AFRL-AFOSR-VA-TR-2019-0160

Excited States Electronic Coupling, and Charge Transfer Properties of Chalcogenide-capped Semiconductor Nanocrystals

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03/27/2019
Final Report

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ RTB2
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 24-06-2019	**2. REPORT TYPE** Final Performance	**3. DATES COVERED** *(From - To)* 01 Jul 2015 to 31 Dec 2018

4. TITLE AND SUBTITLE Excited States Electronic Coupling, and Charge Transfer Properties of Chalcogenide-capped Semiconductor Nanocrystals	**5a. CONTRACT NUMBER**
	5b. GRANT NUMBER FA9550-15-1-0253
	5c. PROGRAM ELEMENT NUMBER 61102F
6. AUTHOR(S) Gordana Dukovic	**5d. PROJECT NUMBER**
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) REGENTS OF THE UNIVERSITY OF COLORADO 3100 MARINE ST 572 UCB BOULDER, CO 80309-0001 US	**8. PERFORMING ORGANIZATION REPORT NUMBER**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203	**10. SPONSOR/MONITOR'S ACRONYM(S)** AFRL/AFOSR RTB2
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2019-0160

12. DISTRIBUTION/AVAILABILITY STATEMENT
A DISTRIBUTION UNLIMITED: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The objective of this project was to investigate the excited-state and charge transfer properties of semiconductor nanocrystals functionalized with ultrashort chalcogenide surface-capping ligands (S2, Se2, and Te2). Colloidal nanocrystals are typically synthesized with long-chain aliphatic molecules, which bind relatively strongly to the nanocrystal surface, thereby passivating and solubilizing the nanocrystal. However, these long, aliphatic surface ligands also weaken the electronic coupling between the nanocrystal and its environment. This is undesirable for applications involving charge transfer. Ultrashort ligands are therefore of great interest, as they allow strong electronic coupling while maintaining the nanocrystal's stability and solubility. However, the effect of ultrashort ligands on the excited states and particularly on charge transfer in nanocrystal systems had not been explored. In this project, we combined theory with experimental work employing steadystate and ultrafast optical spectroscopy to examine how these ligands affect the excited states, electronic coupling, and charge transfer in nanocrystals. We found that binding and unbinding of ultrashort ligands on the nanocrystal surface can introduce electron traps and that these electron traps can enable co-catalyst-free photochemistry by the nanocrystal. We developed a simple analysis to extract the biexciton spectra and lifetime from transient absorption (TA) dynamics and demonstrated that decreased electron-hole wavefunction overlap in S2 capped CdSe quantum dots (QDs) slows down Auger recombination. Using S2 capped CdS nanorods (NRs), we demonstrated enhanced electron transfer to hydrogenase enzyme by three orders of magnitude over MPA capped NRs, which we attribute to stronger electronic coupling enabled by the shorter S2 ligand. Similarly, we demonstrated that hole transfer by S2 capped nanocry

15. SUBJECT TERMS
quantum dot, chalcongenide, ligand, charge transfer

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** BERMAN, MICHAEL
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			
Unclassified	Unclassified	Unclassified	UU		**19b. TELEPHONE NUMBER** *(Include area code)* 703-696-7781

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

DISTRIBUTION A: Distribution approved for public release.

Excited states, electronic coupling, and charge transfer properties of chalcogenide-capped semiconductor nanocrystals

