applied pressures. One can

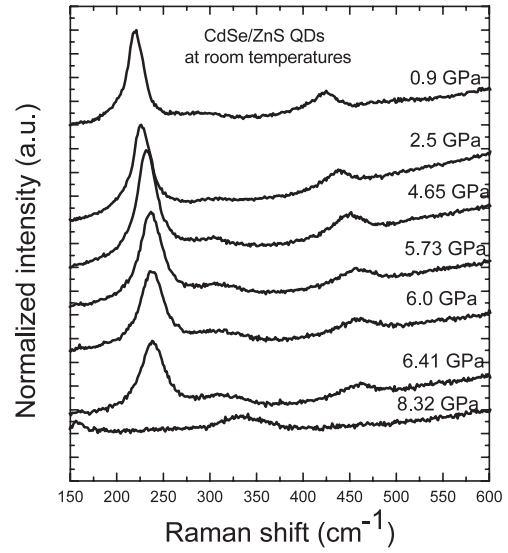
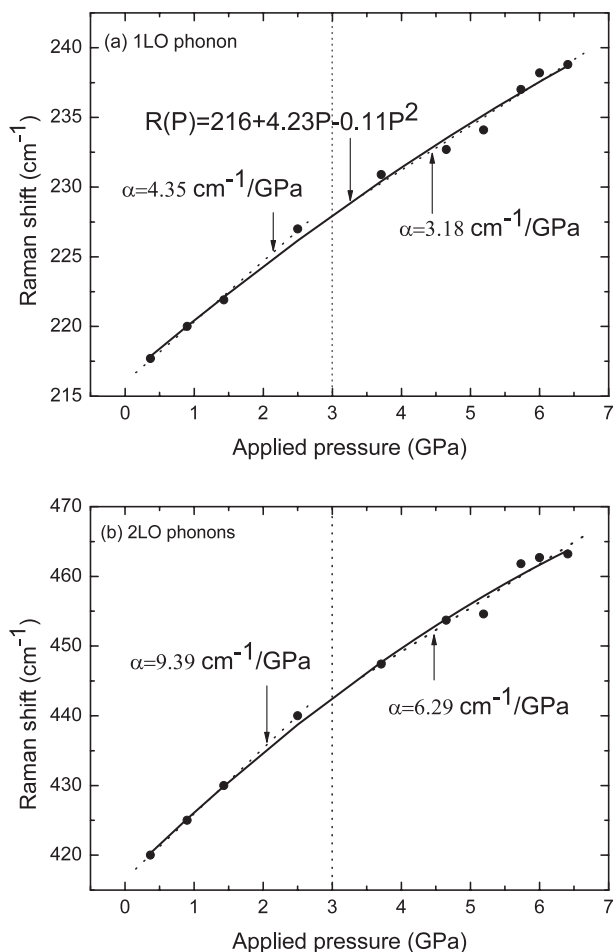


Figure 4. Pressure-dependent Raman spectra of colloidal core/shell CdSe/ZnS QDs at room temperature.

then obtain  $P \left( \frac{\Delta a}{a_0} \right) = \frac{B_0}{B'_0} \left[ \left( \frac{1}{1 + \frac{\Delta a}{a_0}} \right)^{3B'_0} - 1 \right] = -3B_0 \left( \frac{\Delta a}{a_0} \right) + 3B'_0 [3B'_0 - 1] \left( \frac{\Delta a}{a_0} \right)^2 + \text{high-order terms of } \left( \frac{\Delta a}{a_0} \right)$ . In general, for simplicity, the equation can be approximated to the form of  $-3B_0 \left( \frac{\Delta a}{a_0} \right) + 6B_0 \left( \frac{\Delta a}{a_0} \right)^2 + \text{high-order terms of } \left( \frac{\Delta a}{a_0} \right)$  by choosing  $B'_0 \sim 1$ . If the external applied pressure is high enough, the second-order term cannot be neglected. Hence, the pressure-induced quadratic variations of lattice constants can be reflected in the pressure-dependent PL data of figure 2. From the viewpoint of volume change under applied pressures, the bulk modulus is not a constant and increases with increasing pressure. It implies that colloidal QDs are getting harder to be compressed in the relatively high pressure regime. Therefore, the pressure coefficients are getting smaller.

