Research in the UNC EFRC for Solar Fuels

The Dye Sensitized Photoelectrosynthesis Cell (DSPEC)

T.J. Meyer

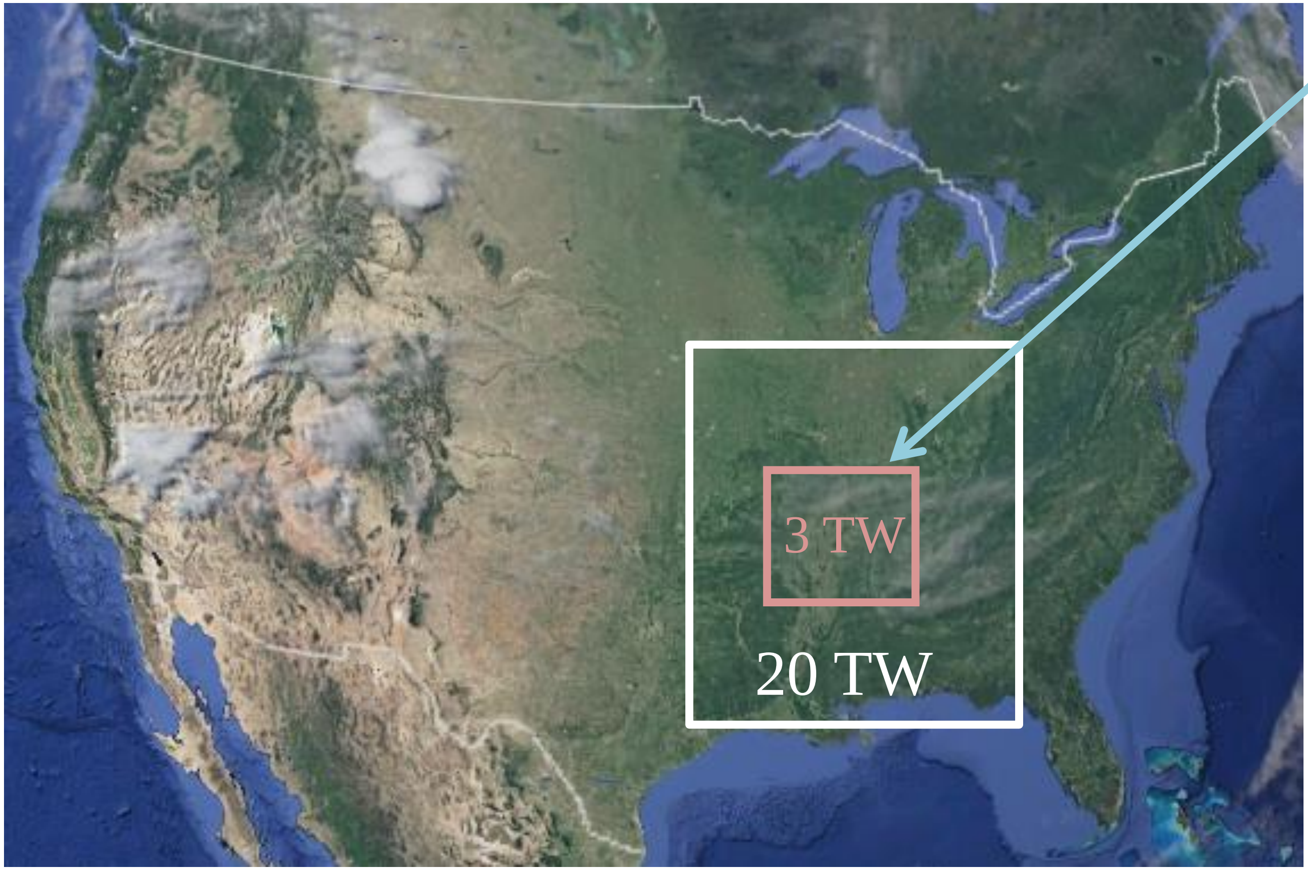
UNC EFRC: SOLAR FUELS

DOE Yellow Team Presentation

May 14, 2015

Solar Energy

~10,000 Times Current Energy Use. But……..



Diffuse:

~60,000 sq. miles to meet current US power demands (3 TW)*

1,000 homes = 32 acres

Intermittent:

6 hours of useful sunlight per day

Requires Energy Storage

*at 10% efficiency, NREL. $60 Trillion at $400/m^2.

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Energy Conversion and Storage with Solar Fuels

Artificial Photosynthesis

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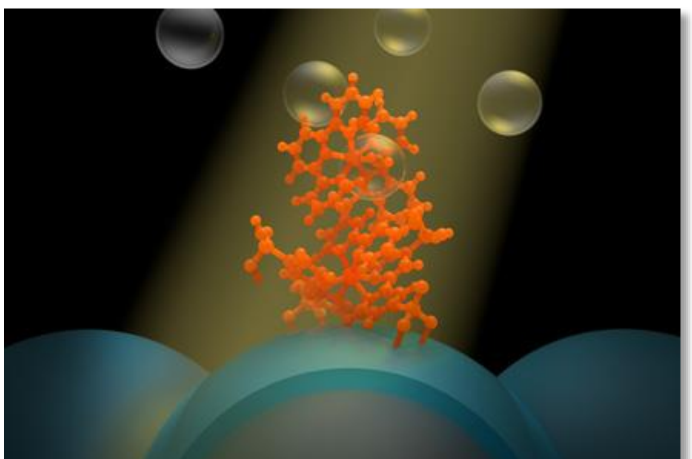
- *Hydrogen, CO, natural gas, liquid hydrocarbons and oxygenates*
- *Use the existing energy infrastructure*

$$2\,H_2O + 4\,h\nu \longrightarrow 2H_2 + O_2$$

$$(\Delta G^o = 4.92\text{ eV},\ n = 4)$$

$$2\,H_2O + CO_2 + 8\,h\nu \longrightarrow CH_4 + 2O_2$$

$$(\Delta G^o = 10.3\text{ eV},\ n = 8)$$



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Dye Sensitized Photoelectrosynthesis Cell DSPEC

DSPEC for H_2O Splitting (1974→1999)

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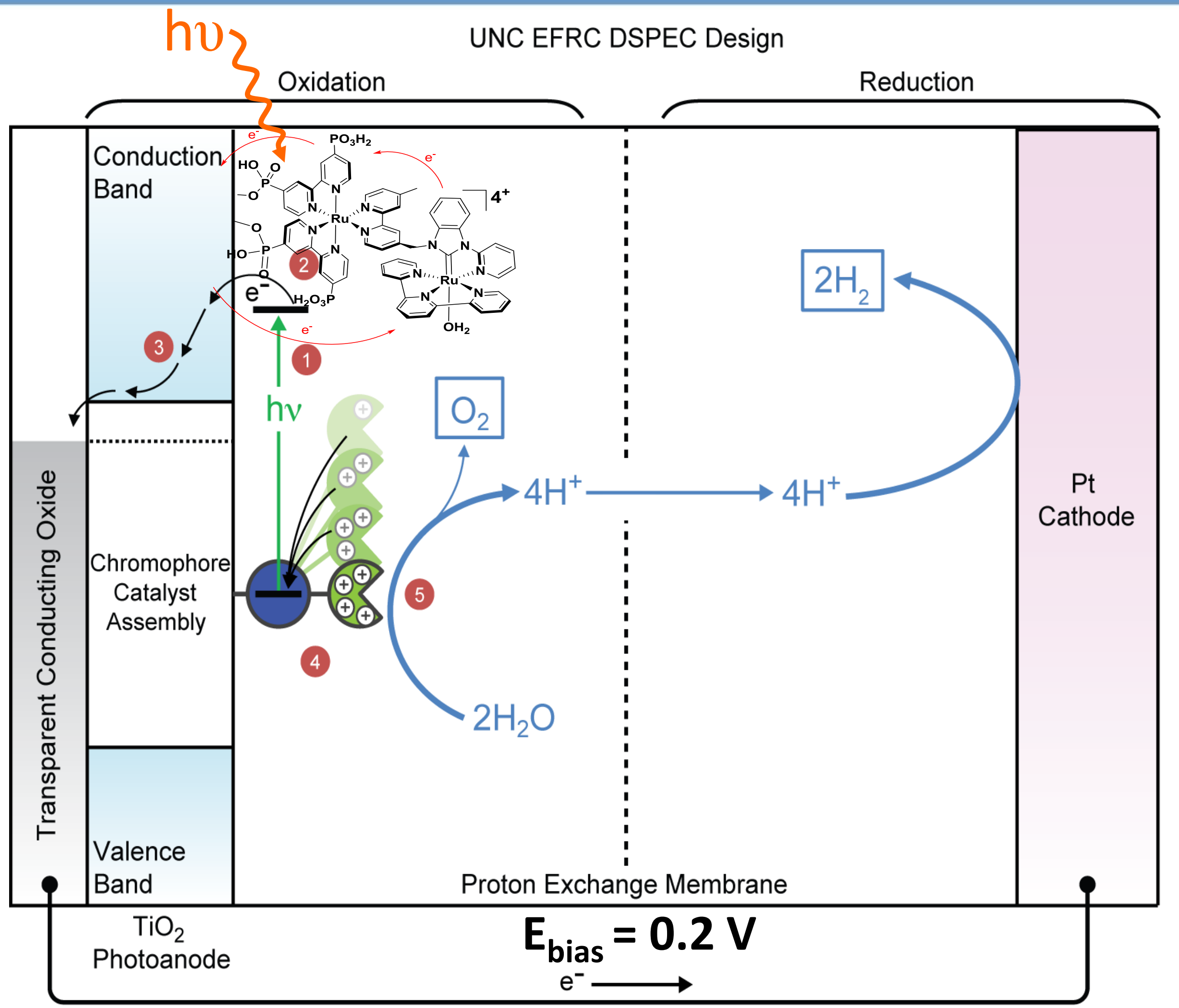

- **KEEP IT SIMPLE!**
- **LET THE MOLECULES DO THE WORK.**

Moss, Treadway, *Inorg. Chem.*, **1999**

Song et al. *Pure and Appl. Chem*, **2011**, 749

Bock, Meyer, Whitten, *JACS*, **1974**, 96, 4710

$$Ru(bpy)_3^{2+}\,(d\pi^6) + h\upsilon \rightarrow Ru^{III}(bpy^{-\cdot})(bpy)_2^{2+*}$$

$$Ru(bpy)_3^{2+*} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^{+\cdot}$$

Tandem DSPEC: CO_2 Reduction to Formate; Syn-Gas (H_2:CO)