FA9550-15-1-0253

Abstract

The objective of this project was to investigate the excited-state and charge transfer properties of semiconductor nanocrystals functionalized with ultrashort chalcogenide surface-capping ligands (S^{2-}, Se^{2-}, and Te^{2-}). Colloidal nanocrystals are typically synthesized with long-chain aliphatic molecules, which bind relatively strongly to the nanocrystal surface, thereby passivating and solubilizing the nanocrystal. However, these long, aliphatic surface ligands also weaken the electronic coupling between the nanocrystal and its environment. This is undesirable for applications involving charge transfer. Ultrashort ligands are therefore of great interest, as they allow strong electronic coupling while maintaining the nanocrystal's stability and solubility. However, the effect of ultrashort ligands on the excited states and particularly on charge transfer in nanocrystal systems had not been explored. In this project, we combined theory with experimental work employing steady-state and ultrafast optical spectroscopy to examine how these ligands affect the excited states, electronic coupling, and charge transfer in nanocrystals. We found that binding and unbinding of ultrashort ligands on the nanocrystal surface can introduce electron traps and that these electron traps can enable co-catalyst-free photochemistry by the nanocrystal. We developed a simple analysis to extract the biexciton spectra and lifetime from transient absorption (TA) dynamics and demonstrated that decreased electron-hole wavefunction overlap in S^{2-} capped CdSe quantum dots (QDs) slows down Auger recombination. Using S^{2-} capped CdS nanorods (NRs), we demonstrated enhanced electron transfer to hydrogenase enzyme by three orders of magnitude over MPA capped NRs, which we attribute to stronger electronic coupling enabled by the shorter S^{2-} ligand. Similarly, we demonstrated that hole transfer by S^{2-} capped nanocrystals is two orders of magnitude faster than by MPA capped nanocrystals. Finally, in the course of creating a complete picture of the excited-state dynamics of NRs, we discovered the diffusive motion of trapped holes on the surface of NRs and described it with a simple but powerful model.

Accomplishments

The objective of this project was to investigate the excited-state and charge transfer properties of semiconductor nanocrystals functionalized with ultrashort chalcogenide surface-capping ligands (S^{2-}, Se^{2-}, and Te^{2-}). Colloidal nanocrystals are typically synthesized with long-chain aliphatic molecules, which bind relatively strongly to the nanocrystal surface, thereby passivating and solubilizing the nanocrystal. However, these long, aliphatic surface ligands also reduce the electronic coupling between the nanocrystal and its environment. This is undesirable for applications involving charge transfer. Ultrashort ligands are therefore of great interest, as they allow strong electronic coupling while maintaining the nanocrystal's stability and solubility. However, the effect of ultrashort ligands on the excited states and particularly on charge transfer in nanocrystal systems had not been explored. In this project, we combined theory with experimental work employing steady-state and ultrafast optical spectroscopy to examine how these ligands affect the excited states, electronic coupling, and charge transfer in nanocrystals. We also used this knowledge to design nanocrystal systems with both enhanced electron and hole transfer.

Finally, in the course of creating a complete picture of the excited-state dynamics of NRs, we discovered the diffusive motion of trapped holes on the surface of NRs and described it with a simple but powerful model.

In the previous funding cycle, we addressed the impact of chalcogenide ligands on the electronic structure of the nanocrystal, finding that electronic coupling of the nanocrystal to its environment in these systems is enhanced. We also found that electron trapping in nanocrystals capped with chalcogenide ligands is enhanced, particularly with Se^{2-} and Te^{2-} ligands. As a continuation of this work in the current funding cycle, we examined how the ligand exchange from long-chain aliphatic ligands to S^{2-} ligands leads to enhanced electron trapping in the nanocrystal. The ligand exchange occurs via a phase-transfer of the nanocrystals from the non-polar to the polar phase. During this phase transfer, the excited-state relaxation of CdSe quantum dots (QDs) does not significantly change. This is confirmed by examining the decay of the bleach signal, measured using TA spectroscopy, in CdSe QDs with S^{2-} and native, long-chain aliphatic ligands (ODPA). This signal corresponds to the population of excited electrons and is similar for both ligands (*Figure 1**a***). The hole dynamics, measured by photoluminescence upconversion, are also similar in both cases and show fast and efficient hole trapping (4 ps) (*Figure 1**b***). Subsequent precipitation and re-suspension in formamide results in electron lifetime shortening, i.e., enhanced electron trapping (*Figure 1c*). The introduction of electron traps can be reversed by the addition of an aliquot containing dissolved S^{2-} ligand to the sample (*Figure 1c*). Our hypothesis is that the enhanced electron trapping upon purification is due to unbinding of a small number of the sulfide ligands. This work provides a pathway toward improved control of surface chemistry and excited-state dynamics with sulfide ligands through an understanding of the relationship between the ligand binding and electron trapping dynamics.

