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Time-resolved intraband relaxation of strongly confined electrons and holes in colloidal PbSe nanocrystals

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The relaxation of strongly confined electrons and holes from higher excited states to their lowest excited states in colloidal PbSe nanocrystals has been time resolved using femtosecond transient absorption spectroscopy. In contrast to II-VI and III-V semiconductor nanocrystals, both electrons and holes are strongly confined in PbSe nanocrystals. Despite the large electron and hole energy level spacings (at least 12 times the optical phonon energy), we consistently observe picosecond time-scale relaxation. Existing theories of carrier relaxation cannot account for these experimental results. We conjecture about mechanisms that could circumvent the expected phonon bottleneck in IV-VI quantum dots.

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INTRODUCTION

A dramatic reduction in the relaxation rate of carriers in three-dimensionally confined quantum systems is predicted to occur if the energy difference between adjacent electron levels (or hole levels) is several times greater than the optical phonon energies.[1,2] (Referring to Fig. 1, relaxation from the $1P_e$ level to the $1S_e$ level is an example of such an “intraband” relaxation process.) The predicted slow relaxation is an interesting issue in nanocrystal physics and is referred to as the “phonon bottleneck.” The existence of a phonon bottleneck would have major implications for applications of quantum dots (QDs). In a QD gain medium, for example, it is desirable that excited carriers relax rapidly to their lowest states, from which radiative recombination occurs. The phonon bottleneck would therefore be likely to hinder the operation of light-emitting devices.

In prior experiments on colloidal QDs, ultrafast intraband carrier relaxation has been observed and a mechanism explaining the process has been widely adopted. This “Auger-like” electron-hole scattering mechanism, described by Efros *et al.*, relies on the high density of hole states in II-VI and III-V semiconductor QDs and fast hole relaxation via phonon emission.[3] In this case, electrons relax on a picosecond to subpicosecond time scale by coupling to the large density of hole states. The strongest evidence in support of the Auger-like process comes from experiments in which this mechanism is intentionally obstructed. When an electron is forced to relax in the absence of a spectator hole, an increase of an order-of-magnitude in the relaxation time is observed.[4–6] It remains a mystery how the intraband relaxation occurs in the absence of the Auger-like mechanism.

QDs of the IV-VI semiconductors PbS, PbSe, and PbTe differ substantially from their II-VI and III-V counterparts. With large electron and hole Bohr radii (for example, in PbSe $a_e = a_h = 23$ nm), both electrons *and* holes are strongly confined. This leads to simple and sparse energy spectra for IV-VI QDs.[7] Therefore, these materials should be ideal for studying electron dynamics in a system with energy levels spaced more than a phonon-energy apart. In contrast, the electron is confined only in small II-VI and III-V QDs, and the hole is *never* strongly confined (for example, in CdSe $a_e = 3$ nm, $a_h = 1$ nm). In addition, the confinement-induced coupling between the three valence bands (heavy-hole, light-hole, and split-off) further complicates the already dense ladder of hole states and leads to congested energy spectra in II-VI and III-V QDs. Intraband electron relaxation in II-VI and III-V nanocrystals[4–6] is dominated by processes that cannot occur in IV-VI materials, so studies of electron relaxation in II-VI and III-V nanocrystals do not provide direct information about the relevant processes in IV-VI QDs.

A consequence of the sparse spectra of IV-VI QDs is that carrier relaxation via the Auger-like process should be impossible. Therefore, it is surprising that prior studies of IV-VI QDs did not observe a phonon bottleneck.[8–10] Here, we report the first experiments to directly time resolve the intraband electron and hole relaxation in strongly confined colloidal PbSe nanocrystals.[11] Transient saturated-absorption measurements were performed to monitor the carrier population with ~100 fs resolution. At low photo-excited carrier density, the $1P$ to $1S$ relaxation time is observed to increase slightly, from 3 to 6 ps, as the QD diameter increases from 4.3 to 6.0 nm. At high carrier density, it is practically constant at 2 to 3 ps for these sizes. In cases where carriers are pumped into much higher excited states, we observe a relaxation time of approximately 3 ps, independent of the carrier density. No known mechanism accounts for these fast relaxations and we conjecture about mechanisms that could circumvent the predicted phonon bottleneck in IV-VI quantum dots.

