Progress Report (2009-2010)

DOE Award DE-FG02-05ER15755 “Atomistic Time-Domain Simulations of Light-Harvesting and Charge-Transfer Dynamics in Novel Nanoscale Materials for Solar Hydrogen Production” to Oleg V. Prezhdo

Funded by the DOE grant (i) we continued to study and analyze the atomistic detail of the electron transfer (ET) across the chromophore-TiO$_2$ interface in Gratzel cell systems for solar hydrogen production. (ii) We extensively investigated the nature of photoexcited states and excited state dynamics in semiconductor quantum dots (QD) designed for photovoltaic applications. (iii) We continued a newly initiated research direction focusing on excited state properties and electron-phonon interactions in nanoscale carbon materials.

Over the past year, the results of the DOE funded research were summarized in 3 review articles. 12 original manuscripts were written. The research results were reported in 28 invited talks at conferences and university seminars. 20 invitations were accepted for talks in the near future. 2 symposia at national and international meetings have being organized this year on topics closely related to the DOE funded project, and 2 more symposia have been planned for the near future.

We summarized the insights into photoinduced dynamics of semiconductor QDs, obtained from our time-domain ab initio studies. QDs exhibit both molecular and bulk properties. 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. By synthesizing the bulk and molecular viewpoints, we clarified the controversies and provided a unified atomistic picture of the nature and dynamics of photoexcited states in semiconductor QDs.

We also summarized our recent findings about the photoinduced electron dynamics at the chromophore–semiconductor interfaces from a time-domain ab initio perspective. The interface provides the foundation for a new, promising type of solar cell and presents a fundamentally important case study for several fields, including photo-, electro- and analytical chemistries, molecular electronics, and photography. Further, the interface offers a classic example of an interaction between an organic molecular species and an inorganic bulk material. Scientists employ different concepts and terminologies to describe molecular and solid states of matter, and these differences make it difficult to describe the interface with a single model. At the basic atomistic level of description, however, this challenge can be largely overcome. Recent advances in non-adiabatic molecular dynamics and time-domain density functional theory have created a unique opportunity for simulating the ultrafast, photoinduced processes on a computer very similar to the way that they occur in nature. These state-of-the-art theoretical tools offered a comprehensive picture of a variety of electron transfer processes that occur at the interface, including electron injection from the chromophore to the semiconductor, electron relaxation and delocalization inside the semiconductor, back-transfer of the electron to the chromophore and to the electrolyte, and regeneration of the neutral chromophore by the electrolyte. The ab initio
time-domain modeling is particularly valuable for understanding these dynamic features of the ultrafast electron transfer processes, which cannot be represented by a simple rate description.

We demonstrated using symmetry adapted cluster theory with configuration interaction (SAC-CI) that charging of small PbSe nanocrystals (NCs) greatly modifies their electronic states and optical excitations. Conduction and valence band transitions that are not available in neutral NCs dominate low energy electronic excitations and show weak optical activity. At higher energies these transitions mix with both single excitons (SEs) and multiple excitons (MEs) associated with transitions across the band-gap. As a result, both SEs and MEs are significantly blue-shifted, and ME generation is drastically hampered. The overall contribution of MEs to the electronic excitations of the charged NCs is small even at very high energies. The calculations supported the recent view that the observed strong dependence of the ME yields on the experimental conditions is likely due to the effects of NC charging.

The electron-hole excitonic nature of high energy states was investigated in neutral and charged Si clusters, motivated by the ME generation (MEG) process that is highly debated in photovoltaic literature. Silicon forms the basis for much of the photovoltaic industry, and our high-level, first principles calculations show that at 2-3 times the lowest excitation energy, the majority of optically excited states in neutral Si7 and Si10 take on ME character. The transition from SEs to MEs is not as sharp in Si as in PbSe clusters, but it is much more pronounced than in CdSe. The closer similarity of Si to PbSe than CdSe was unexpected, since Si clusters were less symmetric than PbSe clusters. Charging suppresses MEG in Si clusters; however, the suppression is less pronounced than in PbSe. A strong ME signal is seen already at 5Eg upon charging. The low ME thresholds and nearly complete switch from SEs to MEs create a good possibility for efficient MEG in neutral Si nanoclusters and reveal hope that reasonable quantum yields can still be obtained despite charging.

