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Mechanisms for intraband energy relaxation in semiconductor quantum dots: The role of electron-hole interactions

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To evaluate the role of nonphonon energy relaxation mechanisms in quantum dots and in particular the role of electron-hole (e-h) interactions, we have studied femtosecond carrier dynamics in CdSe colloidal nanoparticles in which the e-h separation (coupling) is controlled using different types of surface ligands. In dots capped with hole accepting molecules, the e-h coupling is strongly reduced after the hole is transferred to a capping group. By re-exciting an electron within the conduction band at different stages of hole transfer and monitoring its relaxation back into the ground state, we observe a more than tenfold increase in the electron relaxation time (from 250 fs to 3 ps) after the completion of the hole transfer to the capping molecule. This strongly indicates that electron relaxation in quantum dots is dominated not by phonon emission but by the e-h energy transfer.

In bulk semiconductors, intraband carrier relaxation is dominated by electron (hole)-phonon interactions.[1] These interactions also dominate carrier energy losses in two-dimensional (2D) quantum wells[2] and 1D quantum wires,[3] both having quasicontinuous energy spectra as bulk materials. A further reduction in the system dimensionality accompanying the transition to 0D quantum dots (QD's) is associated with a dramatic transformation in the energy spectra which become discrete and atomiclike.[4] Reduced availability of pairs of electronic states satisfying energy and momentum conservation leads to a strong reduction in the efficiency of electron-phonon interactions in QD's, an effect known as the ''phonon bottleneck.''[5] This effect has been expected to dramatically slow down energy relaxation in QD's in comparison with that in systems of higher dimensionality. However, recent ultrafast measurements demonstrate that in both chemically synthesized[6–8] and epitaxial[9] QD's, energy relaxation is extremely fast [picosecond (ps) – sub-ps time scales], indicating a relaxation mechanism which bypasses the ''phonon bottleneck.''

Several nonphonon mechanisms have been proposed for energy relaxation in QD's. These are interactions with defects,[10] Auger interactions with electron-hole (e-h) plasmas outside a QD,[11] and Auger-type e-h interactions involving transfer of the electron excess energy to a hole, with subsequent fast hole relaxation through its dense spectrum of states.[12] The first two of these mechanisms are not intrinsic to QD's and cannot explain, for example, our recent data for colloidal dots.[7] These data indicate that in colloidal nanoparticles, energy relaxation does not show any significant dependence on QD surface properties (i.e., the amount of surface defects) and remain almost identical for different liquid- and solid-state matrices, including transparent optically passive glasses, polymers, and organic solvents, for which no carriers are generated outside the dot.

E-h interactions are intrinsically present in all types of QD's, including both epitaxial and colloidal systems. In the present paper, to evaluate the effect of these interactions on carrier intraband dynamics, we study electron relaxation from the first excited $(1P)$ to the ground $(1S)$ quantized state as a function of the e-h separation, dictated by the QD surface properties.[13,14] In the presence of a ZnS capping layer which creates a confining potential for both electrons and holes,[15] the electron relaxation is not significantly affected by modifications in the hole wave function during hole relaxation. For dots passivated with hole-accepting molecules (pyridine capping), we observe a dramatic increase in the electron relaxation time (from 250 fs to 3 ps) after the electron and hole are spatially separated as a result of the hole transfer to the capping group.

To monitor carrier-induced absorption changes $(\Delta\alpha)$, we use a three-pulse femtosecond (fs) transient absorption (TA) experiment [top of Fig. 1(a)] in which the sample is excited by a sequence of two ultrashort pulses [one in the visible and another in the infrared (IR) spectral ranges] and is probed by broad-band pulses of a fs white-light continuum. The visible interband pump (3 eV photon energy; 100 fs pulse duration) is used to create an e-h pair in the dot, whereas the time-delayed intraband IR pump (tunable within 0.49–1.1 eV; 250 fs pulse duration) is used to reexcite an electron or a hole within the same band [bottom of Fig. 1(a)]. Pump-induced absorption changes are detected over the range 1.2–3 eV using a chirp-free phase-sensitive technique[16] with a lock-in amplifier synchronized to either chopped visible or chopped IR pump beams. Signals obtained by modulation of the visible pump provide information on absorption changes induced by either interband excitation alone (IR pump is ''off''), or by combined inter- and intraband excitations (IR pump is ''on''). Modulating the IR pump, one obtains information solely due to intraband reexcitation. A similar experiment but using a single IR wavelength for both the probe and

