



Gerald J. Meyer

University of North Carolina at Chapel Hill, Chapel Hill NC 27599

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TU Wien, Kontaktraum

1040 Wien, Gußhausstraße 27-29

Building CD, 6th Floor, CD0603



Solar Energy Conversion with Molecular-Semiconductor Hybrid Photoelectrodes

The quest for hybrid photoelectrodes that efficiently upgrade abundant feedstocks to high energy fuels that can be stored is of critical importance. Recently a Solar Hub entitled the Center for Hybrid Approaches in Solar Energy to Liquid Fuels, or CHASE, was funded by the US Department of Energy to advance the fundamental science necessary to realize hybrid photoelectrodes based on molecular catalysts integrated with semiconducting electrodes, see: <https://chase.liquidfuels.org/> This presentation will focus on recent mechanistic advances on individual electron transfer and proton coupled electron transfer (PCET) reactions relevant to photochemistry and to photocatalysis.^{1,2} Recent advances in our mechanistic understanding of dye-sensitized electron transfer reactions occurring in fluid solution and at metal oxide interfaces are manifold and were enabled by the advent of mesoporous thin films, comprised of anatase TiO₂ nanocrystallites, that are amenable to spectroscopic and electrochemical characterization in unprecedented molecular-level detail. The metal-to-ligand charge transfer (MLCT) excited states of Ru polypyridyl compounds typically serve as the dye-sensitizers. Excited-state injection into TiO₂ often occurs on ultrafast timescales with yields that can be tuned from unity to near zero through modification of the sensitizer or the electrolyte composition. Transport of the injected electron and the oxidized sensitizer (hole-hopping) are both operative in the composite mechanism for charge recombination between the injected electron and the oxidized sensitizer. Sensitizers that contain a pendant electron donor, as well as core/shell TiO₂/SnO₂ nanostructures, often prolong the lifetime of the injected electron and provide fundamental insights into adiabatic and non-adiabatic electron transfer mechanisms. Regeneration of the oxidized sensitizer by iodide is enhanced through halogen bonding, orbital pathways, and ion-pairing. A significant ~ 10 MV cm⁻¹ electric field is created by electron injection into TiO₂ nanocrystallites that induces ion migration, reports on the sensitizer dipole orientation, and (in some cases) re-orient or flips the sensitizer. The utilization of conductive oxides also promotes long-lived charge separation with applied bias dependent kinetics that provide quantitative values of the reorganization energies associated with electron transfer and proton-coupled electron transfer (PCET) reactions occurring within the electric double layer.³ The impact of these findings on solar energy conversion will be discussed.

1. **Perspectives in Dye Sensitization of Nanocrystalline Mesoporous Thin Films.** Hu, K.; Sampaio, R.N.; Schneider, J.; Troian-Gautier, L.; Meyer, G.J. *J. Am. Chem. Soc.* **2020**, *142*, 16099-16116.
2. **Dye-Sensitized Solar Cells Strike Back.** Munoz-Garcia, A.; Benesperi, I.; Boschloo, G.; Concepcion, J.; Delcamp, J.; Gibson, E.; Meyer, G.J.; Pavone, M.; Pettersson, H.; Hagfeldt, A.; Freitag, M. *Chem. Soc. Rev.* **2021**, *50*, 12450-12550.
3. **Electronic Coupling and Reorganization Energies for Interfacial Proton-Coupled Electron Transfer to a Water Oxidation Catalyst.** Kessinger, M.; Soudackov, A.; Schneider, J.; Bangle, R.E.; Hammes-Schiffer, S.; Meyer, G.J. *J. Am. Chem. Soc.* **2022**, *144*, 20514-20524.

*All interested colleagues are welcome to this seminar lecture
(45 min. presentation followed by discussion).*