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Spectroscopic Evidence for the Contribution of Holes to the Bleach of Cd-Chalcogenide Quantum Dots

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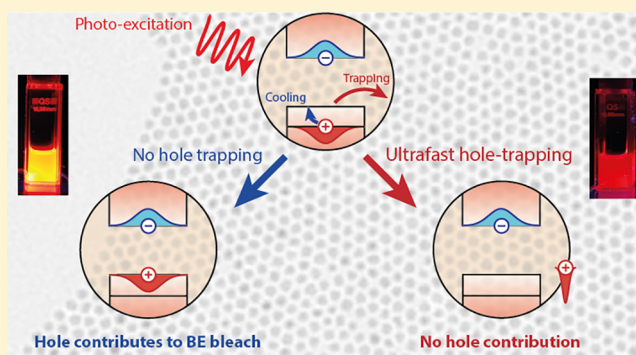
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S Supporting Information

ABSTRACT: In transient absorption (TA) measurements on Cd-chalcogenide quantum dots (QDs), the presence of a band-edge (BE) bleach signal is commonly attributed entirely to conduction-band electrons in the 1S(e) state, neglecting contributions from BE holes. While this has been the accepted view for more than 20 years, and has often been used to distinguish electron and hole kinetics, the reason for the absence of a hole contribution to the BE-bleach has remained unclear. Here, we show with three independent experiments that holes do in fact have a significant impact on the BE-bleach of well-passivated Cd-chalcogenide QD samples. Transient absorption experiments on high photoluminescence quantum yield CdSe/CdS/ZnS core–shell–shell QDs clearly show an increase of the band-edge bleach as holes cool down to the band edge. The relative contribution of electron-to-hole bleach is 2:1, as predicted by theory. The same measurements on core-only CdSe QDs with a lower quantum yield do not show a contribution of holes to the band-edge bleach. We assign the lack of hole bleach to the presence of ultrafast hole trapping in samples with insufficient passivation of the QD surface. In addition, we show measurements of optical gain in core–shell–shell QD solutions, providing clear evidence of a significant hole contribution to the BE transient absorption signal. Finally, we present spectroelectrochemical measurements on CdTe QDs films, showing the presence of a BE-bleach for both electron and hole injections. The presence of a contribution of holes to the bleach in passivated Cd-chalcogenides QDs bears important implications for quantitative studies on optical gain as well as for TA determinations of carrier dynamics.

KEYWORDS: Colloidal quantum dots, femto-second transient absorption spectroscopy, electronic structure, excited-state dynamics



Cadmium chalcogenide quantum dots (QDs) have been among the earliest QD systems to be investigated, and are still at the forefront of QD research, with applications in solar cells,^{1–3} transistors,^{4–6} LEDs,^{7,8} catalysis,^{9–11} and lasing.^{12–14} In particular, recent breakthroughs in electrically pumped core–shell QD lasers¹⁵ confirm the potentials of these QD materials in low-threshold lasing applications. Understanding the behavior of band-edge (BE) absorption in QDs is a necessary step in the development of optoelectronic applications, and has been the focus of years of spectroscopic investigation.^{16–21}

In the presence of excited carriers, the BE absorption of QDs decreases in intensity, an effect called absorption bleach. Numerous reports have claimed that the BE-bleach in Cd chalcogenide QDs seems to be entirely dominated by the presence of electrons in the conduction BE state, with no evidence of a hole contribution to the effect.^{19,22–25} This observation has important consequences for both applied and

fundamental studies on Cd chalcogenides: the lack of a hole contribution implies a negligible amount of stimulated emission, preventing the realization of optical gain; furthermore, complete assignment of the BE-bleach to electrons has been a widely used assumption in the determination of electron kinetics from transient absorption (TA) measurements of bleach decays.^{10,26}

Despite the claim on the lack of a hole-induced bleach, the underlying reason remains ambiguous, with studies suggesting the presence of efficient hole trapping,^{27,28} a high degeneracy of thermally populated hole states,^{23,29} or a combination thereof.²²

Here we present three independent experiments that clearly demonstrate the presence of a significant hole contribution to

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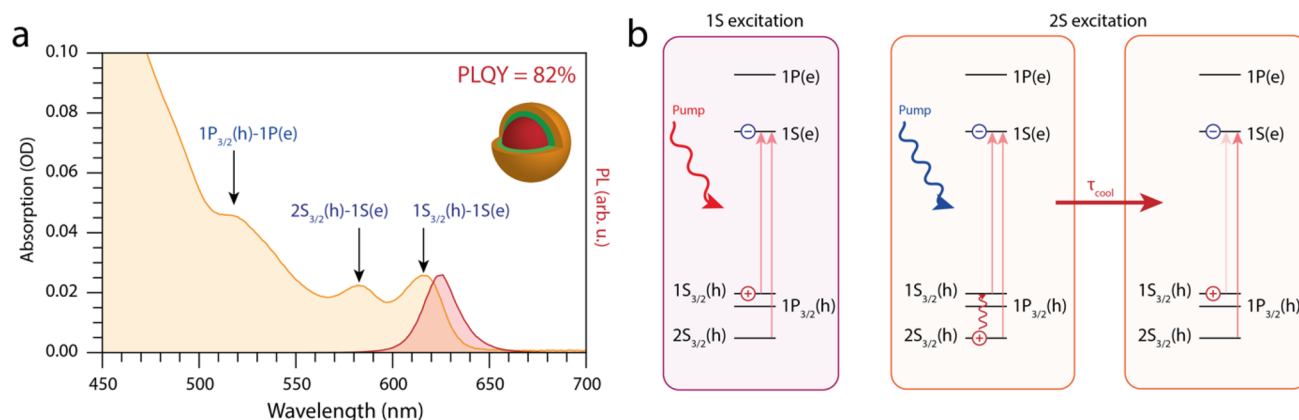


