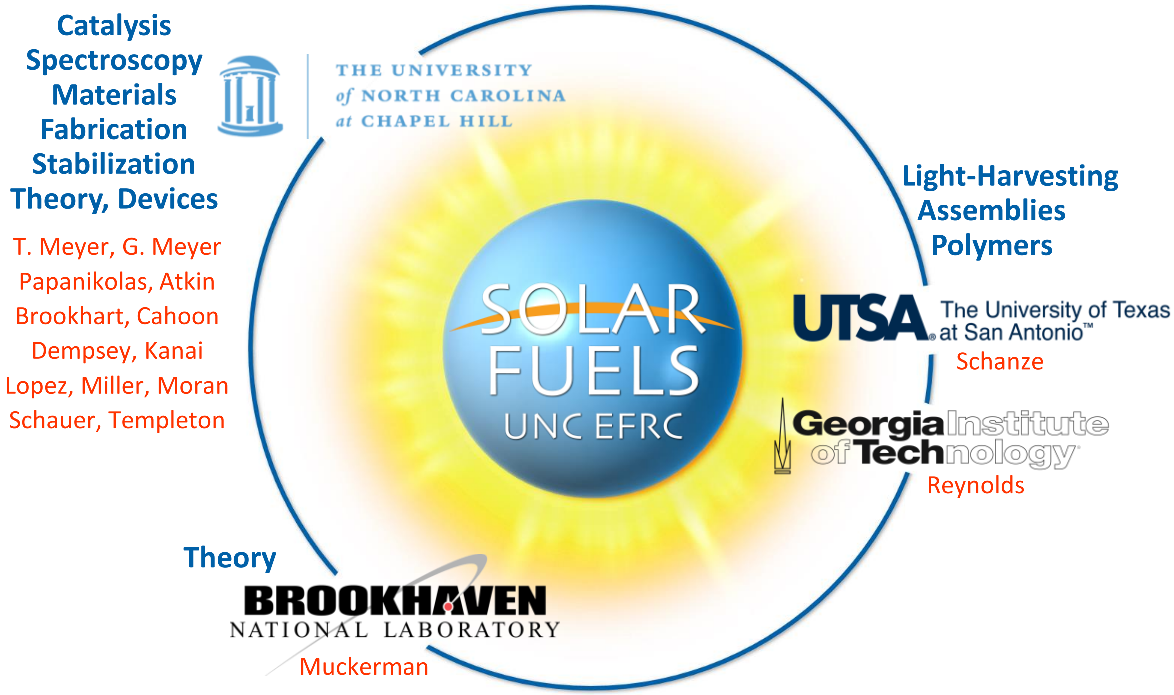
UNC EFRC: CENTER *for* SOLAR FUELS



MISSION

The Center for Solar Fuels conducts research on the dye sensitized photoelectrosynthesis cell (DSPEC) for water splitting, and tandem cells for the reduction of carbon dioxide to carbon-based solar fuels

UNC ENERGY FRONTIER RESEARCH CENTER

www.efrc.unc.edu

RESEARCH PLAN

- A modular approach is applied to design, test, and evaluate high efficiency DSPEC device prototypes for solar water oxidation and CO_2 reduction to formate or syngas H_2:CO mixtures
- Results are integrated from research on water oxidation, CO_2 reduction, light-harvesting chromophores and chromophore arrays, chromophore-catalyst assemblies, mesoporous nanoparticle semiconductor oxide films, and core/shell structures to develop efficient DSPEC device prototypes

THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL · UTSA The University of Texas at San Antonio · Georgia Institute of Technology · BROOKHAVEN NATIONAL LABORATORY · U.S. DEPARTMENT OF ENERGY Office of Science

UNC EFRC TEAM-BASED RESEARCH

Dye Sensitized Photoelectrosynthesis Cell (DSPEC) for Solar Fuels Production

SOLAR FUELS

UNC EFRC SOLAR FUELS

Synthesis (T. Meyer/Miller/Schanze*)