State-of-the-art time domain density functional theory and non-adiabatic (NA) molecular dynamic simulations were used to study phonon-induced relaxation of photoexcited electrons and holes in Ge and Si QDs. The relaxation competes with productive processes and causes energy and voltage losses in QD solar cells. The ab initio calculations showed that quantum confinement makes the electron and hole density of states (DOS) more symmetric in Si and Ge QDs compared to bulk. Surprisingly, in spite of the symmetric DOS, the electron and hole relaxations are quite asymmetric: the electrons decay faster than the holes. The asymmetry arises due to stronger NA coupling in the conduction band (CB) than in the valence band (VB). The stronger NA coupling of the electrons compared to the holes was rationalized by the larger contribution of the high-frequency Ge–H and Si–H surface passivating bonds to the CB relative to the VB. Linear relationships between the electron and hole relaxation rates and the CB and VB DOS were found in agreement with Fermi’s golden rule. The faster relaxation of the electrons compared to the holes in the Ge and Si QDs is unexpected and is in contrast with the corresponding dynamics in the majority of binary QDs, such as CdSe. It suggests that Auger processes will transfer energy from holes to electrons rather than in the opposite direction as in CdSe, and that a larger fraction of the photoexcitation energy will be transferred to phonons coupled with electrons rather than holes. The simulations provided direct evidence that the high-frequency ligand modes on the QD surface play a pivotal role in the electron–phonon relaxation dynamics of semiconductor QDs.

Temperature-dependent dynamics of phonon-assisted relaxation of hot carriers, both electrons and holes, were studied in a PbSe nanocrystal using ab initio time-domain density-functional theory. The electronic structure was first calculated, showing that the hole states were
denser than the electron states. Fourier transforms of the time-resolved energy levels showed that the hot carriers couple to both acoustic and optical phonons. At higher temperature, more phonon modes in the high-frequency range participated in the relaxation process due to their increased occupation number. The phonon-assisted hot-carrier relaxation time was predicted using NA molecular dynamics, and the results clearly showed a temperature-activation behavior. The complex temperature dependence was attributed to the combined effects of the phonon occupation number and the thermal expansion. Comparing the simulation results with experiments, we suggested that the multiphonon relaxation channel is efficient at high temperature, while the Auger-type process may dominate the relaxation at low temperature. This combined mechanism can explain the weak temperature dependence at low temperature and stronger temperature dependence at higher temperature.

Phonon-induced dephasing processes that govern optical line widths, MEG, and MEF fission (MEF) in semiconductor QDs were investigated by \textit{ab initio} molecular dynamics. Using Si QDs as an example, we proposed that MEF occurs by phonon-induced dephasing and, for the first time, estimate its time scale to be 100 fs. In contrast, luminescence and MEG dephasing times were all sub-10 fs. Generally, dephasing is faster for higher-energy and higher-order excitons and increased temperatures. MEF is slow because it is facilitated only by low-frequency acoustic modes. Luminescence and MEG couple to both acoustic and optical modes of the QD, as well as ligand vibrations. The detailed atomistic simulation of the dephasing processes advanced the understanding of exciton dynamics in QDs and other nanoscale materials.

Fluorinated single-walled carbon nanotubes (F-SWNTs) form important intermediates in SWNT sidewall functionalization, leading to a variety of materials and biological applications. By simulating the infrared (IR) signals for the 1,2- and 1,4-addition structures, in which fluorine atoms are arranged in ortho or para positions, respectively, on the aromatic skeleton of the (10,10) SWNT surface, we identified peaks that are unique to each structure. Our full molecular dynamics simulations showed that the \([-C(sp3)-C(sp3)-]\) collective vibrational peak at 400 cm\(^{-1}\) was optically active only in the 1,2-isomer, while the 1300 cm\(^{-1}\) band arising due to the F-C(sp3) stretching motion coupled with the neighboring C(sp2) atoms was seen in the IR spectrum of only the 1,4-isomer. The reported results suggested simple and clear experimental means for distinguishing between the two fluorinated structures and provided a valuable tool for controlled SWNT sidewall functionalization.

