Electronic Structure and Photoexcited-Carrier Dynamics in Nanometer-Size CdSe Clusters

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We use transient optical hole burning and photoluminescence to investigate the static and dynamic electronic properties of 32-Å CdSe quantum dots. We observe a number of discrete electronic transitions, resolve LO-phonon progressions, and obtain homogeneous linewidths and electron–LO-phonon couplings. We find that the band-edge luminescence is *not* from the exciton state but from a surface trapped state. Rapid (~160 fsec) trapping into these surface states results in long-lived (~10–100 nsec) bleach and induced-absorption features in pump-probe experiments.

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Semiconductor crystallites which are small compared to the bulk exciton Bohr radius exhibit three-dimensional electron and hole confinement.[1,2] They show discrete, large-molecule–like electronic states that shift to higher energy with smaller particle size. They are commonly referred to as nanometer-scale clusters or quantum dots. Extensive research on semiconductor quantum wells has shown that restriction of excitons to two dimensions results in spectral confinement of the oscillator strength which can be exploited in the design of nonlinear optical devices. In principle, the further reduction of dimensionality in quantum dots should lead to enhanced nonlinear optical properties.[3] The presence of the crystallite surface as a boundary and source of surface states makes nanometer-scale clusters fundamentally different in principle from epitaxial low-dimensional structures such as quantum wells and quantum wires. This aspect and the question of the response of a small finite lattice to a resident electron-hole pair remain poorly understood.

The effective-mass model, including the effects of Coulomb correlations and the internal structure of the valence band, has been applied extensively to nanometer-scale clusters.[1-7] The lowest excited state, labeled $1s_e$-$1s_h$ and commonly referred to as the exciton state, in principle has both carriers in totally symmetric particle-in-a-sphere eigenstates with nodes at the crystallite surface. The true homogeneous linewidth and electronic character of this state in well characterized nearly monodisperse CdSe crystallites is the central issue of this Letter. Fast transient optical studies of CdS, CdS$_x$-Se$_{1-x}$, and CdSe crystallites, principally in silicate glasses and polymer films, have previously revealed a fast bleaching of exciton absorption, induced absorption attributed to biexciton formation, and photophysical hole burning.[7-11] These samples typically emit from deep trap states, and the observed spectra are complicated by averaging over various and most uncharacterized distributions, such as those of size, structure, defects, stoichiometry, and surface chemistry.

We study chemically synthesized CdSe crystallites dispersed in a Lewis base organic solvent (90% Bu$_3$P, 10% Bu$_3$PO). This type of solvent complexes (e.g., bonds to) metal ions such as Cd and in our system most likely passivates surface Cd atoms. TEM and x-ray analysis shows that this solution contains CdSe crystallites having the bulk wurtzite structure and having less than one stacking fault per crystallite, on average.[12] The mean crystallite diameter in our sample is 32 Å (standard deviation 8%, measurement error dominated). This corresponds to approximately 800 atoms per crystallite, $\sim \frac{1}{3}$ of them being surface atoms. The low-temperature (~15 K) absorption spectrum [Fig. 1(a)] shows a well resolved $1s_e$-$1s_h$ transition at ~525 nm and a shoulder at ~440 nm corresponding to that same transition with the hole in the spin-orbit-split valence band.[13] Low-temperature luminescence with excitation to the blue side of 475 nm to excite all sizes [Fig. 1(a)] is mostly "band edge" with a high quantum yield (>0.1).

Low-temperature PL (photoluminescence) and PLE (photoluminescence excitation) experiments can be used to obtain homogeneous-line-shape information about the inhomogeneously broadened bands of Fig. 1(a). The smallest crystallites in the sample are selectively probed in PLE when monitoring a narrow spectral region on the blue edge of the luminescence band. Figure 1(b) shows a cw PLE spectrum from emission at 530 nm. The shape of this spectrum is nearly independent of the emission frequency on the blue edge of the emission band. The PLE spectrum of Fig. 1(b) is essentially a single-cluster absorption spectrum with small residual inhomogeneous broadening. A number of discrete electronic transitions and an LO-phonon progression are cleanly resolved for the first time in any nanometer-scale cluster. Feature *A* corresponds to the $1s_e$-$1s_h$ transition with LO-phonon substructure well resolved. The weaker features *C* and *D* are tentatively assigned to the formally forbidden $1s_e$-$1p_h$ and $1s_e$-$2s_h$ transitions, respectively. Feature *B* is the previously discussed shoulder (*B*) in the absorption spectrum [Fig. 1(a)], with the spacing between *A* and *B* (~0.45 eV) that of the bulk spin-orbit splitting.[13] Higher excited states such as $1p_e$-$1p_h$ are probably responsible for the broad continuum absorption under