- **Catalysis**: Brookhart, G. Meyer, T. Meyer, **Miller**, Muckerman*, Schauer
- **Assemblies**: G. Meyer, T. Meyer, Papanikolas, Reynolds*, **Schanze***, Templeton

Interfaces & Devices (Papanikolas/Cahoon/G. Meyer)

- **Interface Dynamics**: Atkin, Cahoon, Dempsey, Kanai, G. Meyer, T. Meyer, Moran, **Papanikolas**, Schanze*
- **Photocathode**: Atkin, **Cahoon**, Dempsey, Kanai, G. Meyer, T. Meyer, Papanikolas
- **Photoanode**: Atkin, Cahoon, Dempsey, Lopez, **G. Meyer**, T. Meyer, Moran, Papanikolas, Schanze*

INTEGRATED TEAMS

- Highly integrated, inter-disciplinary, cross-team memberships
- Cross-fertilization, inter-institutional collaboration & synergy
- Faculty-led, biweekly meetings, project oriented
- Continuous internal and external accountability and review

TEAM	TEAM MISSION & RESEARCH FOCUS
CATALYSIS	Catalyst development and mechanistic studies on solution and interfacial catalysts for water oxidation and CO_2 reduction. Evaluation of catalysts in assemblies and device prototypes for photoanode and photocathode applications.
ASSEMBLIES	Design, synthesis, and characterization of molecular, oligomer and polymer chromophore-catalyst assemblies for applications in water oxidation and CO_2 reduction at *n*- and *p*-type semiconductors.
INTERFACIAL DYNAMICS	Dynamics of light-driven interfacial electron transfer in chromophores, assemblies, and chromophore-catalyst assemblies on semiconductor oxide surfaces.
PHOTOCATHODE	Design, synthesis and characterization of hole-transporting semiconductor nanomaterials, core/shell structures, and light-absorbing sensitizers for high-performance photocathode applications integrated with molecular catalysts for CO_2 reduction.
PHOTOANODE	Optimization of solar-driven water oxidation at dye sensitized photoanodes.

