Examining Interfacial Dynamics in Dye-Sensitized Photoelectrosynthesis Cells

Jillian L. Dempsey

Sunlight-to-fuel technologies, such as dye-sensitized photoelectrosynthesis cells, will provide access to a sustainable energy future. The efficiency of solar fuel generating devices is governed by carrier separation, charge transport, and fuel-forming catalysis. As an added challenge, the multi-electron, multi-proton fuel formation reactions for water oxidation, proton reduction and/or CO_2 reduction must be coupled to sequential single-photon excitation processes. To address these challenges, interfacial dynamics in dye-sensitized photoelectrosynthesis cells are being probed through photophysical and electrochemical studies, providing key insights to device efficiency.

We are investigating SnO_2 as a photoanode alternative to TiO_2 for DSPEC applications. SnO_2 and TiO_2 films were sensitized with a ruthenium–polypyridyl chromophore containing phosphonate surface linkers. In these semiconductor–chromophore assemblies, excitation of the chromophore is followed by rapid charge injection into the metal oxide conduction band. Using nanosecond laser flash photolysis together with time-resolved spectroscopic monitoring, we have investigated the interfacial charge recombination dynamics of the injected electrons and the oxidized surface-bound ruthenium chromophores.[1] Recombination rates for RuP–SnO_2 are pH independent and faster than RuP–TiO_2 (which shows a significant pH dependence). Recombination rates for RuP–SnO_2 and RuP–TiO_2 have been correlated with the distribution, identity, and occupation of localized trap states within the nanocrystalline metal oxide films, which are pH specific.

Following this foundational study on SnO_2, photophysical studies were carried out on a high potential, electron deficient porphyrin chromophore with phosphonate substituents for surface anchoring.[2] Direct evidence for photo-generation of the porphyrin cation radical, consistent with excited-state electron injection to SnO_2, is provided by transient absorption difference spectra. Studies of a related SnO_2–chromophore–catalyst assembly which incorporates a ruthenium water oxidation catalyst were also performed. In these assemblies, transient absorption difference spectra reveal the catalyst is oxidized by intra-assembly electron transfer from the ruthenium catalyst to the porphyrin radical cation. In ongoing work, we are exploring new architectures to extend charge separation lifetimes.

References

(1) Knauf, R. R.; Brennaman, M. K.; Alibabaei, L.; Norris, M. R.; Dempsey, J. L. Revealing the Relationship between Semiconductor Electronic Structure

and Electron Transfer Dynamics at Metal Oxide–Chromophore Interfaces. *J. Phys. Chem. C* **2013**, *117*, 25259–25268.

(2) Nayak, A.; Knauf, R. R.; Hanson, K.; Alibabaei, L.; Concepcion, J. J.; Ashford, D. L.; Dempsey, J. L.; Meyer, T. J. Synthesis and Photophysical Characterization of Porphyrin and Porphyrin-Ru(II) Polypyridyl Chromophore-Catalyst Assemblies on Mesoporous Metal Oxides. *Chem. Sci.* **2014**. *Accepted*