Invited Paper

Size-dependent spectroscopy and photodynamics of some II-VI semiconductor nanocrystallites (quantum dots)

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ABSTRACT

The relaxation dynamics of photoexcited CdSe nanocrystallites (quantum dots) are dominated by the surface. Surface electronic properties of CdSe nanocrystallites have been probed using low temperature fluorescence line narrowing and time resolved luminescence. We find that the surface structure creates a random potential for the hole with a size dependent barrier for site to site hopping.

Introduction

Quantum dots of CdSe (20-80 Å in diameter) are characterized by huge surface to volume ratios. Although most theoretical efforts have focused primarily on ideal quantum dots with an infinite potential at the surface,[1] luminescence experiments indicate that the surface plays a crucial role in the relaxation processes in photexcited CdSe quantum dots.[2-5] In this paper we explore the role of the surface in these photodynamics. We use LO phonon replicas in the luminescence to probe the localization of the hole as a function of temperature.

The crystallites were prepared using a variant of a synthesis previously described.[2,6] The absorption spectrum of the sample shows a broad structureless band due to inhomogeneous broadening from the size, shape etc... distributions. Excitation to the blue of this absorption yields a broad emission band from the entire size distribution (Fig. 1). Excitation on the red edge of the first absorption band probes the largest particles in the sample and yields a fluorescence line narrowed spectrum showing LO phonon replicas.

Time resolved measurements on this emission using a time correlated photon counting apparatus with instrumental resolution of 80-100 ps shows that this emission consists of two principal time scales.[2] A fast, temperature insensitive 100 ps component and a long (100's nsec) temperature sensitive component, with ~90% of the fluorescence coming from the long component.

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A strong resonant mixing between a delocalized hole wavefunction and intrinsic tightly localized surface states has previously been postulated to explain this data.[2] The model for the photodynamics of the electron hole pair goes as follows: An electron hole pair is created with the electron essentially delocalized in the particle and with the hole mostly delocalized but with a small amount of surface localization mixed in. (This mixing would correspond to a ~120 fs lifetime for the pure delocalized state.) The hole localizes tightly during the first 100 ps and then hops from site to site on the surface with a time scale of 100 ps.