The electronic structure of PbSe and PbS NCs was calculated by Kang *et al.* using a four-band envelope function formalism.[12] These calculations include estimates of the effects of Coulomb interactions, such as the electron-hole exchange interaction, which are found to be small compared to the confinement-induced level shifts. The lowest several electron and hole states and the lowest dipole-allowed transitions for a 6 nm diameter PbSe QD are shown in Fig. 1.

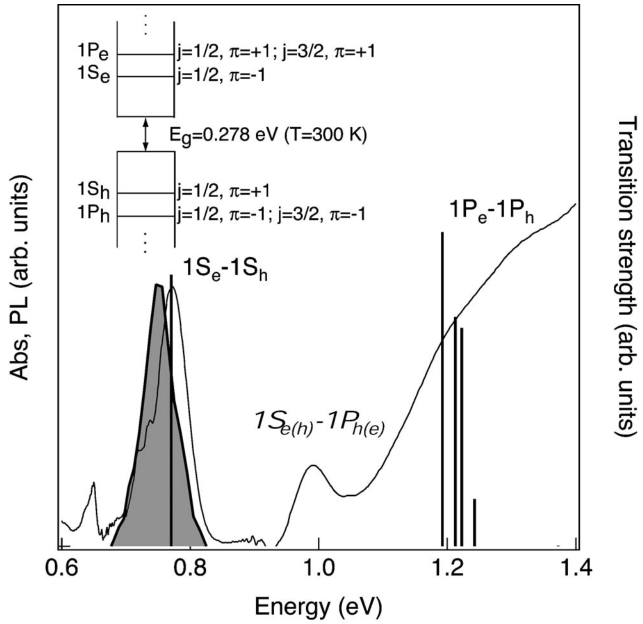

FIG. 1. The absorption (solid line) and photoluminescence (shaded region) spectra for 6 nm PbSe QDs in the colloidal silica film. The lowest several electronic states are calculated using a four-band envelope function formalism (inset). The strengths of the lowest dipole-allowed transitions are indicated by vertical lines. The second absorption feature (italicized label) is discussed in the text. Separate measurements of a blank film show that the absorption peak near 0.6 eV is due to the host.

The states are labeled by total angular momentum (J) and parity (π), but, for simplicity, we adopt the usual nomenclature and refer to the states according to the angular momentum of the envelope function ($\ell=0,1,\ldots$ as $S,P,\ldots$). To date, electronic-structure calculations of lead-salt QDs fail to reproduce convincingly the second absorption peak. Two explanations for this spectral feature have been proposed in the literature: (1) transitions between the S and P states from Kang *et al.*'s model due to a softening of the parity selection rule[13] and (2) transitions between new states that arise from the inclusion of band anisotropy in the electronic structure calculations.[14] We find that the explanation according to parity-forbidden S to P and P to S transitions is in better quantitative agreement with the available data, which include linear absorption spectra[9,13,15,16] and optically induced[9] and electrically induced[17] intraband absorption spectra. In light of these results, we tentatively assign this spectral feature to $1S_{e(h)}$-$1P_{h(e)}$ transitions. However, we should emphasize that the identification of the specific state that is excited in these experiments is immaterial. The energy lost by the carriers is well known, even if the states are not identified precisely.

Dielectric effects may be pronounced in Pb-salt QDs owing to the large mismatch between dielectric constants of the QD and the host.[9] The nonlinear-optical susceptibilities will be reduced substantially by the local-field effects. Thus, small signals are expected in the saturated-absorption experiments. However, we have not quantified this aspect because the absolute signal magnitude is not important for determining the intraband dynamics of interest here.

The vibrational modes are also modified by confinement and in QDs of polar materials, the optical mode with $q=0$ is expected to contribute most strongly to relaxation by phonon emission. As shown in recent experiments by Hyun *et al.*, this mode has an energy of approximately 17 meV over the range of QD sizes studied here.[18] Qualitatively speaking, the separation between the lowest excited states and the next higher ones is several phonon energies; therefore, a phonon bottleneck is expected. Based on our assignment of the second absorption peak, as discussed above, we can say more quantitatively that the $1P_{e(h)}$ to $1S_{e(h)}$ energy spacing is between 12 to 18 phonon energies for the QD sizes studied here.