Figure 1. Schematics of optical bleaching and possible scenarios in core–shell–shell CdSe QDs. (a) Absorption and photoluminescence spectrum of the CdSe/CdS/ZnS core–shell–shell QDs. The different transitions in the CdSe core are labeled according to the literature.^{30–32} (b) Schematic of the optical transitions in the TA experiments. Upon 1S excitation, the band-edge (BE) absorption transition is bleached instantly due to the presence of an electron in the $1S_e$ state and the presence of a hole in the $1S_{3/2}(h)$ state. Upon 2S excitation of the $2S_{3/2}(h)$ - $1S_e$ transition, the BE-bleach should theoretically show an ingrowth over time (sub picosecond), related to fast hole cooling from the $2S_{3/2}(h)$ to the $1S_{3/2}(h)$ state.

the BE-bleach of CdSe and CdTe QDs. According to the present work, the lack of a hole contribution depends on the presence of unpassivated trap states and is not an intrinsic property of II–VI QDs. We performed TA measurements, exciting CdSe/CdS/ZnS core–shell–shell QDs at the 1S [$1S_{3/2}(h)$ - $1S(e)$] transition and 2S [$2S_{3/2}(h)$ - $1S(e)$] transition. Comparison of the two bleach dynamics revealed the presence of a 210 ± 20 fs ingrowth upon 2S excitation, while the growth of the 1S signal is limited by the (130 fs) time resolution of the measurement. As the two excitations differ only for the initial hole state, the difference between the two bleach kinetics demonstrates the presence of a hole contribution to the BE-bleach. The ratio between the electron and hole bleach contribution, extracted from the amplitude of the ingrowth component of the bleach upon 2S excitation, is found to be 2:1. This observation is in excellent agreement with a simple transition-counting model for the bleach of a transition involving a 2-fold degenerate electron state and a 4-fold degenerate hole state. Interestingly, repeating the measurement on core-only CdSe QDs showed identical kinetics for the two excitations, confirming the role of hole trapping in the removal of the hole contribution from the bleach. The latter explains the absence of the observation of a hole bleach in previous reports.^{27,28,3,29}

We provide further evidence for the contribution of holes to the BE-bleach by showing optical gain in solutions of CdSe/CdS/ZnS QDs. The observation of optical gain directly implies the presence of stimulated emission, which in turn is a tell-tale sign of a contribution of holes to the BE-bleach. Comparison of the measured gain with predictions from the transition-counting model shows quantitative agreement.

Finally, we present spectroelectrochemical measurements on films of CdTe QDs. We show that both electron injection (reducing potentials) and hole injection (oxidizing potentials) result in a clear bleach of the BE transition. These results clarify the presence of a hole contribution to the BE-bleach of Cd chalcogenides QD systems, paving the way for quantitative prediction of the gain threshold in this highly investigated material system.

Results and Discussion. QD Synthesis and Material Properties. We synthesized CdSe/CdS/ZnS QDs with a low polydispersity (standard deviation in particle diameter 7%) and

high PL performance, following descriptions in recent literature.^{33,34} The steady state absorption and PL spectra of the core–shell–shell QDs are shown in Figure 1a, labeled following a multiband effective mass approximation description of electronic states in the strong coupling regime.^{30–32} The photoluminescence quantum yield (PLQY) was determined to be 82% (see Supporting Information). The low polydispersity leads to sharp absorption features that allow state selective excitation, which simplifies the analysis of the transient absorption spectra. The high PLQY ensures the sample is hardly affected by carrier trapping.

Evidence of Hole Contribution to the BE-Bleach via Ultrafast TA Measurements. We attempt to determine the contribution of holes to the BE-bleach by selectively exciting either the 1S [$1S_{3/2}(h)$ - $1S(e)$] (616 nm) or the 2S [$2S_{3/2}(h)$ - $1S(e)$] transition (581 nm). Figure 1b shows a schematic of the carrier dynamics expected for the two excitations. Upon optical excitation of the 1S transition, both carriers populate the BE levels, immediately contributing to the BE-bleach, while upon 2S excitation the hole initially populates the $2S_{3/2}(h)$ state and does not contribute to the BE-bleach. After a certain cooling time (τ_{cool}), the hole relaxes to the $1S_{3/2}(h)$ state. In this scenario, with carrier dynamics unaffected by trapping, the presence of a hole contribution to the BE-bleach would result in a difference in the ingrowth-kinetics of the bleach signals in the two excitations.

We performed TA measurements on the sample in the low-fluence regime, in which the pump beam excites an average number of excitons per QD much smaller than unity, while vigorously stirring the solution to avoid photocharging effects.³⁵ Figure 2a,b shows 2D TA color maps for 1S and 2S excitation, respectively. Although the two measurements show identical TA signals in the time window between 1 ps and 3 ns after photoexcitation, clear differences between them can be observed in the early time behavior of the BE-bleach (at 618 nm). To highlight the difference in the two responses, spectral cuts of the 2D TA color maps are shown in Figure 2c,d, displaying the differential absorption signal for different color maps. The transient absorption spectrum in the 1S-excitation measurement (Figure 2c) remains constant after the coherent artifact response.³⁶ The 2S-excitation measurement, shown in Figure 2d, shows a clear growth of the BE-bleach

