Ultrafast dynamics of inter- and intraband transitions in semiconductor nanocrystals: Implications for quantum-dot lasers

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Application of femtosecond transient absorption in the visible and near-IR spectral ranges and time-resolved photoluminescence allows us to separate electron and hole relaxation paths and to map the structure of interband and intraband optical transitions in CdSe and CdS nanocrystals (NC's) with a wide range of surface properties. In contrast to electron relaxation, which is controlled by NC surface passivation, depopulation of hole quantized states is extremely fast (sub-ps-to-ps time scales) in all types samples, independent of NC surface treatment (including NC's overcoated with a ZnS layer). Our results suggest that ultrafast hole dynamics are not due to trapping at localized surface defects such as a vacancy, but rather arise from relaxation into intrinsic NC states or intrinsically unpassivated interface states. [S0163-1829(99)51228-9]

Three-dimensional (3D) quantum confinement results in discrete energy structures and atomiclike selection rules for interband and intraband optical transitions in semiconductor nanocrystals (NC's).[1–3] Structures of interband transitions in II-VI NC's have been extensively studied using linear absorption,[4] photoluminescence (PL) excitation,[5] and transient absorption (TA).[6,7] Time-resolved TA studies have also been applied to probe energy relaxation and recombination dynamics in NC's.[7–9] The large level separation has been predicted to significantly inhibit energy relaxation in NC's due to a ''phonon bottleneck,''[10] which, however, has been argued against by recent experiments.[7,8,11] The relaxation of carriers from the lowest quantized states in NC's can be significantly faster than for radiative decay, due to the enhancement of nonradiative processes associated, e.g., with surface trapping.[8,9] Since both electrons and holes contribute to interband TA signals measured with a visible probe, visible TA data do not allow a reliable separation of electron and hole dynamics, which is essential for understanding the mechanisms for carrier trapping and the origin of trapping sites. Additionally, most of the ultrafast studies of II-VI quantum dots have concentrated on NC/glass samples, which have poorly controlled surface properties. Therefore, it remains unclear whether the fast initial depopulation of quantized states in NC's is entirely due to trapping at surface defects or due to relaxation into intrinsic quantum dot states.

Separation of electron and hole dynamics is possible by using TA with an IR probe tuned in resonance with either electron or hole *intraband transitions*.[12] Of the few IR TA studies of quantum-dot systems,[13,14] all have concentrated on electron intraband transitions, whereas hole energy structures as well as hole dynamics have not been studied to date. In this paper, we report a femtosecond (fs) study of *interband and intraband* (electron and hole) transitions in II-VI quantum dots with a range of surface properties performed combining fs TA in the visible and IR spectral ranges together with time-resolved PL. Our data indicate that in contrast to

electron dynamics, controlled by NC surface passivation, hole dynamics are extremely fast in all samples with apparently different surface properties, suggesting that they are not due to trapping at localized surface defects such as vacancies, but are rather due to relaxation into either intrinsic NC states, or surface states that remain unpassivated even under the range of surface treatments of this work.

TA measurements in the visible spectral range were performed using a fs pump-probe experiment with a white-light fs continuum, as previously described.[15] The pump-photon energy was 3.1 eV, the pump (probe) pulse duration was 100 fs. In IR TA measurements, the probe pulses were derived from an IR optical parametric amplifier, tunable in the range 1.1–2.7 μm. Time-resolved PL was measured using fs up-conversion[16] with an ~150-fs time resolution. We studied CdSe and CdS NC's prepared by colloidal synthesis[17] and high-temperature precipitation in molten glasses.[4] Colloidal CdSe samples were of two types: NC's passivated with molecules of tri-n-octylphosphine oxide[17] (TOPO) and ''overcoated'' NC's containing a final layer of ZnS.[18] NC sizes and size distributions were determined from linear absorption spectra using calibration curves derived from a comparison of optical data with data of transmission electron microscopy and small-angle x-ray scattering.[17] The NC mean radii (R) varied from ~1 to ~4 nm. The NC size dispersion was 4–9 % in colloids and 15–25 % in glass samples. All measurements were performed at room temperature.