EXPERIMENT

High-quality colloidal PbSe NCs were synthesized as reported previously in the literature.[19,20] A colloidal silica host was developed and PbSe QDs of known concentration were dispersed into the matrix in known proportions, poured out between microscope slide separated by spacers, and allowed to cure.[21] The resulting solid films were 240 μm thick and contained approximately 0.1% volume occupancy of QDs. Room-temperature optical absorption spectra of the films (Fig. 1) reveal the same excitonic structure observed from the PbSe QDs before incorporation into the silica host. When the films are excited with a Ti:sapphire laser at 1.55 eV, band-edge photoluminescence is observed as shown in Fig. 1. The absorption cross section was estimated from the measured absorption spectrum and known concentration of QDs within the films. From this, we calculated the pump fluence necessary to create an average of one electron-hole pair per QD for each sample.

Two-color transient absorption measurements were performed to investigate the intraband carrier dynamics. In this experiment, a strong pump pulse incident on the sample generates excited electron-hole pairs. A weak, time-delayed probe pulse monitors the optical density of the sample at the energy of the lowest optical transition. In the limit that $\alpha L < 0.1$ (α is the linear absorption coefficient and L the propagation length), the differential transmittance (DT) of the probe beam, $\Delta T/T_0=(T-T_0)/T_0$, is directly proportional to the sum of the electron and hole populations. Here, T and T_0 are the transmission of the probe beam with and without the presence of the pump beam. The subsequent relaxation of the photo-excited carriers is observed by monitoring the DT as a function of the time delay between pump and probe pulses. We are unable to separate electron and hole contributions to the DT signal because of their similar electronic structures. Therefore, the mirror image transitions are always implied.

The pump and probe pulses were generated in identical optical parametric amplifiers (OPAs), simultaneously pumped by a Ti:sapphire regenerative amplifier. Each OPA was tunable in wavelength from 450 to 3000 nm. The pump and probe pulses were typically 100 fs in duration, and the time resolution of the measurement was better than 300 fs for all combinations of wavelengths employed in this work. The pump beam was mechanically chopped and the probe beam was split equally into signal and reference beams that

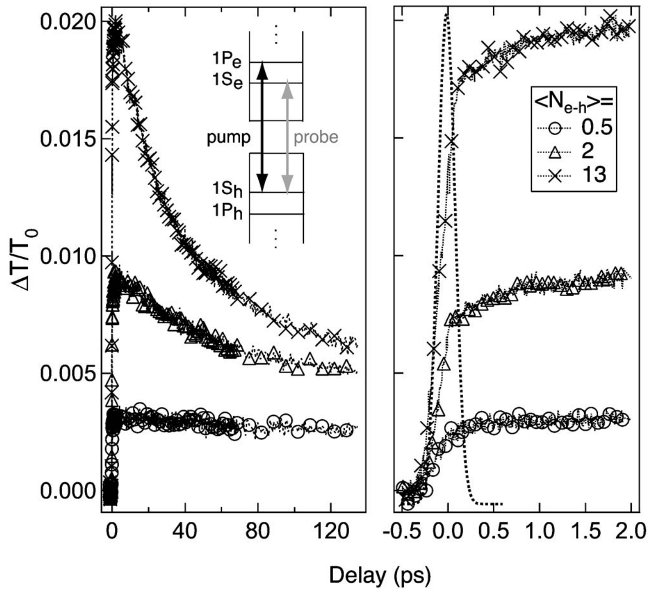

FIG. 2. Room-temperature population dynamics of the 1*S* states, for the indicated densities of photo-excited carriers. The pump pulse is resonant with the $1S_h$-$1P_e$ transition. The mirror-image $1S_e$-$1P_h$ transition is also pumped, but for clarity this is not shown on the energy-level diagram (inset). The expanded time scale (right panel) shows carriers entering the 1*S* states. The dotted line is the instrument response.