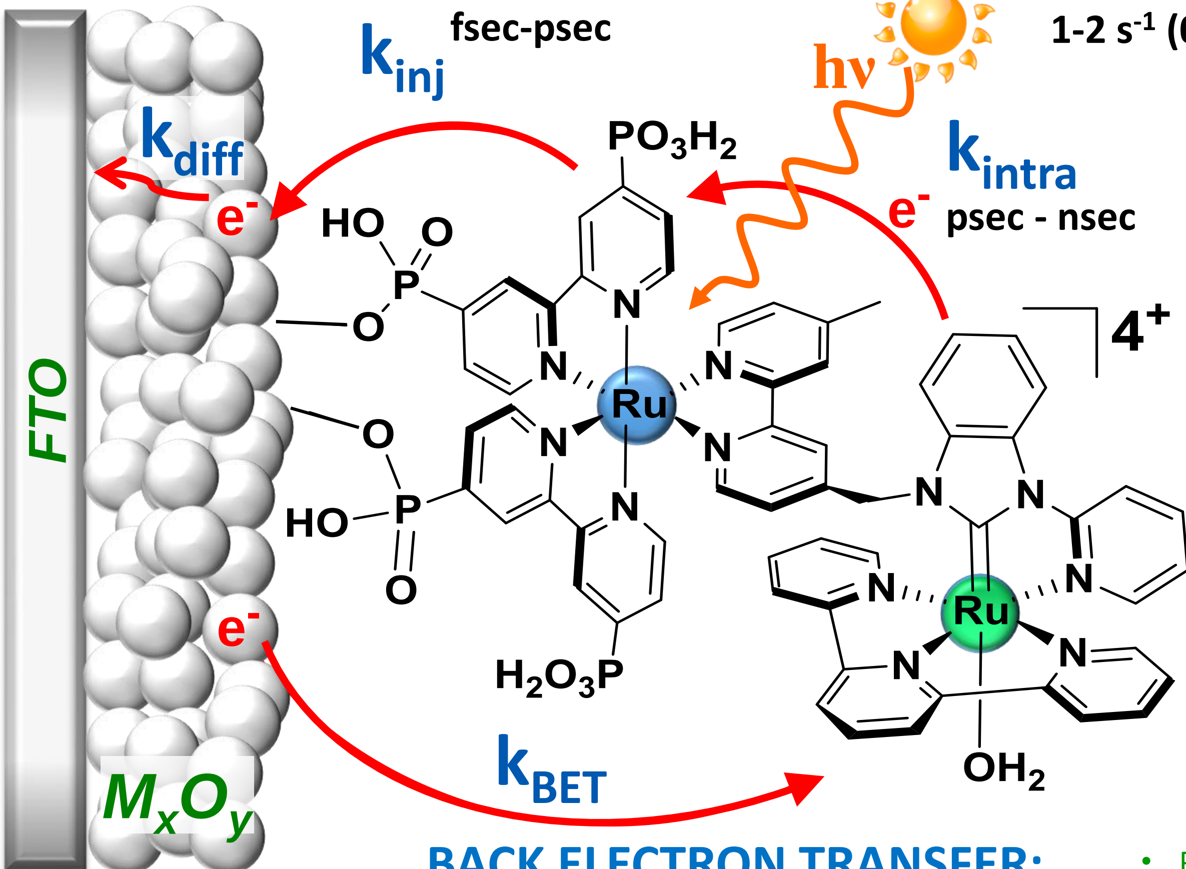
PHOTOANODES for WATER SPLITTING
Interfacial Dynamics – Timescales

SOLAR FUELS

SEMICONDUCTOR:
5-10 μ; ~1 msec

INJECTION:
fsec-psec

LIGHT ABSORPTION:
1-2 s^{-1} (0.25 - 0.5 O_2 s^{-1}; 4 photons)