In Fig. 1, we show visible-to-near-IR spectra of pump-induced absorption changes $\Delta\alpha$ (symbols) for TOPO-passivated CdSe NC's with $R = 1.73$ (a) and 1.17 nm (b) at pump-probe delay times (Δt) 1, 5, and 50 ps. To exclude effects of many-particle interactions on carrier dynamics, these data were taken at low pump intensities corresponding to $N_{eh} < 1$ [N_{eh} is the average number of electron-hole (e-h) pairs excited per NC]. Electron relaxation into the lowest $1S$ state in these samples occurs within less than 1 ps.[8] Popula-
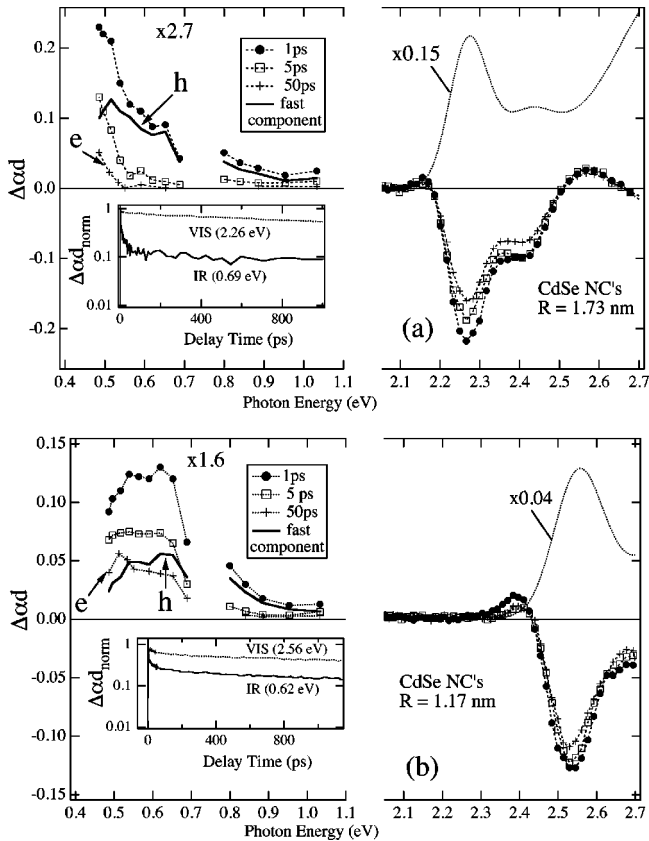
FIG. 1. Visible-near-IR TA spectra (symbols) recorded at different delay times (Δt) between pump and probe pulses for CdSe colloidal NC's (TOPO passivation) with $R = 1.73$ (a) and 1.17 nm (b) (dotted lines are linear absorption spectra). Insets: Comparison of visible ($1S$ transition) and IR TA dynamics. All data were taken at a pump fluence $w_p = 0.32$ mJ cm^{-2}.

FIG. 2. (a) Visible (2.26 eV) and (b) IR (0.69 eV) TA dynamics for CdSe colloidal NC's ($R = 1.73$ nm) with differently prepared surfaces: fresh (circles) and aged (squares) TOPO-capped NC's, and NC's overcoated with a ZnS layer (crosses). Lines are fits to a double-exponential decay.

tion of the $1S$ state leads to state-filling-induced saturation of the $1S(e)$-$nS_F(h)$ interband optical transitions (F is the total hole angular momentum, and n is a number of the state of a given symmetry[4]) with associated bleaching features ($\Delta\alpha < 0$) in the visible portion of TA. For the 1.73-nm sample, we observe two bleaching bands at 2.26 and 2.4 eV, which mark the positions of $1S(e)$-$1S_{3/2}(h)$ ($1S$ bleaching) and $1S(e)$-$2S_{3/2}(h)$ ($2S$ bleaching) transitions, respectively.[5] In the case of the 1.17-nm sample, only one band at 2.53 eV ($1S$ transition) is seen within the observation range. The spectral positions of the TA features closely match those seen in linear absorption (dotted line).

