Sub-Bandgap Photoinduced Transient Absorption Features in CdSe Nanostructures: The Role of Trapped Holes

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ABSTRACT: Transient absorption (TA) is widely used to study the dynamics of various processes, such as trapping, nonradiative decay, or transferring of photoexcited carriers in semiconductor nanocrystals. TA spectra of these systems show photoinduced absorption (PA) features that appear lower in energy than those of the band edge, which have been attributed to sub-bandgap absorptions of photoexcited electrons and holes. Here, we perform atomistic, semiempirical pseudopotential calculations in CdSe nanostructures to compute oscillator strengths for sub-bandgap transitions of conduction band electrons, valence band holes, and surface-trapped holes. We find that sharper peaks in the infrared (IR) range and broader features in the near-IR range (0.5−1.0 eV) are due to near-band-edge transitions of electrons and holes, respectively. Additionally, we focus on the region from 1.45 to 1.9 eV (850−650 nm), in which broad features have been observed and assigned to the PA of holes populating surface traps of nanocrystals. While there has been experimental justification of this assignment, there has been little theoretical investigation. We find that, in this region of interest from 1.45 to 1.9 eV, oscillator strengths for transitions of trapped holes are significantly larger than those of electrons or valence band holes. We conclude that the low symmetry of localized surface trap states and optimal spatial overlap with highly oscillatory states deep in the valence band lead to large electric dipole matrix elements and increased oscillator strengths. Our results are consistent for CdSe and CdS cores, CdSe−CdS core−shell quantum dots, and CdSe nanorods.

INTRODUCTION

Colloidal quantum dots have many attractive properties, such as tunable band gaps, high photoluminescence quantum yields, and the ability to generate multiple charge carriers, that make them promising materials for solar harvesting applications,1−3 photocatalysis,4−6 and other optoelectronic devices.1,7−9 Realization of these applications requires a better understanding of the dynamics of photoexcited charge separation and transfer in colloidal quantum dots. Many experimental studies employ ultrafast transient absorption (TA) spectroscopy as a time-resolved method to study charge carrier dynamics.

In TA, a pump pulse at a certain energy and fluence generates an initial number of electron−hole pairs via optical excitation. After a time delay, a probe pulse is sent through the sample, and the ground state absorption spectrum is subtracted from the excited state absorption. This differential absorbance (ΔA) can be measured as a function of both the probe energy and the pump−probe time delay to understand the dynamics of different populations. Negative ΔA features are due to ground state bleaching, when ground state carriers have been depleted to excited states, or stimulated emission. Positive ΔA features are due to excited state absorption or product absorption.

Understanding chemical processes and kinetics through TA relies on the accurate assignment of differential absorbance features. The study of charge separation and transfer requires monitoring the populations of individual charge carriers, which can be difficult because the optical pump pulse always creates neutral excitations (i.e., electron−hole pairs). Monitoring the population of excited electrons is possible through analysis of the conduction band bleach, which is one of the dominant features in TA spectra of colloidal quantum dots (Figure 1a) and is caused by state filling of the 1S_e state with electrons upon photoexcitation from the pump pulse.9−11 The intensity of this signal only reflects the population of electrons in the 1S_e state, however, and does not provide information about hole populations because of the high degeneracy of the valence band. This high density of valence band states generally makes tracking hole populations more difficult.
To address this challenge, many studies investigating charge separation and transfer in colloidal quantum dots use differential absorbance features that are lower in energy (higher in wavelength) than the band gap to monitor populations of individual carriers. At these lower energies, the probe does not have enough energy to create additional excitons via optical excitation across the band gap. Instead, these energies are probing sub-bandgap photoinduced absorption (PA) transitions of photogenerated electrons or excitons via optical excitation across the band gap. Further, these energies are probing sub-bandgap PA transitions of photogenerated electrons or holes to further in the conduction and valence bands, respectively. These PA features always have positive differential absorbance, but they are much smaller in amplitude than the conduction band bleach and often broad; therefore, attributing these signals to specific transitions or populations can be difficult.