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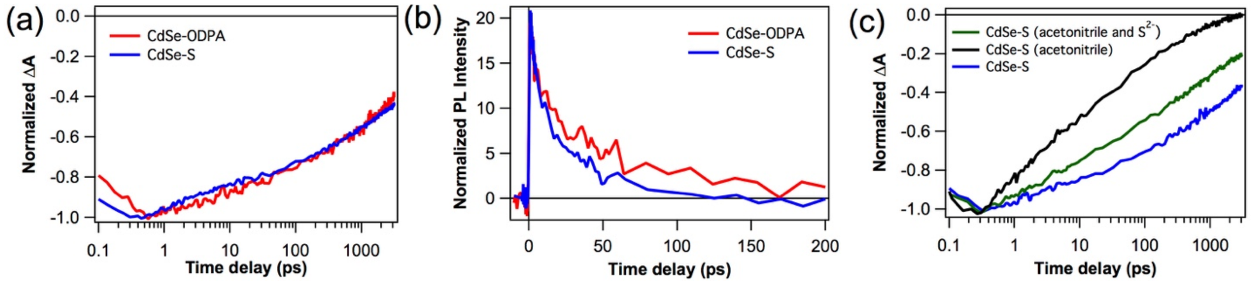

Figure 1. (a) and (b) Ground state TA bleach kinetics and PL decay of CdSe QDs capped with organic and sulfide ligands before purification. (c) Ground state TA bleach kinetics of CdSe-S after ligand exchange (blue), after purification with acetonitrile (black), and after purification followed by addition of S^{2-} (green).

While exploring the use of chalcogenide ligands to enhance charge transfer in systems that couple a nanocrystal as a light absorber to a co-catalyst, we found that the increased amount of electron trapping in S^{2-}-capped nanocrystals has important implications for nanocrystal photochemistry as well. Specifically, we found that CdS and CdSe/CdS nanocrystals passivated with S^{2-} ligands have significant quantum yields of hydrogen production (up to 1%) without employing a co-catalyst, while nanocrystals capped with the longer thiol ligand 3-mercaptoproprionic acid (MPA) did not produce measurable amounts of hydrogen (*Figure 2*). However, the hydrogen production is dependent on the amount of electron trapping introduced during the ligand exchange, discussed in the previous section. In samples where electron traps have not been introduced by precipitating the nanocrystals capped with S^{2-} ligand, no hydrogen

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production is observed. Electron traps in Cd-chalcogenide nanocrystals are thought to originate from unpassivated cadmium sites on the surface. Exposed Cd^0 “islands” on the surface of CdSe nanocrystals with thiol ligands, which appear to form after photoexcitation of the nanocrystal, have also previously been linked to photochemical H_2 production. Our observation of the link between photochemistry and electron trapping in nanocrystals capped with S^{2-} ligands suggest that these ultrashort ligands could have implications for photochemistry beyond their role in electronic coupling and charge transfer, uncovering other unique applications for nanocrystals. This work is currently being prepared for publication.

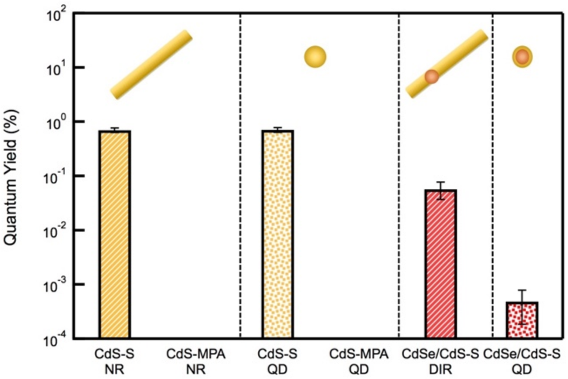

Figure 2. Comparison of H_2 production quantum yields for different morphologies and ligand types (NR = nanorod, QD = quantum dot, DIR = dot-in-rod heterostructure) of CdS and CdS/CdSe nanocrystals capped with S^{2-} or MPA ligands.

We also studied the role of the surface capping S^{2-} ligand in enhancing charge transfer, one of the primary objectives of this project. The role of the ligand in improving hole transfer in nanocrystal systems is particularly deserving of study, as the rate of hole scavenging by a sacrificial reagent has been shown to be the rate-limiting step for H_2 production in Cd-chalcogenide nanocrystal-based systems. Using time-correlated single photon counting to measure the photoluminescence lifetimes, we demonstrated that hole scavenging in CdSe/CdS dot-in-rod and core/shell quantum dot systems employing S^{2-} ligands is two orders of magnitude faster than in systems employing MPA ligands (***Figure 3***). The rate constant for hole transfer to the ascorbate hole scavenger is $2.3 \pm 0.7 \times 10^{10}$ M^{-1} s^{-1} for nanocrystals capped with S^{2-} ligands and $7 \pm 2 \times 10^8$ M^{-1} s^{-1} for nanocrystals capped with MPA ligands. The short sulfide ligands allow faster transfer of trapped holes on CdS surfaces to ascorbate.