The state-filling-induced bleaching of interband optical transitions is proportional to the sum of the occupation numbers of the electron and hole states involved in these transitions. However, at room temperature, the hole population is spread over a large number of valence-band states, and the bleaching signals are dominated by electron populations. This is clearly indicated by the fact that in all colloidal and glass samples, the $1S$ and $2S$ bleaching bands, which involve the same electron ($1S$) but different hole states, show essentially identical dynamics at $\Delta t > 2-3$ ps, dominated by depopulation of the common $1S$ electron level.

In the near-IR spectral range, for both samples shown in Fig. 1, $\Delta\alpha$ is positive indicating excited-state absorption due to intraband transitions. For both the 1.73-nm and 1.17-nm
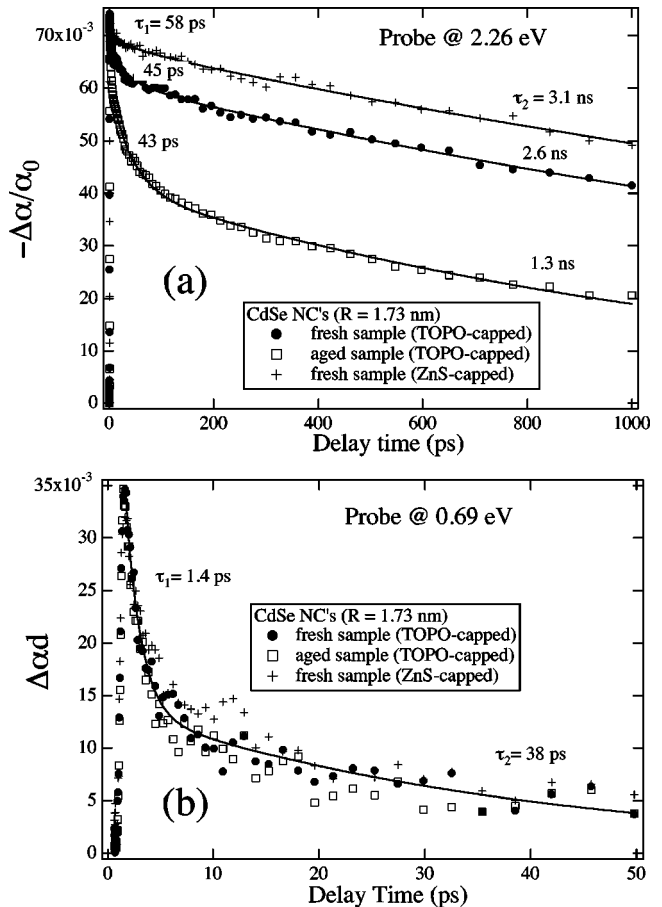
samples shown in Fig. 1, over the IR range studied, the intra-conduction-band contribution can only be due to the $1S$-$1P$ electron transition. In NC's with $R = 1.73$ nm, this transition has an energy of ~ 0.45 eV.[13] Assuming a ~ 0.1 eV transition broadening (estimated for a $\sim 5\%$ size dispersion), the $1S$-$1P$ electron absorption does not contribute significantly to the TA signal measured in the 0.55–0.7-eV range, meaning that it is almost entirely due to intra-valence-band transitions. Consequently, the dynamics of this signal are indicative of hole relaxation behavior.