MOLECULAR CATALYSIS:
> 0.1 s^{-1}

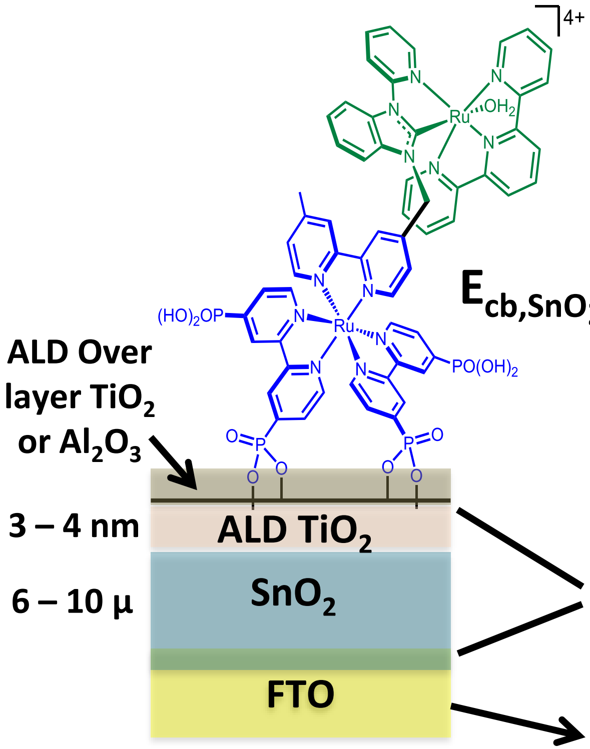
SURFACE BINDING:
Indefinite

BACK ELECTRON TRANSFER:
μsec - msec

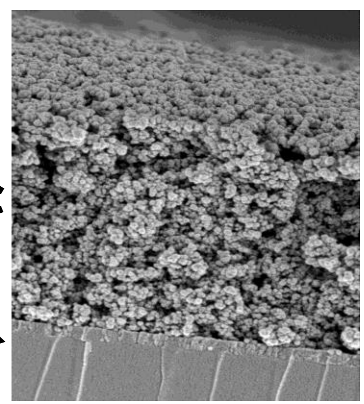
- Papanikolas, Reynolds, Schanze, T. Meyer, Morseth *et al*. *Acc. Chem. Res*. **2015**, *48*, 818
- T. Meyer, Papanikolas, G. Meyer, Brennaman *et al*. *J. Am. Chem. Soc*. **2016**, *138*, 13085

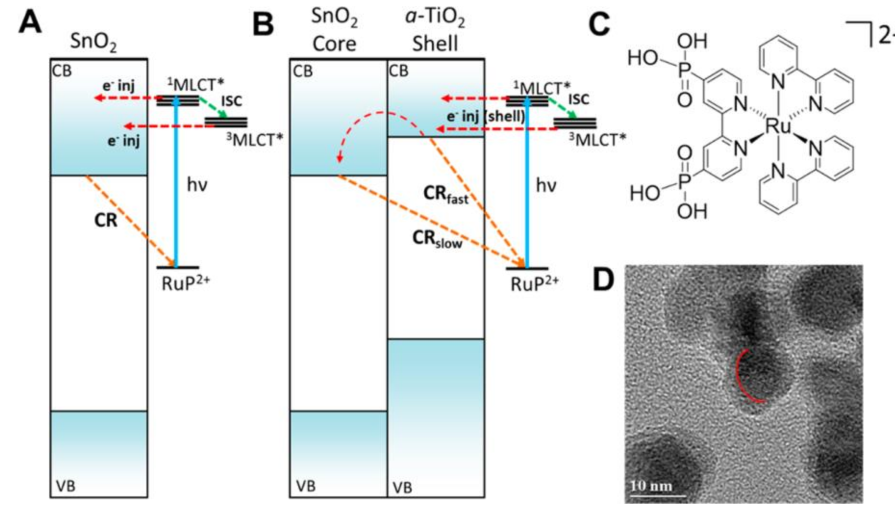
PHOTOANODES for WATER SPLITTING
Core/Shell, Surface Stabilized Electrodes