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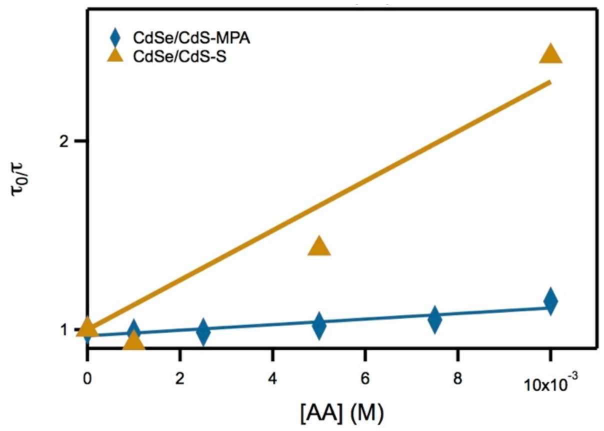

Figure 3. Stern-Volmer plots of the time-resolved photoluminescence lifetime quenching at 580 nm for CdSe/CdS dot-in-rods with S^{2-} (gold) and MPA (blue) ligands measured using TCSPC.

From our previous work, we expected that S^{2-} ligands would enhance electron transfer as well as hole transfer. To demonstrate this, we used a photochemical system that we have worked with for a number of years: CdS NRs capped with MPA ligands and coupled to hydrogenase enzyme (CaI). In this system, the MPA ligand forms the interface between the nanocrystal and the enzyme. In the past, we have used TA spectroscopy and kinetic modeling to quantitatively analyze the excited-state processes that determine the quantum efficiency of electron transfer (QE_{ET}), yielding rate constants for electron-hole recombination, electron trapping, and electron transfer to the enzyme. Electron transfer to the enzyme depends exponentially on the ligand length, so we incorporated the ultrashort S^{2-} ligands into the nanocrystal-enzyme system to enhance its efficiency. We discovered that the rate of electron transfer in the nanocrystal-enzyme system employing S^{2-} ligands undergoes a three order-of-magnitude increase compared to the system employing MPA ligands, from 10^{7} s^{-1} to 10^{10} s^{-1}. This increase in the rate of electron transfer is seen as an extreme shortening of the lifetime of S^{2-} capped CdS NRs relative to the MPA capped NRs (***Figure 4***). Despite the enhanced electron trapping in S^{2-} capped CdS NRs, the significant improvement in the rate of electron transfer means the system employing S^{2-} ligands reaches a maximum in QE_{ET}. Therefore, we have identified S^{2-} as a promising candidate for the ligand of choice in systems coupling nanocrystals to enzymes. This work is currently being prepared for publication.

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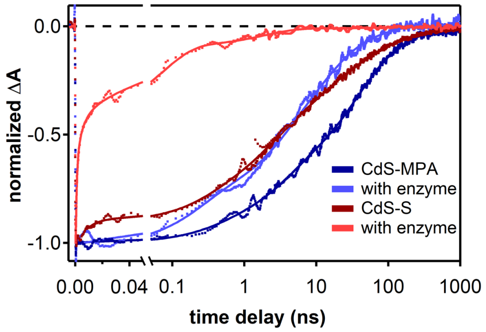

Figure 4. Normalized TA bleach kinetics of CdS NRs with and without hydrogenase using sulfide (red) or MPA (blue) surface capping ligands. The data is plotted on a linear x-axis for the first 50 picoseconds and is logarithmic thereafter.