Bias-Free Water Splitting

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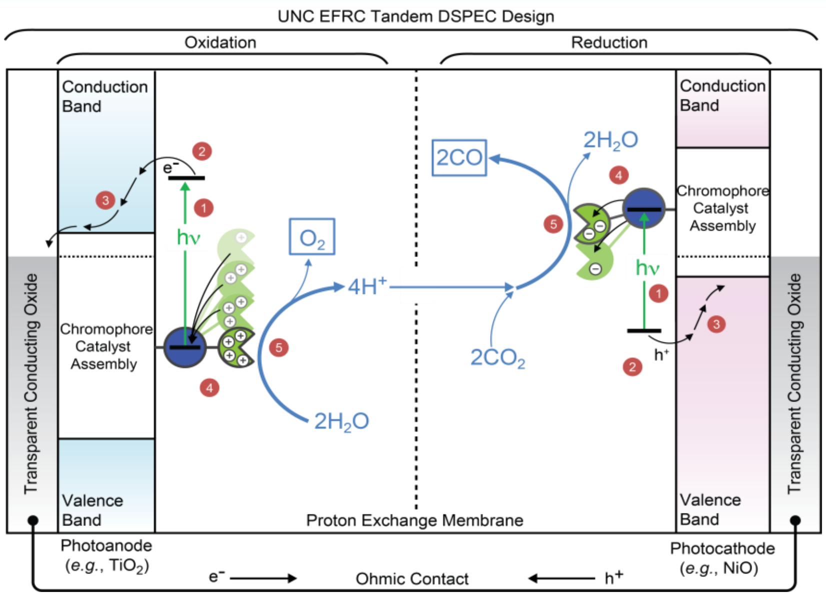
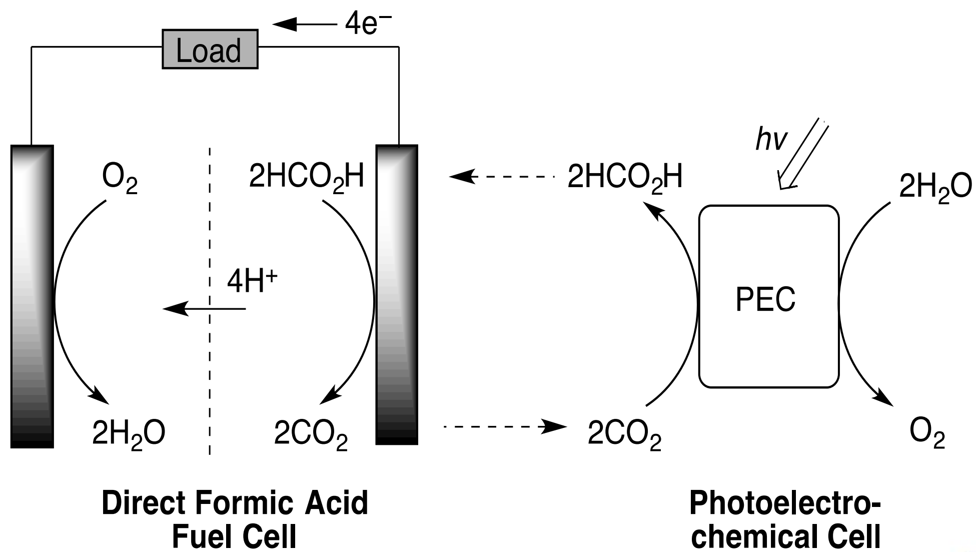


- **Tandem DSPECs for CO_2 reduction and bias-free water splitting**
- **Integrated PEC/formate-oxygen fuel cell for off-grid energy conversion and storage**

- **CO_2/H_2O/H^+ reduction to syngas ($2H_2$:CO)**

  Syngas → CH_3OH → hydrocarbons by Fischer-Tropsch synthesis



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Chromophore-Catalyst Assemblies
Strategies (Kirk Schanze)

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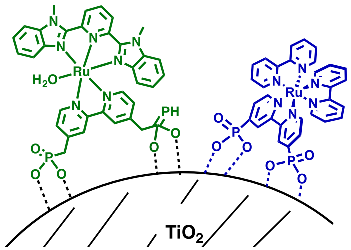
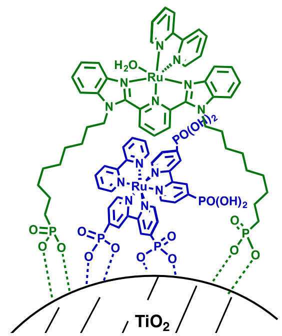


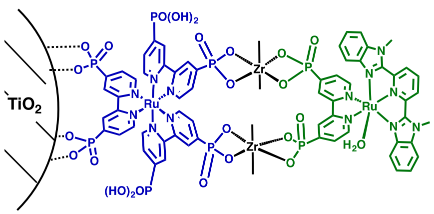
Co-Loaded

JACS, **2013**, 11587
JACS, **2014**, 9773



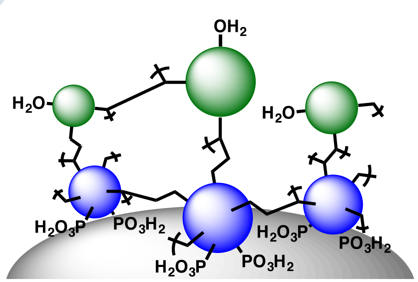
Molecular Overlayers

Inorg. Chem., **2012**, 8637



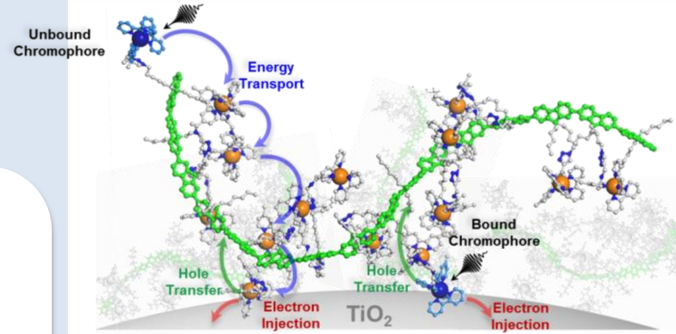
Layer-by-Layer

ACIE, **2012**, 12782
Chem. Sci., **2014**, 3115
JPCA, **2014**, 10301



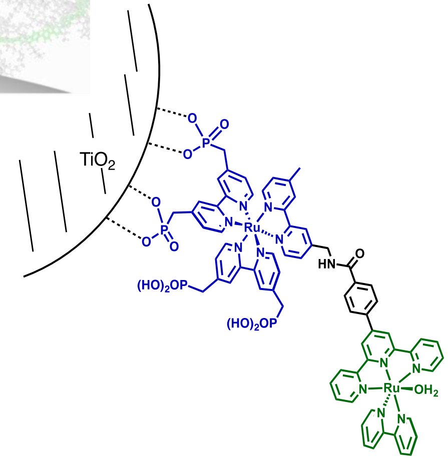
Electro-assembly

JACS, **2013**, 15450
JACS, **2014**, 6578



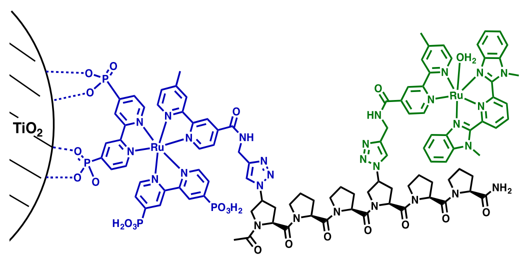
Polymer Scaffolds

Polym. Chem., **2014**, 2363
JPCL, **2012**, 2457



Molecular Assemblies

ACIE, **2009**, 9473
Inorg. Chem., **2012**, 6428
JACS, **2012**, 19189
JACS, **2013**, 2080
JPPC, **2013**, 24250
ACIE, **2013**, 13580
JPCL, **2011**, 1808



Peptide Scaffolds

JCPB, **2013**, 6352
JACS, **2013**, 5250
Inorg. Chem., **2012**, 11324
Inorg. Chem., **2014**, 8120

Surface Assembled

Pre-formed

Interfacial Dynamics on TiO_2 in Water.

TiO_2-[Ru_a^{II}-Ru_b^{II}-OH_2]$^{4+}$ (John Papanikolas)

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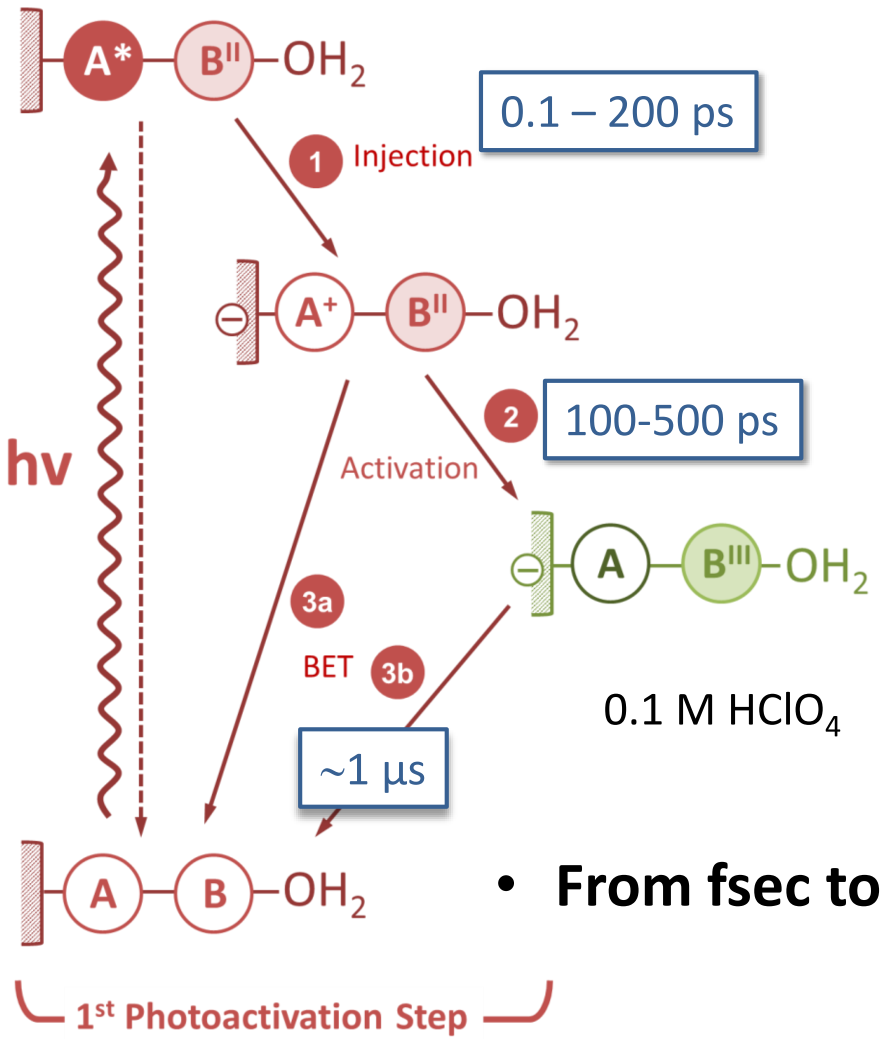
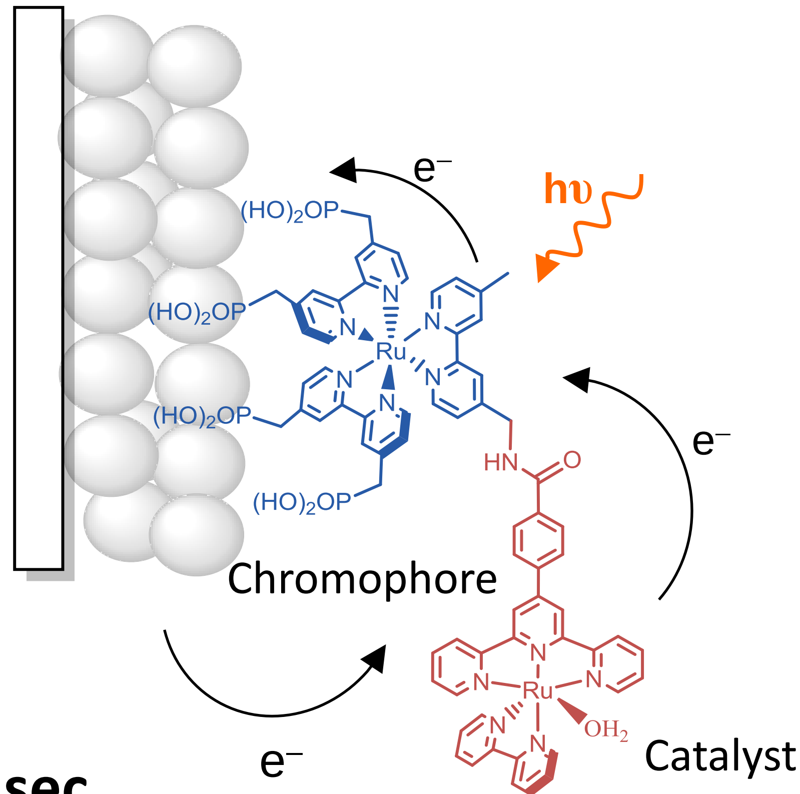
[(4,4'-(PO_3H_2-CH_2)$_2$-bpy)$_2$$Ru_a$(bpy-NH-CO-py)$Ru_b$(bpy)($OH_2$)]$^{4+}$



