

Long-Lived Delocalized Electron States in Quantum Dots: A Step-Scan Fourier Transform Infrared Study

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Received: November 18, 1999; In Final Form: December 13, 1999

Visible light-induced IR absorption in colloidal CdSe quantum dots is observed by step-scan FTIR spectroscopy. Size dependence and the effect of surface modification are investigated. The introduction of surface hole trap states enhances and prolongs the IR absorption in photoexcited quantum dots. Our measurements reveal long-lived (>1 ms) delocalized electron states in 6 nm average diameter dots capped with thiocresol.

The discrete nature of the electronic states in strongly confined semiconductors has generated tremendous interest in quantum dots.¹ They display a wealth of both interesting and practical phenomena.² They provide insights into electronic and optical behavior in a size regime where neither molecular nor bulk description applies. Quantum dots are promising materials in fundamental physics and chemistry, as well as in the future of optoelectronic applications. The use of wet chemical synthesis to prepare nanometer-sized semiconductors as colloids has provided the versatility with which these quantum dots can be manipulated.³ Of the many colloidal nanoparticles, CdSe nanocrystals have been most extensively studied and can be considered the prototypical system of colloidal quantum dots.

While the size dependence of the optical properties of CdSe quantum dots⁴ and the dynamics of their photoexcited carriers⁵ have received much attention, there is an increasing interest in the intraband processes.^{6–8} The size dependence of visible light-induced IR absorption in colloidal CdSe quantum dots capped with TOPO has been first reported in ref 6. The energies and the very large cross sections measured corresponded well to a one-electron transition between delocalized $1 S_e$ and $1 P_e$ states with a localized hole. To date, there have only been a few studies of visible-induced transient IR absorption probing intraband transitions in quantum dots, all of which have concentrated in the picosecond or faster time domains.^{6–9} The sensitivity and the wide spectral range of a Fourier transform infrared (FTIR) spectrometer with time-resolved step-scan methods¹⁰ provide effective means of probing the structures of transient photo-product states at nanoseconds to longer time delays. In this report, we present for the first time step-scan FTIR spectroscopic studies of intraband transitions in CdSe quantum dots.

Colloidal CdSe of several different sizes (35–59 Å in diameter) are investigated. The samples capped with trioctylphosphine oxide (TOPO) are prepared by previously established methods.^{3,11} ZnS-overcoated dots are prepared as described in ref 12. Recapping of TOPO-capped dots with *p*-thiocresol is carried out in a manner similar to that described in ref 13 for 4-(trifluoromethyl)thiophenol. The average size and the size distribution are determined by correlation between the position of the first maximum in the absorption spectra and transmission electron microscopy and small-angle X-ray scat-

tering.¹⁴ The size distribution is between 5 and 10%. For room-temperature solution measurements, samples are dispersed in chloroform and injected into a cell with BaF₂ windows separated by a 25 μ m Teflon spacer. All other samples are prepared as KBr pellets after precipitation of TOPO-capped dots (thiocresol-capped dots) by methanol (hexane), washing several times with methanol (hexane) and drying the resulting powder under N₂ flow.

The transient infrared absorption is measured with a Nicolet Magna 860 FTIR spectrometer operating in step-scan mode. The samples are photoexcited at 532 nm. Pulses of ~ 8 ns duration and ~ 7 mJ energy illuminate a 1 cm² area of the sample. A Ge window is placed in front of the photovoltaic HgCdTe detector to filter out scattered laser light as well as deep-trap emission from the samples. The resolution of the spectrometer is set at 32 cm⁻¹ and the spectral range at 400 to 7800 cm⁻¹. The collection of single-sided interferograms corresponding to this spectral range and resolution requires approximately 640 mirror steps for each scan. The photolysis and stepping repetition rates are approximately 3 Hz. Typically, 10–20 scans, requiring a total of 1–2 h, are averaged together for each sample.