In addition to affecting charge transfer and trapping in the nanocrystal, ultrashort S^{2-} ligands have important implications for Auger recombination. Studying the excited-state dynamics of CdSe QDs capped with either aliphatic octadecylphosphonic acid (ODPA) or ultrashort S^{2-} ligands using TA spectroscopy, we found that the lifetime of the biexciton is elongated by a factor of two in S^{2-} capped CdSe, compared to ODPA capped CdSe. We developed an analysis method allowing the extraction of an isolated biexciton spectrum and time constant from TA data using the assumption that TA data can be described as the sum of a set of decaying spectra. Each spectrum provides a fingerprint of a particular multi- or single-exciton state and decays with the same dynamics as the corresponding exciton state. Because of this, every kinetic trace from the TA data set can be fit to a sum of exponentials with common time constants and variable pre-exponential coefficients. Each time constant is associated with the decay of a particular exciton state, while each set of coefficients can be used to extract the spectral shapes corresponding to each exciton state (***Figure 6***). Using a global fit analysis, the single, biexciton, and multiexciton recombination time constants can therefore be extracted. The biexciton recombination time constant for S^{2-} capped CdSe was found to be 65 ps, a factor of 2 faster than the 35 ps measured for ODPA capped CdSe. We attribute this to the formation of a CdS shell on the surface of the CdSe quantum dot when capped with S^{2-}, as predicted in our previous work. As CdSe/CdS exhibits a quasi-type II band alignment, the conduction band electron is delocalized throughout the nanocrystal, while the hole is confined to the shell. Therefore, when CdSe QDs are capped with S^{2-} ligands, the electron-hole overlap is decreased, resulting in the elongation of the biexciton lifetime. Auger recombination in nanocrystals can compete with charge transfer to a co-catalyst, so slower Auger recombination is a desirable result for systems employing nanocrystals as light absorbers. This work is currently being prepared for publication.

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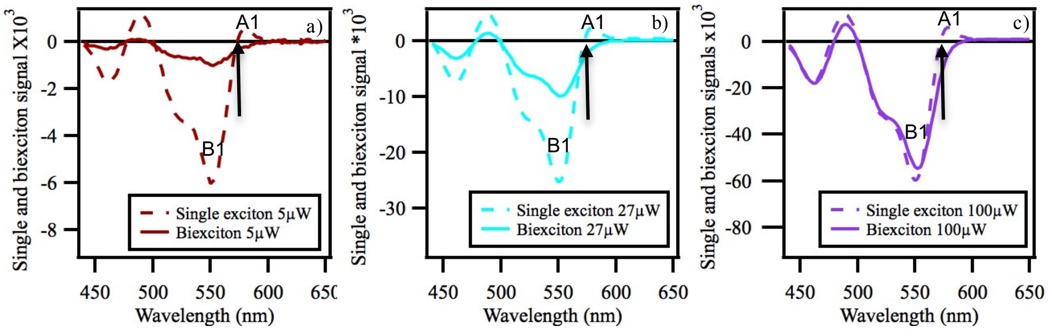

Figure 5. Single and biexciton spectra extracted from fits to TA data collected at 5, 27, and 100 μW.

In addition to our work understanding how ultrashort ligands affect the excited-state dynamics, charge transfer, and photochemistry of nanocrystals, we investigated how surface ligand modification affects phonon dynamics. The phonon characteristics of semiconductor nanocrystals play an important role in coupling to electronic states, impacting exciton relaxation dynamics and charge and energy transport phenomena through the nanocrystal and across interfaces. Some work in this area has examined how long-chain aliphatic ligands influence phonon behavior; however, the impact of ultrashort ligands like Se^{2-} had not been studied. We examined the impact of ligand-exchange from aliphatic ligands (ODPA) to the chalcogenide ligand Se^{2-} on phonon relaxation behavior in CdTe QDs. We prepared and studied CdTe QDs and core/shell CdTe/CdSe QDs, both capped with ODPA as well as chalcogenide Se^{2-}-capped CdTe QDs. We also carried out analogous experiments on CdSe QDs and obtained similar results, so we focus on CdTe here. We used short pulses in TA experiments to generate coherent lattice vibrations in each of these samples. We probed their subsequent behavior by monitoring the kinetics of the band gap bleach feature in the TA spectra at wavelengths sensitive to small spectral changes occurring due to vibrational motion. The resulting decay traces contained oscillations corresponding to vibrations of the longitudinal optical (LO) and longitudinal acoustic (LA) phonons. In our case, in all three samples, LO phonons were present at similar frequencies and exhibited similar damping behavior (***Figure 6***). In contrast, the LA phonons present in the samples capped with aliphatic ligands were severely damped in CdTe QDs capped with Se^{2-} compared to aliphatic-capped QDs. We rationalize this contrast in terms of acoustic phonon energy dissipation into the surrounding environment during the radial breathing mode vibration. The energy dissipation is highly efficient in the case of the inorganic Se^{2-} ligand, while the aliphatic ligands allow partial reflection of the energy back such that several periods of the vibration are observed. Our work suggests that inorganic chalcogenide ligands enhance the mechanical coupling of QDs to their environment, enhancing an energy dissipation pathway. This work was published in 2018: K. J. Schnitzenbaumer, G. Dukovic. "Comparison of phonon damping behavior in QDs capped with organic and inorganic ligands." Nano Letters, 2018, 18 (6), 3667-3674.