0.1 M $HClO_4$

- **From fsec to msec**



Dennis Ashford

Single Site Catalysis of Water Oxidation, 2008

Mechanism. $2H_2O \rightarrow O_2 + 4e^- + 4H^+$ *(Blue Dimer – 1982)*

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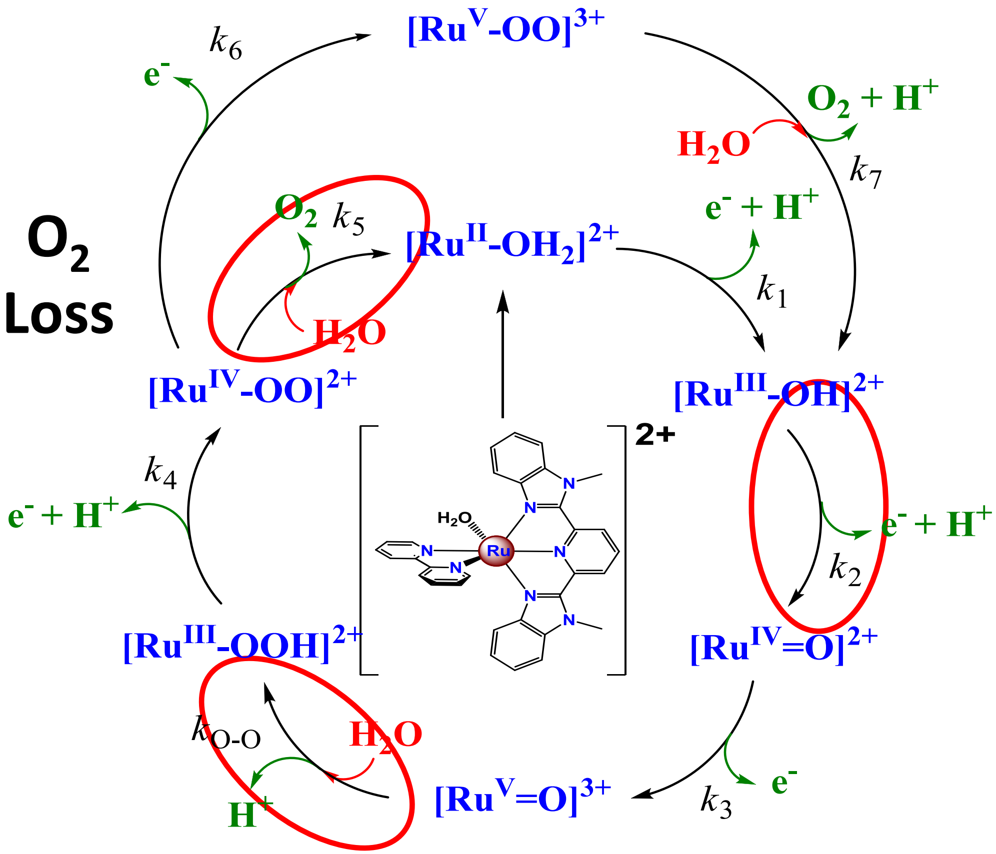
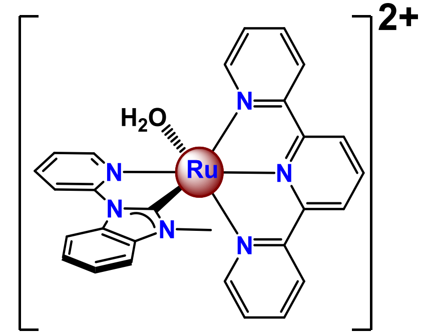


O---O bond formation

PCET (1981)

Binstead et al., *JACS*, **1981**, *103*, 2897



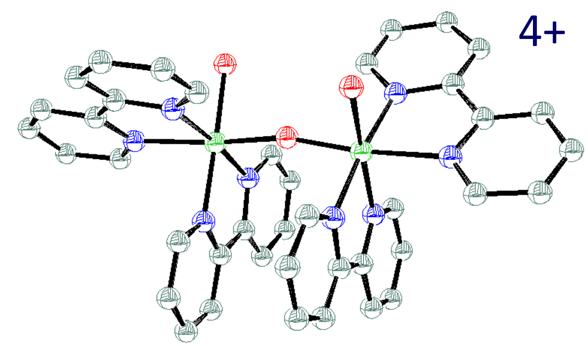
$[Ru(tpy)(Mebim\text{-}py)(OH_2)]^{2+}$

$k_{cat}(2) \sim 2.0\ s^{-1}$

$(0.1\ M\ HNO_3)$

2 weeks - 43,400 turnovers

(pH = 7, 0.1 M $H_2PO_4^-/HPO_4^{2-}$)



$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$

Gersten, et al., *JACS*, **1982**, *14*, 4029

Thummel, *JACS*, **2005**

Concepcion, Chen, *JACS*, **2008**, **2010**; *PNAS*, **2010**, **2012**; *Inorg. Chem.*, **2010**

Specific Base Catalysis
Atom-Proton Transfer (APT) and OH⁻ Attack

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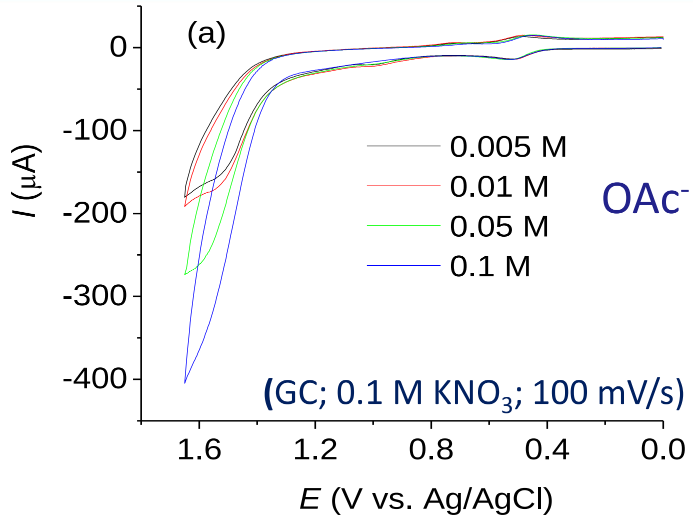
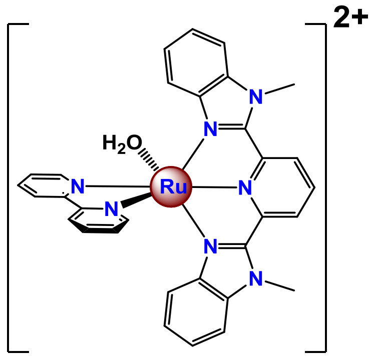


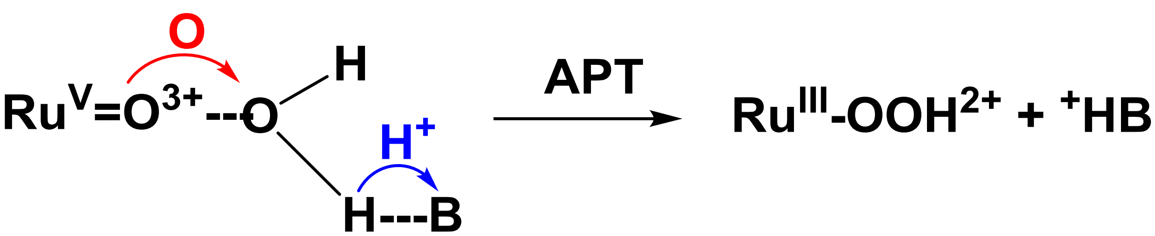
Concerted Atom-proton transfer:

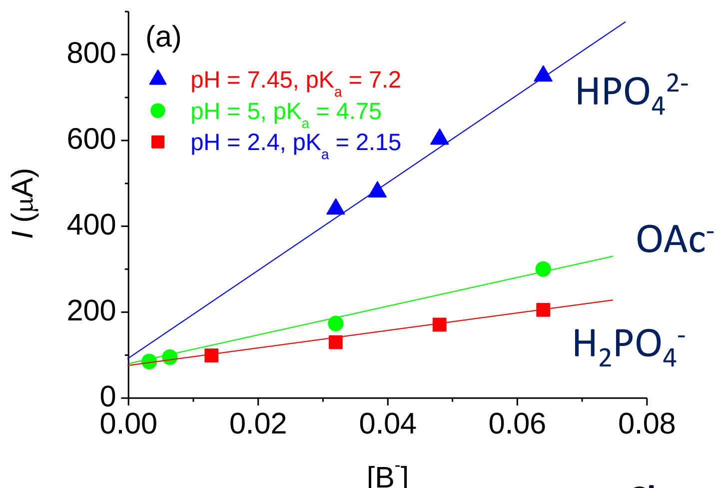
Rate enhancements of > 10^4

2 weeks - 43,400 turnovers

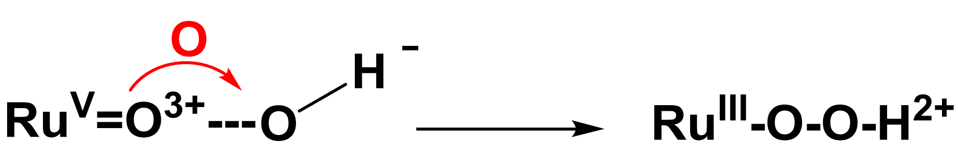
(pH = 7, 0.1 M $H_2PO_4^-/HPO_4^{2-}$)







$$\{Ru^{V}{=}O^{3+} + H_2O \rightarrow M^{III}\text{-}O\text{-}OH_2^{\,3+}\}$$



High pH. Direct OH⁻ attack

Chen, Meyer, Concepcion, Yang, *PNAS*, 2010; Tamaki et al., *JACS*, 2014

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Surface Water Oxidation on *nano*ITO
Water Oxidation Cycle

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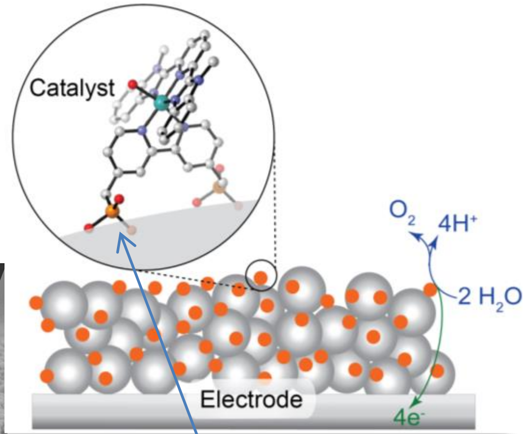
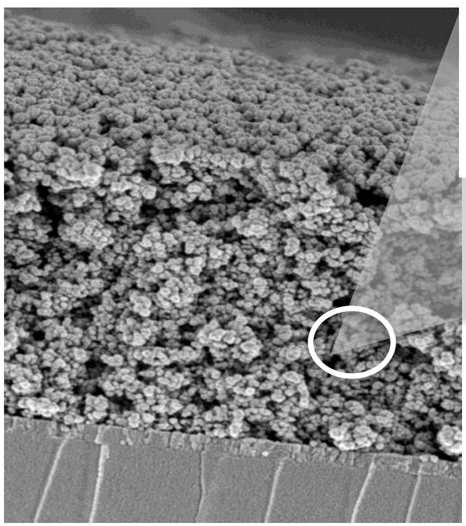
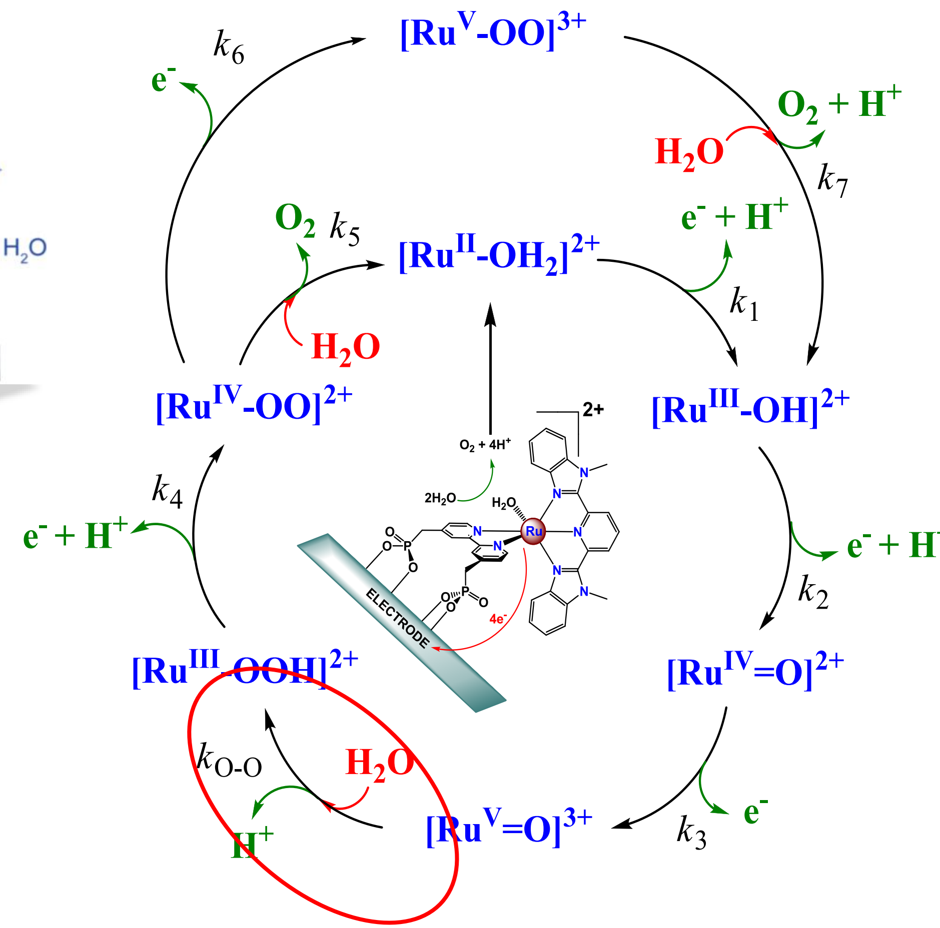




1 µm

Unstable toward hydrolysis in base!

***nano*ITO on FTO ($Sn(IV):In_2O_3$)**



Z. Chen, P. Hoertz, *Dalton Trans.*, **2010**, 6950

Atomic Layer Deposition (ALD) Surface Stabilization

Rate Enhancement of 10^6! (Vannucci, Alibabaei, Hanson)

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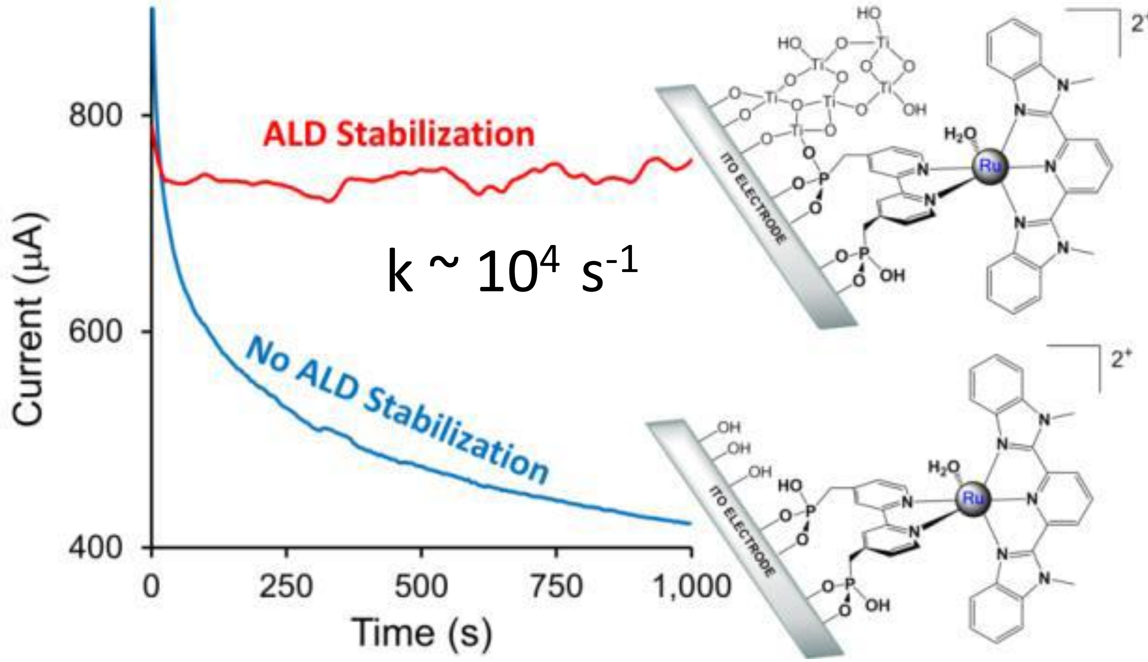
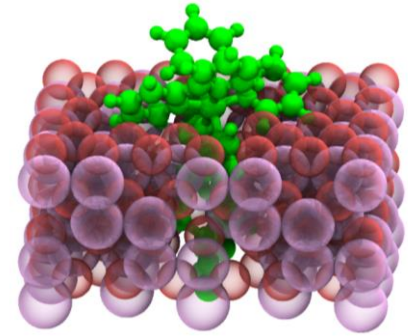
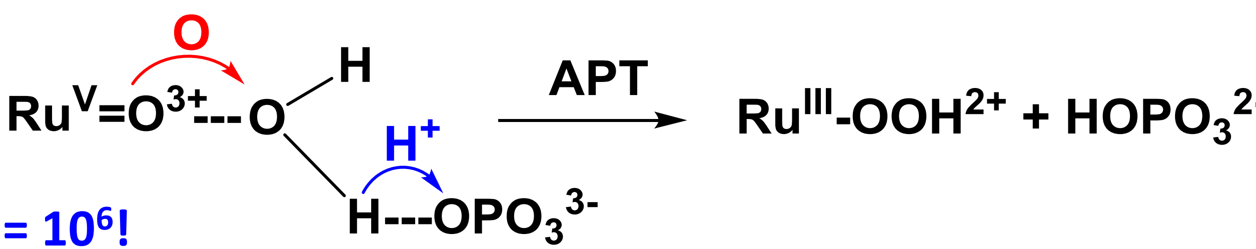




-RuP^{2+} (Al_2O_3)
Alex Lapides,
Chris Dares



Water Oxidation:
k(pH 11; 1M PO_4^{3}))/k(pH1) = 10^6!
Atom-Proton Transfer
to PO_4^{3-}; OH^- attack

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Chromophore-Catalyst Assembly

Mechanism of water oxidation (Norris, Concepcion)

$$nano\text{ITO-}[\text{Ru}_a^{\text{II}}\text{-Ru}_b^{\text{II}}\text{-OH}_2]^{4+} \xrightarrow{-e^-,\ -H^+} nano\text{ITO-}[\text{Ru}_a^{\text{II}}\text{-Ru}_b^{\text{III}}\text{OH}]^{4+}$$

