

Temperature dependence of the photoluminescence emission from thiol-capped PbS quantum dots

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The authors report the temperature dependence of the near-infrared photoluminescence (PL) emission from thiol-capped PbS quantum dots. The high thermal stability of the PL allows the authors to study the thermal broadening of the dot emission over an extended temperature range (4–300 K). The authors show that the linewidth of the dot PL emission is strongly enhanced at temperatures above 150 K. This behavior is attributed to dephasing of the quantum electronic states by carrier interaction with longitudinal optical phonons. The authors' data also indicate that the strength of the carrier-phonon coupling is larger in smaller dots. © 2007 American Institute of Physics. [DOI: 10.1063/1.2711529]

Semiconductor nanocrystals, also known as quantum dots (QDs), are artificial nanostructures with energy spectra and electronic wave functions similar to those observed in atomic physics.¹ In the last two decades, they have been synthesized using different techniques (electron-beam lithography, epitaxy, and colloidal chemistry) and a number of different semiconductor materials. They have been studied in optical and transport experiments and have also formed the basis for devices of potential interest for quantum information processing,² spintronics,³ optoelectronics,^{4,5} and optical imaging in biological studies.⁶ Of the various nanocrystals, PbS-based QDs have emerged as promising candidates for optical applications in the near-infrared region of the electromagnetic spectrum.^{5,7–9} In particular, since the emission wavelength of PbS dots can be controlled and tailored within the spectroscopic window of 1.0–1.2 μm of low absorption of biological systems, water soluble PbS nanocrystals have the potential to be used as biocompatible fluorescent labels and to replace traditional organic fluorescent dyes.

The effect of temperature T on the optical properties of PbS quantum dots is of great importance for their use in room temperature (RT) applications. Recently, an unusually large linewidth (~ 100 meV) for the RT photoluminescence (PL) emission from an individual PbS QD was reported.¹⁰ However, the effect of temperature on the spectral linewidth of either the emission from an individual or an ensemble of PbS dots is still largely unknown. In this work, we study the PL properties of thiol-capped PbS QDs with emission wavelengths tunable from 1.1 to 1.3 μm . The intensity of the PL is only weakly affected by temperature, thus allowing us to study the thermal broadening of the QD emission over an extended temperature range (4–300 K). We find that the optical linewidth W exhibits a strong increase for $T > 150$ K. This increase is attributed to dephasing of the quantum electronic states by carrier interaction with thermally generated longitudinal optical (LO) phonons and is shown to be enhanced in smaller dots.

Our PbS QDs were prepared in aqueous solution following the method described by Bakueva *et al.*¹¹ First we prepared a 15 ml aqueous solution containing 2.5×10^{-4} mol lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2$ and a mixture of thiols, i.e., 1.5×10^{-3} mol thioglycerol and 5×10^{-4} mol dithioglycerol, which act as capping agents. The pH of the solution was adjusted to a value of 11.0 by addition of triethylamine. The synthesis of the dots was completed by adding a 0.1M solution of sodium sulfide Na_2S . By varying the Pb/S molar ratio (MR) from 1:0.2 to 1:0.7, we were able to form colloidal PbS dots of different sizes. The resulting solution was either kept in the laboratory atmosphere or stored in a refrigerator at $T = 278$ K under N_2 atmosphere, and it was examined several times over a period of six months by PL spectroscopy.

For PL experiments, the PbS dots were deposited on a glass substrate. The optical excitation was provided by the 514.5 nm line of an Ar^+ laser. The luminescence was dispersed by a 1/2 m monochromator and detected by a cooled (InGa)As photodiode. For atomic force microscopy (AFM) measurements, the PbS dots were dispersed onto a polished (100)-oriented p -type Si substrate. Following the dilution of the solution with de-ionized water to 1 part in 100, a drop was then deposited on the substrate and spin coated for 30 s at a speed of 250 rpm.