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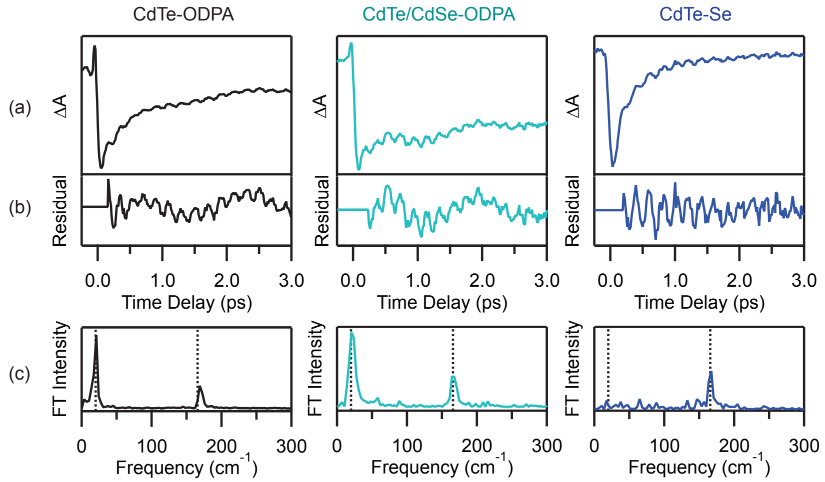

Figure 6. (a) TA bleach kinetics of CdTe-ODPA QDs, CdTe/CdSe-ODPA core/shell QDs, and chalcogenide ligand exchanged CdTe-Se QDs. (b) The oscillations due to exciton-phonon coupling are isolated from the photoexcited carrier dynamics by fitting the TA kinetics to a multiexponential decay. The residual of these fits represent the isolated oscillatory component of the TA signals. (c) Fourier Transform power spectra of the oscillatory components. The two frequencies present in these oscillations, representing the LA (20 cm^{-1}) and LO (166 cm^{-1}) phonons of CdTe QDs, are denoted by the vertical dashed lines.

These findings demonstrate the utility of ultrashort ligands in applications from optoelectronic devices to photochemistry employing nanocrystals as light absorbers. We have demonstrated that S^{2-} ligands in particular combine fast electron and hole transfer rates with an excited-state lifetime long enough to be useful in light-driven systems. We found that ultrashort ligand-capped nanocrystals demonstrate an elongated Auger recombination rate, which could prove useful in enhancing electron transfer to a co-catalyst. We have also developed a comprehensive picture of excited-state relaxation in QDs capped with chalcogenide ligands, including their phonon dynamics.