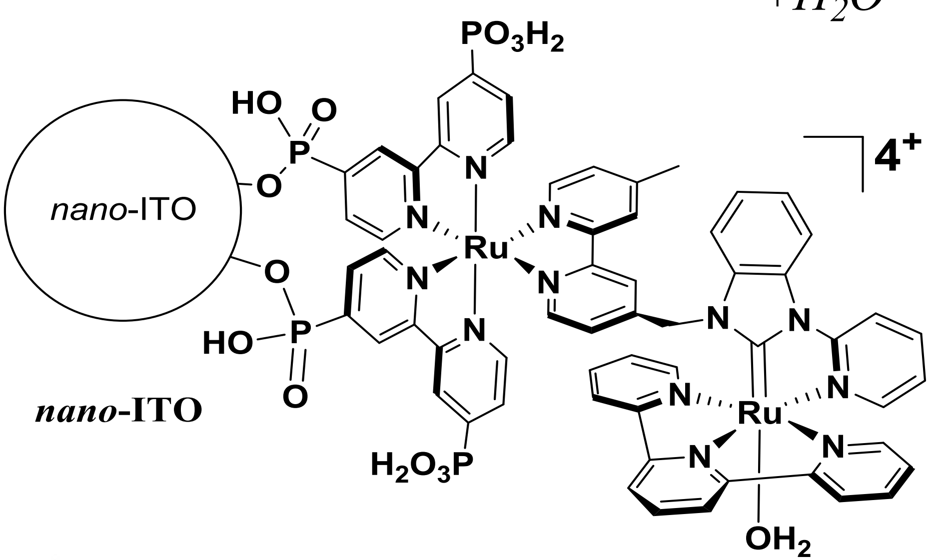
$$nano\text{ITO-}[\text{Ru}_a^{\text{II}}\text{-Ru}_b^{\text{III}}\text{-OH}]^{4+} \xrightarrow{-e^-,\ -H^+} nano\text{ITO-}[\text{Ru}_a^{\text{II}}\text{-Ru}_b^{\text{IV}}\text{=O}]^{4+}$$

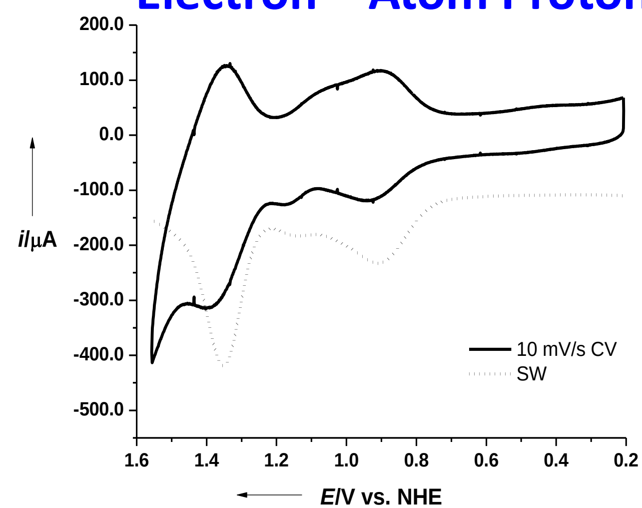
$$nano\text{ITO-}[\text{Ru}_a^{\text{II}}\text{-Ru}_b^{\text{IV}}\text{=O}]^{4+} \xrightarrow[-\text{H}^+]{-e^-} nano\text{ITO-}[\text{Ru}_a^{\text{III}}\text{-Ru}_b^{\text{IV}}\text{=O}]^{5+}$$

$$nano\text{ITO-}[\text{Ru}_a^{\text{III}}\text{-Ru}_b^{\text{IV}}\text{=O}]^{5+} + \text{H}_2\text{O} \xrightarrow[-H^+]{\text{RDS}} nano\text{ITO-}[\text{Ru}_a^{\text{II}}\text{-Ru}_b^{\text{III}}\text{-OOH}]^{4+}$$

$$nano\text{ITO-}[\text{Ru}_a^{\text{II}}\text{-Ru}_b^{\text{III}}\text{-OOH}]^{4+} \xrightarrow[+H_2O]{-H^+,\ -e^-} nano\text{ITO-}[\text{Ru}_a^{\text{II}}\text{-Ru}_b^{\text{II}}\text{-OH}_2]^{4+} + \text{O}_2$$

Electron – Atom Proton Transfer





DSPEC Water Splitting: Timescales
Interfacial Dynamics

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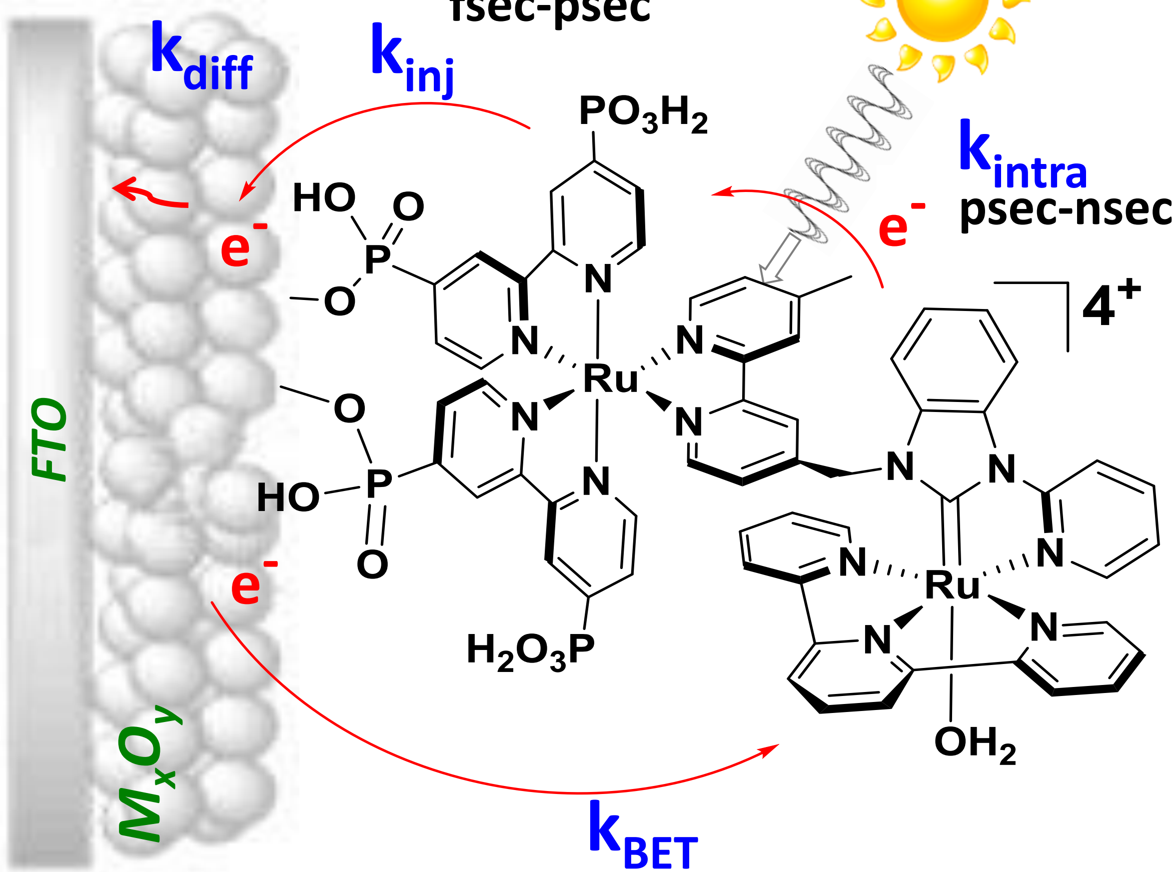
Semiconductor:
5-10 μ; ~ 1 msec

Injection:
fsec-psec

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



Molecular Catalysis:
> 0.5 s^{-1}

Back Electron Transfer: μsec

Surface Binding:
Indefinite

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Solar Water Splitting. Atomic Layer Deposition
Core/Shell Advantage (Alibabaei, Brennaman, Farnum)

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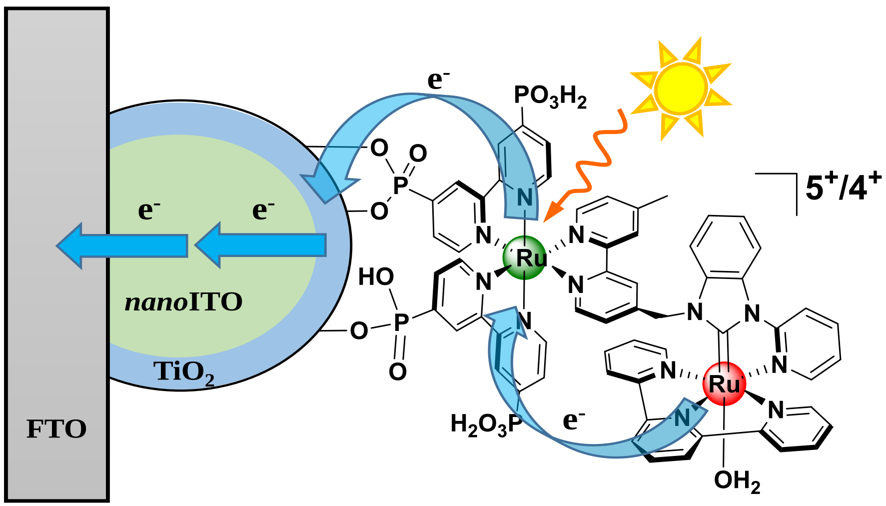
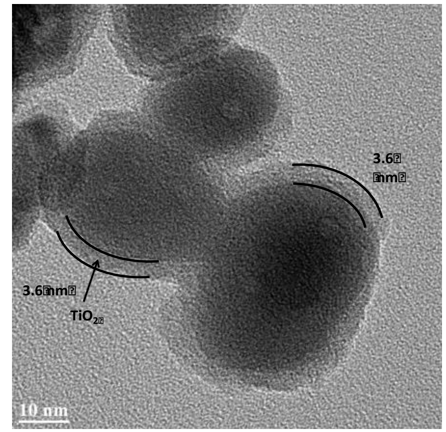




