**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 ME fission (MEF) in semiconductor QDs were investigated by *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:

1. O. V. Prezhdo "Photoinduced dynamics in semiconductor quantum-dots: insights from time-domain ab initio studies", *Acc. Chem. Res.*, **42**, 2005 (2009)
2. O. V. Prezhdo, W. R. Duncan, V. V. Prezhdo, "Photoinduced electron dynamics at semiconductor interfaces: a time-domain ab initio prospective", *Prog. Surf. Sci.*, **84**, 39 (2009)
3. S. Garaschuk, V. Rassolov and O. V. Prezhdo "Semiclassical Bohmian dynamics", *Rev. Comp. Chem.*, in press.

Articles in Peer Reviewed Journals:

4. A. Ueta, Y. Tanimura, O. V. Prezhdo, "Distinct infrared spectral signatures of the 1,2- and 1,4-fluorinated single-walled carbon nanotubes: A molecular dynamics study", *J. Phys. Chem. Lett.*, in press.
5. V. V. Chaban, O. N. Kalugin, B. F. Habenicht, O. V. Prezhdo, "The influence of the rigidity of a carbon nanotube on the structure and dynamics of confined methanol", *J. Phys. Soc. Japan*, in press.
6. S. A. Fischer, A. B. Madrid, C. M. Isborn, O. V. Prezhdo, "Multiple exciton generation in small Si clusters: A high-level, ab initio study", *J. Phys. Chem. Lett.*, **1**, 232 (2010).
7. Kim H.-D., A. B. Madrid, O. V. Prezhdo, "Symmetric band structure and asymmetric ultrafast electron-hole relaxation in silicon and germanium quantum dots: time-domain ab initio simulation", *Dalton Transact., Solar Energy Conversion*, **45**, 10069 (2009).
8. A. B. Madrid, H.-D. Kim, O. V. Prezhdo, "Phonon-induced dephasing of excitons in silicon quantum dots: multiple exciton generation, fission and luminescence", *ACS-Nano*, **3**, 2487 (2009).
9. C. M. Isborn, O. V. Prezhdo, "Quantum dot charging quenches multiple exciton generation: first-principles calculations on small PbSe clusters", *J. Phys. Chem. C*, **113**, 12617 (2009).
10. H. Bao, B. F. Habenicht, O. V. Prezhdo, X. Ruan, "Temperature dependence of hot-carrier relaxation in a PbSe quantum dot: An ab initio study", *Phys. Rev. B*, **79**, 235306 (2009).
11. D. S. Kilin, K. L. Tsemekhman, S. V. Kilina, A. V. Balatsky, O. V. Prezhdo, "Photoinduced conductivity of a DNA-templated composite nanowire", *J. Phys. Chem.*, **113**, 4549 (2009).
12. D. A. Yarotski, S. V. Kilina, A. A. Talin, S. Tretiak, O. V. Prezhdo, A. V. Balatsky, A. J. Taylor "Scanning tunneling microscopy of DNA-wrapped carbon nanotubes", *Nano Lett.*, **9**, 12 (2009).

SYMPOSIA ORGANIZED

10. National Workshop on Nonequilibrium Phenomena, Nonadiabatic Dynamics and Spectroscopy, Telluride Summer Research Center, Telluride, CO, Summer 2011.
9. Symposium on Physical Chemistry of Interfaces and Nanomaterials, International Society for Optical Engineering (SPIE), San Diego, CA, August 1-5, 2010.

8. Symposium on Physical Chemistry of Interfaces and Nanomaterials, International Society for Optical Engineering (SPIE), San Diego, CA, August 2-6, 2009. (Co-organizer with O. Monti and S. Tretiak).
7. National Workshop on Non-adiabatic Dynamics, Telluride Summer Research Center, Telluride, CO, July 20-24, 2009.

INVITED TALKS AT SCIENTIFIC CONFERENCES

Accepted Invitations:

116. Gordon Research Conference on Clusters, Nanostructures & Nanocrystals, Mount Holyoke College, South Hadley, MA, July 24-29, 2011.
115. International Pacifichem Conference, Symposium on "Quantum Coherence and its Control in Condensed Phases", Honolulu, HI, December 15-20, 2010.
114. International Zing Conference on Solar Fuels and Photochemistry, Mexico, December 1-4, 2010.
113. International Workshop on Adiabatic and Non-adiabatic Methods in Quantum Dynamics, European Centre for Atomic and Molecular Computations (CECAM - Centre Européen de Calcul Atomique et Moléculaire), Lausanne, Switzerland, November 1-3, 2010.
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.
111. Time-domain ab initio studies of quantum dots and molecule-bulk interfaces for solar energy harvesting, 240 National Meeting of the American Chemical Society, Symposium on "Inorganic-Organic Photocells", Boston, MA, August 22-26, 2010.
110. Excited state dynamics in semiconducting and metallic quantum dots: A time-domain ab initio perspective, 240 National Meeting of the American Chemical Society, Symposium "Nano Letters: The Next Ten Years", Boston, MA, August 22-26, 2010.
109. Theoretical Studies of Ultrafast Dynamics in Carbon Nanoscale Materials for Energy Harvesting and Storage, 240 National Meeting of the American Chemical Society, Symposium on "Molecular Models for Energy Conversion and Storage", Boston, MA, August 22-26, 2010.
108. 22nd International Conference on Raman Spectroscopy (ICORS 2010), Boston, MA, August 8-13, 2010.
107. Gordon Research Conference on Electron Donor-Acceptor Interactions, August 8-12, 2010.
106. National Meeting of the International Society for Optical Engineering (SPIE), Symposium on Physical Chemistry of Interfaces and Nanomaterials, San Diego, CA, August 2-5, 2010.
105. International Workshop on "Dynamic Processes in Irradiated Materials", Donostia International Physics Center, San Sebastian, Spain, July 26-28, 2010.
104. National Workshop on "Condensed Phase Dynamics", Telluride, CO, July 19-23, 2010.
103. Northwest Regional Meeting of the American Chemical Society, Symposium on "Solar Energy Conversion", Pullman, WA, June 20-23, 2010.
102. 32nd Department of Energy (DOE) Solar Photochemistry Research Meeting, Annapolis, MD, June 6-9, 2010.