In addition to exploring the role of ultrashort ligands in the charge transfer and excited-state dynamics of nanocrystals as described above, we have explored some novel and intriguing discoveries about the nature of trapping in CdS nanocrystals, with partial support from this grant. Photoexcited holes in both morphologies trap efficiently; these trapped holes engage in oxidation photochemistry via hole transfer. However, there a lack of understanding about the dynamics of trapped-holes that makes their chemistry difficult to control. We discovered that the trapped holes on the surface of CdS NRs are mobile, not stationary as was previously assumed. Using TA spectroscopy and theoretical modeling, we demonstrated that trapped holes diffuse across the NR at room temperature, executing a random walk (***Figure 7a***). In CdS NRs of non-uniform width, the electron is confined to the larger "bulb"; the resulting spatial separation between the electron and hole results in a $t^{-1/2}$ power-law decay at long times as the hole and electron recombine. We modeled the time dependence of this recombination using a one-dimensional diffusion-annihilation model (***Figure 7b-c***), which fit the data over four orders of magnitude in time with a single adjustable parameter (***Figure 7d***). We have observed the $t^{-1/2}$ power-law in over twenty different samples of CdS NRs. We propose that this phenomenon is one general to CdS nanocrystals, but had not yet been discovered because it is normally obscured in structures where the wavefunctions of the electron and hole spatially overlap. This work was published in 2016: J. K. Utterback, A. N. Grennell, M. B. Wilker, O. M. Pearce, J. D. Eaves, G. Dukovic. "Observation of trapped-hole diffusion on the surfaces of CdS NRs." Nature Chemistry, 2016, 8, 1061-1066. We next confirmed that trapped-hole diffusion occurs in other morphologies, specifically in CdSe NRs. This work was published in 2018: J. K. Utterback, H. Hamby, O. M. Pearce, J. D. Eaves, G. Dukovic. "Trapped-Hole Diffusion in Photoexcited CdSe Nanorods." Journal of Physical Chemistry C, 2018, 122, 29, 16974-16982. Our theory collaborators on this project, the Eaves group, developed a semiperiodic density functional theory model for the CdS nanocrystal surface, describing the motion of trapped holes along the NR surface. This work was published in 2018: R. P. Cline, J. K. Utterback, S. E. Strong, G. Dukovic, J. D. Eaves. "On the Nature of Trapped-Hole States in CdS Nanocrystals and the Mechanism of Their Diffusion." Journal of Physical Chemistry Letters, 2018, 9, 3532-3537.

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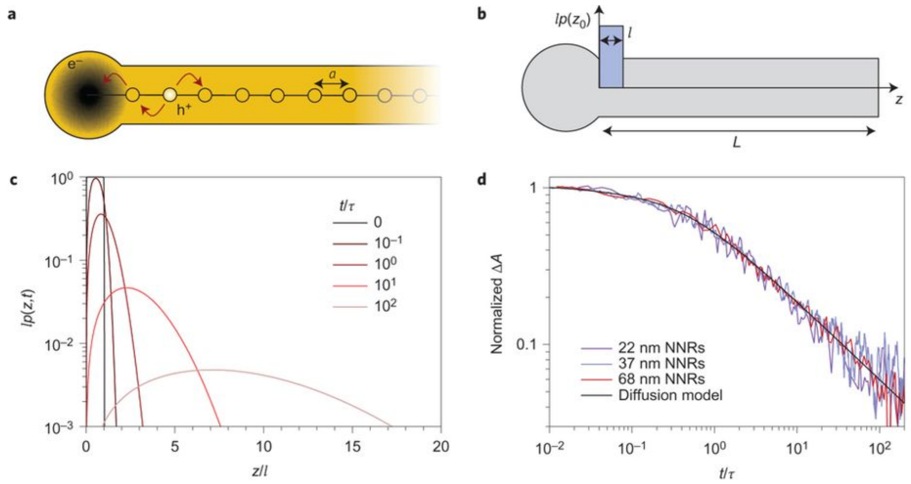

Figure 7. **a)** Schematic representation of trapped-hole diffusion along the rod of a CdS non-uniform NR (NNR). The hole moves with diffusion coefficient D along the rod in a series of steps of length a (red arrows) until it encounters the electron, which is stationary in the bulb, and recombines with it. **b**) Schematic overlay of the initial hole distribution on a NNR, where $l \ll L$. **c**) Probability density of the

trapped hole distribution as a function of time, $lp(z,t)$, from the diffusion model. Using the mean NNR length as an estimate of L, the NNRs in this study satisfy $L > 20l$. **d**) Decay of the bulb signal after 405 nm excitation for three CdS NNR samples of different mean NR lengths fit to the diffusion model. Consistent with the predictions of the model, the TA data from different samples collapse to a master curve when plotted against t/τ.

In summary, in this project we extended our picture of the impact of ultrashort ligands on excited-state properties in QDs and on charge transfer and photochemistry in nanocrystal-based systems. We also made a novel discovery, that trapped holes in CdS and CdSe NRs are not stationary but mobile, and developed a simple but powerful model to describe this motion.