Core/Shell Advantage

3.6 nm shell

***nano*ITO/TiO_2**

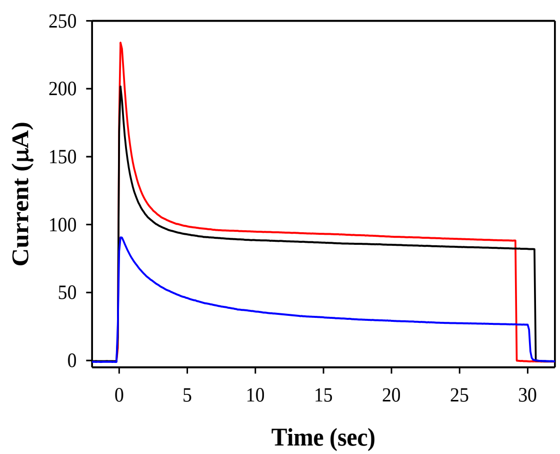
Parsons NCSU

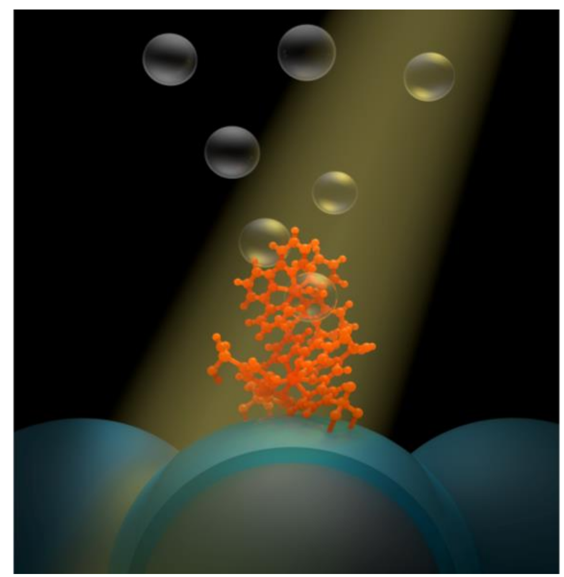
$$\text{FTO}|nano\text{ITO/TiO}_2\text{-[Ru}_a^{II}\text{-Ru}_b^{II}\text{-OH}_2]^{4+}\|\text{Pt} \xrightarrow{4h\upsilon} \text{PtFTO}|nano\text{ITO/TiO}_2\text{-[Ru}_a^{II}\text{-Ru}_b^{II}\text{-OH}_2]^{4+} + \text{O}_2\|\text{Pt} + 2\text{H}_2$$

APCE = 4.5%

455 nm

E_{bias} = -0.2V





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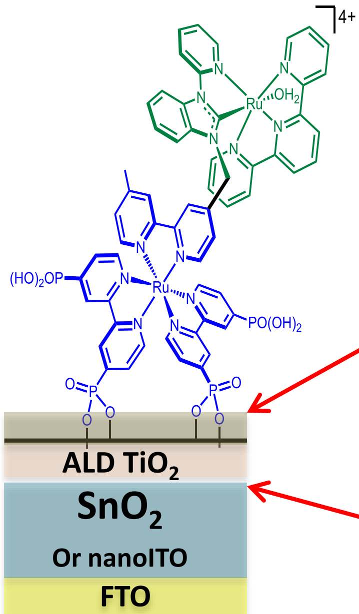
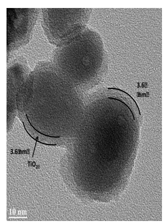
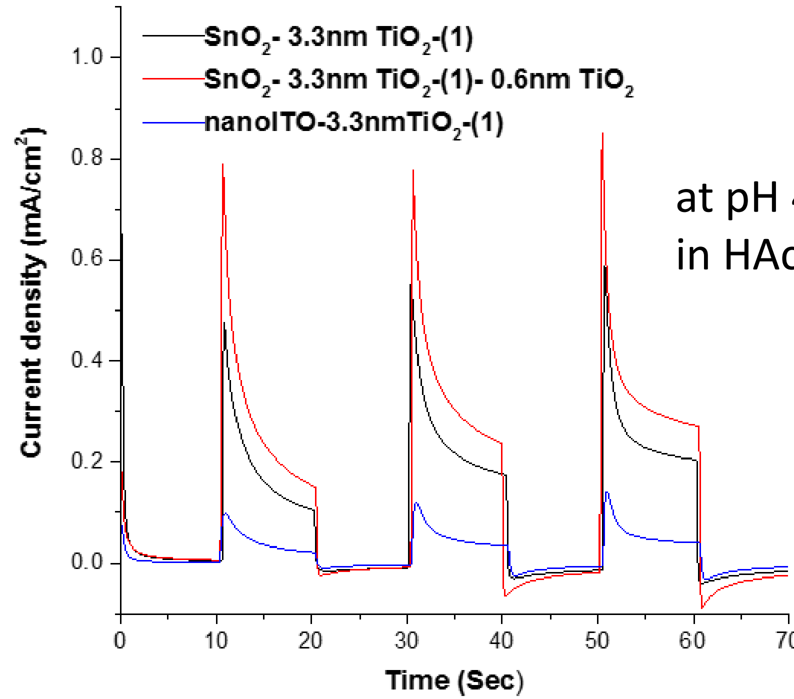
Comparison: SnO_2/TiO_2 and *nano*ITO core/shells *Photoanodes for water splitting (Alibabaei)*



Overlayer
TiO_2 or Al_2O_3

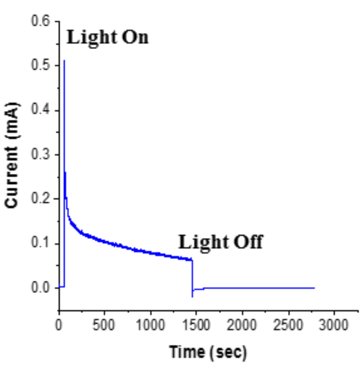


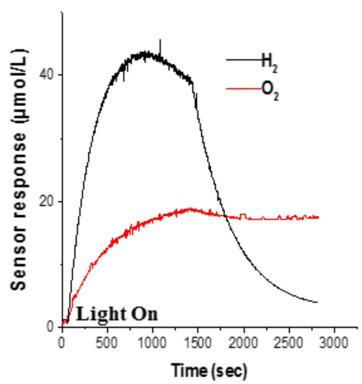
Core/Shell
3-4 nm of TiO_2



at pH 4.6
in HAc/Ac$^-$

TiO_2 (3.3 nm); Pt counter, 200 mV (vs Ag/AgCl) in 0.5 M $LiClO_4$

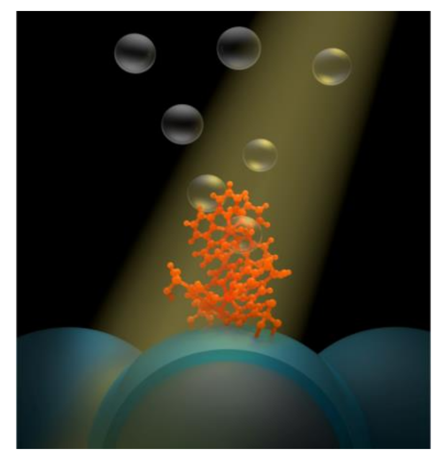




(455nm LED at 46.2 mW/cm^2, E_{bias} = -0.6 V)

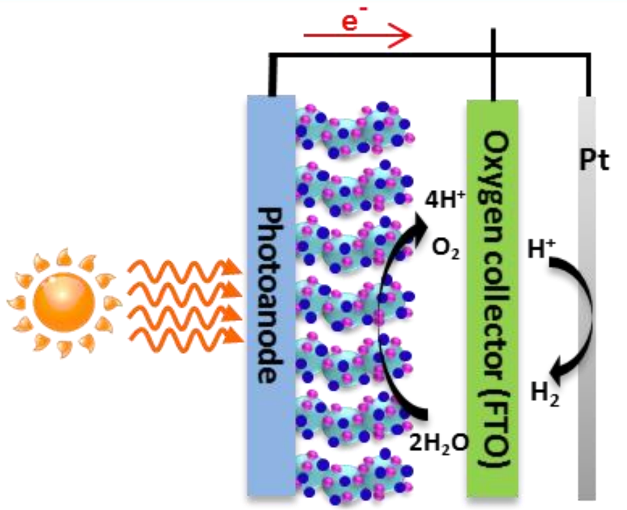
APCE (445nm)

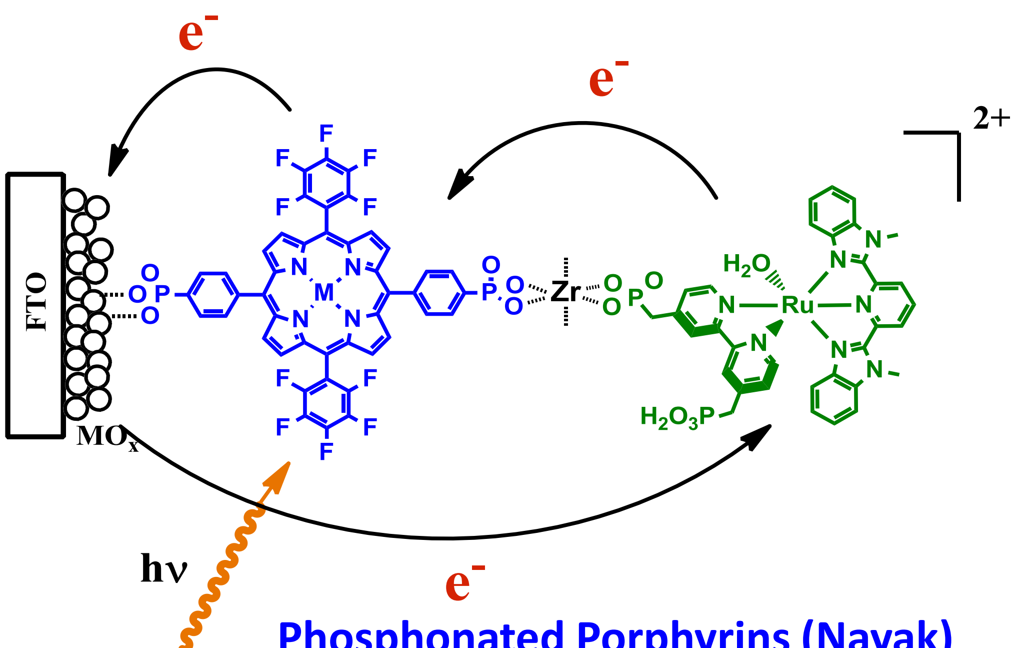
core	*APCE*
nanoITO	4.5%
SnO_2	>20%



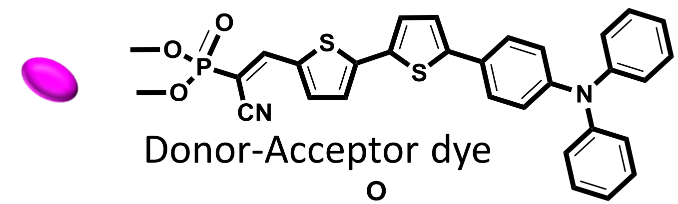
Water Splitting DSPEC: Maximize Efficiency, Stability
Challenges, New Assembly Strategies

