Invited Paper

crystals
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Particles

Photophysics of Capped CdSe Microcrystallites Exhibiting Quantum Confinement

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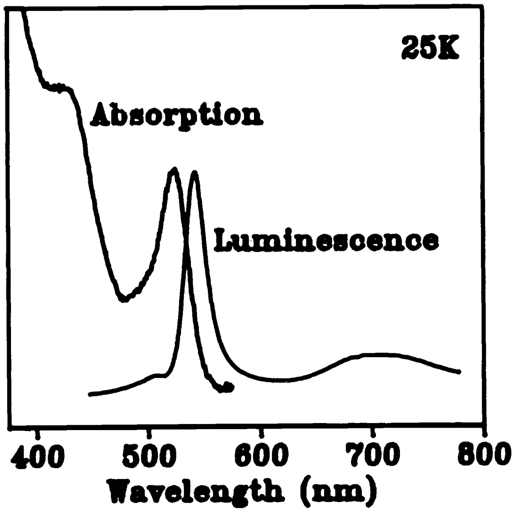
ABSTRACT

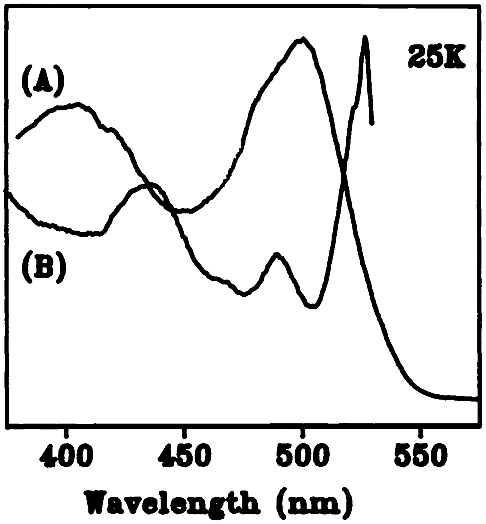
We use nanosecond and picosecond optical spectroscopic techniques to isolate and study the photodynamics of the single particle spectrum of 35Å CdSe nanoclusters exhibiting three-dimensional quantum confinement.

Restriction of carrier wave functions in semiconductor structures of reduced dimensionality results in increased oscillator strength in the excitonic absorption which can be exploited in the design of novel nonlinear optical devices.[1] We review spectroscopic studies of capped CdSe "quantum dots" whose size is small relative to the bulk material exciton radius. Nanosecond and picosecond hole burning and steady-state luminescence spectroscopies are used to characterize the spectral dynamics and isolate the single particle spectrum of these 35 Å diameter CdSe microcrystallites. These clusters, which are grown by a new synthetic method[2], have well developed wurtzite crystal structure[3], high quantum yield of band edge luminescence, low saturation intensities, ($\approx 100 \mu J/cm^2$) and long bleaching recovery times. Our measurements were performed at 25K in dilute glasses.

In this material the "exciton" band, i.e., the homo-lumo transition is shifted ≈1ev to higher energy by quantum confinement effects. The spectral positions of the localized states can be calculated using a simple particle in a sphere model.[4] Figure 1 illustrates the 25K absorption and emission spectra of capped Cdse clusters in our glassy matrix. The gross features in the absorption spectrum are the localized states due to quantum confinement as mentioned above. Generally the crystallite luminescence is quite sensitive to the surface composition and structure. The nature of the emissive behavior and the quantum yield of the emission spectra can change dramatically with solvent. The high quality clusters studied have strong band edge luminescence at ≈ 540nm as shown with a broad weaker emission band at ≈ 700nm.

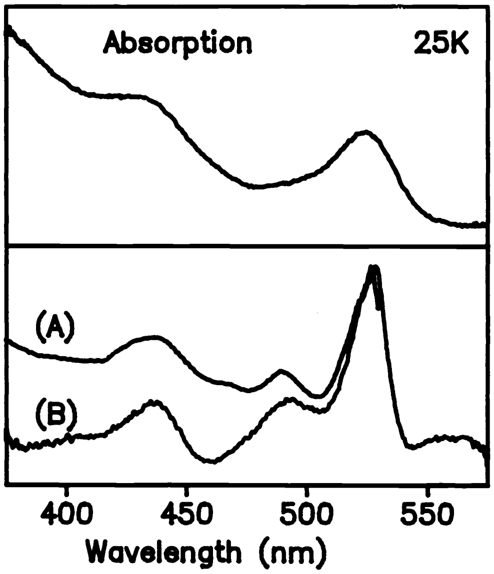


- Figure 1: Low temperature absorption and emission spectra of 35Å CdSe clusters.



