EFRC: CENTER FOR SOLAR FUELS (UNC EFRC)

UPDATED: AUGUST 2016

AWARDS: $17.5M (August 2009 – July 2014); $10.8M (August 2014 – July 2018)

WEBSITES: http://science.energy.gov/bes/efrc/centers/unc/; www.efrc.unc.edu

TEAM: **University of North Carolina at Chapel Hill (Lead):** Thomas J. Meyer (Director), Gerald Meyer (Deputy Director), John Papanikolas (Deputy Director), Joanna Atkin, Maurice Brookhart, James Cahoon, Jillian Dempsey, Yosuke Kanai, Rene Lopez, Alex Miller, Andrew Moran, Cynthia Schauer, Joseph Templeton, Kyle Brennaman, Seth Marquard; **University of Texas, San Antonio**: Kirk Schanze; **Georgia Institute of Technology**: John Reynolds; **Brookhaven National Laboratory**: James Muckerman

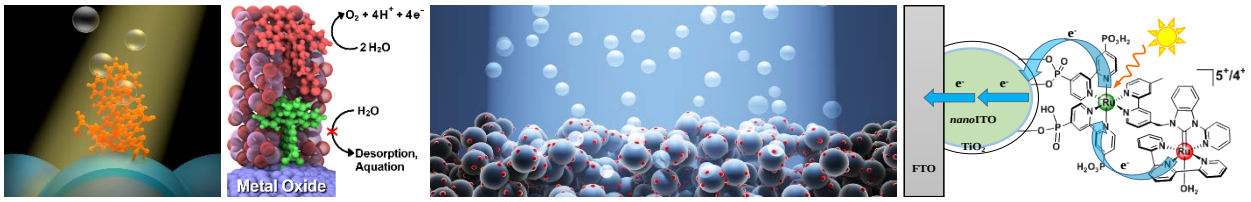
SCIENTIFIC MISSION AND APPROACH

The mission of the UNC EFRC is to conduct research on the dye-sensitized photoelectrosynthesis cell (DSPEC) for water oxidation, and tandem cells for the reduction of carbon dioxide to carbon-based solar fuels for applications in artificial photosynthesis. Research is conducted by five highly integrated teams:

1) **Catalysis**: Catalyst development and mechanistic studies on solution and interfacial catalysts for water oxidation and CO_2 reduction.
2) **Assemblies**: Design, synthesis, and characterization of molecular and polymer chromophore-catalyst assemblies for applications in water oxidation and CO_2 reduction at *n*- and *p*-type semiconductors.
3) **Dynamics**: Develop a detailed understanding of surface mechanisms that guide design of molecular assemblies that improve the performance of photoanodes and photocathodes.
4) **Photocathode**: Development of hole-transporting semiconductor nanomaterials and core/shell structures for high-performance photocathodes integrated with catalysts for CO_2 reduction.
5) **Photoanode**: Continued optimization of solar-driven water oxidation at dye-sensitized photoanodes.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Successfully pioneered the dye-sensitized photoelectrosynthesis cell (DSPEC) for solar fuels production. DSPECs have been developed for sustained, visible light-driven water splitting with core/shell oxide photoelectrodes derivatized with chromophore-catalyst assemblies.
- New single-site catalysts for water oxidation have been developed, and catalysis has been extended to novel surface-bound assemblies and stable first-row transition metal complexes.
- Rapid, robust catalysts have been developed for CO_2 reduction, including selective reduction of CO_2 either to formate or to tunable H_2/CO (syngas) mixtures, in solution or immobilized on a surface.
- Unique approaches to assemblies have been developed and exploited, including coupling multiple light absorbers with polymer scaffolds to mimic the antenna effect in natural photosynthesis.
- A high degree of surface stabilization has been successfully achieved by atomic layer deposition (ALD) and by electropolymerization, extending surface stabilization from minutes to days.
- Developed a range of chromophore-quencher photoanodes on oxide surfaces for water oxidation with per/photon absorbed efficiencies that approach 1%.
- Photocathode performance was greatly enhanced using targeted atomic deposition (TAD) to eliminate defect states in nanomaterials. Dark saturation current density was decreased by more than one order of magnitude, and device photovoltage was increased by up to 230%.
- Established a world-class spectroscopy facility and, with an integrated theory effort, provided dynamic mapping of key photo-events that occur in assemblies bound to oxide surfaces.