In the inset to Fig. 1(a) and in Figs. 2(a) and 2(b) (circles) we compare time transients recorded for the 1.73-nm sample at visible [2.26 eV ($1S$ bleaching)] and near-IR (0.69 eV) spectral energies. In contrast to the relatively slow initial sub-100-ps relaxation of the $1S$ bleaching (electron dynamics), initial relaxation of the near-IR TA (hole dynamics) is extremely fast and occurs on the sub-ps-ps time scale. A pronounced difference in electron and hole relaxation rates allows us to separate electron and hole contributions to IR TA. Since the ``hole'' signal decays on the ps time scale, the 50-ps IR spectrum in Fig. 1(a) is characteristic of the electron $1S$-$1P$ absorption. To derive the fast hole-related portion of TA [thick solid line in Fig. 1(a)], we subtract the spectrum detected at 5 ps from the 1-ps spectrum which gives a band (hole near-IR intraband absorption) peaked at

~ 0.5 eV. Due to quantum confinement, the $1S$-$1P$ electron transition shifts to higher energies in NC's with $R = 1.17$ nm, leading to an increased relative contribution of the slow electron-related portion of TA in the near-IR spectral range [Fig. 1(b) and inset]. From the 50-ps "electron" TA spectrum [Fig. 1(b)], we can assign the energy of the $1S$-$1P$ transition to ~ 0.5-55 eV. The fast TA component reflecting the hole contribution peaks at ~ 0.64 eV.

Analysis of the $1S$ bleaching decay (electron relaxation) shows that it is very sensitive to NC surface properties. In Fig. 2(a) we compare $1S$ bleaching dynamics for three samples with the same NC radius (1.73 nm), but different degrees of surface passivation. These samples are freshly prepared TOPO-passivated NC's (circles), the same NC's but eight months after preparation (squares), and freshly prepared NC's overcoated with four monolayers of ZnS (crosses). For all samples, the $1S$ bleaching shows a two-component decay: initial sub-100-ps relaxation, followed by slow ns decay. In freshly prepared TOPO-capped NC's, the fast component is about 15% of the signal amplitude. The fast component is enhanced up to $\sim 50\%$ in the aged sample, but gets reduced (down to $\sim 7\%$) in the "overcoated" NC's. This comparison clearly indicates that the fast initial electron decay is due to trapping at surface defects. The number of these defects grows with the loss of passivation in aged colloids, resulting in increased availability of sites for electron relaxation. On the other hand, the number of surface defects is significantly reduced in NC's with an epitaxially-grown shell of a wide-gap semiconductor, resulting in the suppression of the fast component in the electron relaxation. Since in TOPO-capped NC's passivating molecules are coordinated to surface metal ions,[17] the electron traps are most likely associated with metal dangling bonds.

In contrast to the initial electron dynamics, which can be controlled by surface passivation, the hole dynamics are practically unaffected by NC surface properties, as clearly seen from comparison of IR traces [Fig. 2(b)] for the samples described in the previous paragraph. All three samples show nearly identical fast decay with a 1.4-ps time constant, indicating rapid depopulation of hole quantized states, independent of the surface passivation. The fast decay of "hole" IR signals (0.5–2 ps) is seen for all colloidal CdSe NC's (TOPO- and ZnS-capped) studied by us ($R = 1$–4 nm). Similar fast relaxation of near-IR signals (0.8–1.5 ps time constants) is also observed in CdSe/glass nanocomposites (NC radii from the 2.2–4.2 nm). The fact that hole dynamics are extremely fast in all types of samples, including "overcoated" NC's, indicates that these dynamics are not due to trapping at localized surface defects, but rather due to relaxation into intrinsic NC states which are likely of surface origin (e.g., hole self-trapped surface states as analyzed in Ref. 19) or intrinsically unpassivated Se or S lone pair sites. The importance of hole surface trapping (localization) in II-VI NC's has been also indicated by several previous experimental studies.[6,13,20]