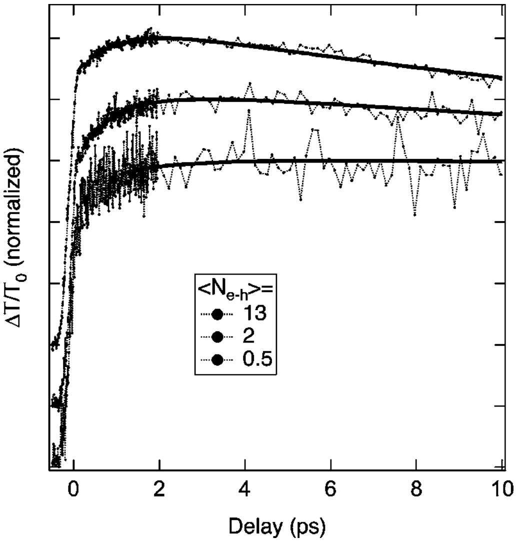

FIG. 3. The population dynamics of the 1*S* states after $1S_{e(h)}$-$1P_{h(e)}$ excitation, for different excitation levels (traces arranged top to bottom as listed in the legend). $\langle N_{e\text{-}h}\rangle$ is the average number of photo-excited electron-hole pairs estimated per QD. The traces are normalized and then offset for clarity. The delay stage step size was changed at 2 ps, giving the appearance of an abrupt change in noise level.

passed through pumped and nonpumped regions of the sample, respectively. The signal and reference beams were measured in balanced detection using matched germanium photodiodes connected to the differential inputs of a lock-in amplifier, and the output signal was digitized and recorded by computer.

The probe beam was always set to the peak absorption energy of the lowest optical transition, $1S_e$-$1S_h$, and the pump was tuned to an energy above this. Two different cases were investigated. In case 1, the pump beam was nominally tuned to the $1S_{e(h)}$-$1P_{h(e)}$ transitions. In case 2, carriers were excited into much higher excited states by pumping with visible light ($\hbar\omega=2.4$ eV). The pump pulse energies were typically varied over the range of tens to hundreds of nanojoules. All of the measurements presented here were conducted at room temperature.

1S-1P excitation

Figure 2 shows a typical measurement when the pump photon energy is resonant with the $1S_{e(h)}$-$1P_{h(e)}$ transition. In the left panel, we observe the population of the 1*S* states increasing on the time scale of the pump pulse, and then decaying within 40 to 100 ps. The relaxation from the 1*S* states in PbSe QDs has been previously studied[9,10] and attributed to multi-exciton Auger recombination[9] as first shown in CdSe QDs.[22] We observe similar behavior. In this work, we focus on carriers entering, rather than leaving, the 1*S* states; therefore, we expand the time scale in the right panel.

Notice that the population increase of the 1*S* states (Fig. 2, right panel) exhibits two components, one increasing within the time duration of the pump pulse and the other rising for several picoseconds thereafter. These dynamics are consistent with the electronic structure (Fig. 2, left panel inset) as follows. First, given that the pumped and probed transitions share a state ($1S_h$, in the case shown), one-half of the probed transition is populated directly by the pump pulse. This leads to the fast component of the population increase that rises with the pump pulse. This interpretation of the fast rise is supported by the absence of such a fast rise when the excitation transition does not share a state with the probed transition. Second, carriers pumped into higher excited states ($1P_e$, in the case shown) eventually relax into their lowest excited state ($1S_e$) at some later time, and this leads to another rising component of the 1*S* states' population. This second component is the intraband contribution to the measured DT signal. The relative magnitudes of the components of the transient will be discussed below.

Figure 3 shows the same DT traces as in Fig. 2, but normalized and offset for clarity. The time after excitation at which the population of the $1S_e$ and $1S_h$ states is maximum is taken as a measure of the intraband relaxation time. The curves are fit to a log-normal function simply to extract that time reliably in the presence of noise in the data. The fitting function is not theoretically significant and is chosen only for convenience. With an estimated average of 0.5 electron-hole pairs excited per QD ($\langle N_{e\text{-}h}\rangle=0.5$), the relaxation occurs in 6 ps. This time decreases as the photo-excited carrier density is increased, and we observe a relaxation time of 2 ps when $\langle N_{e\text{-}h}\rangle=13$. This weak variation in the relaxation time is observed in all of the QDs studied. Clearly, there is no phonon bottleneck and, in fact, the resulting energy-loss rate is within a factor of 3 or 4 of that in bulk PbSe. We repeated these measurements on a range of QD sizes between 4.3 and

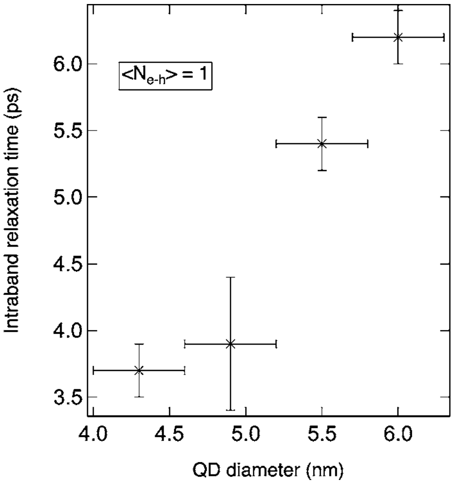

FIG. 4. The intraband relaxation time increases with QD diameter.