UNC EFRC research, from left: Surface-bound chromophore-catalyst assembly for water oxidation; Stabilization of surface-bound assembly by atomic layer deposition; Artificial photosynthesis in a dye sensitized photoelectrosynthesis cell; Photoexcitation of chromophore-catalyst assembly on a core/shell photoanode.

IMPACT

- The UNC EFRC hosts an annual international scientific conference in solar fuels, drawing 300-400 participants each year, and funded to-date by $253K from university and industrial donors.
- UNC EFRC leaders have given 180 invited presentations on energy-related issues to federal and state leaders, universities, industry, and venture capitalists. UNC EFRC researchers have developed and led energy-related outreach programs for schools, teachers, STEM programs, and public science events.
- Support from the UNC EFRC was crucial in creating the new UNC department of Applied Physical Sciences, the first new STEM department in the UNC College of Arts and Sciences in 40 years.
- UNC EFRC research accomplishments have led to $1.75M in follow-on funding from DOE SciDAC-e and ARPA-E programs, a congressional appropriation for instrumentation, and the Research Triangle Solar Fuels Institute, all of which have augmented the scientific impact of the Center.
- The UNC Solar Energy Research Center (UNC SERC) is leading a translational research effort based on technology developed by the UNC EFRC. Market validation studies have led to a translational effort in CO_2 electroreduction to formic acid for decentralized hydrogen production and storage.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, UNC EFRC had published 233 peer-reviewed publications cited over 10,100 times and filed 27 disclosures, 23 US patent applications, and 17 foreign patent applications. 2 patents have been issued and 2 disclosures or patent applications licensed. The following is a selection of impactful papers:

- Concepcion, J. J. *et al.* Mechanism of Water Oxidation by Single-Site Ruthenium Complex Catalysts. *J. Am. Chem. Soc.* **132**, p1545-p1557, doi:10.1021/ja904906v (2010). [**247 citations**]
- Kang, P. *et al.* Selective Electrocatalytic Reduction of CO_2 to Formate by Water-Stable Iridium Dihydride Pincer Complexes. *J. Am. Chem. Soc.* **134**, p5500-p5503, doi:10.1021/ja300543s (2012). [**89 citations**]
- Ashford, D. L. *et al.* Photoinduced Electron Transfer in a Chromophore-Catalyst Assembly Anchored to TiO_2. *J. Am. Chem. Soc.* **134**, p19189-p19198, doi:10.1021/ja3084362 (2012). [**53 citations**]
- Alibabaei, L. *et al.* Solar water splitting in a molecular photoelectrochemical cell. *Proc. Natl. Acad. Sci. USA* **110**, p20008-p20013, doi:10.1073/pnas.1319628110 (2013). **[91 citations**]
- Kang, P. *et al.* Single catalyst electrocatalytic reduction of CO_2 in water to H_2 + CO syngas mixtures with water oxidation to O_2. *Energy Environ. Sci.* **7**, p4007-p4012, doi:10.1039/c4ee01904k (2014). [**15 citations**]
- Alibabaei, L. *et al.* Visible photoelectrochemical water splitting into H_2 and O_2 in a dye-sensitized photoelectro-synthesis cell. *Proc. Natl. Acad. Sci. USA* **112**, p5899-p5902, doi:10.1073/pnas.1506111112 (2015). [**30 citations**]
- Knauf, R. R. *et al.* Charge Recombination Dynamics in Sensitized SnO_2/TiO_2 Core/Shell Photoanodes. *J. Phys. Chem. C* **119**, p28353-p28360, doi:10.1021/acs.jpcc.5b10574 (2015). [**5 citation**]
- Flynn, C. J. *et al.* Site-Selective Passivation of Defects in NiO Solar Photocathodes by Targeted Atomic Deposition. *ACS Appl. Mater. Interfaces* **8**, p4754-p4761, doi:10.1021/acsami.6b01090 (2016). [**4 citations**]
- Zigler, D. F. *et al.* Disentangling the Physical Processes Responsible for the Kinetic Complexity in Interfacial Electron Transfer of Excited Ru(II) Polypyridyl Dyes on TiO_2. *J. Am. Chem. Soc.* **138**, p4426-p4438, doi:10.1021/jacs.5b12996 (2016). [**5 citations**]
- Leem, G. *et al.* Light-Driven Water Oxidation using Polyelectrolyte Layer-by-Layer Chromophore-Catalyst Assemblies. *ACS Energy Lett.* **1**, p339-p343, doi:10.1021/acsenergylett.6b00171 (2016). [**2 citations**]