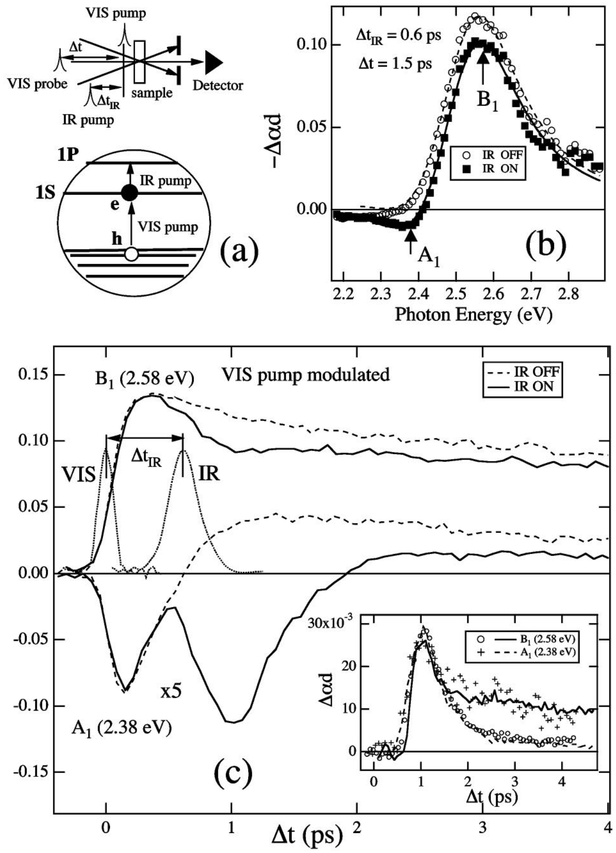

FIG. 1. (a) Schematics of a three-pulse pump-probe experiment (see text for details). (b) Spectra of absorption changes induced by a visible pump pulse alone (circles) and by visible and IR pulses together (squares). Lines are fits assuming that in all photoexcited QD's electrons are in the $1S$ ground state (dashed line), or that in 20% of the photoexcited QD's electrons are in the $1P$ state (solid line). (c) TA dynamics at 2.58 eV (B_1) and 2.38 eV (A_1) recorded with (solid lines) and without (dashed lines) the IR post-pump (modulation of the visible pump); dotted lines are cross correlations of the visible and IR pump pulses with a probe pulse. Inset: comparison of responses to the IR post-pump derived by subtracting time transients shown in the main frame (symbols) and recorded directly by modulating the IR pump (lines) (see text for details).

the post-pump was reported previously in Ref. 13.

We studied CdSe colloidal QD's fabricated by the organometallic precursor route.[17] ZnS overcoated and pyridine capped QD's were prepared as previously described.[18] In the present paper, we concentrate on small-size QD's with a mean radius $R=1.15$ nm (size dispersion $\sim 5\%$) for which the visible pump photon energy is nearly resonant with the transition coupling the lowest electron $1S$ state and the $2S_{3/2}$ hole state (for notation of electron and hole quantized states in spherical QD's see, e.g., Ref. 19).

Interband-pump-induced absorption changes in QD's are primarily due to state filling and Coulomb multiparticle interactions.[20,21] State filling results in the bleaching of optical transitions coupling occupied states. Coulomb interactions lead to a shift of both occupied and unoccupied transitions, manifested as derivativelike features in TA spectra with a bleaching at the original position of the transition and photoinduced absorption (PA) below or above it, depending on the direction of the shift. The PA is usually observed most clearly for unoccupied transitions and significantly suppressed by the state-filling induced bleaching for transitions coupling occupied states.[21]