Furthermore, because these sub-bandgap PA transitions are so low in energy, they often require probe energies in the infrared (IR) or near-IR (NIR) spectra. A sharper PA peak has been observed in the IR spectrum around 0.26 eV (4600 nm) in 4.5 nm CdSe cores, and broad features have been measured in the near-IR spectrum around 0.62–1.1 eV (2000–1100 nm) in CdSe and CdS cores. These features have been attributed to intraband transitions of band edge electrons and holes, respectively. With probes in the visible region, several experiments have observed a broad, positive PA feature that appears at 1.45 eV (850–650 nm) in CdSe and CdS, and broad features in the NIR are dominated by PA of valence band transitions or populations of holes trapped at surface states of the nanocrystal. They observe a more rapid decay of this PA signal in the presence of a hole-accepting ligand phenothiazine (PTZ) and no change in kinetics in the presence of an electron-accepting ligand benzoquinone (BQ). This feature is associated with holes, not electrons. Additionally, they find that the rise time of this feature is slower than ~200 fs, which is slower than expected cooling rates, and the decay kinetics match those of trap emission bands in photoluminescence spectroscopy, indicating the feature can be attributed specifically to trapped holes. While similar types of features have been studied computationally in small semiconductor clusters, this broad feature in semiconductor nanocrystals has not been assigned by first-principle or model calculations, and the origin of these photoinduced transitions, especially in the visible region, is not well understood.

Figure 1a shows the TA spectra of 3.0 nm CdSe and 2.3 nm CdSe–3 ML CdS core–shell quantum dots with band edge excitations at a high fluence, for which an average of two excitons are created upon excitation. At the illustrated pump–probe delay of 7 ns, the average number of excitons remaining is less than one. Both spectra feature the large, negative conduction band bleach as well as the broad, positive PA feature from 1.65 to 2.05 eV, which is highlighted in the inset. This experimental data is representative of previously reported observations of broad, positive features in the visible region of TA studies of similar systems. PA features can generally be attributed to the photoinduced absorption of (i) band edge electrons to higher in the conduction band, (ii) band edge holes to deeper in the valence band, and (iii) surface-trapped holes to the valence band, as illustrated in the model energy diagram in Figure 1b.

Here, we perform atomistic calculations on CdSe and CdS nanocrystals of experimentally relevant sizes to compute the oscillator strengths (OSs) of transitions from each of these three states, thereby investigating the energies and relative amplitudes of PA features, with a focus on those in the 1.45–1.9 eV (850–650 nm) region, in these systems. We find that sharper features in the IR region are due to the 1S−1Ptransition of conduction band edge electrons, and broad features in the NIR are dominated by PA of valence band holes; broad features in the 1.45–1.9 eV region are due to PA of surface-trapped holes.

**METHODS**

We perform atomistic electronic structure calculations within the semiempirical pseudopotential method to obtain quasiparticle states of CdSe, CdS, and CdS–CdS core–shell quantum dots as well as CdSe nanorods. Note that, while the discussion throughout the paper uses notation of the effective mass model to describe single-particle states (i.e., 1S, 1P, etc.), these calculations have been performed within an atomistic approach.

Experimentally, midgap hole trap states arise from unpassivated chalcogenide atoms on the surface of the nanocrystal. Within the semiempirical pseudopotential method, all surface Cd, Se, and S atoms are generally modeled with passivation ligand pseudopotentials, which push the energy of surface states out of the band gap. Therefore, a surface hole trap is modeled by a Se or S atom that is unpassivated, which creates a localized midgap state about 0.5 eV above the valence band maximum. These energies are consistent with electron microscopy, absorption, and emission measurements on CdSe and CdS nanocrystals, which have shown that dangling Se and S bonds create surface traps with similar energies.

Electron trap states are less common, both in theoretical models and in experimental systems, than midgap hole trap states in CdSe and CdS systems. Electrons have a relatively small effective mass (about 5 times smaller than holes in CdSe and CdS), so they are unlikely to form localized, midgap trap states, even when Cd atoms are left unpassivated.