SOLAR FUELS

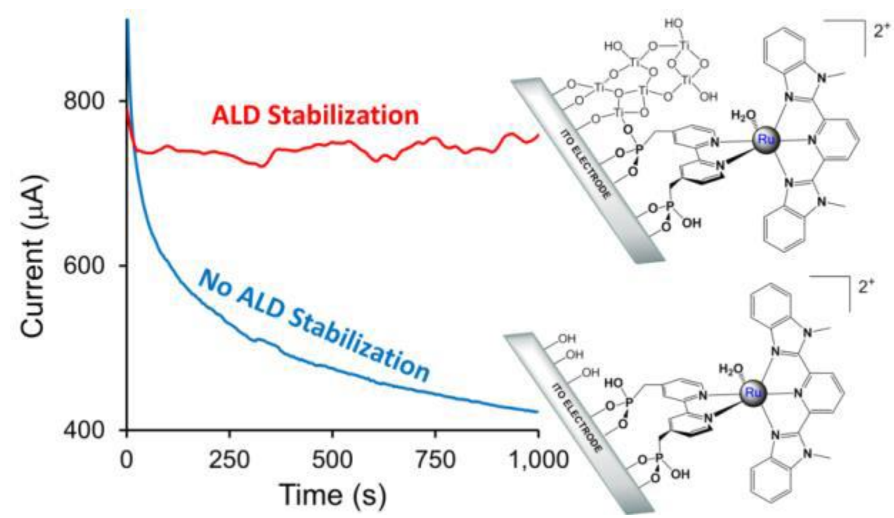


$$E_{cb,SnO_2} = E_{cb,TiO_2} + 0.4\ V$$





Core/Shell Electrodes



ALD Surface Stabilization

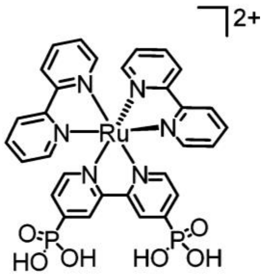
APCE (445nm) ~20%
Solar H_2 < 1%

- T. Meyer, Sherman *et al. ACS Energy Lett.* **2017**, *2*, 124
- T. Meyer, Alibabaei *et al. Proc Natl Acad Sci USA* **2015**, *112*, 5899
- T. Meyer, Alibabaei *et al. Proc. Natl. Acad. Sci. USA* **2013**, *110*, 20008

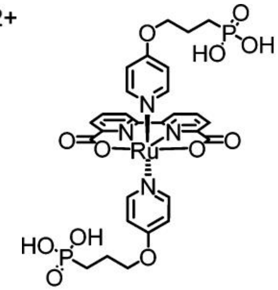
PHOTOANODES for WATER SPLITTING
All-in-one Tandem Water Splitting DSPEC

SOLAR FUELS

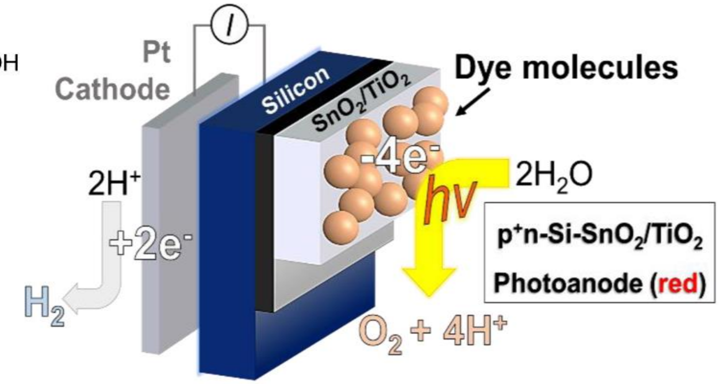
Chromophore



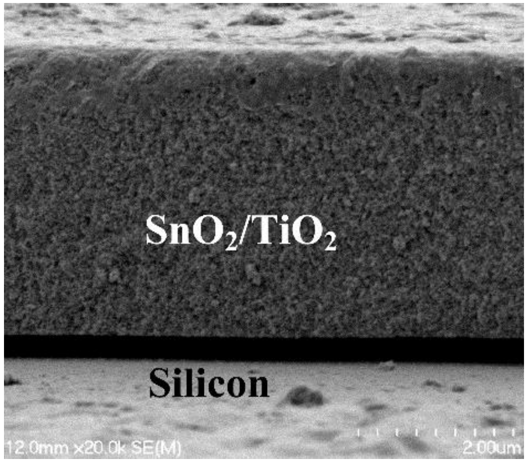
Catalyst



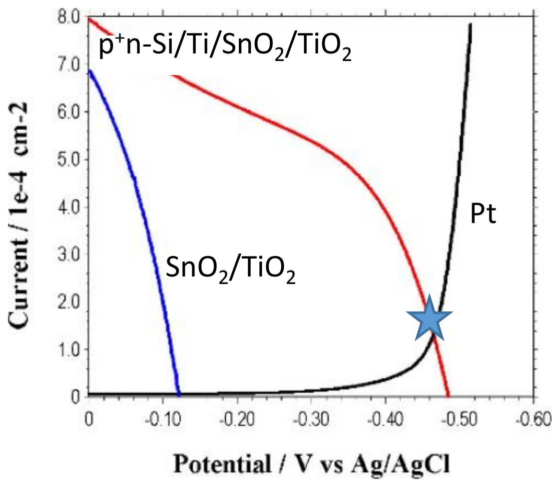
Device



$Si/Ti/SnO_2/TiO_2$



Unbiased water splitting



ACHIEVEMENT

Unbiased water splitting cell with molecular chromophores and catalysts combining mesoporous SnO_2/TiO_2 and a silicon p-n junction