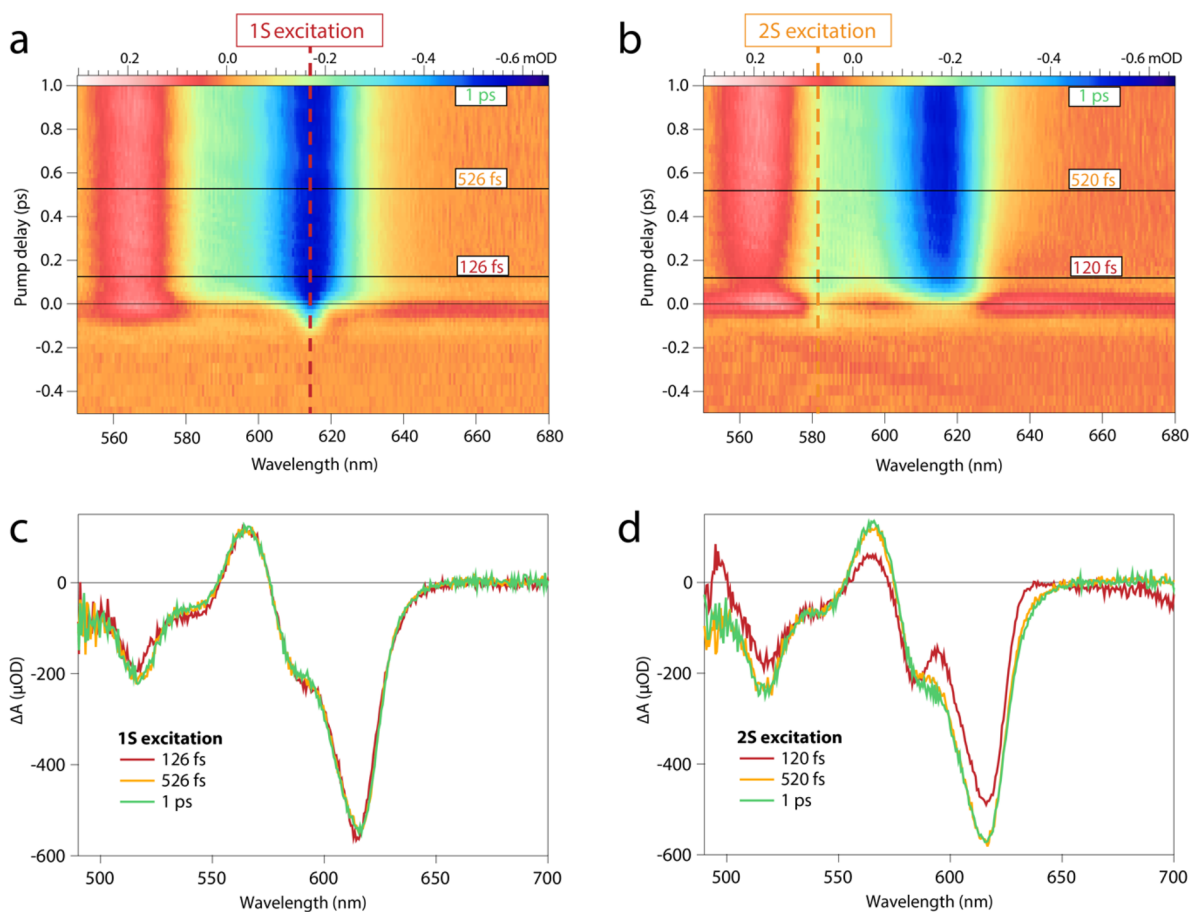


Figure 2. 2D TA measurements on the CdSe/CdS/ZnS QDs during the first picosecond upon 1S and 2S excitation. (a) 2D TA image for excitation resonant with the 1S and (b) 2S transition. Excitation of the 1S transition shows an instantaneous appearance of the BE-bleach. (c) Differential absorption of the CdSe QD BE upon 1S and (d) 2S excitation. Excitation of the 2S transition shows a clear ingrowth of the BE-bleach signal in the first hundreds of femtoseconds after photoexcitation, indicative of hole cooling from the $2S_{3/2}(h)$ to the $1S_{3/2}(h)$ state.

occurring in the first hundreds of femtoseconds after photoexcitation. As the only difference between the two measurements is the initial hole state, this clearly demonstrates a significant influence of the hole on the BE-bleach: as holes cool down to the BE state, the BE-bleach increases. Below we perform a quantitative analysis on these transient absorption measurements. We focus only on the region of the 1S transition since spectral overlap between different transitions prevents unambiguous quantitative description of the transient absorption signals at a higher energy.

Quantitative Modeling of the Hole Contribution to the BE-Bleach. In order to quantify the impact of the hole on the BE-bleach, we fitted the sum of two Gaussians to the time-dependent differential absorption spectrum close to the energy of the BE absorption (Figure 3a), to account for the partial overlap of the 1S and 2S bleach features. Although the description of the TA signal at the energy of the 2S transition is neglecting spectral overlap with higher energy components, the precise shape of the 2S bleach has a little influence on the determination of the 1S bleach component (see Supporting Information). Figure 3b shows the time dependence of the 1S bleach component for 1S and 2S excitation. Again, a clear difference is observed in the dynamics of the BE-bleach between the two measurements, with the 2S excitation showing a clear ingrowth during the first 500 fs, while upon 1S excitation the BE remains constant after a 130 fs resolution-limited increase. After cooling is completed, the bleach per

absorbed photon in the two excitations is the same, confirming that the number of carriers reaching the band edge in the two excitations is the same (see Supporting Information). The ingrowth of the BE-bleach in the 2S-excitation measurement is fitted with the sum of a step function (1S electrons) and an exponential increase (1S holes), convolved with a Gaussian Instrument Response Function (IRF, see Supporting Information). The fit yields a time constant for the ingrowth of 210 ± 20 fs, in agreement with the expected fast dynamics of hole relaxation³⁷ (see Supporting Information).

