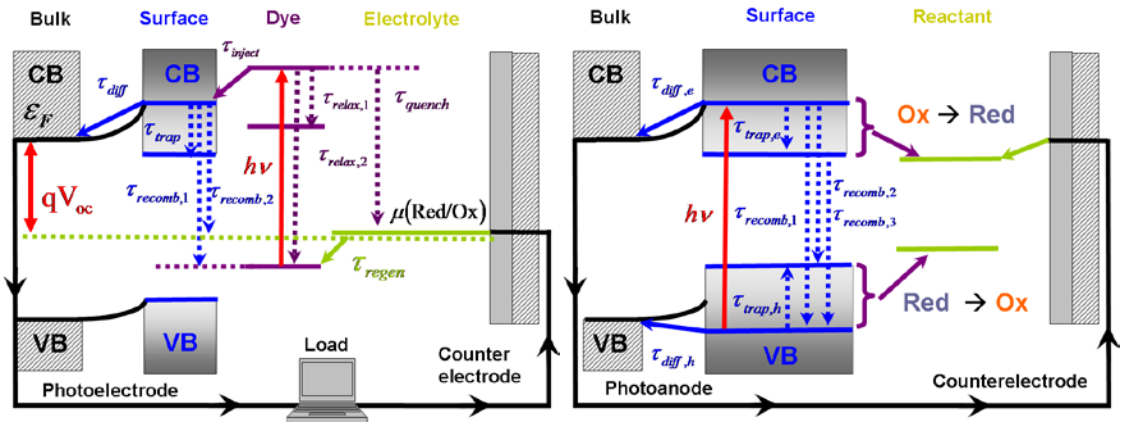
Final Report, Oleg. V. Prezhdo

DOE Award DE-SC0006527 "Atomistic Time-Domain Simulations of Light-Harvesting and Charge-Transfer Dynamics in Novel Nanoscale Materials for Solar Energy Applications"

During the previous DOE funding cycle, our research focused on materials for two types of solar cells (SC): interfaces involving bulk inorganic semiconductors[1-6] and quantum dots[7-17] (QD). In close connection with experiment, we applied our state-of-the-art ab initio time-domain approaches in order to model the photoinduced dynamics in these materials. Additionally, we investigated solvent effects,[18-24] and worked on public release of the simulation methodologies[25-28] developed in our group. The complete list of the 30 DOE sponsored publications[1-30] is presented below. The research results were reported at over 30 invited conference presentations and university seminars.

Electron dynamics at semiconductor interfaces play a central role in photovoltaics and photo-catalysis. Describing electron behavior in these systems is difficult because it requires a union between disparate interface components, infinite solid-state materials and finite systems such as molecules, studied by different communities, chemists and physicists. Our theoretical efforts bridged the gap by analyzing systems that serve as good general models of the interfacial electron dynamics.



(a) (b)

Figure 1. Energy diagram and competing processes in (a) photovoltaic and (b) photochemical cells.[4]

The electron and energy dynamics at semiconductor surfaces are surprisingly rich and involve many processes.[4] In a Grätzel photovoltaic cell, Fig. 1a, a chromophore absorbs a photon, $h\nu$. The photoexcited electron evolves along many pathways: injection into the conduction band (CB) of the semiconductor, τ_{inject}; relaxation to a lower state of the chromophore, $\tau_{relax,1}$, or to its ground state, $\tau_{relax,2}$; quenching by electrolyte, τ_{quench}. The last two routes should be avoided to maximize the SC efficiency. Once injected into the semiconductor CB, the electron can diffuse to bulk, τ_{diff}, and be used to perform work – this pathway maximizes solar-to-electric energy conversion. Alternatively, the electron can be captured by surface trap states, τ_{trap}, and recombine with the positive charge by interacting with electrolyte, $\tau_{recomb,1}$, or the chromophore, $\tau_{recomb,2}$. The latter two processes decrease

efficiency by reducing the number of charge carriers. The electrolyte serves to close the electrical chain by transferring electrons from the opposite electrode to the chromophore. Diffusion of bulk electrolyte affects chromophore regeneration, τ_{regen}, and ultimately light-to-electric energy conversion. The basic principle of operation in the photocatalytic (photochemical) cell is similar to that of the photovoltaic cell, Fig. 1b, with some differences.[4]

We formulated the general principles governing the complex electron dynamics at bulk-semiconductor interfaces, Fig. 1, by considering specific examples.[1-6] The ultrafast time-scale of the electronic and vibrational processes at the interfaces makes it difficult to invoke traditional theories. Instead, we performed explicit time-domain simulations with an atomistic representation of the interface. Our approach directly mimics the time-resolved experimental data and provides a detailed description of the processes as they occur in real time. We took into consideration chemical structure, determined the role of the vibrational motions and electron-phonon coupling, uncovered a variety of electron dynamics scenarios, and ultimately, established the basic criteria that provided an understanding of this complicated process. The insights attained in our theoretical studies let us formulate practical suggestions for improving SC properties and for controlling dynamics at semiconductor interfaces.