To understand the origin of the PA signal in these systems, we compute the oscillator strengths (OSs) of intraband transitions from the conduction band edge, valence band edge, and hole trap states. For a transition from state i to state j, the OS is calculated as

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**Figure 1.** (a) Experimental TA spectra of a 3.0 nm CdSe core (maroon) with a 540 nm excitation wavelength and 7.0 ns pump–probe delay and 2.3 nm CdSe–3 monolayer (ML) CdS core–shell (purple) with a 545 nm excitation and 7.0 ns delay. The inset illustrates the broad, positive PA feature. (b) Energy level schematic of a CdSe core showing single-particle states. PA could be attributed to the photoinduced absorption of (i) the conduction band edge electrons and holes to further in the conduction and valence bands, respectively, (ii) valence band edge (blue), or (iii) surface trap states (orange).
\[ f_\eta = \frac{4m_e}{3\hbar^2}(\varepsilon_j - \varepsilon)\mu_\eta^2 \]  
where \( m_e \) is the mass of the electron, \( e \) is the charge of the electron, and \( \mu_\eta \) is the electric dipole matrix element given by
\[ \mu_\eta = \varepsilon \int \psi_i(r) r \psi_j(r) \, dr \]
where \( \psi_i(r) \) is the single-particle wave function for state \( i \) with energy \( \varepsilon_i \). The absorption cross section \( \sigma \) reflects the probability of absorption of each transition from a given state as well as the number of possible transitions. \(^{39}\) It can be obtained as a function of the transition energy \( \omega \) by performing a Boltzmann-weighted average over initial states \( i \) and summing over all possible transitions \( j \),
\[ \sigma(\omega) \propto \frac{1}{Z\sqrt{2\pi\gamma}} \sum_i e^{-\beta\varepsilon_i} \times \sum_j f_j \exp \left( -\frac{1}{2} \left( \frac{\omega - (\varepsilon_j - \varepsilon)}{\gamma} \right)^2 \right) \]
Here, \( \gamma = 0.042 \text{ eV} \) is the inhomogeneous broadening factor, and \( Z = \sum_i e^{-\beta\varepsilon_i} \) is the partition function of initial states. \( \beta = 1/\kappa_B T \) at room temperature, 298 K. Only the partition function for the valence band edge has contributions from multiple states, as the spectrum of hole states is relatively dense, even near the band edge.

### RESULTS AND DISCUSSION

PA features were investigated in CdSe cores with a diameter of 4.0 nm as a representative system, because their PA features have been well characterized; they are often used in experimental studies of charge separation and transfer. The charge densities of the conduction band edge electron, valence band edge hole, and surface-trapped hole are illustrated in Figure 2a, and the absorption cross sections with transition energies for each of these states are shown in Figure 2b.

Near-band-edge transitions are the most significant for the PA signal from the conduction band edge. In particular, the \( 1S_e - 1P_e \) transition at 0.27 eV (4600 nm), which corresponds to the 0.26 eV IR feature observed and characterized for 4.5 nm CdSe cores,\(^ {17} \) appears as a sharp peak with a very high amplitude. The \( 1S_e - 2P_e \) transition is higher in energy (1.1 eV) and in agreement with calculations for CdSe cores of a similar size.\(^ {40-42} \)

These conduction band PA features are sharp, reflecting the density of states near the conduction band edge, which is sparse due to quantum confinement and the relatively small electron effective mass. The energies of these sharp transitions are size dependent. Specifically, they will be higher in energy for smaller structures, in which the confinement energy is larger and the energy spacing between conduction band states is larger. Additionally, while transitions with changes in orbital angular momentum beyond \( \pm 1 \) are allowed outside of the effective mass approximation, due to the breaking of spherical symmetry, they are still weak and have a negligible contribution to the PA. Because of the relatively large \( 1S_e - 1P_e \) splitting, the TA pump creates electrons that populate only the \( 1S_e \) state, and the only significant PA signals are those corresponding to \( 1S_e - nP_m \) transitions. At very high fluences, where the pump creates more than two excitons and the \( 1P_e \) state is also populated, additional features corresponding to \( 1P_e - nD_l \) transitions are expected to appear.
Transitions near the band edge are also the most prominent features of the PA signal of the valence band edge. These features begin to appear at very low energies (0.01–0.5 eV), as the valence band is more dense near the band edge due to a larger effective mass and 2-fold degeneracy. Because of this high density of states, the TA pump creates holes not necessarily at the valence band maximum (1S<sub>3/2</sub> state) but at any of these near-band-edge states, according to a Boltzmann probability, as shown in eq 3. Consequently, many transitions at a variety of energies satisfy a change in orbital angular momentum equal to ±1 and therefore have a larger OS, resulting in broad and relatively size-independent PA features for the valence band hole.