The ratio between the hole bleach (ΔA_h) and the exciton bleach (ΔA_x), extracted from the fit, amounts to 0.32 ± 0.02 . This value can be compared to the prediction based on a widely used model based on state filling of degenerate energy levels,^{14,15,38,39} schematically shown in Figure 3c. Assuming equal oscillator strength for all the energy-degenerate transitions, the total absorbance is given by a sum over identical contributions A^* for each transition, represented as red, upward arrows in Figure 3c. The presence of an electron and/or a hole in one of the two states involved in a transition induces state filling, as well as stimulated emission, both leading to a reduction of the net absorption. In the low-fluence limit relevant for comparisons with the measurements, the steady state absorbance A_0 and the excited-state absorbance A' in the presence of an occupation, n_e and n_h , of the electron and hole states can be written as

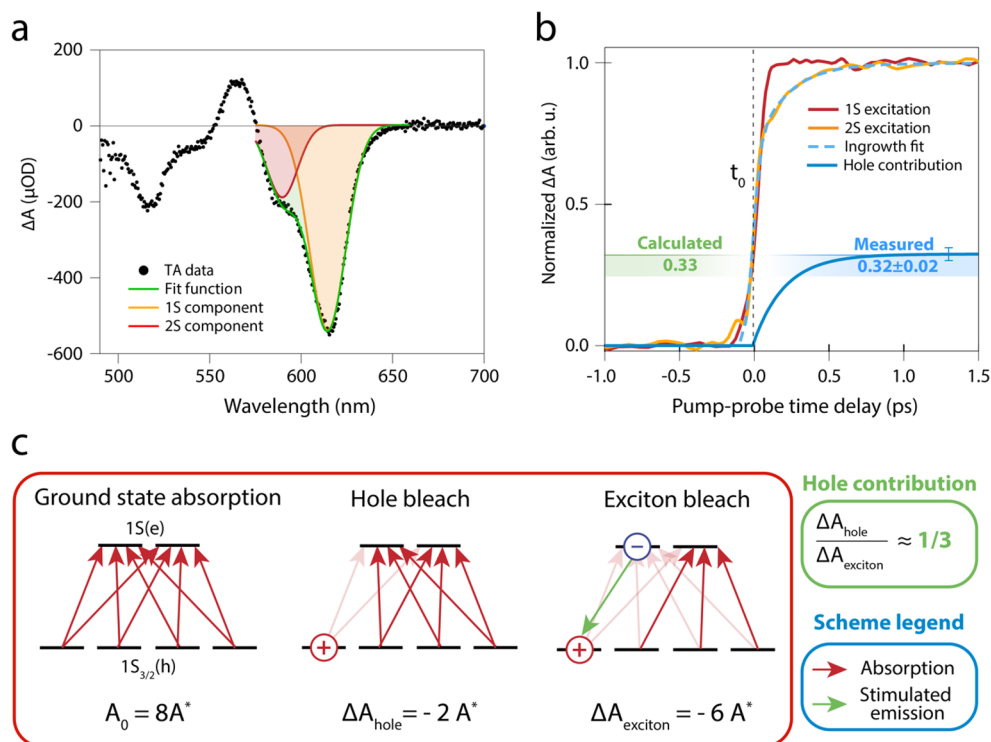


Figure 3. Analysis of the BE bleach in TA experiments upon 1S and 2S excitation of the CdSe/CdS/ZnS NCs. (a) We fit two Gaussians to the BE-bleach, which correspond to the $1S_{3/2}(h)$ - $1S(e)$ and $2S_{3/2}(h)$ - $1S(e)$ transitions, and extract the contribution of each transition to the TA signal for different pump-probe delay times. (b) Normalized amplitude of the BE-bleach upon exciting the 1S and 2S transition (red and orange). 2S excitation leads to an ingrowth of the BE-bleach on a time scale of hundreds of femtoseconds, whereas for 1S excitation the BE-bleach appears instantly. Fitting the 2S-excitation signal with a step increase due to the electron and an exponential ingrowth due to the hole (convolved with the IRF, see [Supporting Information](#)) produces a good agreement with the data (dotted light blue) and allows to quantify the time dependence of the hole contribution (dark blue). (c) Schematic of the transition-counting model used to extract the contributions of the electron and exciton to the magnitude of the BE-bleach.

$$A_0 = A^* g_e g_h \quad (1)$$

$$A' = A^* [(g_e - n_e)(g_h - n_h) - n_e n_h] \quad (2)$$

where g_e (g_h) represents the electron (hole) degeneracy. The term proportional to $n_e n_h$ originates from stimulated emission, represented by a green, downward arrow in [Figure 3c](#). It follows from [eqs 1 and 2](#) that the differential absorbance, $\Delta A = A' - A_0$, in the presence of an exciton ($n_e = 1$, $n_h = 1$) and in the presence of a hole ($n_e = 0$, $n_h = 1$) can be expressed as

$$\Delta A_X = -A^*(g_e + g_h) \quad (3)$$

$$\Delta A_h = -A^* g_e \quad (4)$$

Within this model, the ratio of the hole and exciton BE-bleach, $\frac{\Delta A_h}{\Delta A_X} = \frac{g_e}{g_e + g_h}$, is entirely determined by the degeneracy of the BE states. Setting the BE degeneracies to the theoretically predicted values ($g_e = 2$ and $g_h = 4$)⁴⁰ results in a ratio of the hole-to-exciton bleach $\frac{\Delta A_h}{\Delta A_X} \approx 1/3$, in a quantitative agreement with the value (0.32 ± 0.03) we measured. Although the simple model neglects the presence of angular momentum selection rules for optical transitions, accounting for angular momentum conservation, leads to the same quantitative results (see [Supporting Information](#)). We conclude that the bleach dynamics of near-unity PLQY CdSe core-shell QDs can be entirely explained in terms of the commonly accepted values for the BE degeneracies of single-particle electron and hole

states in CdSe QDs,^{14,38,41} ruling out the presence of a high-degeneracy quasi-continuum of BE hole states.