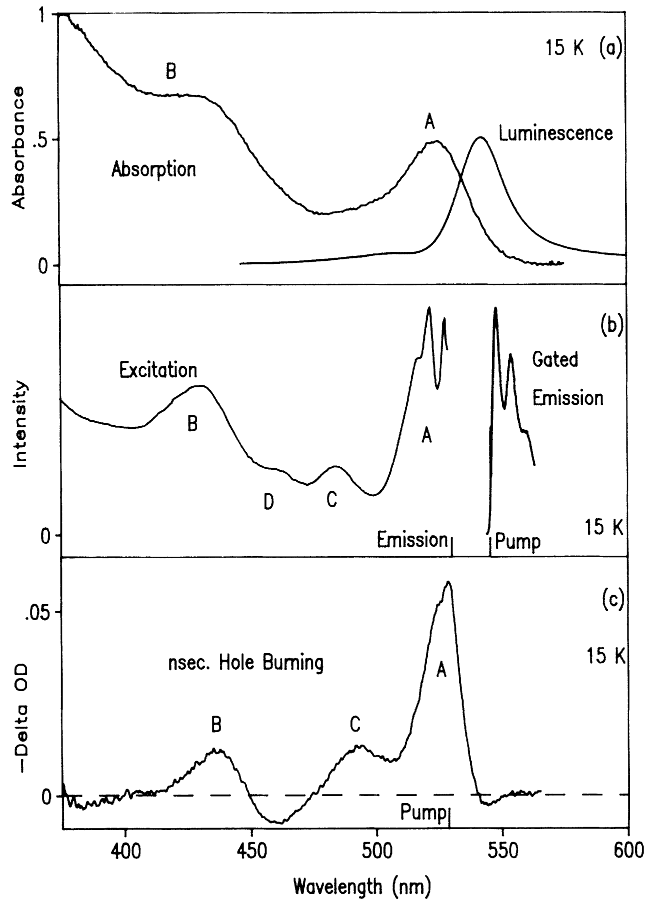

FIG. 1. (a) Absorption and fluorescence spectra for the CdSe nanometer-scale cluster sample (average size 32 Å). (b) PLE and gated-emission spectra. Emission at 530 nm with a ~10-cm^{-1} bandpass was monitored for PLE. A 10-nsec pulse at 545 nm was used as excitation for the gated emission with a 20-nsec gate and a delay of ~30 nsec between pump and emission. Leftover pump light can be seen as a small spike near the bottom of the blue edge of the emission. (c) Bleach spectrum from the nsec pump-probe experiment. Note that the y axis is $-\Delta$OD. Positive-going peaks correspond to the absence of ground-state absorption and negative peaks are induced absorptions. A 10-nsec pump pulse at 535 nm was used. The probe was a nsec white-light source detected using a 10-nsec gate with a delay of ~40 nsec between pump and probe. All the data were taken with the sample at ~15 K. The assignment of the broad electronic features and the sharp phonon progressions is given in the text.

feature *B*.

The largest clusters in the sample are selectively excited by pumping on the red edge of the $1s_e$-$1s_h$ absorption band. Figure 1(b) shows the emission using a ~10-nsec pump pulse at 545 nm. This emission decays on a 100-nsec scale in a multiexponential manner. A purely radiative τ of ~0.5 nsec would be expected based on the $1s_e$-$1s_h$ absorption cross section. There is also an unambiguous energy shift between the pump frequency and the luminescence zero-LO-phonon line of ~75 cm^{-1}, nearly independent of the pump-laser frequency. These results show that the emitting state is *not* the exciton state, unexpectedly and despite the simple appearance of band-edge emission. The long multiexponential decay suggests one or both carriers localized in surface states with small overlap between the electron and hole wave functions. The three vibronic features seen are spaced by ~200 cm^{-1} which is consistent with the bulk LO frequency (210 cm^{-1}).[13] The emission spectrum in Fig. 1(b) tracks the pump frequency in this region as smaller crystallites are excited at higher energy.

Complementary optical hole-burning experiments were also performed at ~15 K on nanosecond (~10 nsec/pulse) and subpicosecond (~350 fsec/pulse) time scales. In these pump-probe experiments, a spectrally narrow and intense pump-laser pulse is tuned inside the $1s_e$-$1s_h$ absorption band. A small distribution of crystallites whose $1s_e$-$1s_h$ absorption overlaps with the pump wavelength is excited. The ΔOD (bleach) spectrum then records both enhanced transmission due to the absence of ground-state absorption and induced absorption corresponding to the absorption spectrum of photoexcited clusters. The information in PLE and hole burning is complementary; the PLE spectrum contains mostly ground-state absorption information while the bleach spectrum results from both ground- and excited-state absorptions. The dependence of the ΔOD on power was found to be linear for pump intensities $\lesssim 50\ \mu$J/cm^2.