During the first three weeks after the synthesis, we observed that for a given MR, the PL emission from the dots tends to shift to longer wavelengths (by up to 30 nm). This behavior is likely to arise from ripening effects that lead to formation of nanocrystals with larger size and hence longer wavelength emission. This process can be reduced by storing the solution at low temperature $T < 280$ K. Figure 1 shows the typical RT PL spectra of all samples investigated in this work. By increasing the Pb/S MR from 1:0.2 to 1:0.7, the luminescence from the PbS dots is tuned in the wavelength range of 1.1–1.3 μm . The shift of the dot emission towards longer wavelengths with increasing MR is due to the increase of the QD size. Our AFM study indicates that the dots have approximately spherical shape with diameter d increasing from about 3 to 12 nm for Pb/S MR increasing from 1:0.2 to 1:0.7 (see Fig. 1).

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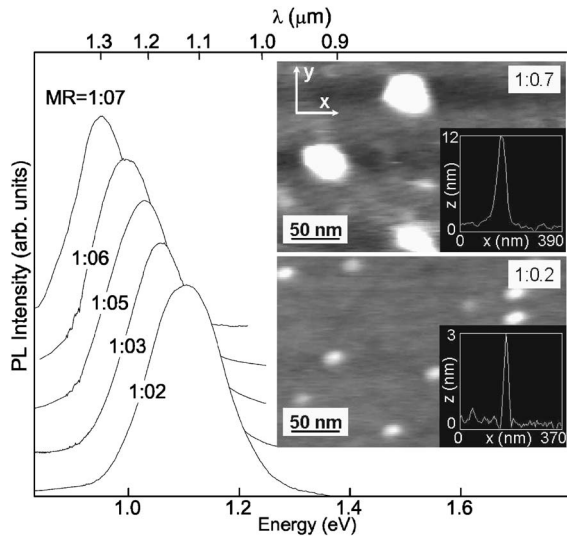


FIG. 1. (Color online) RT PL spectra of thiol-capped PbS dots with various Pb/S MRs. The inset shows AFM images of PbS dots with Pb/S MRs equal to 1:0.2 and 1:0.7. Each AFM image shows the height profile for a representative dot in the ensemble.

Figure 2 shows the PL spectra at various T for a representative sample. Increasing T has three main effects on the PL spectrum: (1) The peak intensity of the QD PL emission reveals a maximum at $T=50$ K and thereafter it decreases monotonically (top inset of Fig. 2). (2) The peak energy E of the QD emission blueshifts and its T dependence for $T > 150$ K can be described by the coefficient $\alpha = \partial E / \partial T = 0.3$ meV/K (middle inset of Fig. 2). The value of α is smaller than that of bulk PbS ($\alpha = 0.5$ meV/K).¹² We attribute this difference to the atomiclike character of the dot energy levels and the strong quantum confinement of the exciton, whose Bohr radius (20 nm) is considerably larger

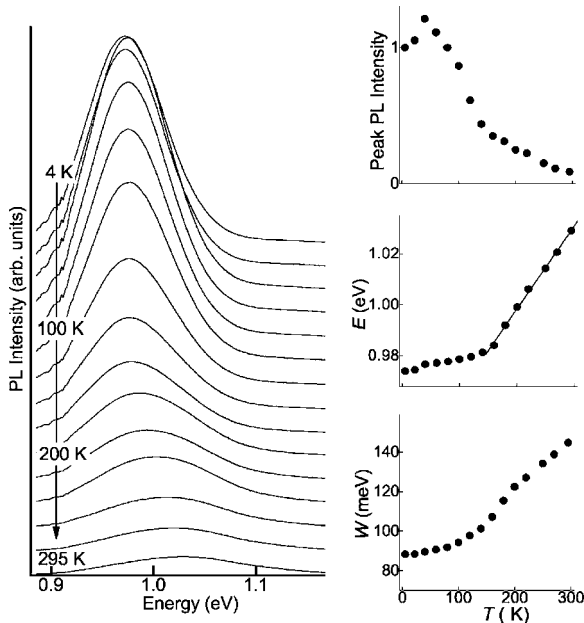


FIG. 2. (Color online) PL spectra at various temperatures and excitation power $P=100$ W/cm² for thiol-capped PbS QDs with Pb/S MR equal to 1:0.5. The insets show the T dependence of the peak intensity (top inset), energy peak, E (middle inset), and full width at half maximum, W (bottom inset), of the QD PL emission. The line in the middle inset is a linear fit to the data of E vs T .

