Auger-Mediated Electron Relaxation Is Robust to Deep Hole Traps: Time-Domain Ab Initio Study of CdSe Quantum Dots

Dhara J. Trivedi,† Linjun Wang,‡ and Oleg V. Prezhdo*‡

†Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627, United States
‡Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States

ABSTRACT: By slowing down electron–phonon relaxation in nanoscale materials, one can increase efficiencies of solar energy conversion via hot electron extraction, multiple exciton generation, and elimination of exciton trapping. The elusive phonon bottleneck is hard to achieve, in particular, due to Auger-type energy exchange between electrons and holes. The Auger channel can be suppressed by hole trapping. Using time-domain ab initio simulation, we show that deep hole traps cannot fully eliminate the Auger channel. The simulations show that the hole-mediated electron relaxation is slowed down only by about 30%, which is in agreement with the recent experiments. The Auger energy exchange and hole relaxation to the trap state occur on similar time scales. Hole trapping is slow, because holes themselves experience a weak bottleneck effect. The study establishes the fundamental mechanisms of the electron and hole relaxation processes with and without hole traps. It shows that more sophisticated hole trapping strategies, for example, involving shell layers, are required in order to achieve the phonon bottleneck and to reduce electronic energy losses.

KEYWORDS: CdSe quantum dots, hot electron relaxation, Auger processes, phonon bottleneck, nonadiabatic molecular dynamics, time-dependent density functional theory

Quantum confined semiconducting materials, such as quantum dots (QDs), nanorods, and nanotubes, have given rise to a new generation of light harvesting and charge separation systems for solar energy conversion.1−10 Absorption of a photon in these materials creates bound electron–hole pairs, known as excitons. These excitons have to dissociate into free charge carriers via, either generating electrical current or converting chemically simpler molecules into fuels. The size-tunable band gap has proven to be a very valuable light harvesting feature of colloidal QDs. QDs and other nanoscale materials exhibit novel physical phenomena, such as multiple exciton generation11 and Auger-assisted electron transfer,12 which can be used to enhance solar cell efficiencies.

The energy of hot excitons is rapidly lost to heat in bulk semiconductors. The electron–phonon coupling is the key channel of energy relaxation. The quantization of the electronic energy levels near the band edge, induced by spatial confinement in colloidal semiconductor QDs, results in large energy splittings of electronic states and discrete atom-like electronic transitions. This is in contrast to the continuous broadband spectra of bulk semiconductors. The well separated electronic energy levels lead to a large mismatch between the electronic and vibrational energy quanta, impeding electron–phonon relaxation and resulting in the phenomenon known as the phonon bottleneck.11,13 Under special conditions, the intraband energy relaxation time can be as long as several nanoseconds in QDs.14,15 Most typically, time-resolved experiments have shown rapid bulklike relaxation.16−18

Several mechanisms that leads to fast relaxation of electronic excitations in QDs have been proposed. First and foremost signature, the density of states obtained at the atomistic level of description is orders of magnitude higher than that resulting from a particle-in-a-box type description.19 The atom-like S- and P-levels provide envelope functions and characterize optical selection rules. Even though multiple transitions underline each envelope,19 the atomistic calculations show discrete energy levels near the band edge, suggesting a possibility for the phonon bottleneck. The two most commonly discussed mechanisms of breaking the phonon bottleneck are (i) the Auger-type process, during which the excited electron exchanges energy with the heavier hole, which then quickly relaxes via its dense state manifold;20−22 and (ii) the surface-mediated process in which surface defects and ligands provide intermediate states and create strong electron–phonon coupling.23−25 It has been suggested that the Auger pathway can be eliminated by hole trapping. The strategy has been applied with intermittent success, resulting in contradicting time-resolved measurements performed by many experimental groups. No matching time-domain atomistic simulations have been reported thus far. Such simulations are capable of establishing detailed mechanisms underlying the complex
electron-vibrational dynamics in colloidal QDs with and without traps. In this Letter, we show that deep hole traps affect the Auger channel of electron–hole energy exchange only weakly, and therefore alternative strategies are required. Relaxation of the hole from the edge of the valence band (VB) to the deep trap states is insufﬁciently fast to compete with the Auger process. To some extent, the hole itself experiences the phonon bottleneck because the energy gap between the VB edge and the trap is large. The simulation mimics directly the recent experiments of Sipple et al.,26 focusing on CdSe QDs capped with either inert oleic acid or 1,6-hexanedi-thiol (HDT) ligands that create deep hole traps. We ﬁnd that the hole trapping is slightly slower than the Auger electron–hole energy exchange and that the deep trapping strategy decreases the Auger channel by only about 30%. These theoretical results are in excellent agreement with the experimental data. We also ﬁnd that the Auger process depends signiﬁcantly on the density of states in the QD VB, while the trapping process is independent of the VB state density. Introduction of both shallow and deep hole traps on the QD surface is unlikely to eliminate the Auger relaxation channel. It will speed up hole trapping, while at the same time providing a sufﬁciently high density of states for the trapped hole to participate in the Auger energy exchange with the electron. Our analysis indicated that the method developed by Pandey and Guyot-Sionnest,37 that is, introducing a shell between the core electron and the trapped hole, provides a viable strategy for eliminating the Auger relaxation channel.