Since the Cd-Se LO phonon is a polar

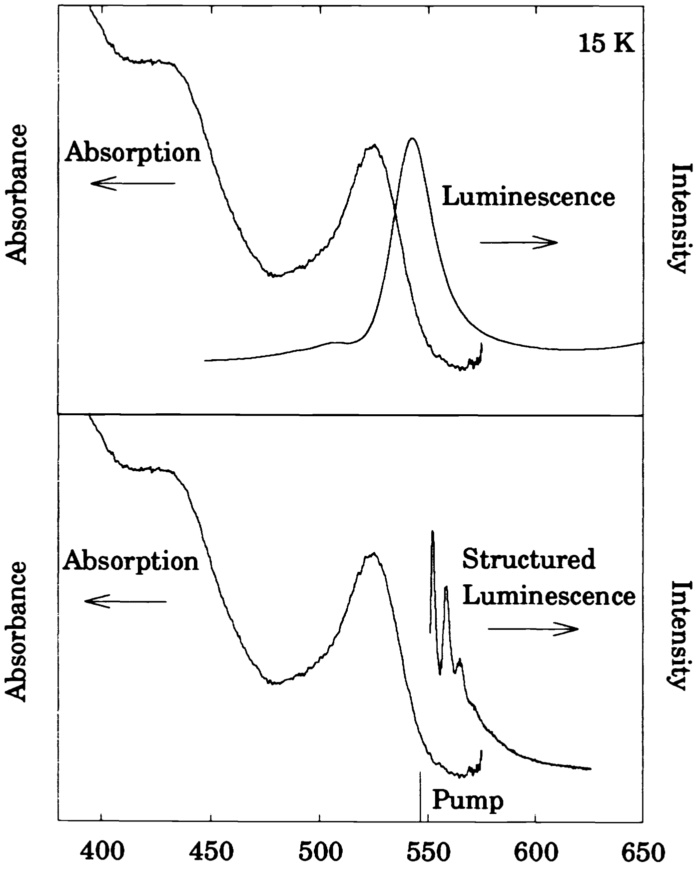

Fig. 1. (Top) Absorption and luminescence spectra of 32 Å CdSe crystallites at 15 K. The excitation is at 440 nm. (Bottom) Same absorption spectrum but the luminescence excitation is now at 545 nm for size selection. This leads to significant line narrowing and the appearance of LO phonon replicas. (from Ref. 2.)

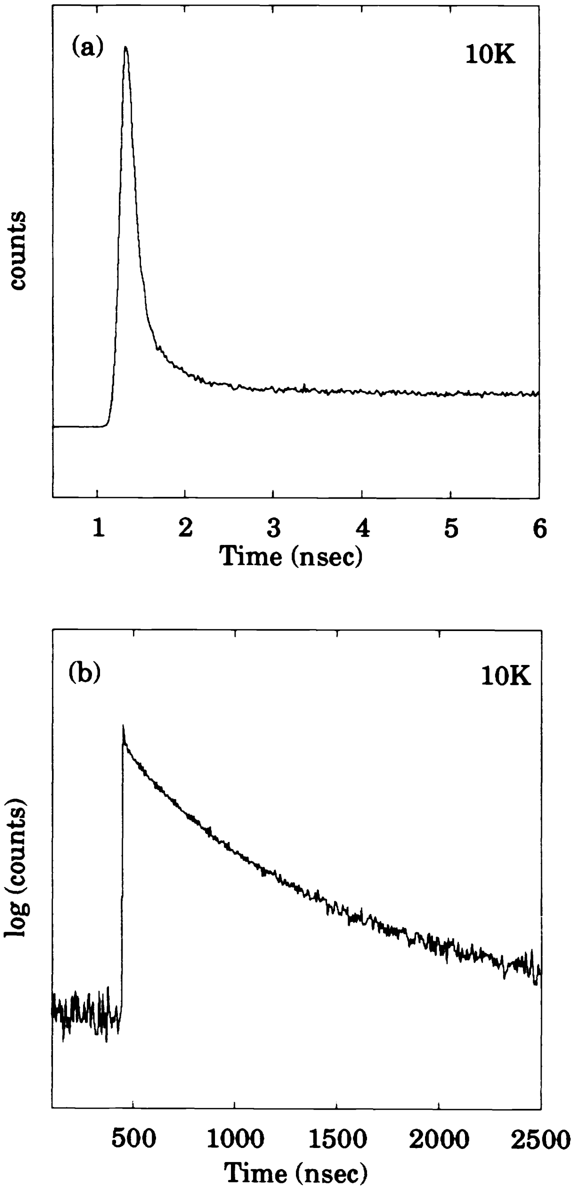

Fig. 2. (a) Decay of zero phonon line showing a fast ~100 ps component and a long μs component. (b) Logarithm of the long component of the zero phonon line. (from Ref. 2.)