Absence of Hole Contribution to the BE-Bleach for Unpassivated QDs. It is likely that the presence of a high density of surface traps incomplete surface passivation via thinner shells or lack of time resolution contributed to hide the BE hole bleach contribution in previous TA studies of CdSe QDs. We studied the importance of good surface passivation for the determination of the hole bleach, via comparison between the high-PLQY, core-shell-shell CdSe/CdS/ZnS QDs, shown in [Figure 3](#), and low-PLQY (6.5%), core-only CdSe QDs. Recent work by our group^{26,42} and others⁴³ has shown that PL quenching for core-only Cd-chalcogenide QDs is dominated by the presence of localized hole states in the band gap, leading to ultrafast hole trapping. These trap states originate from undercoordinated chalcogenide atoms at the surface of the QDs,^{26,42,43} which can be passivated by Z-type ligands.⁴⁴

[Figure 4a,b](#) shows 2D TA color maps for the core-only CdSe NCs, excited at the 1S and the 2S transition, respectively. A striking similarity is observed in the dynamics of the BE-bleach between the two measurements. [Figure 4c](#) compares the temporal evolution of the BE-bleach for the two excitations, revealing that the bleach components follow the same kinetics in both measurements. This implies that the hole trapping rate exceeds both the cooling rate (i.e., $\tau_{\text{trap}} \ll \tau_{\text{cool}}$) and the time resolution of the measurement (for a more quantitative discussion on the trapping dynamics, see [Figure S9](#)). Thus,

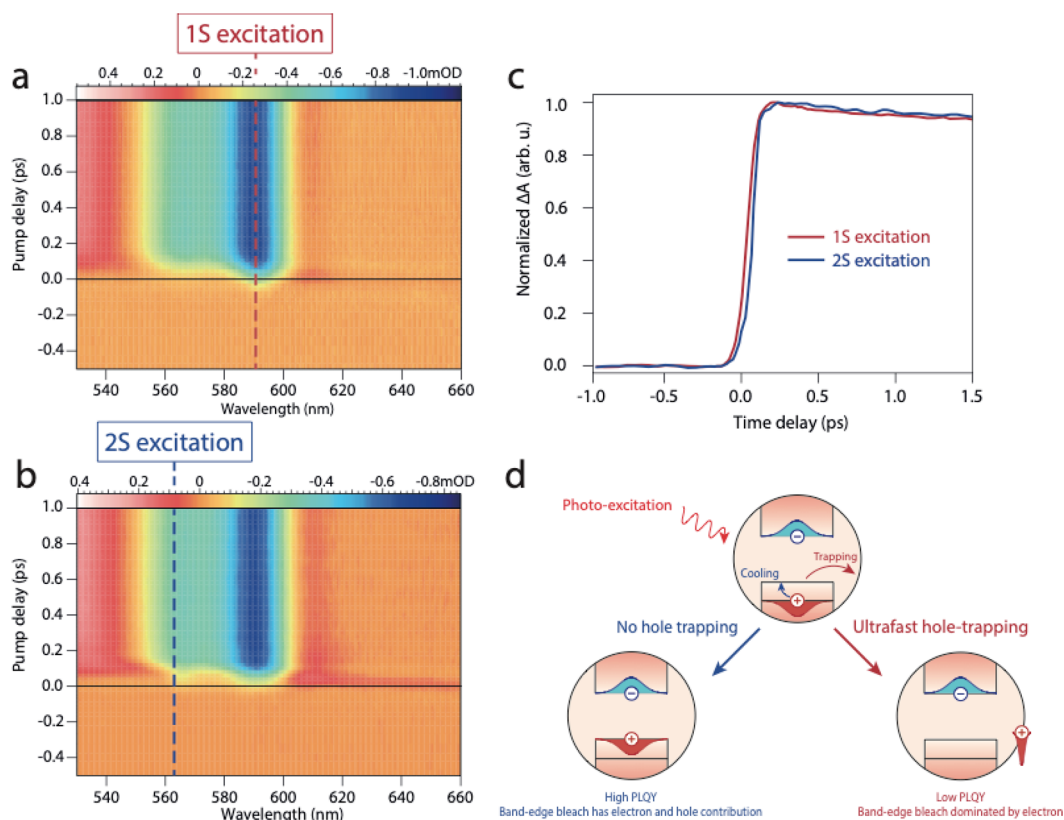


Figure 4. Analysis on the core-only, low-PLQY CdSe QDs upon 1S and 2S excitation, showing fast hole trapping. (a) 2D TA images for 1S and (b) 2S excitation, up to 1 ps after photoexcitation on the core-only CdSe QDs. In both cases, we do not see an ingrowth of the BE-bleach. (c) Amplitude of the BE-bleach upon exciting the 1S (red) and 2S (yellow) transitions. Note that the bleaches appear simultaneously and instantly after photoexcitation in both cases; i.e. we do not observe the hole cooling, which is in contrast with the BE-bleach of the high-PLQY NCs from Figure 4. (d) Schematic representation of hole relaxation pathways after photoexcitation. In high-PLQY samples, with little to no hole trapping, the hole relaxes to the BE level [$1S_{3/2}(h)$], where it contributes accordingly to the BE-bleach in the fs-TA experiments. In samples where there is fast hole trapping, the hole is rapidly localized in a trap state and does not contribute anymore to the BE-bleach signal in our fs-TA experiments.

the TA measurement probes QDs populated by a trapped hole and a conduction BE electron, irrespective of the initial excitation. These results demonstrate that the contribution of holes to the BE-bleach is completely obscured by fast hole trapping in low-PLQY samples.

