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Dye Sensitization of Semiconductor Particles

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DOE Patent Clearance Granted

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The aim of this project has been to use time-resolved spectroscopy to study electron transfer between titanium dioxide particles and adsorbed dye molecules. In these experiments the dye molecule is excited by an ultrafast (ca. 200 fs) laser pulse and the formation and decay of the dye radical cation is monitored with a near-IR probe laser pulse. This is a standard pump-probe measurement that primarily provides information about the reverse (semiconductor-to-dye) electron transfer process. The faster forward (dye-to-semiconductor) electron transfer process is difficult to observe by this technique because: (i) it is extremely fast, and (ii) there is no clear observable in our experiments (reactants, intermediates and products all contribute to the absorption in the near-IR region). The issues we addressed are how factors such as the crystal structure of the particles, the size of the particles, and their surface potential affect the rate of the back electron reaction.

The first part of this project ("Effect of Structure on Electron Transfer Reactions Between Anthracene Dyes and TiO₂ Nanoparticles." I. Martini, J. H. Hodak, and G. V. Hartland *J. Phys. Chem. B* **102**, 9508-9517 (1998)) was completed before the start of the DOE funding. We found that differences in rate for the different crystal structures of TiO₂ are due to differences in the coupling between the dye molecules and the semiconductor particles. Experiments with different isomers of anthracene carboxylic acid bound to titanium dioxide and zirconium dioxide were also performed. In this case differences in the back electron transfer rate are attributed to differences in the driving force for electron transfer, due to the different redox potentials of the dye molecules and the different conduction band energies of the semiconductor. We have also shown that the size of the semiconductor particles has no effect on the semiconductor-to-molecule electron transfer rate. Specifically, anatase TiO₂ particles in the 4 nm to 40 nm size range have identical back electron transfer times. These results imply that the electrons are rapidly trapped into sites adjacent to the dye radical cation, and that recombination occurs with the dye radical cation from these sites. This result was published in "Dynamics of Semiconductor-to-Dye Electron Transfer for Anthracene Dyes Bound to Different Sized TiO₂ Particles." I. B. Martini, J. H. Hodak, and G. V. Hartland *J. Phys. Chem. B* **103**, 9104-9111 (1999) (Ref. (1) below).

In the latter part of this project we concentrated on examining how the rates of electron transfer depend on the surface potential of the semiconductor particles. The surface potential was varied by adjusting the pH. For both anatase and rutile TiO₂, the way the surface potential depends on pH and ionic strength of the solution is well known (it is described in most standard texts on colloid and interface science!). Specifically, the conduction band potential changes by ca. 50 mV for every pH unit. Thus, to see significant effects in electron transfer rates the pH must be varied by at least 3-4 units. Unfortunately it is very hard to find dye molecules that remain bound over a wide range

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of pH units, and it is also hard to keep the solutions stable against precipitation. (Performing experiments in films raises problems about the exact value of the surface potential.) Thus, although we were able to measure back electron transfer rates at different pHs, the results were not uniformly reproducible and not publishable. The last set of experiments attempted was to use Stark spectroscopy to investigate the electronic structure of molecules attached to the surface of the particles. Stark measurements can yield information about the dipole moment of the adsorbed molecules which, in turn, provides important information about the electronic coupling between the molecule and the surface. The electronic coupling plays a central role in theories about electron transfer, thus, these experiments offer the possibility of providing detailed information about this interaction. The current status of this project is that the Stark spectrometer has been constructed, and initial experiments have been carried out to test the instrument. On the other hand, our time-resolved studies of semiconductor particles have moved on to examining the interaction between metal colloids and semiconductors, in collaboration with Dr. Prashant Kamat of the Notre Dame Radiation Laboratory. The focus of this work is to understand the effect of the presence of the semiconductor on the time scale for electron-phonon coupling in the metal particle. I am currently seeking support for this work through the NSF (there is significant overlap with my NSF grant which covers the photophysics of metal particles).

Papers Acknowledging DOE Support through Grant DE-FG02-98ER14898:

- 1) I. B. Martini, J. H. Hodak, and G. V. Hartland "Dynamics of Semiconductor-to-Dye Electron Transfer for Anthracene Dyes Bound to Different Sized TiO₂ Particles." *J. Phys. Chem. B* **103**, 9104-9111 (1999).

Papers presented at Professional Conferences related to this Project:

- 1) 23rd DOE Solar Photochemistry Research Conference, Tahoe City, California, June, 1999 (Poster presentation).
- 2) IPS-2000 Solar Photochemistry Meeting, Snowmass, Colorado, August, 2000 (Poster presentation).
- 3) 24rd DOE Solar Photochemistry Research Conference, Tahoe City, California, June, 2001.

Students supported by DOE Funding:

Ignacio B. Martini; Ph. D., 1999; Thesis Title: "Ultrafast Study of Electron Transfer at the Semiconductor-Liquid Interface."

Maria T. Canalas; M. Sc.; 2001; Thesis Title: "Construction of a Stark Spectrometer."

Debi Pant; Post-doctoral; 5/1999-6/2000.