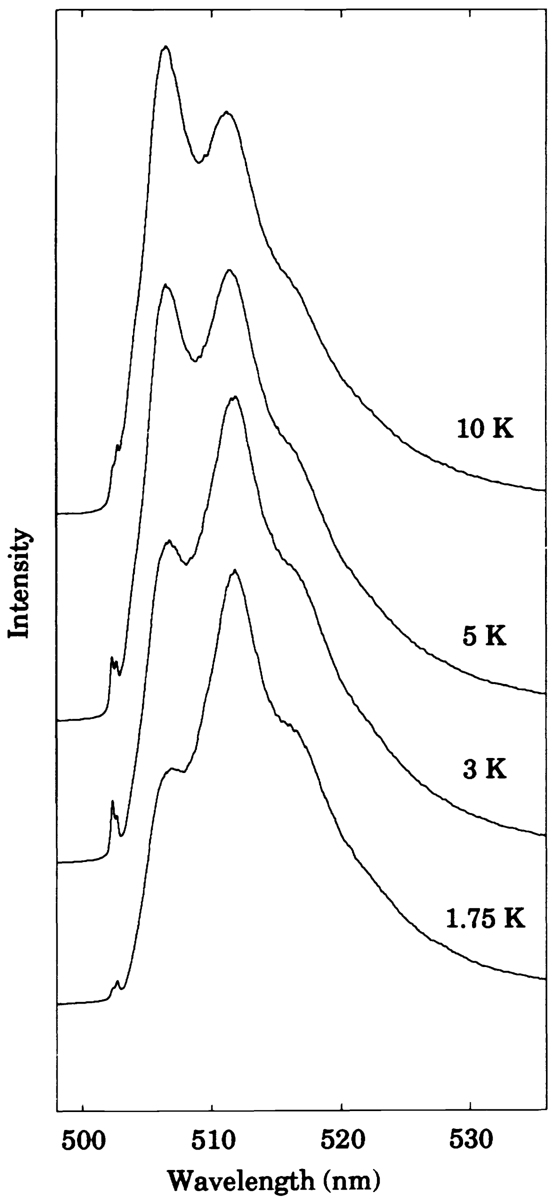

Fig. 3. Temperature dependence of luminescence for 23 Å diameter CdSe quantum dots. The ratio of the zero to one phonon line changes dramatically between 1.75 K and 10 K. The sharp line near the base of the zero phonon lines is left over laser scattering.

vibration, it can couple to charge imbalances inside the photoexcited crystallite. This coupling (Frölich coupling) is what allows us to see phonon replicas in the first place.[7] As the localization of the hole increases, the charge separation between the electron and the hole also increases, yielding an increase in the number of phonon replicas in the luminescence and an increase in the integrated intensity of the first to zero phonon lines. This ratio of first to zero phonon line then provides an experimental measure of the localization of the hole on the surface.

Temperature Dependent Luminescence

The temperature dependence of the structured luminescence is shown in Fig. 3 for 23 Å diameter particles. There is a dramatic change in the ratios of the zero to first LO phonon lines from 1.75 to 10 K. We can estimate the charge distribution in the relaxed luminescing state using a simple model where the electron is delocalized inside the particle but the hole is localized inside a small sphere of radius r located tangent to the surface of the particle. In a displaced harmonic oscillator model the coupling strength S (Huang-Rhys) parameter is the square of the ratio of the first to zero phonon line integrated intensities.[8,9] We can calculate S for a given hole radius r. This hole radius is then used as fitting parameter to match the experimental data. Figure 4 shows the experimentally obtained coupling strength S and the calculated hole radius. Note the dramatic change at ~8 K.

The quantum dot has its surface passivated with tri-n-octylphosphine oxide that binds to the surface Cd atoms. The Se *p* orbitals are either uncoordinated or passivated with tri-n-octylphosphine. These *p* orbitals have been postulated as being energetically shallow surface hole traps which give rise to the μs tail in the luminescence lifetime. We suggest that it is these states which in the unevenly shaped nanocrystallites gives rise to a disordered band for the hole (a Mott-Anderson picture[10]). Disordered bands or random potentials are characterized by two kinds of states: localized states where the probability amplitude decays exponentially form the center of localization, and delocalized states. At low temperatures, the hole is localized near the bottom of a local minimum for the potential. As the temperature is raised the hole is thermally activated across the potential barriers on the surface, delocalizing it. The overlap between electron and hole wavefunctions increases, reducing the coupling to the lattice vibrations as seen in the ratio of the integrated intensities of the one phonon to zero phonon lines.