Hole Cooling in Z-Type Ligand ($InCl_3$) Passivated CdSe Core-Only QDs. We have attributed the lack of hole cooling in unpassivated core-only QDs to ultrafast hole trapping, also leading to low PLQY in these samples. This interpretation suggests it should be possible to observe hole cooling in core-only CdSe QDs when their PLQY is high enough; i.e., the hole trapping is sufficiently slow or absent from a portion of the QD population. Below, we show that Z-type ligand passivation of the surface of core-only CdSe QDs increases their PLQY, and allows us to observe the cooling of the hole from the $2S_{3/2}$ into the $1S_{3/2}$ hole state in TA experiments.

Proper passivation of the CdSe QD surface can in principle lead to high-PLQY core-only samples.⁴⁵ We passivated the surface of CdSe QDs cores with $InCl_3$, a Lewis acid that acts as a Z-type ligand, following work that was recently published by our group.⁴⁴ The steady state absorption and PL spectra are shown in Figure 5a. After the $InCl_3$ surface treatment, the PLQY of the CdSe QDs sample increased from 2% to 21%. Figure 5b shows the BE-bleach for 1S and 2S excitation of these passivated CdSe QDs dispersed in toluene. A clear ingrowth of the BE-bleach amplitude is observed when photoexciting the 2S transition; i.e., the hole cools down

from the $2S_{3/2}$ hole state to the $1S_{3/2}$ hole state, whereas the growth of the BE-bleach upon 1S excitation is limited by the time resolution. Fitting the data with the same model presented for the high-PLQY core-shell-shell QDs, we obtain a ratio for the hole-to-exciton bleach in the $InCl_3$ passivated CdSe cores of 0.10 ± 0.02 , with a hole cooling time of 190 ± 40 fs, closely matching the value obtained on the core-shell-shell QDs.

We associate the increase in PLQY to the suppression of the trapping process in part of the QD population, due to an improved chemical passivation of surface traps.⁴⁴ In the passivated QDs, holes contribute to the BE ingrowth, while in the unpassivated portion of the population the BE signal is dominated by the electron contribution. As a result, the amount of hole contribution to the BE signal for the $InCl_3$ passivated cores is expected to be lower than in the core-shell-shell sample, in line with the difference in PLQY. Figure 5c presents the amplitude of the BE-bleach after exciting the 2S transition of the unpassivated QDs, the $InCl_3$ passivated QDs and the core-shell-shell QDs. The ingrowth follows a clear trend with increasing PLQY; better passivation of the CdSe QDs leads to a higher contribution of holes to the BE-bleach. As we passivate possible hole traps on the surface of the QDs better, a larger fraction of photoexcited holes survive the cooling process from the $2S_{3/2}$ to the $1S_{3/2}$ state.

Figure 5d shows the amplitude of the BE-bleach upon 1S excitation of the unpassivated cores, $InCl_3$ -treated cores and