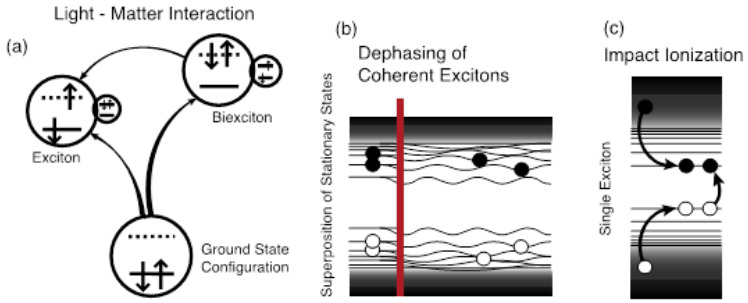


Figure 2. Light, electron and phonon interactions in nanocrystals.[8] (a) Doubly excited configurations provide a quantitative measure of observing multiple-excitons in the photo-excited state. (b) Lattice vibrations induce dephasing of superpositions of single and multiple excitons. (c) Energy is transferred from a high-energy exciton to promote an additional electron across the band gap.

Excited state dynamics in nanoscale semiconductors determine their utility in SC applications. QDs exhibit both molecular and bulk characteristics. Unlike either bulk or molecular materials, QD properties can be modified continuously by changing QD shape and size. However, the chemical and physical properties of molecular and bulk materials often contradict each other, which can lead to differing viewpoints about the behavior of QDs. For example, the molecular view suggests strong electron-hole and charge-phonon interactions, as well as slow energy relaxation due to mismatch between electronic energy gaps and phonon frequencies. In contrast, the bulk view advocates that the kinetic energy of quantum confinement is greater than electron-hole interactions, that charge-phonon coupling is weak, and that the relaxation through quasi-continuous bands is rapid. Our simulations allowed us to bridge the bulk and molecular viewpoints, to clarify controversies, and to provide a unified atomistic picture of the photoexcited state dynamics in semiconductor QDs.[7-17] Our atomistic description of QDs complemented the phenomenological models and provided important atomistic details. The ab initio approach is particularly useful for studying geometric and electronic structure of QDs, because it treats bulk, surface, ligands, and defects on equal footing and incorporates electron correlation effects. Our simulations most closely mimicked the complex light-induced evolutions of charges and phonons,[8] Fig. 2. We showed that the underlying atomic structure, thermal fluctuations, and surface effects lift

electronic state degeneracies predicted by phenomenological models and that excitonic electron-hole interactions are strong in small QDs. Stoichiometric surfaces self-heal. However, only molecular ligands and core/shell designs can eliminate traps associated with dangling chemical bonds, missing atoms, and other defects. We showed that ligands can create charge traps[16] and provide high frequency phonons.[16] Our simulations indicated that phonon-induced dephasing[9, 10, 19] of electronic excitations is ultrafast, ranging from tens to hundreds of femtoseconds. The dependence of the relaxation on the excitation energy and the density of states clarified the controversies regarding the phonon bottleneck in the photoexcited electron relaxation.[9] We rationalized the ultrafast generation of multiple-excitons without the phonon bottleneck by strong Coulomb interactions between the charge carriers.[8] The QD charging and defects explained the large variation in the experimental data.

Public domain software for non-adiabatic molecular dynamics was released during the past funding cycle. DOE is encouraging efforts aimed at large-scale computational screening and prediction of materials properties. Such efforts involve multiple scientists, who need accesses to necessary software. With this goal in mind, we released PYXAID (PYthon eXtention of Ab Initio Dynamics), making available the key methods developed and used in our group to study excited state dynamics in SC materials at the time-domain, atomistic level of description.[25, 26]

Publications resulting from the previous DOE funding cycle:

(1) Wang, L. J.; Long, R.; Prezhdo, O. V., Time-Domain Ab Initio Modeling of Photoinduced Dynamics at Nanoscale Interfaces. *Annual Reviews of Physical Chemistry* **2015**, in press.
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(3) Guo, Z. Y.; Prezhdo, O. V.; Hou, T. J.; Chen, X.; Lee, S. T.; Li, Y. Y., Fast Energy Relaxation by Trap States Decreases Electron Mobility in Tio2 Nanotubes: Time-Domain Ab Lnitio Analysis. *Journal of Physical Chemistry Letters* **2014**, *5*, 1642-1647.
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(7) Hyeon-Deuk, K.; Kim, J.; Prezhdo, O. V., Ab Initio Analysis of Auger-Assisted Electron Transfer. *Journal of Physical Chemistry Letters* **2015**, *6*, 244-249.
(8) Jaeger, H. M.; Hyeon-Deuk, K.; Prezhdo, O. V., Exciton Multiplication from First Principles. *Accounts of Chemical Research* **2013**, *46*, 1280-1289.
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