The study focuses on the relaxation dynamics of electron from the 1Pe state to the 1Sv state in a pure CdSe QD and a CdSe QD ligated with HDT. The experimentally observed relaxation time is in the subpicosecond to picosecond range,26–28 indicating absence of the phonon-bottleneck effect in both cases. It is suggested that the Auger process plays a key role. The electron rapidly exchanges energy with the hole, Figure 1a. The experimental data indicates that ligands do affect the electron relaxation, because they are capable of trapping the hole, and thereby eliminating the Auger channel, Figure 1b. However, the relaxation time scale changes insigniﬁcantly. The experimental work of Sipple et al.26 reports 220 fs for the electron relaxation in pristine CdSe QDs and 290 fs for the electron relaxation in CdSe QDs with HDT hole traps. The reported hole trapping time is 350 fs. A similar time scale for the hole trapping has been achieved by Klimov et al.22 The study is performed with the Cd33Se33 “magic” cluster with a diameter of 1.3 nm. It is very stable29 and is one of the smallest CdSe clusters supporting the crystalline topology.30,31

The study of exciton dynamics has been made possible by the recently developed global flux surface hopping (GFSH) approach, which generalizes the most popular method of nonadiabatic molecular dynamics (NAMD) to higher order processes, such as superexchange and many-particle transitions. The GFSH has been implemented within the time-dependent Kohn–Sham (TDKS) framework.32 The simulations are performed in the adiabatic representation. It is most natural with ab initio electronic structure methods, which produce eigenstates of the electronic Hamiltonian for ﬁxed nuclear positions, and diagonalize out all off-diagonal Coulomb coupling terms. Transitions occur due to nonadiabatic coupling, which is directly related to the Coulomb coupling of the diabatic representation, as discussed in ref 34.

The simulations are performed with the Vienna ab initio simulation package (VASP),35 using the PBE functional,36 projector-augmented-wave (PAW) pseudopotentials,37 and a converged plane wave basis. A periodically replicated cubic cell with at least 8 Å of vacuum between QD replicas is used. The structures are fully optimized at 0 K and are heated to 300 K with repeated velocity rescaling. Three picosecond microcanonical MD trajectories are generated for each cluster using the Verlet algorithm with the 1 fs time step and Hellman–Feynman forces, providing input for NA dynamics. The GFSH was implemented using Python eXtension for ab initio dynamics (PYXID).38,39 The entire computational methodology is repeated for the Cd33Se33 QD with the HDT hole trap. In addition, the relaxation dynamics are performed with models, which represent larger size QDs using higher densities of states (DOS).