101. National Meeting of the Canadian Society for Chemistry, Workshop on "Coherence and Decoherence in Molecular Processes", Toronto, Canada, May 29 - June 2, 2010.
100. International Workshop on Quantum Transport and Dynamics in Materials and Biosystems: From Molecular Mechanisms to Mesoscopic Functionality, European Centre for Atomic and Molecular Computations (CECAM - Centre Européen de Calcul Atomique et Moléculaire), Dublin, Ireland, May 12-15, 2010.
99. International Workshop on "Bio-Functionalized Nanomaterials: Bio Helps Nano", Santa Fe, NM, April 26-28, 2010.

Past Talks:

98. Time-Domain Ab Initio Studies of Photoinduced Dynamics in Quantum Dots and Chromophore-Semiconductor Interfaces. National Meeting of the American Physical Society, Focus Topic Session on "Physics and Materials for Inorganic Photovoltaics", Portland, OR, March 15-19, 2010.
97. Semiclassical and Quantum-Classical Approaches to Nonadiabatic Molecular Dynamics. International Workshop on "Quantum-Classical Modeling of Chemical Phenomena", Center for Scientific Computation and Mathematical Modeling (CSCAMM), University of Maryland, March 8-11, 2010
96. Nonadiabatic Dynamics with Time-Domain Density Functional Theory. 2010 Mesilla Chemistry Workshop on "Electronic Non-Adiabatic Dynamics", February 7-10, 2010.
95. Novel Nanoscale Materials for Solar Energy Harvesting and Storage: Time-Domain Ab Initio Studies. 2nd Annual Scientific Meeting on "Solar Fuels and Energy Storage, the Unmet Needs", The Solar Energy Research Center, University of North Carolina at Chapel Hill, January 15-16, 2010.
94. Photoinduced Dynamics at Chromophore-Semiconductor Interfaces: A Time-Domain Ab Initio Perspective. International Workshop in "Molecular Photoreactivity on Metal-Oxide Surfaces from First Principles", Madrid, Spain, December 4-5, 2009.
93. Dynamics on the Nanoscale: Time-Domain Ab Initio Studies. International Conference "Modern Problems of Solution Physical Chemistry and Electrochemistry", 80th anniversary of Institute for Chemistry, Kharkiv University, Kharkov, Ukraine, December 1-4, 2009.
92. Parallel Computing Implementation of Nonadiabatic Molecular Dynamics for Time-Domain Density Functional Theory, Workshop on High-Performance Computational Nano Science (HPCNano), Supercomputing Conference, Portland, Oregon, November 15, 2009
91. Photoinduced processes at molecule-semiconductor interfaces and quantum dots for photovoltaic applications, Symposium on "Functionalizing Nanostructures towards Novel Paradigms for Energetics", 26th European Conference on Surface Science (ECOSS 26), Parma, Italy, August 30, September 4, 2009.
90. Semiclassical approaches for excited state dynamics in nanoscale materials, International Symposium on Quantum Simulations, Center for Scientific Computing and Department of Mathematics, University of Warwick, UK, August 24-28, 2009.
89. Fundamental processes in quantum dots for solar energy conversion, National Meeting of the American Chemical Society, Symposium on The Physical Chemistry of Photon to Fuel Conversion, Washington, D.C., August 16-20, 2009.

88. Excitation dynamics in carbon nanotubes and graphene nanoribbons, Symposium on Carbon Nanotubes, Graphene, and Associated Devices, International Society for Optical Engineering (SPIE), San Diego, CA, August 2-6, 2009.
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.
86. Dynamics on the nanoscale: time-domain ab initio studies, International Workshop on Condensed Phase Dynamics, Telluride, July 20-24, 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.
83. Excitation dynamics in semiconductor quantum dots. International Conference on Dynamics and Structure in Physics and Chemistry, honoring 70th birthday of Prof. I. V. Krivoshei, Kharkov, Ukraine, May 25-28, 2009.
82. Time-domain ab initio studies of excitation dynamics in carbon nanotubes and nanoribbons. National Meeting of the American Physical Society, Nanotube Session, Pittsburgh, March 16-20, 2009.
81. Theoretical modeling of novel photovoltaic materials: Chromophore-semiconductor interfaces and quantum dots. International School on Hybrid Organic/Inorganic Materials for Applications in Photovoltaics, Valencia, March 9-11, 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.
79. Novel approaches to non-adiabatic molecular dynamics of nanomaterials. International Workshop on Chemical Dynamics: Challenges and Approaches, IMA, University of Minnesota, Minneapolis, MN, January 12-16, 2009.

## INVITED UNIVERSITY SEMINARS

Accepted Invitations:

71. Lawrence Livermore National Laboratory, University of California - Berkeley, 2010 Computational Chemistry and Materials Science Summer Institute: Materials Research for Energy, August 2-3, 2010.
70. Department of Chemistry, Southern Illinois University, April 16, 2010.

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.
62. The biological catch-bond: Where is the catch? Department of Chemistry, University of California, Los Angeles, CA, January 26, 2009.