For colloidal QDs under high pressures, the blue shift of the PL peak position is not only caused by the lattice contraction but also by the enhanced quantum confinement. For the quantum confinement effect, the changes in electronic energy under applied pressures are given by  $\Delta E = \frac{\hbar^2 \pi^2}{2\mu R^2} \left( \frac{1}{f} - 1 \right)$  [16], where  $f$  is the volume compressive ratio due to pressure,  $\mu$  is the reduced mass of the electron and hole and  $R$  is the radius of the QDs. By employing the typical parameters of CdSe QDs with 4 nm in radius and setting  $f$  to be about 0.8, the change of the electron energy induced by the increase of quantum confinement due to the applied pressures up to the phase transformation is still much smaller. This implies the blue shift of the PL peak position caused by the quantum confinement effect can be neglected.

Raman scattering measurement is a very sensitive and powerful tool to probe the lattice property of crystalline structures. To further study the pressure-induced quadratic variations of lattice constants, Raman spectra were also recorded at the same time. Figure 3 shows the Raman spectrum of colloidal CdSe/ZnS QDs at the pressure of 1.43 GPa at room temperature. From left to right, two obvious peaks can be found, and are assigned as 1LO and 2LO phonons of CdSe. Figure 4 shows pressure-dependent Raman spectra of



**Figure 5.** Raman peak positions of (a) LO and (b) 2LO phonons of CdSe as a function of applied pressure.

colloidal CdSe/ZnS QDs under various high pressures. With the increasing pressure, both phonon peaks shift to higher frequency up to 7 GPa. Above this pressure, these CdSe related Raman peaks disappear abruptly. Combining PL with Raman scattering, it is appropriate to conclude that the structure transformation occurs at this pressure. Figures 5(a) and (b) show the peak positions of Raman shift for the LO and 2LO phonons of CdSe as a function of applied pressures. Both curves are all in a quadratic relationship. The solid line is a quadratic fit by the equation  $\omega(P) = \omega_0 + \alpha P + \beta P^2$  to overall experimental data. The pressure coefficients of linear and quadratic terms for LO phonons are  $4.2 \text{ cm}^{-1} \text{ GPa}^{-1}$  and  $-0.1 \text{ cm}^{-1} \text{ GPa}^{-2}$ . The linear term is consistent with previous results of bare CdSe colloidal QDs [6]. This is clear evidence for hydrostatic pressures applied to the colloidal QD core even over-coated with a ZnS thin layer. We can also observe that there are two pressure regimes with different slopes which divide at the pressure of 3 GPa. From the pressure-dependent Raman spectra, the Gruneisen parameter can be derived by

the equation  $\gamma = \frac{B_0}{\omega_0} \frac{d\omega}{dP}$ , where  $B_0$  is the bulk modulus and equal to 53 GPa for CdSe bulk [7].  $\omega_0$  is the Raman shift at ambient pressure. One then obtains  $\gamma = 1$ , and the LO phonon frequency at ambient pressure is  $216 \text{ cm}^{-1}$ , which is larger than the bulk value of  $213 \text{ cm}^{-1}$ . The increased value is due to additional compressive stress resulting from the over-coated ZnS. Previous work has reported that QDs over-coated with ZnS are able to increase the Raman shift with a value of  $2 \text{ cm}^{-1}$  [17].

#### 4. Conclusion

We have studied the electronic and vibrational states of colloidal core/shell CdSe/ZnS QDs at room temperature with high pressure optical measurements. Pressure-induced quadratic variations of lattice constants can be observed explicitly from both the PL and Raman spectra up to  $\sim 7$  GPa. This quadratic relationship is consistent with the theoretical prediction. The pressure coefficients of linear and quadratic terms are  $32 \text{ meV GPa}^{-1}$ ,  $-1 \text{ meV GPa}^{-2}$  for PL and  $4.2 \text{ cm}^{-1} \text{ GPa}^{-1}$ ,  $-0.1 \text{ cm}^{-1} \text{ GPa}^{-2}$  for Raman measurements, respectively.

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