For CdS NC/glass samples, in addition to TA measurements, we performed studies of PL dynamics. In contrast to state-filling-induced TA signals, which are proportional to the sum of the electron and hole occupation numbers, PL is proportional to the product of these numbers; therefore PL dynamics are dominated by carriers with the shortest relax-
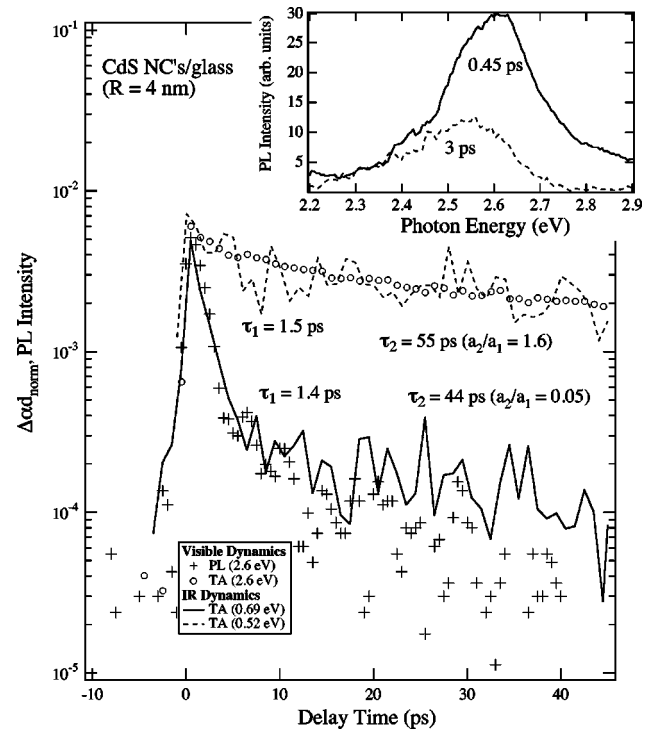

FIG. 3. Comparison of visible-TA and PL dynamics ($1S$ transition) with IR-TA dynamics in CdS/glass ($R \approx 4$ nm) sample ($w_p = 0.02$ mJ cm^{-2}). Time constants (τ_1 and τ_2) and amplitudes (a_1 and a_2) are taken from fits of the IR traces to a function $y = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2}$ (not shown for clarity). Inset: PL spectra detected at 0.45 and 3 ps after excitation.

ation time.[20] In Fig. 3, we show a comparison of PL and visible TA dynamics (both for the 1S transition) with IR TA dynamics for CdS NC's with $R \approx 4$ nm. The $1S$ bleaching is dominated by a component with a 55-ps time constant, due to electron surface trapping. The PL relaxation occurs on a much shorter (~ 1 ps) time scale, indicative of fast hole relaxation, analogous to that in CdSe samples. Interestingly, the 0.56-eV TA trace is almost identical to that for the $1S$ bleaching, indicating the dominant contribution of electrons into the IR signal at this spectral energy. With increasing probe spectral energy, the TA relaxation becomes faster, and at 0.69 eV, it closely matches that of PL, indicating that both are dominated by hole dynamics. Fast hole relaxation is accompanied by a low-energy PL shift (~ 60 meV) which provides an estimate of the hole localization energy (see the inset to Fig. 3).