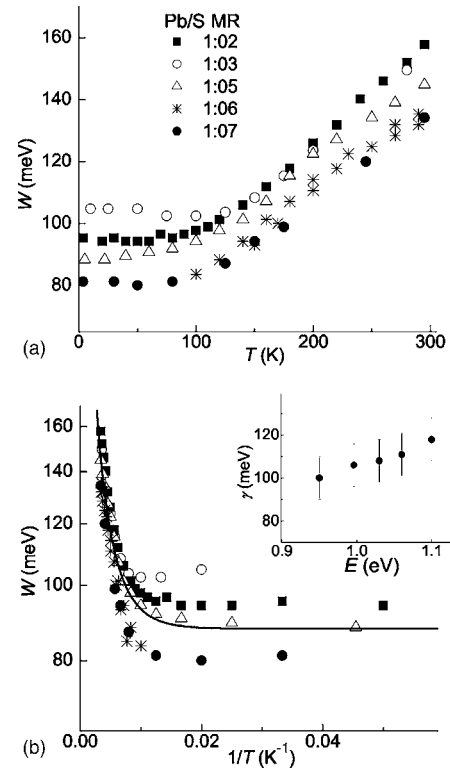


FIG. 3. (Color online) (a) T dependence of W for all samples investigated in this work. (b) Plot of W vs $1/T$. The line represents the curve $W = \gamma n + W_0$, where n is the Bose distribution function for LO phonons, and γ and W_0 are two constants. The inset shows the dependence of γ on the peak energy E of the QD PL emission measured at RT.

than the dot diameter (< 10 nm).⁷ (3) The blueshift and quenching of the dot emission are accompanied by a significant increase of the full width at half maximum, W , of the dot emission (bottom inset of Fig. 2).

The enhancement of the QD PL intensity observed for increasing T below 50 K indicates a thermally activated redistribution of carriers in the dot in the presence of defects: with increasing T , carriers trapped in a defect in or around the dot overcome shallow energy barriers and fall into the ground state of the dot, thus increasing the PL intensity. A further increase of T from 50 to 295 K decreases the PL intensity by only a factor of 10; this T dependence and high thermal stability of the PL emission were observed for all our samples. These are important features for device applications and indicate a low level of thermal escape of carriers from the ground state of the dot towards the excited states and a relatively low density of nonradiative recombination centers.

We now focus on the T dependence of W for samples with different Pb/S MRs. For $T < 150$ K, we observed different T dependencies and/or values of W ($W = 80 - 100$ meV) [see Fig. 3(a)]. In contrast, for $T > 150$ K, all samples show a characteristic thermally activated increase of W . This behavior is revealed more clearly in Fig. 3(b), which plots W vs $1/T$. It can be seen that at high T , the T dependence of W is well described by an exponential dependence.

In order to understand the effect of the temperature on W , we need to consider the mechanisms that can give rise to the broadening of the emission from an ensemble of dots. At low T , carriers are frozen randomly into the dot states and

PL spectrum reflects the distribution of the dot energies. Although the optical linewidth depends largely on the dispersion of the dot size and spectral diffusion due to charge trapping on dot defects, the thermally activated increase of W indicates that at high T the optical linewidth is also controlled by an intrinsic scattering process due to carrier interaction with phonons. The coupling of carriers to phonons in a QD leads to a PL emission, which consists of a zero-phonon line (ZPL) and a broad band due to LO phonon sidebands and a continuum of acoustic-phonon-assisted transitions.^{1,13–16} The contribution of phonon sidebands to the QD PL spectrum was found to be important for CdSe QDs (Ref. 13) and much weaker for nanocrystals based on (InGa)As (Ref. 15) and GaAs.¹⁶ Previous PL studies have also shown single broad PL emissions for both individual PbS and ensembles of dots¹⁰ with PL line shapes typically reproduced by a single Gaussian function. Therefore, we infer that the measured thermally activated broadening of the dot emission observed in all our PbS QDs does not arise from the contribution of phonon sidebands, but instead from homogeneous broadening of the ZPL for each dot in the ensemble caused by interaction with the increasing thermal population of optical phonons.

