II.K.2 Real-Time Atomistic Simulation Studies of Light Harvesting and Charge Transport for Solar Hydrogen Production

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Objectives

The state-of-the-art computational approaches most recently developed in our group have been applied to several closely related photovoltaic systems that hold a great promise for light harvesting, charge separation and solar-driven generation of molecular hydrogen. With a wealth of time-resolved experimental data on the electron transfer dynamics available in these systems, the mechanisms responsible for the charge transport and energy relaxation are not yet established or remain controversial. Our expertise in nonadiabatic molecular dynamics simulation allowed us to address the fundamental aspects of the photoexcitation dynamics. The simulation studies resulted in a predictive framework for the design of novel, efficient and cost-saving hydrogen producing solar cells.

Technical Barriers

Our scientific objectives are aimed at designing cheaper and more efficient solar cells for hydrogen production. In particular, we established the mechanisms of the photoinduced charge separation and recombination at the chromophore-TiO_2 interface, which forms the basis for Gratzel type hydrogen solar cells. The insights learned in the studies allowed us to formulate a number of suggestions for improving the Gratzel cell design in order to increase cell's voltage, current and, ultimately, hydrogen yield. We also characterized the mechanisms of multiple exciton generation and the energy relaxation processes that compete with it in quantum dot hydrogen solar cells. It turned out that the properties of quantum dots for photovoltaic applications are very different from what was thought originally and, therefore, our research was an essential first step for using quantum dots in order to increase (potentially double) the efficiency of hydrogen producing cells.

Abstract

Fundamental mechanisms of solar energy harvesting and flow in novel nanoscale materials for solar hydrogen production have been investigated in a series of theoretical studies with emphasis on the simulation in real time, at the atomistic level and in direct connection with experiment. Particular attention will be given to: ***Dye-semiconductor*** solar cells (SCs) that are one of the most promising alternatives to the traditional SCs, due to inexpensive components and high photocurrents. ***Quantum dots*** (QDs) that replace molecular donors, are tunable with size, form better heterojunctions with solid conductors, and have a unique potential to produce photon-to-electron yields greater than one, increasing photocurrent, and to utilize hot carriers, increasing photovoltage. ***Nanocarbons*** that can serve as electron acceptors in solar cell assemblies, possess good chemical stability and large surface area suitable for modification with multifunctional groups. Understanding the electron dynamics and excited state relaxation mechanisms in these nanostructures will provide guidelines to their use for solar hydrogen production.

Progress Report

The DOE funding allowed us to

(i) Investigate the atomistic details of the electron injection across the chromophore-TiO_2 interface in Gratze$_l$ type SCs systems for solar hydrogen production. The analysis of the structure, electronic properties and electron-vibrational dynamics in the chromophore-TiO_2 systems allowed us to formulate general principles characterizing the interface. The photo-excited states leading to the interfacial electron transfer (ET) could be classified into three types, including states well inside the TiO_2 conduction band (CB), where efficient electron injection was possible with weak chromophore-semiconductor; new low energy photoexcited states involving direct ET from the molecule into the surface that was possible with strong chromophore-semiconductor coupling; and chromophore excited states near the TiO2 CB edge that could inject the electron into the low density of states region of the CB allowing one to improve SC voltage.

(ii) Initiate new research directions focusing on excitation dynamics in QDs and carbon nanotubes (CNTs), which hold great promise for improvement of

the solar energy conversion and generation of hydrogen. We simulated exciton relaxation a zigzag semiconducting CNT in time domain using density functional theory. Hole dynamics were more complex than the electron dynamics: in addition to the optical phonons, holes coupled to lower frequency breathing modes and decayed over multiple time scales. We investigated the relaxation dynamics of charge carriers in a 32 atom PbSe QD. The simulations showed slow, nearly symmetric relaxation of electrons and holes through multiple intermediate states. Both electrons and holes interacted with low frequency phonons. Holes decayed only slightly faster than electrons rationalizing the highly efficient carrier multiplication in PbSe nanocrystals reported recently in relation to improved solar power conversion for hydrogen production.

(iii) Develop new tools for theoretical analysis of the charge carrier dynamics that form the basis for the photovoltaic hydrogen producing devices. We developed a novel approach for detailed analysis of hole-electron distributions in many-electron molecular systems such as the chromophore-semiconductor interface, QDs and CNTs. The approach reveals non-trivial effects of electronic redistribution due to electron-hole interactions, which are important in all systems. The vibrational coherence transfer between the electronic states was described theoretically by application of the quantized Hamiltonian dynamics. The observed coherent modulation of the frequency of the probe signal is represented with simple analytic models.

Future Directions

The future studies will address in detail the following closely related systems that are under active experimental investigation.

- **Electron injection, relaxation and transport in chromophore-semiconductor assemblies. Minimizing voltage and current losses in Gratzel cells.** The mechanisms of the photoinduced electron transfer from molecular donors to semiconductor acceptors and the subsequent evolution of the injected electrons in dye sensitized semiconductor solar cells remain a topic of active discussion. Our current study shows a great variation of electron transfer events even for a single chromophore at an ideal TiO_2 surface. Surface defects, solvent configuration and chromophore-semiconductor binding affect SC efficiencies. We will extend our pioneering work in a systematic way in order to investigate how these factors can affect the solar hydrogen production efficiency.
- **Conjugated polymer/inorganic semiconductor SCs. Optimizing interfacial electron-hole separation and minimizing recombination.** Conjugated polymers offer a good alternative simultaneously to the sensitizer dyes and electrolyte in the Gratzel cells. Efficient electron-hole separation across the polymer-inorganic interface and prevention of the electron-hole recombination at the interface are critical for the SC generation of hydrogen. Formation of excitons in the polymer film next to or father away from the semiconductor surface, the evolution of the excitons towards the surface, formation of electron-hole pairs across the polymer/semiconductor interface, evolution of electrons and holes in the inorganic and organic phases, and electron-hole recombination will be addressed.
- **Quantum dot solar cells. Achieving better photon-to-electron yields through multiple electron-hole pairs.** Advantages of QDs over the dye molecules include the tunability of optical properties with size and better heterojunction with the solid conductors. Particularly important is the unique potential of QD-sensitized SCs to produce photon-to-electron quantum yields greater than one. In order to achieve this goal multiple charge carriers must be generated and extracted from QDs faster than they can relax by electron-phonon, Auger and other mechanisms. Recent experimental studies indicate that multiple excitons can be generated and detected in PbSe, PbSe, CdSe and Si QDs, even though the relaxation to the lowest energy exciton can be very fast. We will investigate the mechanism of the multiple exciton generation, the origin of the quantization induced reduction of the exciton relaxation rates, and the role of the Auger and other processes.
- **Excitation dynamics in novel carbon materials for solar hydrogen production.** Experiments indicate that fullerenes and CNTs can be employed as electron acceptors in SC assemblies. CNTs in particular possess good chemical stability and a large surface area that can be functionalized with electron donors, including both molecular chromophores and inorganic QDs. In contrast to other carbon-based conductors such as conjugated polymers, nanocarbons show exceptional charge mobilities and are resilient to current-induced failure. Understanding of the charge separation dynamics at interfaces involving nanocarbons is key to their application for solar hydrogen production and will be addressed.

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