The surface-trapped hole has a negligible absorption cross section for all transition energies less than 0.75 eV. This is because, while the hole-trapped state is localized to the surface, hole states near the valence band edge have the largest wave function amplitudes near the center of the nanocrystal, as shown in Figure 2b. While the OSs for transitions from the trapped hole state remain small, they persist for higher-energy transitions, unlike those of the conduction and valence bands.

The absorption cross sections vary significantly over the full energy range 0.0–3.0 eV, but the PA from each state dominates the overall PA signal at different energy regimes (Figure 2c). At the lowest energies (0.0–0.25 eV, greater than 5000 nm), valence band holes dominate the PA. In the IR region, the 1S<sub>3/2</sub>−1P<sub>1/2</sub> transition is dominant around 0.27 eV (4600 nm). At higher energies (0.5–1.0 eV, 2500–1250 nm), the valence band hole again has the largest contribution to the overall PA spectrum, corresponding to the broad feature around 0.7 eV observed in 4.0 nm CdSe and CdS cores. At energies higher than 1.5 eV (wavelengths shorter than 830 nm), trapped holes dominate the overall PA signal.

To better understand the PA signal due to trapped holes and its dependence on system size, we computed the absorption cross section for CdSe cores of different diameters, 2.5, 3.3, and 4.0 nm, and focused on the energy range of interest (1.45–1.9 eV, 850–650 nm). As depicted in Figure 3, the trapped hole absorption cross section comprises a broad feature that is larger in amplitude than that of band edge electrons and holes. This phenomenon persists for CdSe cores of different diameters, 2.5, 3.3, and 4.0 nm, but is more obvious for larger cores.

This trend can be explained by the decreased confinement energy in larger systems, which causes the momentum of the excited electron or hole to increase with increasing nanocrystal size for a given excitation energy. These higher-momentum states have a significant amplitude throughout the nanocrystal, while lower-momentum states have a larger amplitude concentrated in the center and fewer nodes, as illustrated in Figure 4. Therefore, the magnitude of the electric dipole matrix element, given by eq 2, is larger between the higher-momentum states in larger cores and surface trap states that are highly localized to the surface. Aside from contributions of the hole to the PA signal, the smallest core includes a sharper feature in this energy region due to the 1S<sub>3/2</sub>−2P<sub>1/2</sub> transition, which is not present in larger structures due to decreased quantum confinement and a lower-energy spacing between the 1S<sub>3/2</sub> and 2P<sub>1/2</sub> states (Figure 3).

Finally, we performed calculations on a 5 nm CdS core, 2.3 nm CdSe≈3 ML CdS core–shell quantum dot, and 2.1–10 nm CdSe nanorod, as these systems have been studied in the context of charge transfer as promising candidates for solar energy harvesting and other applications. Figure 5 indicates that the PA signal in the region from 1.45 to 1.9 eV is again dominated by surface-trapped holes in these systems. In fact, the dominance of the trapped hole signal over the valence band signal is even more pronounced than those in the CdSe cores.

![Figure 3. Absorption cross section in arbitrary units in the energy region of interest (1.45–1.9 eV, 850–650 nm) for CdSe cores with diameters of 2.5 (top), 3.3 (center), and 4.0 (bottom) nm. The smallest core has a peak corresponding to the 1S<sub>3/2</sub>−2P<sub>1/2</sub> transition. The larger systems, these peaks are lower in energy due to smaller confinement energies. For all systems, the hole trap has the largest absorption cross section. This effect becomes more pronounced as the size of the system increases. The total OS is integrated over the transition energy range from 1.45 to 1.9 eV.](https://dx.doi.org/10.1021/acs.jpcc.0c04746)

