Photoexcited electron and hole dynamics in semiconductor quantum dots: phonon-induced relaxation, multiple exciton generation and recombination

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Abstract. Photoexcited dynamics of electrons and holes in semiconductor quantum dots (QD), including phonon-induced relaxation, multiple exciton generation, and recombination (MEG and MER), were simulated by combining *ab initio* time-dependent density functional theory and non-adiabatic (NA) molecular dynamics. These nonequilibrium phenomena govern the optical properties and photoexcited dynamics of QDs, determining the branching between electronic processes and thermal energy losses. Our approach accounts for QD size and shape as well as defects, core–shell distribution, surface ligands and charge trapping, which significantly influence the properties of photoexcited QDs. The method creates an explicit time-domain representation of photoinduced processes and describes various kinetic regimes owing to the non-perturbative treatment of NA couplings in the quantum dynamics. QDs of different sizes and materials, with and without ligands, are considered. The simulations provide direct evidence that the high-frequency ligand modes on the QD surface play a pivotal role in the electron–phonon relaxation, MEG, and MER. The insights reported here suggest novel routes for controlling the photoinduced processes in semiconductor QDs and lead to new design principles for increasing efficiencies of photovoltaic devices.

1. Time-domain *ab initio* simulation of excited-state dynamics in quantum dots

Confinement of charge carriers in quantum dots (QDs) of sizes smaller than the Bohr exciton radius of the corresponding bulk material determine the electronic properties of the QD, leading to a variety of applications. High cross-sections for light absorption make QDs excellent materials for photovoltaic devices. Similarly to molecular systems, spatial confinement of electronic states in a QD creates relatively strong charge-phonon couplings, and efficiencies of QD photovoltaic devices and lasers depend upon charge-phonon relaxation rates. The phonon-mediated relaxation of electrons and holes in QDs is the focus of many experimental and theoretical investigations.

In our study, state-of-the-art time domain density functional theory (DFT) and non-adiabatic (NA) molecular dynamics simulations are applied to study phonon-induced relaxation of photo-excited electrons and holes in Ge and Si QDs.[1,2] Our *ab initio* calculations showed that the quantum confinement makes the electron and hole density of states (DOS) more symmetric in the Ge and Si QDs compared to the bulk semiconductors as figure 1(a) shows. Figure 1(b) demonstrates that, in spite of the symmetric DOS, the electrons decay faster than the holes, and so the electron and hole relaxations are quite asymmetric. Such excited-state dynamics cannot be predicted only by the static band structure calculations, suggesting importance of the real-time NA dynamics simulation including the phonon dynamics. This asymmetry arises due to the stronger NA couplings caused by the phonon

dynamics in the conduction band (CB) than in the valence band (VB). The stronger NA couplings of the electrons compared to the holes was rationalized by the more delocalized electron density over the hydrogen surface ligands and thus by the larger contribution of the high-frequency Ge–H and Si–H surface bonds to the CB. Our results demonstrate that surface passivation is another option to control excited electron and hole dynamics in nano materials. Figure 1(b) also shows a linear relationship between the electron and hole relaxation rates and the CB and VB DOS. This can be regarded as a new type of Fermi's golden rule since the rates are now proportional not to the square of the static Coulomb couplings but to the square of the dynamical NA couplings.

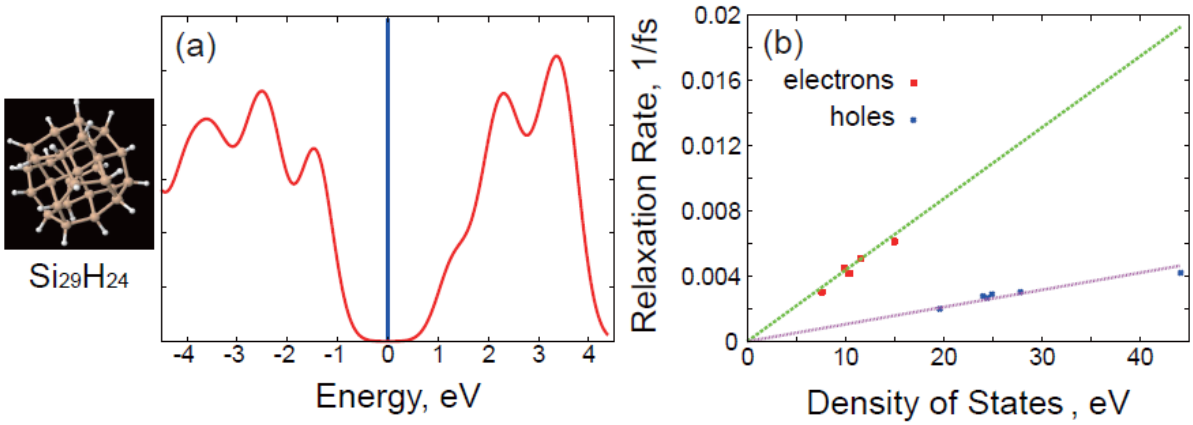

Figure 1: (a) Density of electron and hole states in the Si QD. The electron and hole DOS are quite symmetric due to the quantum confinement. The CB is about twice as high as the VB in the corresponding bulk DOS. The energy gap E_g is calculated as 2.1 eV. (b) Asymmetric relaxation of the electron and hole in the symmetric DOS. The rates scale linearly with the DOS, leading to Fermi's golden rule.

