

Dye-Sensitized Hole and PCET Transfer for Water Oxidation

Renato N. Sampaio¹, Ludovic Troian-Gautier¹, Gerald J. Meyer¹

¹ Department of Chemistry, University of North Carolina at Chapel Hill,
Chapel Hill NC USA.

E-mail: gjmeyer@email.unc.edu

There exists a critical need to identify materials that can be utilized to convert sun light into a sustainable energy source. A molecular approach has been to sensitize wide bandgap semiconductor mesoporous thin films to visible light with dyes. Such dye-sensitized nanostructures can provide electrical power generation as well as gaseous hydrogen fuel through water splitting. This presentation provides recent highlights of research directed towards solar fuel generation through dye-sensitized water oxidation.

Dye-sensitized solar cells have received considerable attention since the advent of mesoporous TiO₂ thin films described by Grätzel and O'Regan.^[1] Recently a kinetic pathway for electron transfer from the semiconductor to the oxidized dye was identified through the rational design of molecules where the distance and driving force were held near parity and only a bridge unit was varied.^[2] These molecules were comprised of a Ru chromophore linked through a rigid xylyl- or phenyl- thiophene bridge. Spectroscopic analysis revealed that electronic coupling through the phenyl bridge was a factor of ten greater than through the xylyl bridge. Taken together the data indicated an interfacial electron transfer pathway by a super-exchange hole-transfer mechanism. If time permits, the detailed mechanisms(s) for intramolecular hole transfer will be described.

Visible water splitting has been demonstrated for chemically linked sensitizer-catalyst molecules in dye-sensitized photoelectrosynthesis cells.^[3] In these cells, water oxidation requires the absorption of four photons and transient absorption measurements have provided insights into the first two light driven steps with both nanocrystalline TiO₂ and core-shell SnO₂-TiO₂ electrodes. An interesting observation was that light excitation of the mixed-valent molecule, [S-Ru^{III}-OH₂]⁵⁺, at pH = 1 resulted in excited state injection followed by a slow one electron, two proton transfer reaction that occurred on the seconds time scale: $\text{TiO}_2\text{-[S}^+\text{-Ru}^{\text{III}}\text{-OH}_2\text{]}^{5+} \longrightarrow \text{TiO}_2\text{-[S-Ru}^{\text{IV}}\text{=O]}^{3+} + 2 \text{H}^+$. Under more alkaline conditions, electrolyte buffers enhance water oxidation by a proposed atom-proton transfer reaction. The importance of proton coupled electron transfer reactions for light driven water oxidation as well as the utility of core-shell nanostructures for charge recombination inhibition will be discussed.

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