In Fig. 1, we show spectra (b) and dynamics (c) of pump induced absorption changes ($\Delta\alpha d$, d is the sample thickness) of ZnS-capped QD's. Two sets of data (with and without the IR post-pump) were recorded, both with modulation of the visible pump. The delay between visible and IR pump pulses (Δt_{IR}) was 0.6 ps. The IR pump was tuned to 0.55 eV, corresponding to the intra-conduction-band $1S-1P$ resonance. To avoid complications associated with effects of multiparticle interactions (such as Auger recombination), the visible-pump excitation density was ~ 0.5 e-h pairs per dot on average. The intensity of IR pulses was sufficient to reexcite $\sim 30\%$ of dots initially excited by the visible pump. In addition to reexciting electrons, IR pumping also causes reexcitation of holes in a portion of the dots due to the overlap of electron and hole intraband absorptions.[22] However, by monitoring IR-pump-induced changes in the interband $1S$ bleaching (see data shown below) one selectively probes only dots with reexcited electrons. This is due to the fact that because of a high density of valence-band states, the $1S$ bleaching is dominated by electron populations.[7]

The TA spectra shown in Fig. 1(b) are dominated by state-filling induced bleaching (B_1) of the lowest $1S$(e)-$1S_{3/2}$(h) interband transition ($1S$ transition). IR postexcitation leads to a reduction of the bleaching amplitude and an increase of the PA feature (A_1), below the $1S$ transition [see also time transients in Fig. 1(c)]. Both effects indicate reexcitation of the electron from the $1S$ to a higher energy state in a portion of QD's. In the reexcited dots, the $1S$ TA is primarily due to a low-energy transition shift (biexciton effect)[20,21] observed as the A_1 PA. Experimental spectra [symbols in Fig. 1(b)] can be well fit [lines in Fig. 1(b)] using a model accounting for state filling and biexciton effects[21] and assuming that either all photoexcited electrons are in the ground $1S$ state [IR pump is ''off''; dashed line in Fig. 1(b)] or that in 20% of initially excited QD's the electrons are reexcited into the $1P$ state [IR pump is ''on;'' solid line in Fig. 1(b)].

Very illustrative are the dynamics of B_1 and A_1, shown in Fig. 1(c). In the absence of the IR pump, the B_1 shows a fast ~ 150 fs growth followed by a monotonic nonexponential decay. The A_1 has an even shorter pump-pulse-limited rise, followed by a very rapid sub-ps decay. Without the IR reexcitation, this feature is due to a small portion of the largest QD's from the size distribution which are pumped not into the $1S$ but into the $1P$ electron state. An instantaneous Coulomb-interaction-induced shift of the $1S$ transition in these dots leads to the observed fast buildup of the A_1.[21] The sub-ps decay of this band is due to increasing contribution from the state-filling-induced bleaching resulting from electron relaxation into the $1S$ ground state.[6]

Application of the IR pulse leads to an abrupt decrease in the B_1 bleaching signal and a complementary increase in the A_1 PA, both due to depopulation of the $1S$ electron state in dots from the center of size distribution for which the IR pump photon energy is close to the energy of the $1S-1P$ intraband transition. A decay of perturbations associated with the IR pump provides a direct measure of the electron intraband relaxation back into the ground $1S$ state. To extract electron intraband dynamics, one can either subtract time transients recorded with the IR pump ''on'' and ''off,'' or to directly record them using a modulated IR beam. As illustrated in the inset to Fig. 1(c), both approaches give the same result [compare symbols (subtraction) and lines (IR pump modulation)], however, with a better S/N ratio for the second method.

In addition to a fast sub-ps decay (due to intraband relaxation), the IR-pump-induced signals exhibit a slow background which grows *superlinearly* with respect to the amplitude of the initial sub-ps component. In Ref. 13, a similar background was observed in pyridine-capped samples, which was attributed to the formation of charge transfer QD$^-$/pyridine$^+$ complexes, for which the $1P$ electron relaxation was inhibited due to the reduced e-h coupling (see below). However, the fact that we detect this background also in strongly-excited ZnS-capped dots (e-h charge separation is inhibited) indicates that the slow portion of the TA signal can also be due to accumulation of electrons in some high-energy long-lived states (e.g., interface related), populated by the IR pump via nonlinear excitation processes (such as two-photon absorption or an excitation via two consecutive steps). Thus one cannot make an unambiguous conclusion about the formation of the long-lived $1P$ excited state based solely on observations of the slow background in intraband time transients. In order to provide direct evidence for the fact that electron relaxation in QD's is governed by e-h interactions, we study ''dynamical'' modifications in electron intraband relaxation caused by sub-ps variations in e-h coupling. This coupling changes either via hole relaxation within the manifold of the QD states (ZnS cap) or by hole transfer to a capping group (pyridine cap).