Figure 1A shows the room temperature optically induced IR absorption of thiocresol-capped CdSe nanocrystals (solid line) and (CdSe)/ZnS (core)shell nanocrystals capped with TOPO (dashed line) in CHCl₃ at short (<20 ns) delays. The two samples are of similar optical density in the visible. The curves are least-squares fits to a single Gaussian. The corresponding visible-induced IR absorption maxima are 0.39 and 0.37 eV for thiocresol-capped and ZnS-overcoated dots, respectively. Overcoating CdSe with ZnS has been shown to significantly improve the quantum efficiency of the band edge luminescence by passivating surface trap states.¹² Thiocresol on the other hand introduces surface hole traps leading to almost complete quenching of the band edge luminescence.⁸ As expected, faster dynamics are seen for ZnS overcoated dots (Figure 1B). The curves in Figure 1B are three-exponential fits and the longest measured time constants are 2 μ s (0.7%) for ZnS-coated dots and 11 μ s (7.6%) for thiocresol-capped dots. Introduction of surface hole states by thiocresol decreases the electron and hole wave function overlap, reducing radiative and nonradiative recombination rates. This effectively prolongs the optically induced IR absorption.

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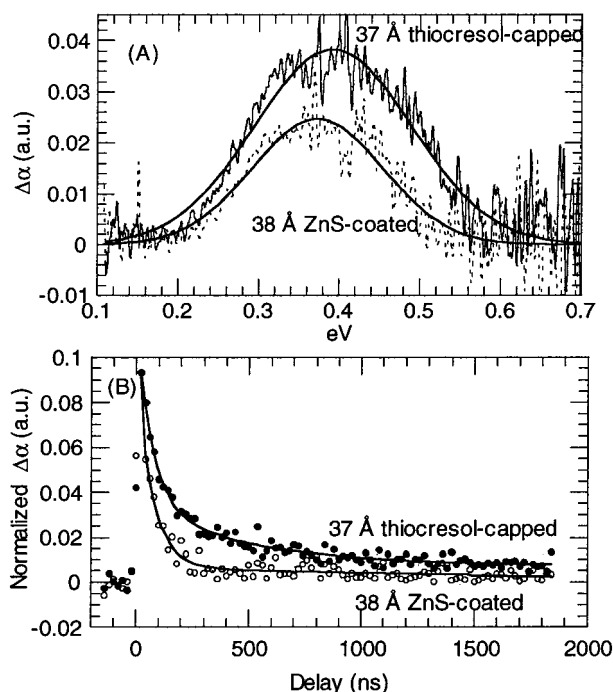


Figure 1. Visible light-induced IR absorption of thiocresol-capped and ZnS-overcoated CdSe nanocrystals dispersed in chloroform at 295 K (A). Both spectra are averages of the IR absorption at short time delays (20–200 ns) where there is maximum signal. Each spectrum is fitted to a single Gaussian. (B) is the time trace of the transient IR signal at maximum absorbance change ($\Delta\alpha$) arbitrarily normalized for comparison. The curves are three-exponential fits.

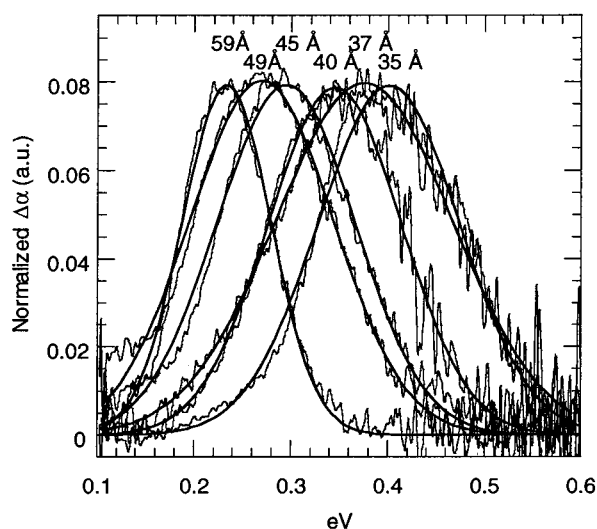


Figure 2. Room temperature visible light-induced transient FTIR spectra of thiocresol-capped CdSe nanocrystals of indicated sizes in KBr. The spectra are taken at short time delays (averaged over ~20–200 ns delays) where there is a maximum signal. There are no significant differences in the spectral position or the line widths of the transient IR absorption at 295 or 80 K.