The DOS of the bare and HDT capped Cd33Se33 QD are shown in Figure 2a,b. The optimized structures of the systems are given as inserts. The DOS of the ligand-free and passivated QDs show a major difference near the edge of the valence band (VB). The ligand creates a new state lying at 0.3 eV above the VB maximum. The state can trap the photogenerated hole.26,40 Because 0.3 eV is signiﬁcantly greater than kBT at ambient temperatures, it is a deep trap. The ﬁrst peak in the conduction band (CB) is present in both pure and ligated QDs. It represents the 1S-electron state, deﬁned according to the effective-mass representation.41 The higher energy peaks can be attributed to the P, D, and so forth electronic levels of QD. Note that the energy gap between the 1S electron state and the
The optimized geometries are shown in the insets. The remainder of the CB is on the same order of magnitude as gap between the hole trap state and the VB. The DOS is higher in the VB than the CB, as predicted by the effective-mass theory. The high VB DOS guarantees that the hole undergoes rapid relaxation by coupling to phonons. This feature is essential for the rapid hole-mediated Auger relaxation of the electron, because otherwise the hole can transfer energy back to the electron.

Figure 3 shows the spatial density of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the systems under investigation. The left panel of the middle row shows the density of the trap state. The trap is localized strongly at the interface between the QD and the HDT ligand, and in particular, on the bridging S atom. The fact suggests that the simulation can be simplified by removing the long aliphatic chain of the ligand. This hypothesis is tested with the Cd$_{32}$Se$_{33}$S QD, which contains only the bridging S atom. Remarkably, the DOS of the Cd$_{32}$Se$_{33}$S QD is very similar to that of the ligated dot, Figure 2b,c. The trap state is still present in Cd$_{32}$Se$_{33}$S, and its energy is close to that in the ligated QD. The spatial densities of the hole trap are also quite alike; compare the corresponding HOMO orbitals in Figure 3. Therefore, the subsequent simulations of the photoinduced electron–phonon dynamics in the presence of the hole trap are performed with Cd$_{32}$Se$_{33}$S. Significant computational savings arise both because the vacuum region of the simulation cell is now smaller, significantly decreasing the basis set size, and because statistical averaging is greatly simplified by avoiding the need to sample conformations of the flexible aliphatic chain of the ligand.

The relaxation of the photoexcited electron from the 1P$_e$ to 1S$_e$ state, observed in the experiment, is represented by the transition between the second and first unoccupied orbitals, LUMO+1 and LUMO, respectively. Figure 4a shows the evolution of the orbital energies for part of the Cd$_{33}$Se$_{33}$ trajectory. The calculated mean energy gap between the 1P$_e$ and 1S$_e$ states is 0.4 eV, which agrees well with the experimental observations of 0.1−0.3 eV for CdSe QDs. The calculated value is larger because the investigated QD is smaller than the experimental QDs. At the initial relaxation stage, the energy lost by the electron is gained by the hole, confirming the Auger-assisted relaxation process. The hole never gets the full energy lost by the electron, because the hole energy is dissipated by phonons. The relaxation time for the hot electron is 2.5 ps in this case, Figure 4c, which is an order of magnitude larger than the experimental value of 220 fs. The relaxation is slow in the calculation, because the QD is small. Auger rates depend strongly on the DOS of hole states. We repeated the time-domain ab initio simulation by increasing the hole DOS 5- and 10-fold. The resulting electron relaxation times decrease to 1.5 and 1.3 ps, respectively, Figure 4c. By volume scaling, a 2-fold increase in the QD diameter corresponds to an 8-fold increase of DOS. The diameter of Cd$_{33}$Se$_{33}$ is 1.3 nm, and the 10-fold increased DOS corresponds to 2.8 nm. Recall that the experimental QDs are ~4 nm in diameter. Further, the 1P$_e$ to 1S$_e$ is smaller in the experiment. These two factors favor faster dynamics in experiment relative to simulation.

Next, we consider the photoinduced dynamics of Cd$_{32}$Se$_{33}$S, Figure 5. The hole DOS contains the trap level. Hole relaxation into the trap competes with hole excitation by Auger energy exchange with electron. The competing pathway slows down the electron relaxation process. However, the rate decrease is insignificant to achieve the phonon bottleneck. The data shown in Figure 5b,d represents the system with a 10-fold increase in DOS. Exponential fits of the data in Figure 5b shows that the electron relaxation slows down from 1.3 ps in CdSe to 1.8 ps in CdSeS.