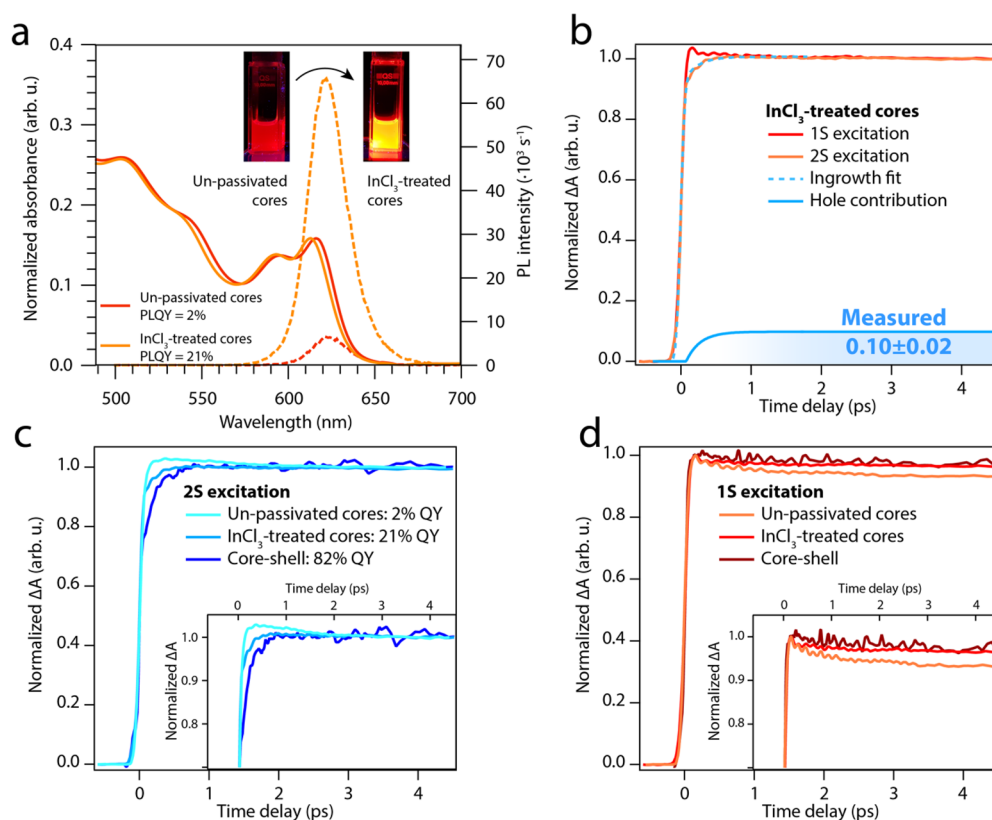


Figure 5. Evidence of hole contribution to the BE-bleach in Z-type ligand (InCl_3) passivated core-only CdSe QDs with TA. (a) Absorption and PL spectra of the unpassivated and InCl_3 passivated core-only QDs. The PLQY is increased by an order of magnitude. (b) Comparison between 1S and 2S excitation on CdSe cores, which are passivated with InCl_3 . The ingrowth of the BE-bleach due to the relaxation of the hole from the 2S to 1S state is clearly visible and constitutes 10% of the total BE-bleach amplitude. (c) Comparison of the BE-bleach amplitude between unpassivated core-only CdSe QDs, InCl_3 passivated QDs, and the core-shell QDs earlier presented in this Letter. The inset shows a photograph of the unpassivated (2% PLQY) and InCl_3 passivated (21% PLQY) QDs. (d) BE-bleach amplitude after 1S excitation on the same samples presented in panel c.

core-shell-shell QDs. Although all samples have a decay component with a picosecond lifetime, InCl_3 -treated cores and unpassivated cores show sign of faster decay components, possibly associated with the ultrafast hole trapping process assumed in our description. However, the presence of multiple coherent bleach oscillations, typically associated with phonon-emission processes,^{46–48} and limits in the time resolution of the measurements prevents quantitative determination of the character of the fastest decay component (see Supporting Information).

The experiments on these InCl_3 -passivated QDs show that holes do indeed contribute to the BE-bleach in CdSe QDs cores, with an amplitude determined by the degree of QD passivation.

Evidence of a Hole Contribution to the BE-Bleach via Optical Gain and Spectroelectrochemistry. Another spectroscopic signature of a significant hole contribution to the BE-bleach can be found in the presence of optical gain at the energy of the 1S transition. Figure 6a shows a high-fluence TA measurement on the CdSe/CdS/ZnS QDs, performed exciting the system at 400 nm with a fluence of 1.86×10^{14} photons/cm² per pulse, resulting in an average of 2.07 excitons per QD. Figure 6b compares the steady state absorbance of the measured sample (black) to excited-state absorbances for different excitation fluences ($\langle N \rangle = 0.86$ in orange and 2.07 in red), obtained adding the differential absorbance at 4.5 ps after photoexcitation to the steady state spectrum. For the higher

fluence measurement (red), the excited-state absorbance is negative on the low-energy side of the 1S absorption feature, an effect which would not be possible in the absence of a hole contribution to both stimulated emission and state filling of the 1S transition. The red trace in Figure 6b shows that net gain is observed in the presence of approximately two excitons per QD. In the absence of a hole contribution to the BE-bleach, a doubly excited QD with 2-fold degenerate conduction BE should have zero absorption (i.e., the material is transparent at the BE energy), but would not show gain.

We applied the transition-counting model, corrected for Poissonian excitation statistics (see Supporting Information), to a QD with 2-fold degenerate conduction BE and 4-fold degenerate valence BE. For an excitation density of $\langle N \rangle = 2.07$, this model predicts a fractional bleach $\Delta A/A_0 = 1.21$, in close agreement with the fractional bleach of 1.19 observed from the TA measurement (see Supporting Information). This result shows that our quantitative assignment of the hole contribution in the low-fluence BE-bleach remains valid in the high-fluence regime: the transient absorption signal at the BE is well-described by the sum of the contributions of electrons, with a degeneracy of 2, and holes, with a degeneracy of 4.

Perhaps the conceptually clearest proof of holes contributing to a BE-bleach comes from experiments where only holes are injected. In principle, hole injection could be done electrochemically and the changes in absorption could be recorded.