The transient IR absorption also reveals the remarkable size-tunable properties of quantum dots. Figure 2 shows the room temperature optically induced IR absorption of several sizes of thiocresol-capped CdSe nanocrystals in KBr.¹⁵ Each spectrum is fitted to a Gaussian. There are no significant differences in the spectral position and line widths at 80 K. In Figure 3, the size dependence of the intraband transitions is shown. The open squares are measurements at 80 K and filled circles are at room temperature. All samples shown are thiocresol-capped CdSe dots in KBr unless otherwise noted. The filled triangles are

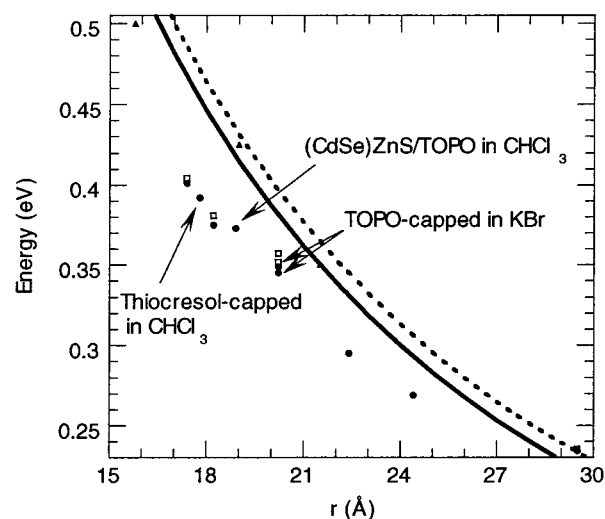


Figure 3. Size dependence of the visible-induced IR transition energies. Filled circles are measurements at 295 K. Open squares are measurements at 80 K. All samples are thiocresol-capped CdSe embedded in a KBr pellet unless otherwise noted. Filled triangles are experimental results from ref 6. The solid line (dashed line) is the calculated energy for the $1 S_e - 1 P_{ez}$ ($1 P_{ex,y}$) transition from ref 6.

results from ref 6. The solid line is the calculated $1 S_e - 1 P_{ez}$ transition and the dashed line is the calculated $1 S_e - 1 P_{ex,y}$ transition energy with corrections for the Coulomb interaction between a delocalized electron and a surface-localized hole, as described in ref 6. $1 P_{ez}$ ($1 P_{ex,y}$) corresponds to $1 P_e$ states along (perpendicular to) the axis where the localized hole lies. There is a discrepancy of ~0.04 eV between results obtained in ref 6 and our current experiments. While there is no time dependence of the spectral position of the visible-induced IR absorption at times >20 ns, there may be spectral shifts that occur between picosecond and nanosecond time scales. At this stage, there is not enough experimental evidence to speculate on what causes the discrepancy between picosecond and nanosecond time regimes, and resolving this discrepancy is left up to future studies.

The most striking feature of thiocresol-capped CdSe quantum dots is the long lifetimes of the delocalized electron states that they exhibit. While at room temperature there is no evident trend in the lifetimes of the delocalized electron states with respect to size, at 80 K larger dots seem to exhibit longer lifetimes (Figure 4A,B). Even at room temperature, all of the thiocresol-capped dots show significant IR absorption 1 μ s after the optical excitation. Figure 5 shows the time evolution of visible-induced IR absorption of 59 Å diameter CdSe dots capped with thiocresol at 80 K. The inset shows that there is approximately 30% of the initial (at 10 μ s delay) visible-induced IR absorption at 720 μ s delay. The longest lived component from the least-squares fit to three exponentials of the time decay curve is 1.5 ms. Although fairly long-lived electron states may be expected in TOPO-capped dots on the basis of their long fluorescence lifetimes (~1 μ s), what is observed in the step-scan FTIR studies is 3 orders of magnitude longer. We attribute this extremely long-lived delocalized electron state to the efficient hole trapping enhanced by surface modification with thiocresol and by the absence of electron trapping states. This electron state is a delocalized state (as opposed to a surface trap state) since there is a distinct size dependence, and for a given size, different surface modifications do not change the spectral position of the IR absorption. At lower temperatures, these electron states may exhibit even longer lifetimes.