We find that the T dependence of W can be described by the relation $W = \gamma n + W_0$, where $n = 1 / [\exp(\hbar\omega_{LO}/k_B T) - 1]$ is the Bose distribution function for LO phonons of energy $\hbar\omega_{LO}$, γ is a constant, and W_0 represents the inhomogeneous contribution to W .¹⁷ As shown in Fig. 3(b), at high T (>150 K) all data are well described by this expression by setting $\hbar\omega_{LO}$ equal to the energy of LO phonons in PbS ($\hbar\omega_{LO} = 26$ meV),¹² $\gamma = 110 \pm 20$ meV, and $W_0 = 90 \pm 10$ meV. We find that the strength of carrier-phonon coupling, as measured empirically by γ , tends to be larger for dots with the higher PL emission energies [see Fig. 3(b)].

In a QD, the interaction of electrons with phonons is expected to be qualitatively different from that occurring in bulk systems. Inelastic interactions such as phonon-assisted excitation of carriers to excited states or energy relaxation processes are unlikely to occur in PbS dots as we estimate that the confinement energy for electrons and holes is much larger than $\hbar\omega_{LO}$.¹⁸ In contrast, elastic collisions involving the virtual absorption and emission of a LO phonon by carriers do not require a specific energy separation between the discrete levels of the dot. Elastic collisions by phonons do not change the energy of the carrier, but they do change the phase of the carrier wave function, thus causing a broadening of the spectral lines.^{19–21} For a spherical PbS QD, the exciton-phonon coupling strength is expected to be small due to the almost identical form and size of the electron and hole wave functions.²² The calculated exciton wave function and its coupling to lattice vibrations depend on the strength of carrier confinement^{23,24} and can be influenced by local electric fields arising from trapping of charges in QD defects.²⁴ An increase of the strength of carrier-phonon coupling with increasing carrier confinement was observed in Cd(SSe) nanocrystals,²⁵ while an opposite trend was shown for CdTe-based quantum wells²⁶ and CdS QDs.²⁷

Our data indicate that the strength of carrier-phonon coupling, γ , is larger for dots with the higher emission energies (>1 eV at RT) and smaller size ($d < 7$ nm) [see Fig. 3(b)] in qualitative agreement with theory.²³ We also find that these dots exhibit the largest values of W . Therefore, we propose that the local environment of the dot (i.e., trapped charges on

defects) acts not only to broaden the optical linewidth at low T but also to enhance the interaction of carriers with the lattice, thus leading to an additional broadening of the dot PL emission.

In conclusion, we have observed a thermally activated increase of the linewidth W of the emission from thiol-capped PbS quantum dots and explained this behavior in terms of dephasing of the electronic states by interaction with longitudinal optical phonons. We have found that the size of the dot and its environment affect the strength of this interaction, a finding of relevance for the design and exploitation of PbS nanocrystals in RT applications.

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¹*Semiconductor Nanocrystals: From Basic Principles to Applications*, edited by A. L. Efros, D. J. Lockwood, and L. Tsybeskov (Kluwer Academic Dordrecht/Plenum, New York, 2003), 1, 1.

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¹⁷From the low T (<150 K) dependence of W , we extrapolate that at RT the linear contribution to W due to longitudinal acoustic (LA) phonons should be much smaller (<5 meV) than that due to LO phonons (>50 meV). Therefore in the analysis of the T dependence of W , we have neglected a linear term due to coupling of the exciton to LA phonons.

¹⁸Our estimate of the ground and excited energy states of the QD is based on the effective mass approximation and a PbS nanocrystal with spherical shape, diameter $d = 10$ nm, and potential barriers of infinite height.

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