![Figure 4. Projections of single-particle wave functions onto the x-axis of the valence band edge (blue), surface hole trap (orange), and a state 1.7 eV below the valence band maximum (green) in a 2.5 nm CdSe core (top) and 4.0 nm CdSe core (bottom). The deep valence band state is higher in momentum and more oscillatory in the 4.0 nm CdSe core due to a lower confinement energy. Also, note that, for both systems, the valence band states have inversion symmetry about x = 0, while the surface trap state does not have the symmetry.](https://dx.doi.org/10.1021/acs.jpcc.0c04746)
shown above. This is again due to the fact that all these structures are even larger than the 4 nm CdSe core, so higher-energy states are more oscillatory with a significant amplitude throughout the nanocrystal. Interestingly, the dominance of the trapped hole contribution to the PA signal in the region from 1.45 to 1.95 eV is independent of the location of the surface trap, even for the highly anisotropic nanorods (Figure S1). This effect can again be explained by the increased amplitude of higher-energy valence band states near the surface of the nanorods, where the surface trap states are localized.

Our results show that for transition energies greater than 1.45 eV in a variety of systems, the photoinduced absorption cross section of trapped holes is much larger than those of band edge electrons or holes. Deeper into the conduction and valence band are higher-momentum states that have more oscillatory wave function envelopes with relatively equal amplitudes throughout the nanocrystal. Band edge electrons and holes, however, have radially symmetric wave function envelopes that have a higher amplitude at the center. Surface-trapped holes break radial symmetry and have a larger amplitude in a more localized area of space, as depicted in Figure 4. Therefore, the integral for the electric dipole matrix element has a larger value for transitions between the symmetric high-energy valence band states and the localized trapped hole state, leading to a larger absorption cross section for large (greater than 1.45 eV) transition energies.

These conclusions will not depend significantly on the absolute energy of the hole trap state, and they should be consistent for shallow traps that have energies closer to the valence band maximum. The PA amplitude for shallow traps will be slightly decreased, due to the dependence of the oscillator strength on the energy between initial and final states, but the contribution of the trapped hole to the overall PA signal will remain significant.

Our findings are consistent with absorption sum rules, which state that the OS between a state and all other states must sum to 1.43 Because the OSs for low-energy transitions near the band edge are so strong for electrons and holes, the OSs for transitions to higher-energy states are weaker. On the other hand, surface trap states have very low OSs for these low-energy transitions, so they are relatively larger for transitions greater than 1.45 eV.

CONCLUSIONS

The dynamics of photoinduced charge separation and transfer in CdSe and CdS nanostructures is often studied using TA spectroscopy. While the analysis of sub-bandgap PA features can be used to understand the kinetics of individual charge carriers, many of these signals are low in energy and require probes in the NIR or IR regions. One PA signal that does appear in the visible range around 1.45–1.9 eV (850–650 nm) is often assigned to the photoinduced absorption of holes trapped to the surface.

Through theoretical investigation of PA features due to band edge electrons and holes and surface-trapped holes, we see that the use of the broad PA feature greater than 1.45 eV (less than 850 nm) to measure the populations of trapped holes is justified. Additionally, unlike the conduction band bleach feature, which saturates quickly under multie excitonic conditions due to filling of the 1S state, the total PA signal is purely additive in the trapped hole region, assuming that the surface traps are spatially separated. This facilitates the understanding of hole-trapping dynamics at high fluences, as the mapping remains linear between the PA amplitude and the number of trapped holes. There is a nonzero contribution, however, of valence band edge holes to the PA signal at 1.45 eV, and this will likely become significant for small cores and for systems with few to no surface traps, i.e., near-unity quantum yield particles.

This work highlights the physical origins of the optical signal of hole traps in TA spectra in CdSe and CdS nanostructures, facilitating investigations of charge separation and transfer in these systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c04746.

Procedures used to construct the nanocrystal configurations and to compute single-particle states within the semiempirical pseudopotential method; figures illustrating the independence of the photoinduced absorption signal with the location of the trapped hole for the 4.0 nm CdSe core and 2.1–10 nm CdSe nanorod; description of the transient absorption setup and measurements; and information about the measured samples, including sample preparation procedures, linear absorption spectra, and photoluminescence measurements (PDF).

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Notes

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