6.0 nm and found that the intraband relaxation time increases slightly with QD size (Fig. 4).

High-energy excitation

We also explored the effect of exciting carriers far above their $1P$ states. The primary advantage in this configuration is that the pump pulse no longer populates a state that is probed; so unlike the previous case, the intraband relaxation should be unambiguous. Accordingly, the population increase of the $1S$ states (Fig. 5) now consists of only a single component. When a 4.9 nm diameter QD is pumped at 2.4 eV, we find that the $1S_e$-$1S_h$ population develops in approximately 3 ps at both low ($\langle N_{e\text{-}h}\rangle < 1$) and high ($\langle N_{e\text{-}h}\rangle = 10$) carrier densities.

DISCUSSION

We now turn to a discussion of the physical mechanisms that underlie the carrier relaxation. First, we reiterate that the emission of at least 12 optical phonons would be required for relaxation by coupling of electrons to polar phonons. Thus, the contribution of multiphonon[23] or polaron[24] effects in the relaxation are ruled out. As noted earlier, the Auger-like mechanism that is accepted in II-VI semiconductor QDs will not produce efficient energy relaxation owing to the symmetric electron and hole spectra. The relaxation could be facilitated by the presence of additional states that bridge the energy-level separation. One possible source of such states may be the eight equivalent L-valleys in PbSe. The splitting of these degenerate states is calculated within the tight-binding model to be as large as ~ 100 meV in the smallest QDs[16] and these calculations appear to be consistent with the structured photoluminescence spectra observed in low-temperature measurements on PbSe QDs.[25] Even with such splitting, however, the energy separation between the $1P$ and $1S$ manifolds is still several phonon energies.[26] To our knowledge there are no other intermediate states to serve as the "ladder" for such a relaxation. Given this failure to explain our observations, we consider additional mechanisms.

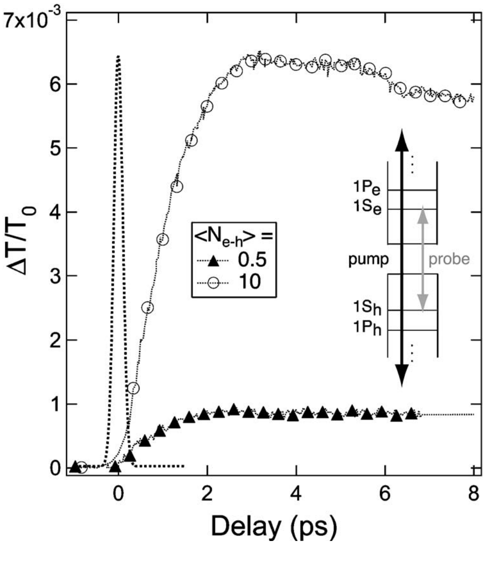

FIG. 5. Population dynamics of the $1S$ states for a 2.4 eV energy pump and the indicated photo-excited carrier densities.

We first consider the case of intraband relaxation with carriers excited into states far above $1P$ (Fig. 5). This relaxation, along with its apparent insensitivity to the carrier density, might be explained by impact ionization. In this process, a carrier with energy in excess of twice the $1S_e$-$1S_h$ energy difference ($\Delta E_{1S\text{-}1S}$) relaxes to its $1S$ state by exciting additional electrons from $1S_h$ to $1S_e$.[27] Thus, two or more cooled carriers may result from a single highly excited one. Schaller *et al.* have attributed the appearance of multi-exciton signatures in the decay of the $1S$ states with $\langle N_{e\text{-}h}\rangle < 1$ to impact ionization.[28] In some sense, impact ionization is the reverse of Auger recombination and can naturally be expected to occur when Auger processes are unlikely, i.e., in lead-salt QDs. At low carrier density and high-energy excitation ($\hbar\omega = 2.5^{*}\Delta E_{1S\text{-}1S}$), we also observe a fast decay component from the $1S$ states, as expected in the presence of impact ionization. We do not observe this decay for the $1S$-$1P$ excitation. Briefly, we note that the precise mechanism responsible for the appearance of multiple excitons from a single photon is a point of current debate, as evidenced by a recent paper attributing this effect to direct multi-exciton generation.[29]