Figure 5c characterizes the phonon modes participating in the electron relaxation and hole trapping. The nonadiabatic electro-phonon coupling is directly related to the second derivative of the energy along the nuclear trajectory. Therefore, the vibrational modes that most strongly modulate the energy levels will create the largest coupling. Fourier transform of the energy gap between the 1S$_e$ and 1P$_e$ states of the electron (red line) reveals that the electron couples to the phonons with frequencies between 50 and 100 cm$^{-1}$. Phonons contributing to the hole trapping are characterized by Fourier transform of the energy gap between the edge of the VB and the trap state (green line). More modes participate in this case,
because the trap defect introduces disorder and local vibrational modes. The magnitude of the peaks in Figure 5c is higher for the holes, indicating that coupling to phonons is stronger in this case. Note that coupling to phonons does govern hole trapping, while electron relaxes by Auger coupling to holes rather than by phonons.

Figure 5d represents the hole population in the VB edge state in the CdSe and CdSeS QDs. The populations decrease as a result of both hole excitation by energy transfer from the electron and, in the case of Cd32Se33S, hole trapping. Exponential fit of the two lines give 400 and 600 fs for Cd33Se33 and Cd32Se33S, respectively. The difference in the rates, 1/400 fs minus 1/600 fs, gives the hole trapping rate of 1/1200 fs. The hole trapping time is on the same order as the electron relaxation time, as in the experiment. The result confirms the key conclusion of the paper that deep traps cannot restore the phonon bottleneck to the electron relaxation by out-competing the Auger process. Note that the simulation times are 4–5 times longer than the experimental numbers, primarily because the studied systems are smaller and have lower DOS. Nevertheless, the relative magnitudes of the times scales are in excellent agreement with the experiment.

The rates of both Auger processes and hole trapping depend on the QD size. Hole trapping is a charge transfer process. The size dependence of charge transfer between a QD and a ligand is analyzed in ref 45. The main affect arises due to decrease of the donor–acceptor coupling, which scales approximately as inverse of QD volume. Reference 42 analyzes Auger rates as a function of system size. Auger rates depend on Coulomb coupling and density of states. The Coulomb coupling also scales approximately as inverse of QD volume. Thus, the donor–acceptor coupling for hole trapping and the electron–hole coupling for the Auger process scale the same way. The difference arises due to the density of final states. It is independent of the QD size for the hole trapping and increases with the QD size for the Auger process. Therefore, the qualitative arguments indicate that deep hole traps should become even less efficient in eliminating the Auger relaxation channel with increasing QD size.

In summary, the reported theoretical analysis shows that deep hole traps only partially eliminate the faster Auger channel of electron relaxation. The energy gap between the VB edge and the trap state is too large, and the trapping process is insufficiently fast. The local phonon modes of the trap do enhance the hole-phonon coupling. Increasing the number of trap sites on the QD surface can accelerate the trapping; however, the experiments have not shown this effect yet. One can consider a combination of shallow and deep trap states, for instance, by using several types of ligands. While such strategy will accelerate the trapping dynamics, it will also open up new Auger channels. Holes trapped on a QD surface still interact strongly with the electron, and a high density of trap states will effectively extend VB to lower energy. In order to achieve rapid hole trapping and to decouple the trapped hole from the...
electron, one should consider more complex architectures, for instance, as in the work of Pandey and Guyot-Sionnest. There, deep trap states were separated from the core by a shell layer. At the same time, the shell has energy levels between the VB edge and the trap, accelerating hole trapping. The simulations reveal the complex interplay between the competing Auger electron relaxation, charge-phonon interactions, and ligand hole trapping, providing a comprehensive picture of the complex photoinduced dynamics in semiconductor QDs. The simulations provide important insights to enhance extraction efficiency of hot charge carriers for photovoltaic and photocatalytic applications. Most conclusions apply to nanoscale systems in general.

### AUTHOR INFORMATION

#### Notes
The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS
Funding from the U.S. Department of Energy, Grant DE-SC0006527 is gratefully acknowledged. This work was supported in part by the Russian Science Foundation, project No. 14-43-00052.

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