IMPACT

Combination of molecular chromophore-catalysts with conventional silicon represents a new paradigm for design of tandem water splitting cells

DETAILS

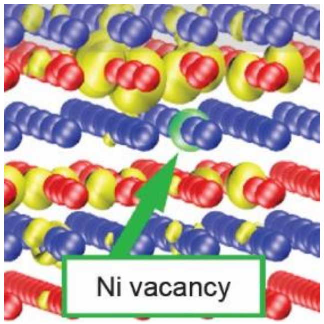
- Mesoporous SnO_2/TiO_2 films are derivatized with ruthenium-based chromophores and catalysts, which perform light absorption and water-oxidation catalysis
- Silicon p^+-n wafers provide the additional photo-potential needed for water splitting, with proton reduction at a Pt cathode

T. Meyer, Cahoon, Sheridan *et al*. *Nano Lett.* **2017**, *17*, 2440

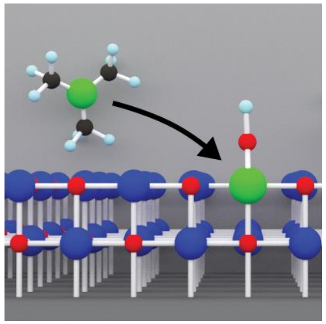
THE PHOTOCATHODE
Passivating Photocathode Materials by TAD

SOLAR FUELS

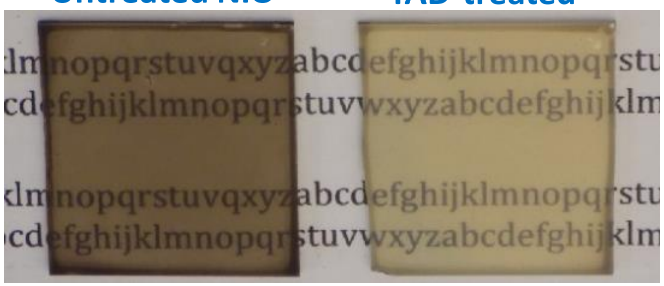
Ni vacancy defect states



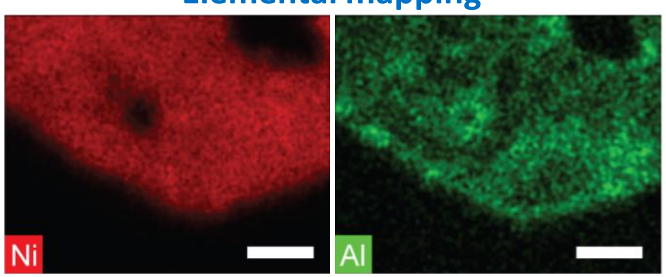
TAD deposition at defect sites



Untreated NiO **TAD-treated**



Elemental mapping



ACHIEVEMENT

Selective passivation of Ni vacancy defects in the widely used cathode NiO leads to dramatic optical and bleaching of thin films and to large improvements in the performance of dye-sensitized devices.

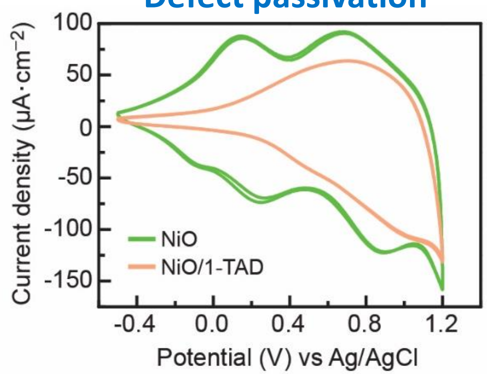
IMPACT

A new vapor-phase process termed **Targeted Atomic Deposition (TAD)** was used to passivate defects. The TAD process could be widely applied to defect passivation in semiconductor nanomaterials.