In Fig. 2, we show $1P$-to-$1S$ electron relaxation dynamics recorded for ZnS (a), and pyridine (b), capped samples at different delay times between visible and IR pump pulses, varied from 70 to 600 fs. For a majority of QD's, electrons are pumped by the visible pulse directly into the lowest quantized $1S$ state, where they remain until being reexcited by the IR pulse. On the other hand, holes, which initially populate the excited $2S_{3/2}$ state, can rapidly relax due to transitions into lower-energy quantized states inside the dot or the charge-transfer to a capping group. Therefore, by varying the IR reexcitation time one can evaluate the effect of modification in the hole wave function (during hole relaxation/transfer) on electron intraband dynamics.

In ZnS-overcoated dots, the $1P$-to-$1S$ relaxation is extremely fast (270 fs time constant) for all Δt_{IR} delays from 70 to 600 fs. In sharp contrast, in the pyridine-capped dots, electron dynamics show a strong dependence on the delay between visible and IR pulses. At short delays ($\Delta t_{IR}=70$ fs), the relaxation constant is 250 fs, close to that in ZnS-capped dots. With increasing the visible-IR pump delay, the electron relaxation time gradually increases up to 3 ps at $\Delta t_{IR}=430$ fs. A further increase in Δt_{IR} does not lead to significant changes in electron intraband dynamics.

Importantly, the threshold delay of about 400 fs found in three-pulse experiments is very close to the hole-transfer time to a capping molecule inferred from visible TA measurements of pyridine-capped dots. The pyridine cation (formed by hole transfer) is observed in TA spectra as a long-lived broad PA band below ~2.5 eV (Fig. 3). In contrast to the short-lived biexciton-related PA feature at 2.38 eV in the spectra of ZnS-capped dots, the PA detected in pyridine-capped samples is characterized by a delayed growth and a significantly longer lifetime determined by recombination of the dot/pyridine charge-transfer complex (inset to Fig. 3). The growth of the pyridine-cation PA is completed within ~450 fs, strongly suggesting that the significant changes in electron relaxation observed in pyridine-capped dots are due to changes in the e-h coupling, resulting from hole transfer to the capping group.

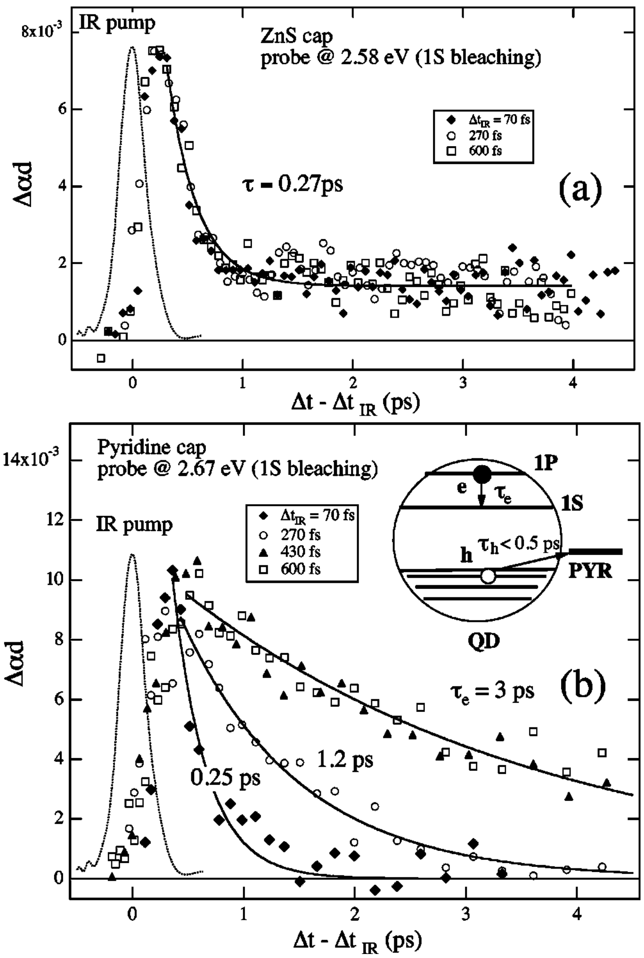

FIG. 2. Dynamics of the IR-post-pump-induced $1S$ bleaching changes (electron intraband dynamics) detected at different delay times between visible and IR pump pulses for ZnS- (a) and pyridine-capped (b) dots. Inset to panel (b): Schematics of electron and hole relaxation/transfer processes in pyridine-capped dots.