- Surface assembly, new strategies
- Surface stabilization
- Avoid losses from oxidized chromophores
- Control rates and interfacial dynamics
- Extend light absorption further into the visible
- Implement tandem configurations

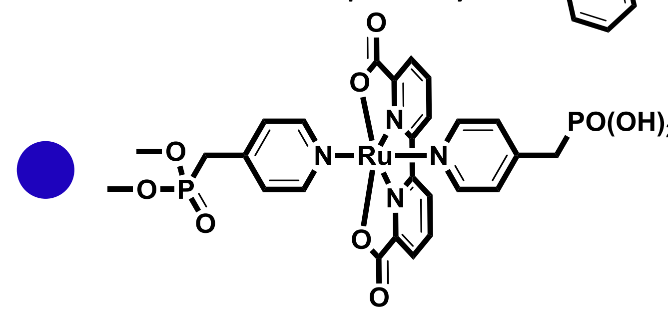




Phosphonated Porphyrins (Nayak)



Donor-Acceptor dye



Water Oxidation Catalyst

Organic Dyes (Wee)

Chromophore-Catalyst Assemblies

New Assembly Strategies *(Ashford, Chem. Rev., 2015)*

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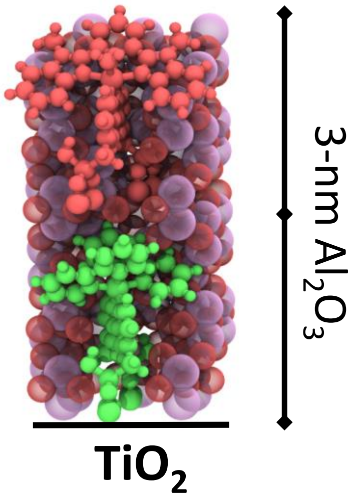
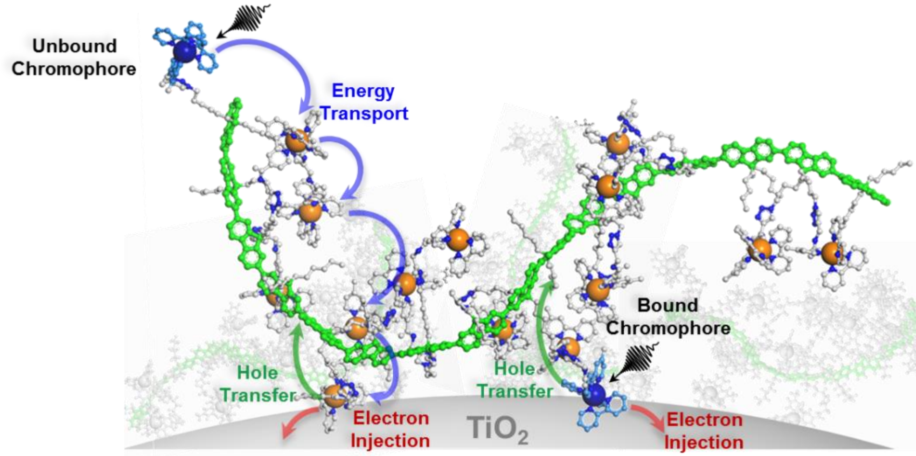
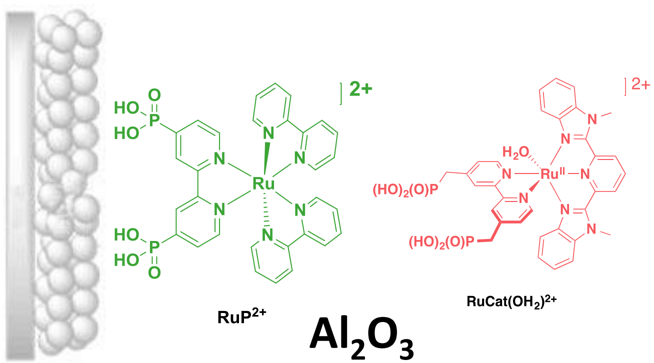
$TiO_2|RuP^{2+}(10AO)\text{-}RuCat\text{-}OH_2^{2+}$

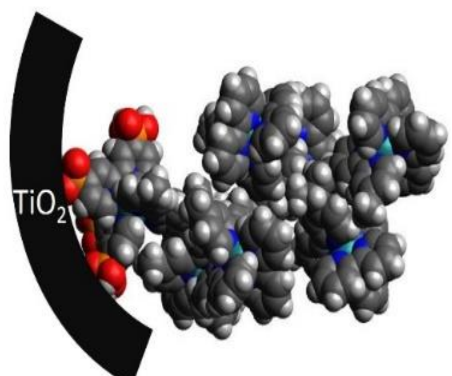


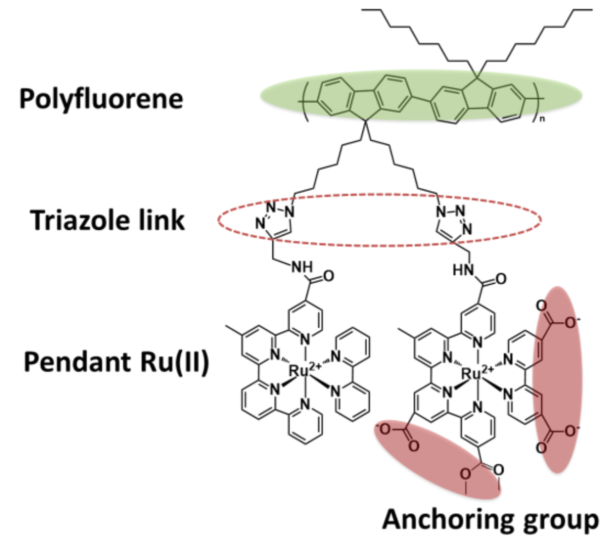


Derivatized Polymers (U Florida, Georgia Tech)



ALD "Mummy" Assemblies (Lapides)





Intra-Cavity Electro-Assemblies (Fang)

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Electro-Assembly DSPEC
TiO_2-RuP- Ru(bda)

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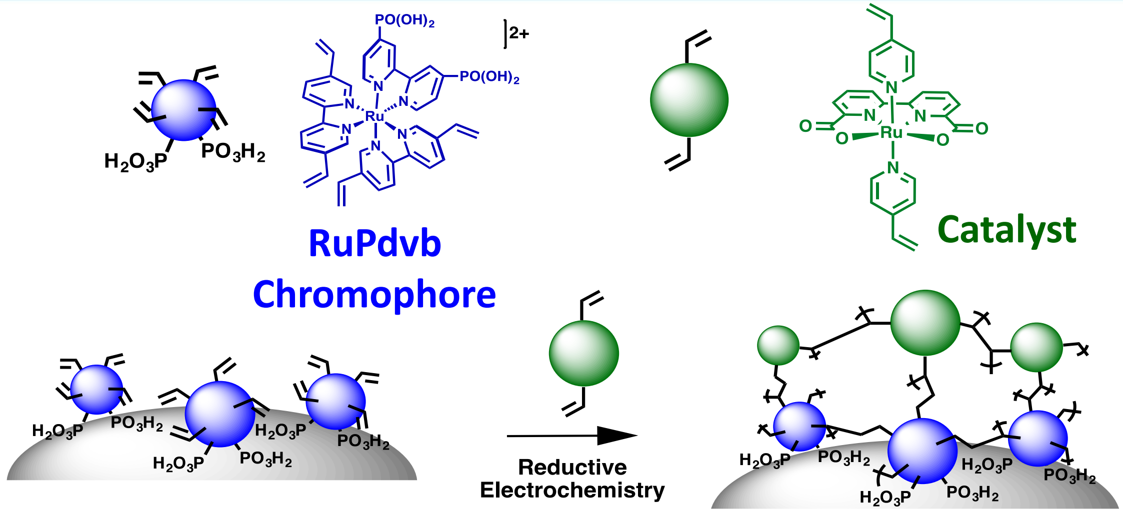
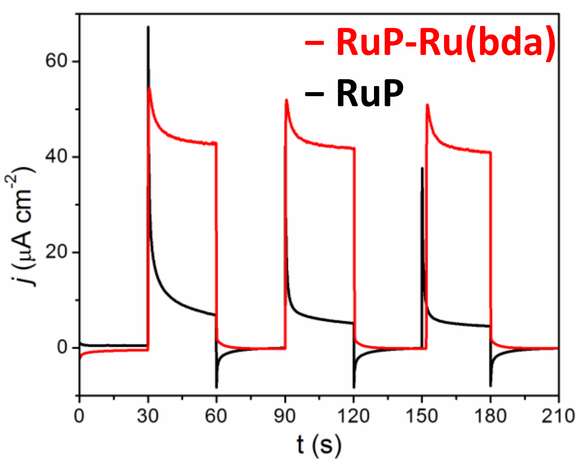
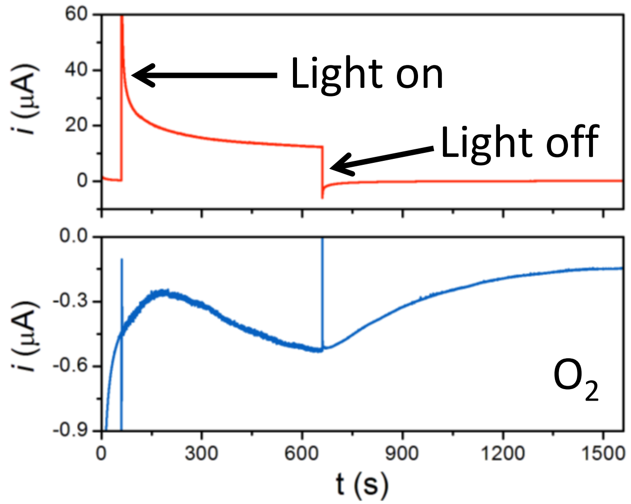
Ashford, Sherman et al. *ACIE*, **2015**



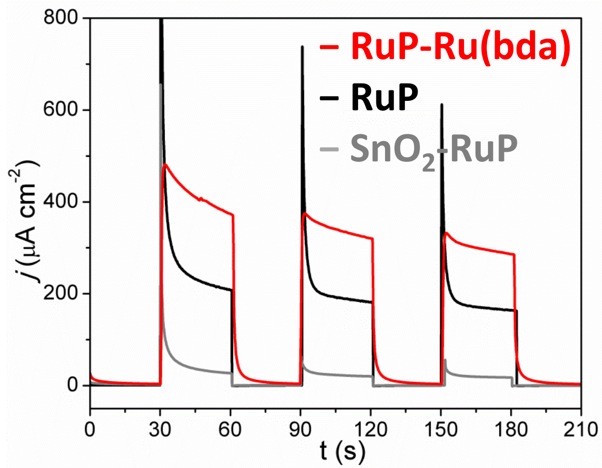
0.1 M $H_2PO_4^-/HPO_4^{2-}$ pH 7; 0.4 M $NaClO_4$; AM1 White light 100 mW cm^{-2}; E_{bias} = -0.4V vs. SCE