In summary, we have shown that surface modification of quantum dots can lead to enhanced and prolonged transient IR

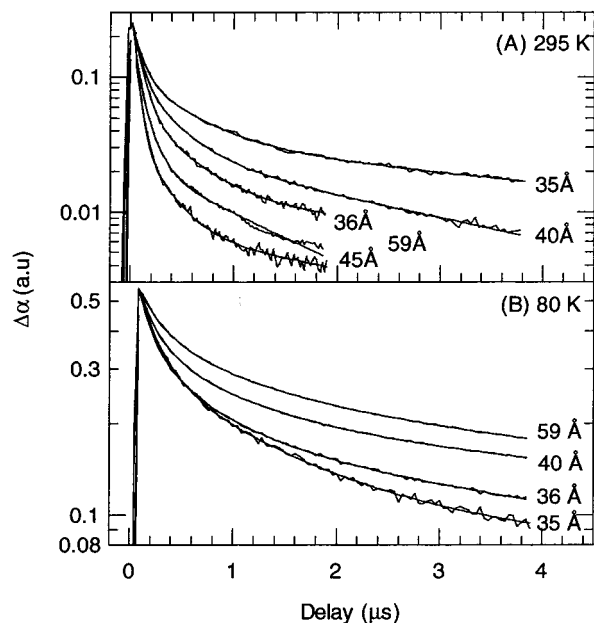


Figure 4. Time evolution of thiocresol-capped CdSe nanocrystals in KBr at 295 K (A) and at 80 K (B). The same fits are shown as in Figure 1B. The baselines for both figures lie below 0.001 absorption change and are omitted for clarity.

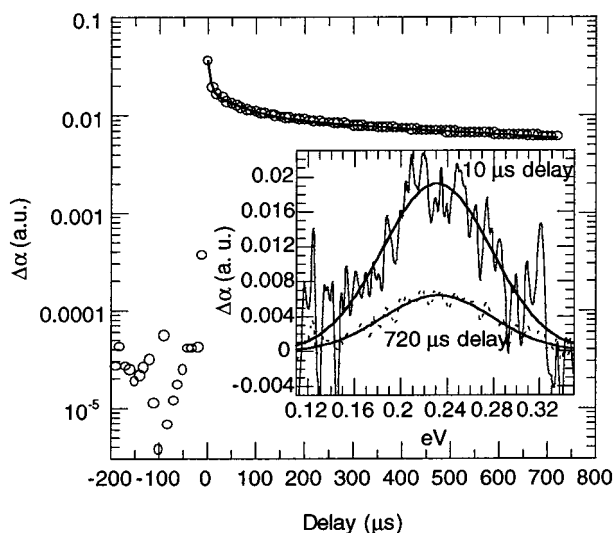


Figure 5. Time evolution of the optically induced IR absorption of 59 Å diameter CdSe nanocrystals capped with thiocresol measured at 80 K. The sample is prepared as a KBr pellet. The curve is a least-squares fit to three exponentials, which gives the longest component with a time constant of 1.5 ms. The inset shows the transient FTIR spectra at 10 μs (solid line) and 720 μs (dotted line) delays. Each spectrum is fitted to a Gaussian.

absorption in agreement with results of ref 8. Very long (>1 ms) delocalized electron states are observed. The size-tunability of the intraband transitions along with facile surface modifications makes colloidal quantum dots a promising material in

understanding the carrier dynamics of quantum-confined systems as well as in applications in infrared optoelectronic devices. The combination of step-scan FTIR and transient intraband absorption promises to be very fruitful in addressing charge-transfer processes in nanocrystalline materials.

Acknowledgment. M.S.B. and S.S. acknowledge the W. M. Keck foundation for the purchase of specialized equipment. This work was funded by the National Science Foundation under grant No. DMR-9731642. We made use of the MRSEC Shared Facilities supported by the National Science Foundation under grant No. DMR-9400379.

Supporting Information Available: The absorption spectra of the samples studied and the fluorescence spectra of one of the samples with different surface modifications. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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