We compared the behavior of liquid methanol confined by an open ended SWNT under four different simulation conditions by using molecular dynamics. We concluded that using the approximation of rigid or/and fixed SWNT did not lead to any systematic errors in properties of the confined liquid. The results showed that simulations using rigid carbon nanotubes provide a reliable description of molecular diffusion and other solvent properties in a variety of applications, such electro-chemical devices, membranes and sensors that rely on these properties.

Negatively charged phosphine groups on the backbone of DNA are known to attract gold nanoclusters from a colloid, assembling the clusters at fixed intervals. Bridging these intervals with porphyrin-dye linkers forms an infinite conducting chain, a quantum wire whose carrier mobility can be enhanced by photoexcitation. The resulting nanoassembly can be used as a photovoltaic device or as a gate: a wire with a controllable conductivity. The electronic structure of the porphyrin-gold wire is studied here by density functional theory, and the conductivity of the system was determined as a function of the photoexcitation energy. Photoexcitations of the dye were found to enhance the wire conductivity by orders of magnitude.
Invited Reviews and Feature Articles:


Articles in Peer Reviewed Journals:


SYMPOSIA ORGANIZED


INVITED TALKS AT SCIENTIFIC CONFERENCES

Accepted Invitations:


112. International Workshop on Titania, European Centre for Atomic and Molecular Computations (CECAM - Centre Européen de Calcul Atomique et Moléculaire), Bremen, Germany, September 6-10, 2010.


108. 22nd International Conference on Raman Spectroscopy (ICORS 2010), Boston, MA, August 8-13, 2010.


Past Talks:


87. Photoinduced processes at molecule-semiconductor interfaces: a time-domain ab initio perspective, Symposium on Physical Chemistry of Interfaces and Nanomaterials, International Society for Optical Engineering (SPIE), San Diego, CA, August 2-6, 2009.
85. Excitation dynamics in quantum dots and carbon nanotubes, National Meeting on “Excited State Processes in Electronic and Bio Nanomaterials” (ESP-2009), New Mexico, USA, June 29-July 2, 2009.
84. Quantum dot solar cells. 31st Solar Photochemistry Program Meeting, Department of Energy, Annapolis, MD, June 7-10, 2009.
80. Time-domain studies of quantum dynamics in complex chemical systems. International Workshop on Coherence, Control, and Dissipation, IMA, University of Minnesota, Minneapolis, MN, March 2-6, 2009.

INVITED UNIVERSITY SEMINARS

Accepted Invitations:

Past Talks:
69. Excitation dynamics in carbon nanotubes and quantum dots: time-domain ab initio studies, Department of Chemistry & Biochemistry, University of Texas at Austin, October 8, 2009.
68. Photoinduced dynamics in quantum dots and chromophore-semiconductor interfaces for solar energy applications, Department of Chemistry, University of Utah, September 28, 2009.
67. Excitation dynamics in carbon nanotubes and quantum dots: time-domain ab initio studies, Department of Chemistry, University of Rochester, August 22, 2009.

66. Photoinduced dynamics in nanoscale materials for solar energy harvesting, Department of Physics, Summer Colloquium, George Washington University, June 22, 2009.

64. Dynamics on the nanoscale: time-domain ab initio studies of excitation dynamics in quantum dots and carbon nanotubes, Department of Chemistry, University of Rochester, April 27, 2009.

63. Dynamics on the nanoscale: time-domain ab initio studies of excitation dynamics in quantum dots and carbon nanotubes, Department of Chemistry, University of South Carolina, Columbia, SC, February 13, 2009.