2. Multiple exciton generation and recombination dynamics in semiconductor quantum dots

Further advantages of QDs in photovoltaic devices are due to the possibility of generating multiple electron-hole pairs (excitons) upon absorption of a single photon as in figure 2. This is called multiple exciton generation (MEG), and provides great potential for increasing solar energy conversion efficiencies relative to those in bulk systems since the MEG provides new mechanisms for utilizing excess photon energy and avoiding energy loss to heat. We recently developed a real-time atomistic simulation method for studying the MEG and its inverse process, multiple exciton recombination (MER).[2,3,4] Our atomistic simulation is performed by directly solving the time-dependent Schrödinger equation based on multiple exciton bases with NA coupling and band energies obtained by the time-domain DFT calculation on nano materials. Our method calculates various real-time dynamics of the MEG and MER treating NA phonon couplings non-perturbatively, and the MEG and MER are allowed to occur simultaneously. Our atomistic simulation method can take into account QD size, shape, defects, core-shell distribution, surface ligands, and charge trapping, which significantly influence the photoexcited dynamics in nano materials. These are all advantages of our method which static electronic calculations of band structures and perturbative rate theories such as Fermi's golden rule cannot account for.

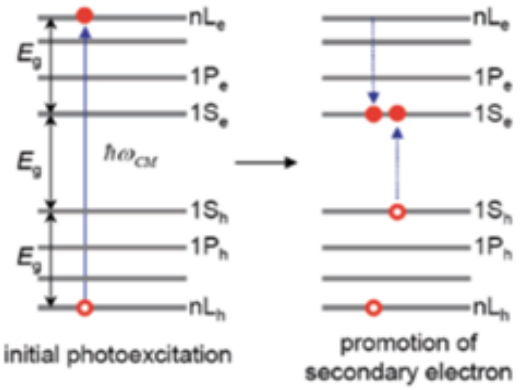

Figure 2: Schematic depiction of the MEG

As a result, we found the following important insights. (1) The MEG rapidly accelerates with initial excitation energy, reflecting strong energy dependence of double exciton (DE) density of states.[2,3,4] (2) At early times, the MEG exhibits Gaussian relaxation rather than exponential decay because the initial dynamics involves fewer states and is not statistically enough. The exponential dynamics, assumed in the standard rate theories, starts at a later time and becomes more important in larger QDs where a number of states are involved in the MEG dynamics. [2,3] (3) Phonon-assisted MEG is observed at energies below a purely electronic threshold due to presence of high-frequency ligand vibrations. The lack of the energy to generate DEs is compensated by the high-frequency phonon modes.[2,3] (4) Dissipation by phonons is essential for the MER since lower-energy DEs can be a main gateway to recombine into single excitons (SEs) due to the larger SE/DE DOS ratio around the lower-energy DEs.[4] (5) The MER simulated starting from a DE is significantly slower than the MER involving an optical excitation of a SE, followed by the MEG and then the MER (See figure 3). The latter time scale agrees well with the experiments [5-8], emphasizing the importance of superpositions of many DEs prepared by the preceding MEG for the efficient MER. [4]

The above detailed descriptions of the interplay between the MEG and MER coupled to phonon modes provide important insights for the excited-state dynamics in semiconductor QDs and in other nano materials, and also for improving efficiency of solar energy conversion using them.

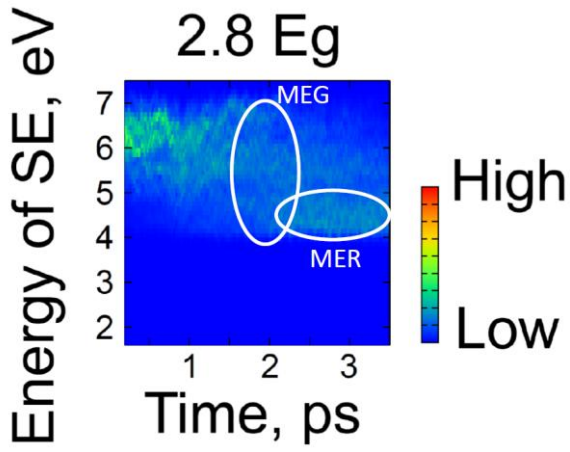

Figure 3: SE population dynamics accompanying the DE dynamics. The initially excited SE evolves into other SE and DE states. The decrease in the SE population seen at the intermediate time corresponds to the MEG. The recursion of the SE population at the later time corresponds to the MER, demonstrating that our method accounts for the MEG and MER simultaneously. The MER appears around 2 E_g, supporting the Auger recombination picture proposed in the experiments.

References

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