Next, we focus on the other case we investigated experimentally. The relaxation that we attribute to $1P \rightarrow 1S$ requires a different explanation. Prior studies of intraband relaxation in QDs[5,6] only considered low excitation, $\langle N_{e\text{-}h}\rangle < 1$; no dependence on carrier density was reported, and the Auger-like mechanism was invoked to explain the relaxation. Our experiments exhibit a dependence on the carrier density, with the relaxation time decreasing from 6 ps at the lowest carrier density to 3 ps for $\langle N_{e\text{-}h}\rangle \sim 1$, finally reaching 2 ps for $\langle N_{e\text{-}h}\rangle = 13$. At fixed carrier density, smaller QDs exhibit faster intraband relaxations. The decreasing relaxation time with increasing carrier density suggests that a carrier-carrier interaction plays a role. Given that we have already ruled out the Auger-like process due to symmetry in the energy-level structure, these experimental results suggest that another electron-hole scattering mechanism influences the dynamics, although further work is required to test this hypothesis.

In the absence of a systematic understanding of these experimental results, we now conjecture about the existence of relaxation channels outside the picture of interior electron states and vibrational modes. For example, surface atoms and ligands may be involved in the decay. Darugar *et al.* have studied the relaxation in CdSe QDs and quantum rods, and find that electrons in QDs relax faster than electrons in quantum rods of the same diameter.[30] This trend is the opposite of what one would expect by consideration of quantum confinement, and these authors show that this is consistent with the change in excited electron density on the nanoparticle surface with size. Assuming sufficient coupling between the excited electrons and large surface molecules, they suggest this as a route to efficient carrier thermalization.[30] This mechanism could explain the slightly faster relaxation we observe in the smaller QDs; the oleic acid molecules that terminate the QDs could be involved in the relaxation, but this is speculation at this point. Regardless of the mechanism that underlies the relaxation of electrons in these QDs, the experimental data exhibit evidence that suggests that some electrons relax through a channel that is not observable in our experiment. We would expect the fast- and slow-rising components to contribute equally to the total signal magnitude, on the basis of the symmetric electronic structure. However, the measurements indicate that the $1S$ states are almost seven times more likely to be populated by direct excitation than by the $1P$ to $1S$ relaxation. This suggests the presence of an alternate decay channel, which drains electrons from the $1P$ states without populating the $1S$ states. However, such a mechanism is difficult to reconcile with the high fluorescence quantum yield of the $1S$-$1S$ transition that is observed. More work is clearly needed to resolve these puzzling observations.

Before concluding, we point out the similarity in intraband relaxation times reported in this work for electrons and holes in PbSe QDs and those observed for electrons in II-VI and III-V semiconductor QDs when the Auger-like electron-hole scattering mechanism is intentionally obstructed.[4–6] Together, these results suggest the existence of a nonradiative relaxation channel on the picosecond time scale that is accessible to strongly confined electrons and/or holes in colloidal QDs, *independent of material system*. Again, relaxation through surface channels may be a way to explain these similar intraband relaxations in nanoparticles made from vastly different semiconductors. Renewed efforts to incorporate the surface's role into the relaxation mechanisms may be needed.

CONCLUSIONS

In conclusion, we have time resolved the relaxation of electrons and holes in colloidal PbSe NCs. In stark contrast to other semiconductor NCs, both electrons and holes are strongly confined in PbSe QDs. Therefore, the Auger-like electron-hole scattering cannot be invoked to explain the intraband relaxation of charge carriers. In cases where carriers are pumped into high excited states, we observe a relaxation time of ~3 ps, independent of the carrier density. We tentatively attribute this behavior to carrier cooling via impact ionization. When the P states are directly populated with, on average, less than one electron or hole per QD, the $1P$ to $1S$ relaxation time increases from 3 to 6 ps as the QD size is varied between 4.3 and 6.0 nm in diameter. The size dependence of this relaxation may be correlated with the change in electron density on QD surface as previously suggested in the literature. This could explain the similarity of the relaxation times observed in PbSe QDs and in surface-modified colloidal II-VI and III-V QDs. Known mechanisms based on interior electron states and vibrational modes cannot account for the experimental results, which suggests that surface atoms and ligands may play a major role.

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