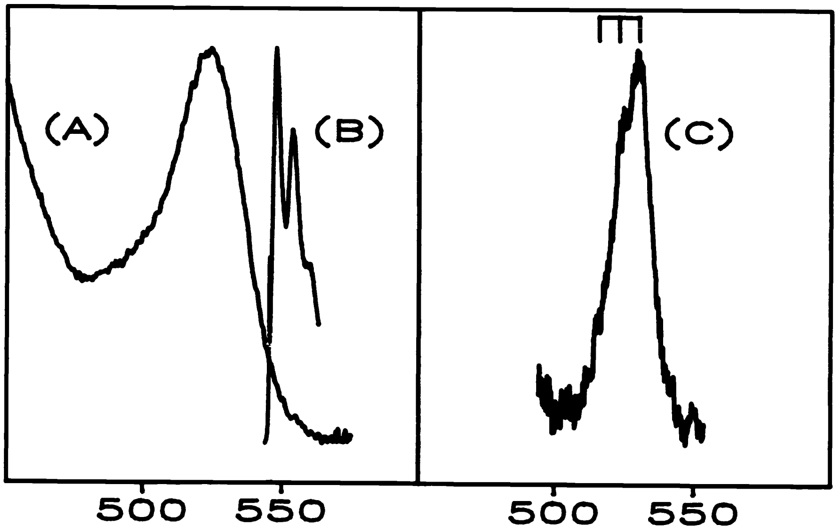
- Figure 2: Luminscence excitation spectra of band edge (A) and deep red emission (B). The large difference in excitation profile is indicative of the differing photophysics for the emitting species.

Luminescence excitation spectra as shown in figure 2 indicate that these two emissive features have distince spectral character. Unfortunately picosecond time resolved emission behavior is highly non-exponential and extremely long lived (>100ns) for both features. One can gauge the degree of inhomogeneous broadening due to cluster polydispersity in the system both by investigating the transient photophysical holeburning spectra as well as looking more closely at the luminescence excitation behavior as shown in Figure 3. There is strong bleaching of the $1_{Se}-1_{Sh}, 1_{Se}-1_{Ph}$ transitions as well as the spin-orbit split state, these features are also clearly resolved in luminescence excitation. More importantly in saturation we resolve instrumentally limited,(500fs), induced absorption to the blue of the homo-lumo transition which decays on a 10-100ns time scale. The long spectral hole and emission lifetimes are consistent with a dynamical picture including a "trapped" species. These trap states, which fall within the bandgap of the material result from the interaction of the cluster electronic states with the surface of the crystallite, (note ≈30% of the atoms are on the surface). The dynamics observed suggest that the initially photogenerated electron-hole pair created rapidly relaxes to a trapped carrier state, (<500fs). Clusters, (like bulk semiconductors), can accommodate multiple electron-hole pairs.



- Figure 3: Comparison of luminescence excitation (A) and transient bleaching spectra (B). The line narrowing nature of the two techniques allows recovery of the spectral features normally masked by inhomogeneous broadening. (The absorption is shown for comparison.)

The oscillator strength of the second pair excitation is critically dependent upon the electronic configuration of the cluster. In addition to direct coulomb interaction between delocalized pairs, localization of the electron and hole to different spatial regions of the cluster can result in a dipole field of 10^3or10^4 V/cm.. The photoinduced absorption therefore, can be readily understood as a reduction in oscillator strength of the second electron-hole transition due to the presence of these effects.

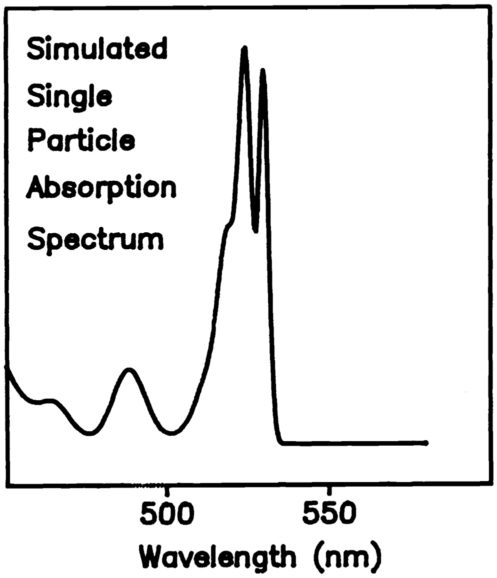


- Figure 4: Vibronic structure of cluster spectra due to coupling of the excited state to the 200cm^{-1} LO phonon. The vibrational progression is clearly evident in both the gated emission at the band edge, (B), and the bleach spectrum, (C), of the homo-lumo transition. (A) is the absorption spectrum.

This description is consistent with recent theoretical work of Hu *et al*,[5] as well as early bleaching studies in CdS clusters.[6]

In addition, the high quality of our samples allows us for the first time to resolve the vibronic structure of the $1_{Se}{-}1_{Sh}$ transition due to coupling to the 200cm^{-1} LO phonon mode. Its effect on the emission and holeburning spectra is clearly illustrated in figure 4.

Detailed analysis of the time-resolved and steady-state spectral data allows us to extract a ≈150cm^{-1} hole width for the zero-phonon line of the exciton transition and construct a single cluster spectrum which is shown in figure 5.



- Figure 5: Simulated single particle spectra as extracted from a fit of all spectral data. The homogeneous width of the zero phonon line of the lowest exciton transition is ≈150cm^{-1}.

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