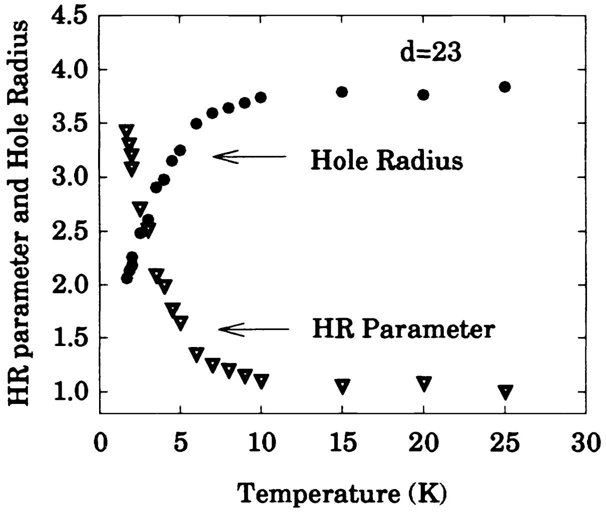

Fig. 4. Hole radius and Huang-Rhys (HR) parameter vs. temperature for 23 Å diameter CdSe quantum dots. The HR parameter is obtained experimentally. The model described above is used to calculate the hole radius.

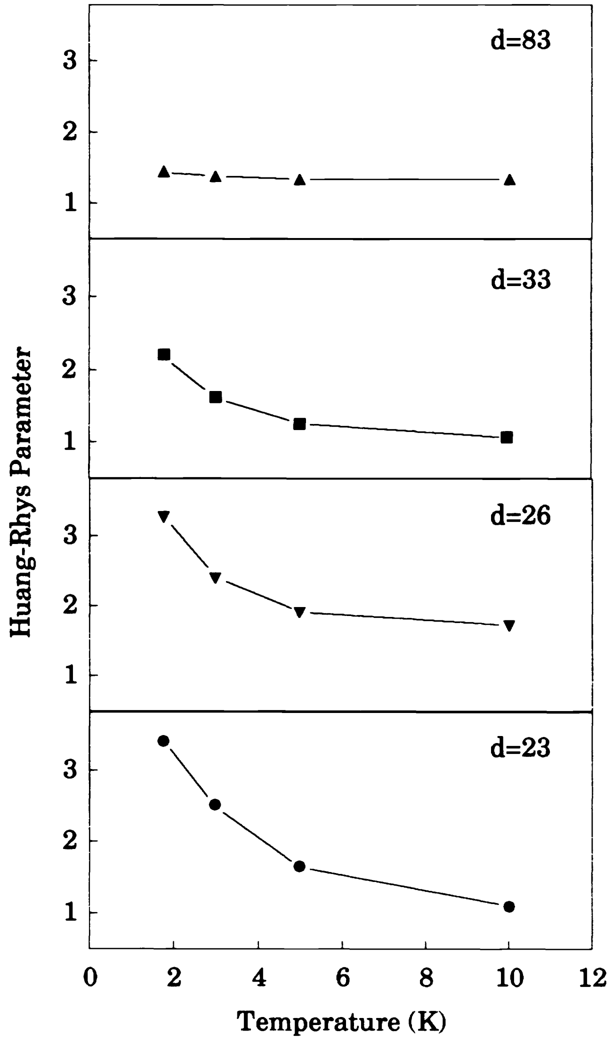

Fig. 5. Temperature dependence of Huang-Rhys parameter for a series of diameters. The solid lines are guides to the eye.

We can verify the consistency of our model by varying the particle diameter. We find that when the diameter of the particles reaches 83 Å the fluorescence line narrowed spectrum is essentially temperature independent. These particles have much smaller surface to volume ratios than the 23 Å particles and the core of the particles begins to dominate the electronic properties. Figure 5 clearly shows the effect of changing the surface to volume ratio on the temperature dependence of the Huang-Rhys parameter.

Acknowledgments

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