The bleach spectrum [Fig. 1(c)] exhibits discrete features and consists of the $1s_e$-$1s_h$ absorption (*A*) centered around the pump frequency showing a small shoulder near the peak which is LO-phonon substructure. Features *B* and *C* coincide with those in the PLE spectrum. The induced absorptions between *B* and *C* and to the red side of *A* correspond to excited-state absorptions. The absence of bleach to the blue side of *B* indicates that ground- and excited-state absorptions are of equal magnitude in this region. All the features in the hole-burning spectrum of Fig. 1(c) appear with an instrumentally limited rise time of ~500 fsec. There is negligible decay in this spectrum even after our maximum delay of 300 psec in our subpicosecond experiments. The shape of the bleach spectrum is virtually independent of pump frequencies which fall within the inhomogeneously broadened $1s_e$-$1s_h$ absorption band. We do not see any spectral evolution in our subpicosecond pump-probe experiment once the pump and probe are temporally separated: The bleach spectrum with a delay of 1 psec between pump and probe in our subpicosecond experiment looked identical to that in our nanosecond experiment (~40-nsec delay) performed on a different apparatus.

We do see spectral evolution in our subpicosecond experiments when the pump and probe beams are temporally overlapped, however. The sharp bleach feature around the pump frequency in Fig. 2 is only present dur-

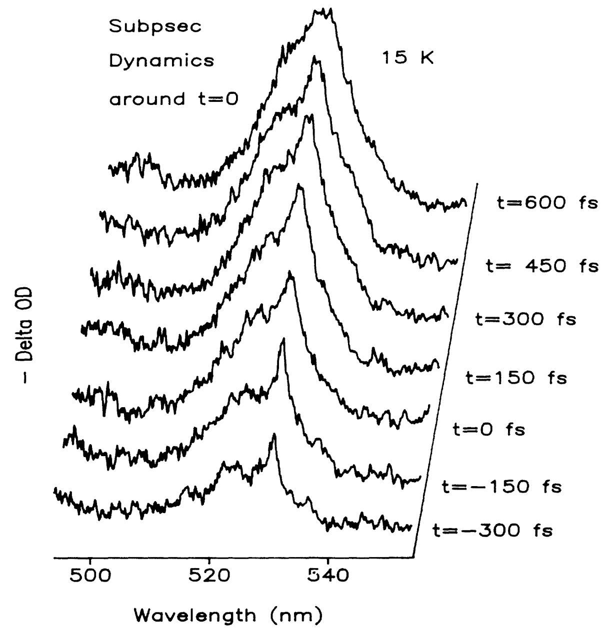

FIG. 2. Spectral evolution of the bleach spectrum during pump and probe temporal overlap. The coherence spike is cleanly resolved as described in the text. The time axis indicates delay between pump and probe beams.

ing temporal overlap of the pump and probe. We assign this structure to a probe-pump-matter interaction in $\chi^{(3)}$ which produces a hole linewidth which is narrower than the homogeneous Frank-Condon linewidth. This is commonly referred to as a coherence spike or artifact.[14,15] Using the formalism of Refs. 14 and 15, quantitative modeling of these data requires a fast (< 500 fsec) depopulation of the initial exciton state into some long-lived trap state, presumably the long-lived state observed in luminescence.

Combining the pump-probe and emission results leads us to conclude that the induced absorptions observed in the bleach spectrum are the result of exciting an *e-h* pair in clusters where the first *e-h* pair has relaxed into localized surface states. Bleaching of the exciton transition due to static fields set up by surface localized carriers has been previously suggested.[9] The small (~ 75 cm^{-1}) shift between excitation and emission in Fig. 1(b) indicates energy relaxation from the $1s_e$-$1s_h$ state to the surface states. This small shift, however, also indicates that the localized surface states are almost isoenergetic with the $1s_e$-$1s_h$ state. We conjecture that the hole localizes on threefold-coordinated surface Se atoms. This type of surface state in the bulk has been calculated to be just below the top of the valence band.[16] Structured band-edge luminescence from nanometer-scale cluster samples clearly does not, by itself, necessarily imply free-carrier recombination.