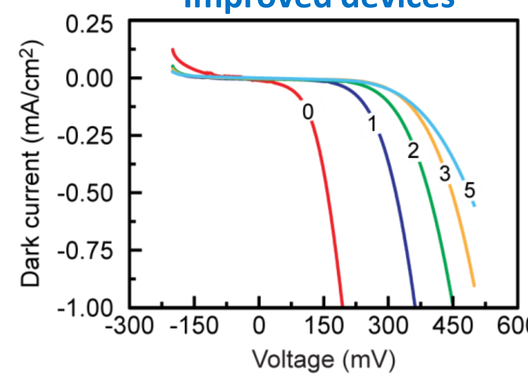
DETAILS

- First-principles calculations identified oxygen-localized defect states as a result of Ni vacancies
- Vapor-phase trimethyl aluminum, at a temperature too low for layered deposition, selectively reacted with the oxygen dangling bonds at defect sites, removing trap states and bleaching thin films of NiO

Defect passivation



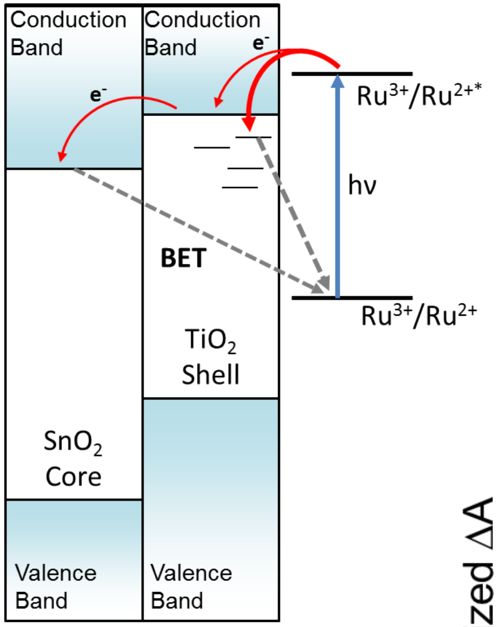
Improved devices



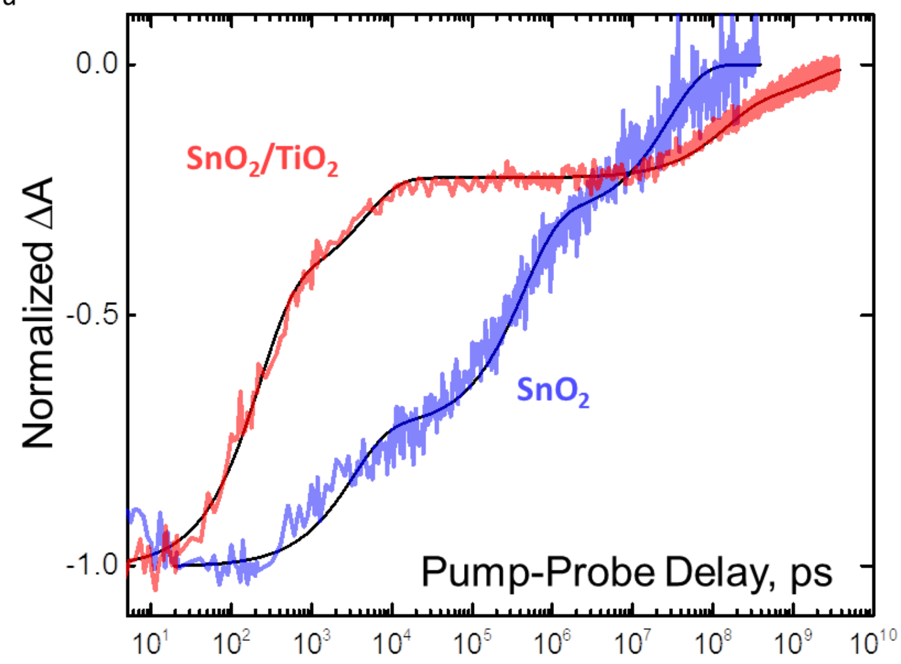
Cahoon, Kanai, T. Meyer, Nozik, *et al.* *ACS Appl. Mater. Interfaces* **2016**, *8*, 4754
Cahoon, Kanai, *et al.* *J. Phys. Chem. C* **2016**, *120*, 16568