This is consistent with the electron-relaxation mechanism involving Coulomb-interaction-mediated e-h energy transfer, as theoretically analyzed in Ref. 12. In the case of ZnS-capped samples, the holes are confined within the dot during the first 600 fs after excitation.[22] Therefore the e-h coupling does change significantly on this time scale, consistent with our observations of Δt_{IR}-independent electron dynamics [Fig. 2(a)]. On the other hand, in pyridine-capped dots, the e-h coupling is strong immediately after photoexcitation (holes are inside the dot), but is reduced dramatically after the hole transfer to the pyridine, which explains the more than tenfold slowing down in the electron intraband relaxation [Fig. 2(b)]. However, even in the charge-separated system, the electron relaxes back to the ground state on a ps

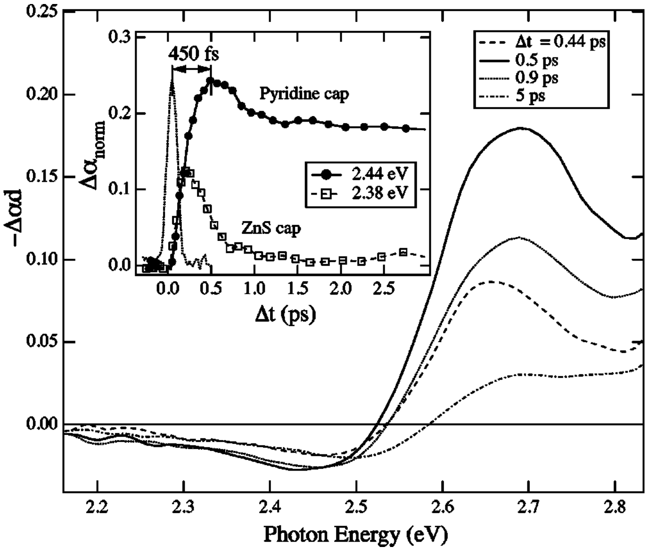

FIG. 3. Time-resolved spectra of absorption changes in pyridine-capped dots induced by the visible interband pump. Inset: Comparison of dynamics of PA features below the 1*S* resonance for ZnS- (squares) and pyridine- (circles) capped dots.

time scale which is much faster than expected for phonon-dominated relaxation.[5] This indicates that even in the case of a significant spatial separation between an electron and a hole, Coulomb e-h interactions can be strong enough to provide an efficient channel for electron energy losses. This can be rationalized as arising from the fact that the Coulomb coupling does not require a direct overlap between electron and hole wave functions and scales relatively slowly (inversely) with the e-h separation. The fact that the electron relaxation mechanism is not strongly affected by the direct overlap between the electron and hole wave functions is also indicated by relaxation data for ZnS-capped QD's. The time transients in Fig. 2(a) recorded at $\Delta t_{IR} \leqslant 600$ fs, as well as the results obtained for longer Δt_{IR} delays (not shown here), demonstrate that changes in the hole wave function during the hole relaxation do not lead to significant changes in electron intraband dynamics. However, in bigger dots (studied, e.g., in Ref. 13), one may expect a stronger effect of the modification in the hole wave function on electron dynamics. This is due to the fact that in large QD's, the difference between initially excited and relaxed hole states can be more pronounced than in the 1.15-nm dots studied in this paper.

In conclusion, we have applied fs TA experiments to directly study electron intraband dynamics in CdSe QD's as a function of e-h coupling strength. To control this coupling, we use different types of surface passivation, which either confine an electron and a hole inside a dot (strong e-h coupling) or lead to efficient charge separation due to a hole transfer to a capping group (reduced e-h coupling). In dots capped with hole-accepting molecules, we observe a dramatic increase in the electron relaxation time (from 250 fs to 3 ps) after the completion of a hole transfer to the capping group. This clearly indicates that electron relaxation in QD's is dominated by processes involving e-h interactions, but not electron-phonon interactions, which play the major role in bulk materials.

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