TiO_2



Collector (ITO) electrode
-0.85 V vs. SCE



SnO_2/TiO_2 Core/Shell

Electrocatalyzed CO_2 Reduction
Selectivity, Aqueous, Rapid, Robust (Alex Miller)

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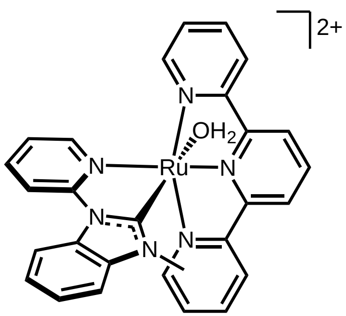
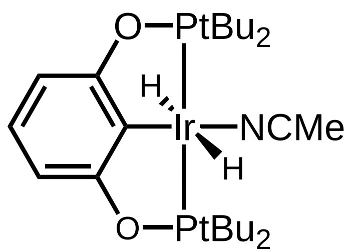
Controlling Electrocatalytic CO_2 Reduction Selectivity In Water

- Ru catalysts reduce CO_2 to syn gas with **tunable H_2:CO ratio**
- Ir catalysts reduce CO_2 to **formate** with no H_2 or CO byproduct
- **Nanoparticle film** catalysts produce CO, formate, CH_4

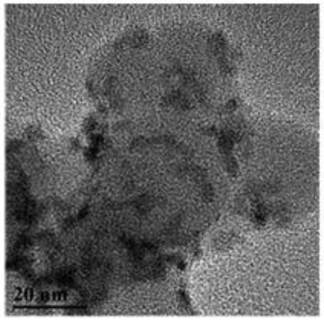


(Chen, Kang)

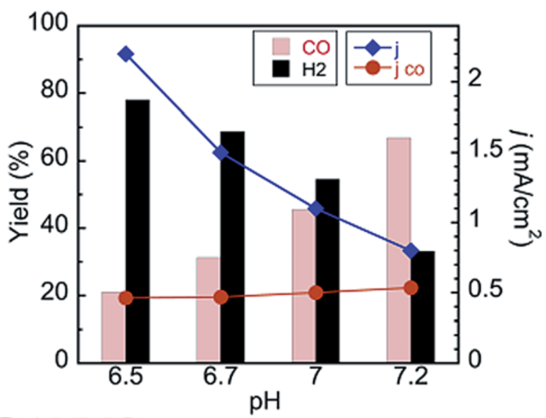
Proc. Natl. Acad. Sci., **2012**, *109*, 15606
Energy Environ. Sci., **2014**, *7*, 4007
Chem. Commun., **2014**, *50*, 335

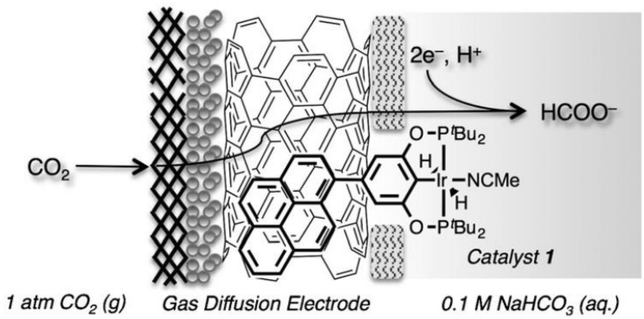


J. Am. Chem. Soc., **2012**, *134*, 5500
Chem. Sci. **2013**, *4*, 3497



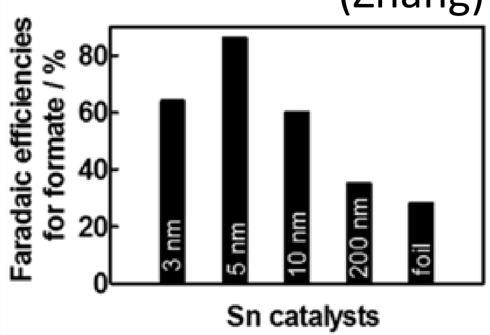
J. Am. Chem. Soc. **2014**, *136*, 1734





Continuous, large-scale formate production
Angew. Chem. Int. Ed. **2014**, *53*, 8709

(Zhang)



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Photocathodes for CO_2 Reduction
NiO and beyond NiO (Jim Cahoon)

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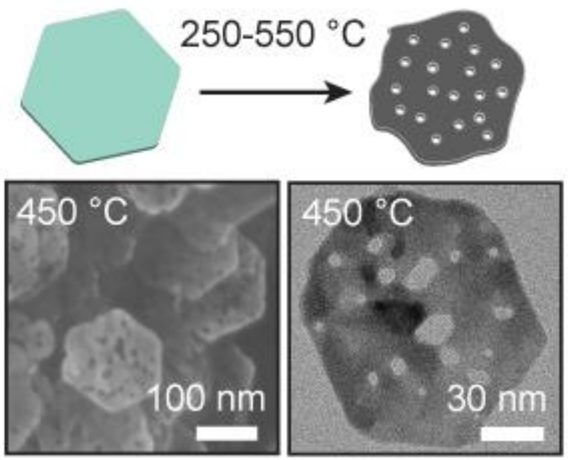
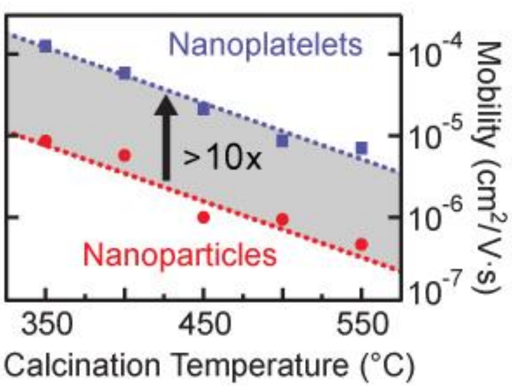
Redesigned "2D" NiO

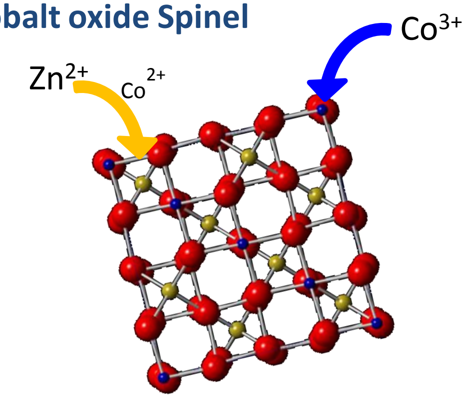


Improved Charge Transport and Device Performance



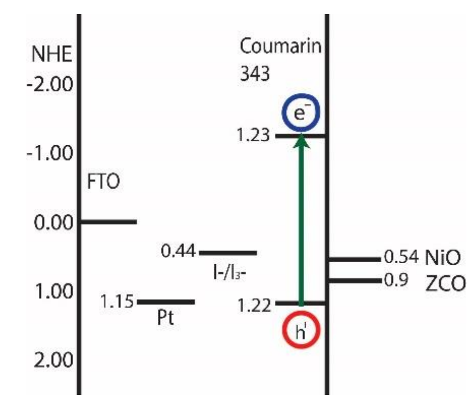
New cathode oxides

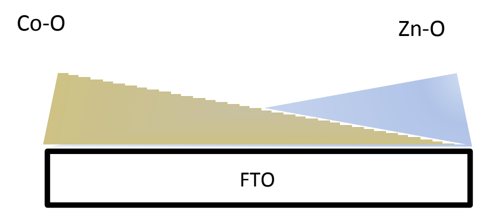
Zinc-cobalt oxide Spinel



Substitution of Zn^{2+} into tetrahedrally coordinated Co^{2+} results in p-type behavior.

P-type DSSC





Mercado and Nozik

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UNC Energy Frontier Research Center
Solar Fuels

SOLAR FUELS

U.S. DEPARTMENT OF ENERGY | Office of Science

SCIENTIFIC ACHIEVEMENTS

- DSPEC: Modular approach, assembly design
- Application of core/shell structures to water splitting
- Water oxidation catalysis
- Assembly based interfacial dynamics
- Selective reduction of CO_2 to formate or syngas

- 206 peer-reviewed publications (h-index 35) – 65% co-authored by >1 senior investigator
- 24 patent applications
- World-class user facilities in catalysis, spectroscopy, photolysis, device fabrication, synthesis - staffed by Ph.D. research scientists

TRAINING THE ENERGY WORKFORCE OF THE FUTURE

- Trained or in training:
  - ✓ 60 postdoctoral fellows
  - ✓ 80 graduate students
  - ✓ 30 undergraduates
- 50 graduate degrees awarded
- > 120 careers in industry, academia, government, policy, public sector

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MODULAR INTEGRATED TEAM-BASED RESEARCH

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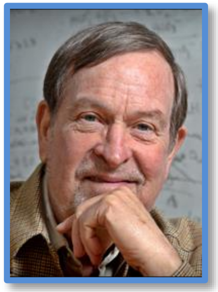


Tom Meyer
Director, UNC

John Papanikolas
Deputy Director, UNC

Jerry Meyer
Deputy Director, UNC

UNC EFRC SOLAR FUELS

- **Synthesis** (T. Meyer/Miller/Schanze*)
  - **Catalysis**: Brookhart, Glish, T. Meyer, ***Miller***, Muckerman*, Murray, Schauer, Templeton
  - **Assemblies**: T. Meyer, Papanikolas, Reynolds*, ***Schanze****, Templeton, Waters
- **Interfaces & Devices** (Papanikolas/Cahoon/G. Meyer)
  - **Interface Dynamics**: Cahoon, Dempsey, Kanai, G. Meyer, T. Meyer, Moran, ***Papanikolas***
  - **Photocathode**: ***Cahoon***, Dempsey, Kanai, G. Meyer, T. Meyer, Nozik*, Papanikolas
  - **Photoanode**: Cahoon, Dempsey, Lopez, ***G. Meyer***, T. Meyer, Moran, Nozik*, Papanikolas

Maurice Brookhart
UNC

Jim Cahoon
UNC

Jillian Dempsey
UNC

Gary Glish
UNC

Yosuke Kanai
UNC

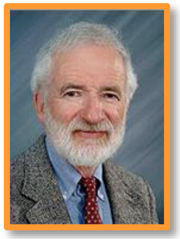
Rene Lopez
UNC

Andy Moran
UNC

Alex Miller
UNC

Jim Muckerman*
BNL

Royce Murray
UNC



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UC Boulder/NREL

John Reynolds*
Georgia Tech

Kirk Schanze*
U Florida

Cindy Schauer
UNC

Joe Templeton
UNC

Marcey Waters
UNC

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Annual UNC EFRC Research Review with External Advisory Board – May 2014

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