The relaxation data shown above are also relevant to the important technological issue of room-temperature optical gain and lasing in NC media. Previously, optical gain[21–23] and lasing[21] in CdSe NC's have been demonstrated at cryogenic temperatures. To explore the possibility of achieving room-temperature gain, we studied the TA pump dependence for colloidal CdSe NC's (TOPO and ZnS capped) of various sizes with PL quantum yield up to $\sim 30\%$. In the inset to Fig. 4, we show a normalized $1S$-absorption change ($-\Delta \alpha / \alpha_0$, α_0 is the linear absorption) at $\Delta t = 2$ ps vs pump fluence w_p. The gain threshold corresponds to $-\Delta \alpha / \alpha_0 = 1$. None of the samples shows crossover from absorption to gain even at very high pump densities corresponding to $N_{eh} > 10$. Interestingly, in the plot of $-\Delta \alpha / \alpha_0$ vs N_{eh} (main frame of
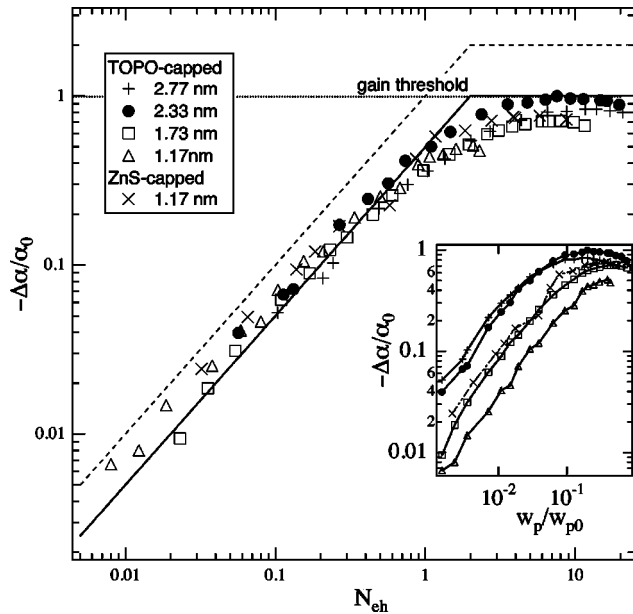
FIG. 4. Pump dependence of the normalized $1S$ absorption changes (symbols) in CdSe colloidal samples (TOPO- and ZnS-capped) with R from 1.17 to 2.77 nm plotted vs N_{eh} (main frame) or normalized pump fluence (inset) ($w_{p0} = 15.6$ mJ cm^{-2}). Lines are model curves for state filling in the system for which the lowest optical transition couples a populated electron state to either a populated (dashed line) or unpopulated (solid line) hole state.

Fig. 4), all experimental data points fall along one ''universal'' curve which shows a linear growth below $N_{eh} = 1$, and saturation at a level $-\Delta\alpha/\alpha_0 \approx 1$ above $N_{eh} = 1$. These data are compared with the dependence expected for state filling in a system for which the lowest optical transition couples a populated electron state to either a populated (dashed line) or unpopulated (solid line) hole state. This comparison strongly suggests that already at 2 ps after excitation all holes are removed from quantized states, consistent with our IR data indicating ultrafast hole trapping. Interestingly, time-resolved visible-TA data indicate that $1S$ optical gain is not observed even on the short 1-ps time scale, suggesting that during the energy relaxation the hole reaches the manifold of surface states before the electron relaxes into the $1S$ state. We also do not see any signatures of the ''biexciton'' gain[24] which should be located at spectral energies below the $1S$ transition. The latter is consistent with data of Ref. 22, indicating that the gain due to the biexciton-exciton transition is only observed at low temperatures ($T < 170$ K for 2.5-nm CdS NC's).

In conclusion, we have performed time-resolved PL and visible-to-near-IR TA studies of II-VI semiconductor NC's which allow us to directly compare the dynamics of inter- and intra-band transitions between quantized states. We observe extremely fast depopulation of hole quantized states (sub-ps and ps time scales) in all types of samples, independent of NC surface properties, indicating that hole trapping sites are not defect-related but rather are intrinsic to nanocrystal quantum dots. In contrast to this observation, initial fast electron relaxation is extremely sensitive to the degree of surface passivation, suggesting that it is due to trapping at surface defects, associated most likely with metal dangling bonds. We observe a ''universal'' size-independent TA pump-intensity dependence, indicating saturation of the $1S$ absorption bleaching before a crossover to gain occurs. This provides additional strong evidence that ultrafast depopulation of hole quantized states is a general feature of II-VI quantum dots.

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