This mechanism is confirmed by quantitative modeling of the PL, PLE, and hole-burning spectra. A single set of parameters reproduces the three experiments. Figure 3 presents extracted single-cluster spectra and a fit to the experimental data. The $1s_e$-$1s_h$ transition contains a number of LO-phonon replicas [from the PLE spectrum in Fig. 1(b)] which merge to form an absorption tail to the blue. The homogeneous linewidth of the zero-phonon peak is found to be ~ 130 cm^{-1}, over 20 times larger than in bulk exciton spectra. (A ~ 100-cm^{-1} width for the $1s_e$-$1s_h$ state has also been recently reported in resonance Raman fits of similarly sized CdS crystallites.[17]) The ratio of the first- to zero-LO-phonon integrated intensity is 1.4, which is a factor of ~ 6 smaller than the bulk value. This decrease in electron-LO phonon coupling in nanometer-scale clusters compared to the bulk has been previously found in resonance Raman experiments[17,18] and has been predicted by analysis of Frohlich coupling.[3] The linewidth in luminescence, about 20 cm^{-1}, is far narrower than in absorption. The experimental linewidths in PL and PLE are actually dominated by the absorption linewidths due to the sample inhomogeneous broadening (~ 930 cm^{-1}, consistent with the sample size distribution). The ratio of the first- to zero-LO-phonon peaks in luminescence is ~ 0.3. Remarkably, electron-phonon coupling is smaller in luminescence from the surface localized states than in absorption into the $1s_e$-$1s_h$ state. The large linewidths in absorption are consistent with a fast (< 500 fsec) decay into these surface states. Assuming that these linewidths are dominated by T_1 processes yields an exciton lifetime of ~ 160 fsec. The much smaller linewidths in luminescence reflect the stationary nature of the emitting states and the fact that they are entirely different from the ab-

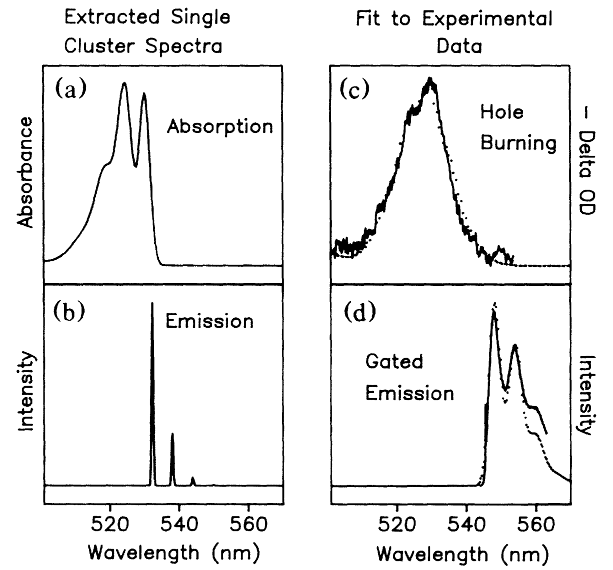

FIG. 3. (a),(b) Simulated single-cluster absorption and fluorescence spectra and (c),(d) fits to the subpicosecond bleach ($t = 1.5$ psec) and to the gated-emission spectra.

sorbing state. The fit spectra (dotted lines) in Fig. 3 were obtained by simulating the hole-burning and the PL experiments using the extracted single-cluster parameters. The large width of the hole burned $(\sim 550\ \mathrm{cm}^{-1})$ in the $1s_e$-$1s_h$ absorption band is a result of a combination of residual electron-LO phonon coupling and the lifetime-broadened homogeneous linewidths of the individual LO-phonon replicas.

In this Letter we describe a comprehensive set of optical experiments on a well characterized sample of 32-Å-diam CdSe quantum dots. The high quality of our sample is demonstrated by the wealth of spectral features obtained in PLE and PL. Integrating *all* the data allows us to cleanly extract single-cluster absorption and band-edge fluorescence spectra, yielding homogeneous linewidths and electron-LO phonon couplings. Unexpectedly, we find that the band-edge emission is *not* from the exciton state, but from a state where one or both carriers are trapped and localized on the surface. This trapped state is responsible for the bleach and induced-absorption features observed in our pump-probe experiments. The presence and importance of surface states in nanometer-scale clusters reveals a fundamental difference between dispersed quantum dots and quantum wells which have epitaxial surfaces. The broad linewidths and dilution of oscillator strength in LO-phonon progressions point to a potential difficulty in using these clusters as nonlinear optical materials where sharp, high-oscillator-strength spectral features are required. Less polar semiconductors such as the III-V's may reduce the LO progressions. Epitaxial growth of some optically inert material around the nanometer-scale clusters to prevent formation of surface states[19] may also help to experimentally realize the potential of quantum dots.

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