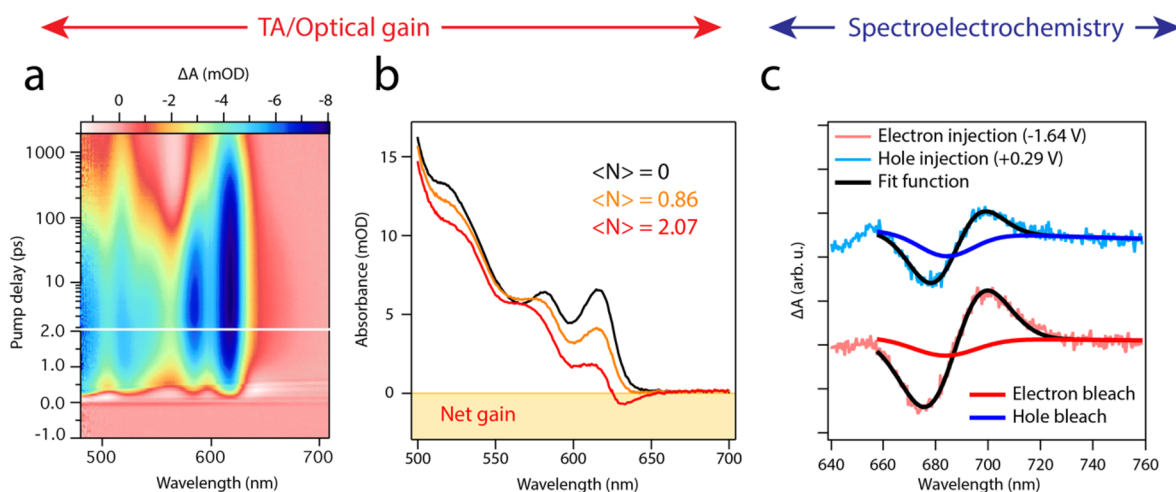


Figure 6. Additional spectroscopic evidence of hole contribution to the BE-bleach. (a) High-fluence TA color map of the CdSe/CdS/ZnS QDs, excited at 400 nm with a fluence of 6.54×10^{14} photons/cm² per pulse, showing a maximum of the BE-bleach 4.5 ps after photoexcitation. (b) Comparison between the excited-state absorption spectrum ($A_0 + \Delta A$), obtained from the differential absorbance shown in panel a at 4.5 ps, and the steady state absorption (A_0 , black), clearly showing the presence of optical gain at $\langle N \rangle = 2.07$ excitons/QD. (c) Spectroelectrochemical measurement on a film of CdTe QDs, showing the differential absorption spectrum of the sample at reducing potentials (electron injection, red curve) and oxidizing potentials (hole injection, blue curve, offset for clarity). The bleach amplitude was extracted from a fit of the signal with a Gaussian and a derivative-like feature, due to the presence of a Stark shift induced by localized charges.⁴⁹

However, electrochemical hole injection leads to rapid deterioration of CdSe QDs,⁵⁰ possibly due to irreversible oxidation of Se surface ions and dissolution of Cd²⁺.⁵¹ However, we found that for CdTe QDs stable hole injection is possible, allowing spectroelectrochemical determination of the hole bleach spectrum. The presence of a hole contribution to the BE-bleach should be extendable to other Cd-chalcogenides QDs, as they all share the same character of the BE transition.

Figure 6c shows differential absorption spectra obtained during a spectroelectrochemical measurement of a film of CdTe QDs. A potential difference is applied between the sample and a Ag pseudoreference electrode, which allows us to control the Fermi level inside the QD film. Applying both a reducing potential (electron injection, red) and oxidizing potential (hole injection, blue), we observed spectral changes at the BE energy. These spectral changes are caused by the superposition of a bleach feature and of a derivative-like feature, associated with a Stark shift induced by the presence of trapped electrons.⁵² We fitted the BE signal in the two traces, separating the bleach component (red and blue lines in Figure 6c) and the Stark-shift component (see Supporting Information). The similarity in the spectral shape of the BE signals and the presence of a bleach component in both the spectra demonstrates that holes have a contribution to the BE-bleach similar to the contribution of electrons. Furthermore, we extracted the BE-bleach at each potential from a fit of the differential absorbance spectra, showing the presence of two distinct onsets in the bleach amplitude, corresponding to electron and hole injection (see Supporting Information). This clearly shows that electrochemical hole injection results in a measurable BE-bleach in CdTe QDs.

Conclusions. To summarize, we have provided three independent pieces of evidence that holes contribute to the BE-bleach in Cd-chalcogenide QDs. We measured TA in the low-fluence regime on high-PLQY CdSe core-shell-shell QD solutions, identifying a component in the bleach kinetics associated with hole cooling. The relative weight of the

photogenerated hole to the BE-bleach amounts to half the weight of the electron, consistent with a simple theoretical model for the bleach of degenerate transitions. Measurements on low-PLQY CdSe core-only QDs do not show a dependence on the initial hole state. InCl₃-treated QDs, which have an intermediate PLQY between cores and core-shell-shell particles, show the presence of a hole component in the bleach, with a smaller amplitude than in the core-shell-shell QDs. These observations support the conclusion that ultrafast hole trapping in samples with incomplete passivation obscures the hole contribution to the BE-bleach. We also show that optical gain of the BE transition can be achieved for relatively low excitation densities ($\langle N \rangle = 2$), which implies a significant contribution of a BE hole to the BE-bleach. Furthermore, we measured a bleach upon electrochemical hole injection in CdTe QDs, confirming that holes contribute to the BE-bleach of Cd chalcogenides QDs even in the absence of BE electrons.

Once demonstrated, the presence of a hole bleach can be used for spectroscopic analysis, allowing to differentiate between BE and trapped holes. Furthermore, our results suggest that measurements of TA BE-bleach can be employed to investigate the kinetics of hole processes in high-PLQY Cd chalcogenides QDs, by monitoring the kinetics of the hole contribution to the bleach. Finally, we showed remarkable agreement between calculations of the fractional bleach in the presence of hole contribution and our experimental results. This observation paves the way to more quantitative studies of the buildup of optical gain in these materials, which will give solid handholds to improve these materials for applications in low-threshold gain media.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.nanolett.9b00164](https://doi.org/10.1021/acs.nanolett.9b00164).

Synthesis of the NCs employed in this work, techniques used to characterize the NCs (TEM, steady state

absorption, PL), setups used for the TA and spectroelectrochemical measurements, extraction of the hole contribution to the BE-bleach, determination of the absorption cross section, calculation of the fractional bleach with Poissonian excitation, extraction of the bleach component from spectroelectrochemical measurements, and analysis of the coherent oscillations in the bleach signal (PDF)

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Notes

The authors declare no competing financial interest.

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