UNC EFRC RESEARCH CAPABILITIES
Photoexcited Dynamics: From fsec to msec

SOLAR FUELS



Through combination of transient absorption methods, UNC EFRC can follow photoinduced dynamics on timescales ranging from **fsec** to **msec**



Example:
Observe combination of psec and msec recombination following injection on SnO_2/TiO_2 core/shell nanoparticles

- Papanikolas, T. Meyer, Gish *et al. J. Phys. Chem. Lett*. **2016**, *7*, 5297
- Papanikolas, Schanze, Reynolds, Morseth *et al. J. Phys. Chem. B* **2016**, *120*, 7937
- Papanikolas, T. Meyer, Bettis *et al. J. Phys. Chem. A* **2014**, *118*, 10301

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UNC EFRC – A *CENTER* ETHOS

- Integrated Teams, EFRC IP MOU, Inter-Site Visits
- Annual UNC SERC Scientific Conference serc.unc.edu SERC UNC SOLAR ENERGY RESEARCH CENTER
- Annual Research Review (External Advisory Board)
- Inter-institutional Videoconferencing zoom Video Conferencing
- SharePoint Collaborative Workspace/Portal
- Orientation, Workshops, Training, Education, Outreach

SOLAR FUELS UNC EFRC

CENTER for SOLAR FUELS TECHNICAL TALKS

Gerald J. Meyer *C-IV-3* *Tue 2:10pm*	**A General Approach for Generation of Catalytic High Valent Metal Oxo Species Reveals Photoinduced One Electron, Two Proton Transfer Reactivity**
Kirk S. Schanze *H-I-1* *Mon 3:00pm*	**Molecular and Polymer Chromophore-Catalyst Assemblies for Solar Fuels Production**
John M. Papanikolas *H-I-4* *Mon 4:00pm*	**Ultrafast Injection and Recombination Dynamics at SnO_2/TiO_2 Core/Shell and NiO Interfaces for Solar Fuels Production**
Taylor H. Moot, Lesheng Li *H-IV-1* *Tue 1:30pm*	**Identification and Passivation of the Defect States in NiO for Photovoltaic and Solar Fuel Applications (Student/Postdoc Competition)**

CENTER for SOLAR FUELS POSTERS

CATALYSIS TEAM Ying Wang Sergio Gonell-Gómez	**Water Oxidation and CO_2 Reduction Catalysis for Solar Fuels Production** *PII-C-3 Tue 3:30pm*
ASSEMBLIES TEAM Gyu Leem Ludovic Troian-Gautier	**Chromophore-Catalyst Assemblies for Solar Fuels Production** *PI-H-5 Mon 5:00pm*
DYNAMICS TEAM Melissa K. Gish Lenzi J. Williams	**Interfacial Electron and Hole Transfer Dynamics of Dye-Sensitized Metal Oxide Architectures** *PI-H-11 Mon 5:00pm*
PHOTOCATHODE TEAM Taylor H. Moot Lesheng Li	**Probing Photocathode Materials and Interfaces to Enable Tandem Dye Sensitized Photoelectrosynthesis Cells** *PII-H-1 Tue 3:30pm*
PHOTOANODE TEAM Renato N. Sampaio	**Accessing the Photophysics of Water Oxidation Photoanodes** *PII-H-11 Tue 3:30pm*