

Artificial Photosynthesis: Where are we now? Where can we go?

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Abstract:

Widespread implementation of renewable energy technologies, while preventing significant increases in greenhouse gas emissions, appears to be the only viable solution to meeting the world's energy demands for a sustainable energy future. The final energy mix will include conservation and energy efficiency, wind, geothermal, biomass, and others, but none more ubiquitous or abundant than the sun. Over several decades of development, the cost of photovoltaic cells has decreased significantly with lifetimes that exceed 25 years and there is promise for widespread implementation in the future. However, the solar input is intermittent and, to be practical at a truly large scale, will require an equally large capability for energy storage. One approach involves artificial photosynthesis and the use of the sun to drive solar fuel reactions for water splitting into hydrogen and oxygen or to reduce CO₂ to reduced carbon fuels. An early breakthrough in this area came from an initial report by Honda and Fujishima on photoelectrochemical water splitting at TiO₂ with UV excitation. Significant progress has been made since in exploiting semiconductor devices in water splitting with impressive gains in spectral coverage and solar efficiencies. An alternate, hybrid approach, which integrates molecular light absorption and catalysis with the band gap properties of oxide semiconductors, the dye-sensitized photoelectrosynthesis cell (DSPEC), has been pioneered by the University of North Carolina Energy Frontier Research Center (UNC EFRC) on Solar Fuels. By utilizing chromophore-catalyst assemblies, core/shell oxide structures, and surface stabilization, the EFRC recently demonstrated a viable DSPEC for solar water splitting.

Keywords:

Artificial Photosynthesis; Solar Fuels; Photoelectrochemical; Dye-Sensitized; Water Oxidation; Carbon Dioxide Reduction

1. Introduction:

Energy is a unifying theme across the physical and natural sciences, geopolitics, and economics. How we use, distribute and manage our energy resources is at the forefront of the global agenda. There is steadily increasing demand as global affluence increases, and the nagging deleterious effects of climate change if renewable resources aren't used to supply this increasing demand. As a perspective of present and future needs, in September 2000 the United Nations millennium development goals (MDGs) promised to halve the global population living in extreme poverty by 2015. The result has been remarkably successful, decreasing the number

of people subsisting on \$1 a day from 43% in 1990 to 21% by 2010.¹ In the summer of 2013, a list of post-2015 MDGs were recommended to the UN, most notably the eradication of extreme poverty by 2030. As shown in many studies, an increase in the global standard of living will result in increasing energy consumption. In Sub-Saharan Africa alone the economy is estimated to quadruple by 2040 with an 80% increase in energy demand.²

Until now, the global community's energy demands have been largely met by fossil fuels. On the short term, the concept of "Peak Oil" and the predicted decline of oil reserves has been overcome by the advent of modern exploration techniques and the use of horizontal drilling and hydraulic fracturing technologies allowing access to oil and shale gas reserves that were previously out-of-reach. Use of the new technologies comes with an environmental risk, including the impact of methane leakage on global warming³ and potential contamination of ground-water. In addition, many of the predictions for shale gas reserves relied on coarse-grain modeling⁴ with more recent fine-grain analyses resulting in more conservative forecasts. They predict a peak in production in 2020 followed by slow declines thereafter.^{4,5}

In any case, the combustion of fossil fuels has been implicated in the increasing levels of atmospheric CO₂ and the resulting detrimental effects on the global climate. At the time of this writing, delegates from 196 countries are meeting at the 20th Conference of the Parties to the UN Framework Convention on Climate Change to detail objectives that will insure that the rise in global temperature will not rise more than 2°C by developing policies that reduce greenhouse gas emissions.⁶ Computer models show that further increases could result in catastrophic damage to the planet with drought, melting ice sheets, and shrinking glaciers leading to rising sea levels and food and water shortages.⁶ The cause for alarm is as much economic as environmental. An increase of ~20 inches in sea level would result in the displacement of an estimated 150 million people from submerged port cities by 2070 (including areas of Shanghai and New York City), with property losses of \$35 trillion.⁷

To prevent a temperature rise beyond 2°C global emissions must be controlled peaking within the next ten years and declining to half of the current level by 2050. The international community is responding, with the US pledging to reduce 2005 level emissions by 28% by 2025, the EU planning to cut their emissions by 40% of 1990 levels by 2030, and China reaching peak emissions by 2030.⁸

Continued reliance on fossil fuels will soon present a global paradox with eradication of poverty and decreasing global emissions in direct competition. If the increasing demand for energy is met with traditional fossil fuels without CO₂ capture and storage, reduced emission goals will fail. To achieve both, new technologies are needed to meet the energy demands of developing economies without increasing the global rate of greenhouse gas emissions.

The need will be met by integrating a variety of energy sources – wind, biomass, geothermal, hydro, etc. – but the major renewable, carbon free energy source is the sun. In one hour the sun provides ~10,000 times the energy currently consumed by the world in a year. In the past five years the cost of providing electricity, using either solar or wind power, has plummeted making these renewable options less expensive than coal or natural gas in some markets including the Great Plains and Southwestern United States.⁹ These advances have been triggered by new technology and have been fueled, in part, by generous tax subsidies that have decreased the cost of utility-scale solar electricity to 5.6 cents/kW-h and wind to 1.4 cents/kW-h. By comparison, the cost for natural gas is currently 6.1 cents/kW-h and for coal is 6.6 cents/kW-h. Without subsidies, the cost of solar would rise to 7.2 cents/kW-h and wind to 3.7 cents/kW-h.

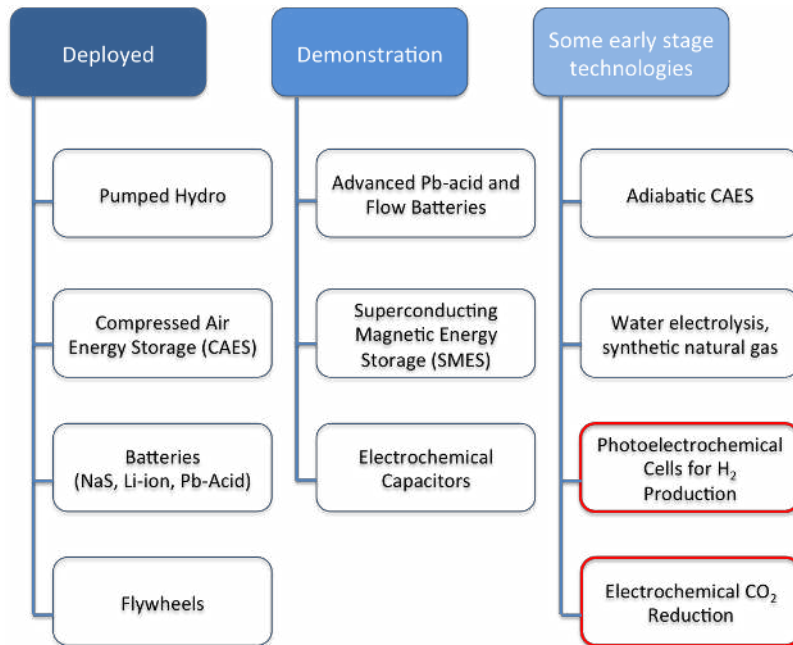


Figure 1. Examples of energy storage technologies and their relative stages of development. Technologies based on artificial photosynthesis are highlighted in red. Adapted from Department of Energy “Grid Energy Storage”¹⁰

More importantly, the real cost of photovoltaic cells (PV) decreased by a factor 59 between 1976 and 2008 with device lifetimes that now exceed 25 years.¹¹

Although promising and growing in importance in the global energy economy, both solar and wind energy suffer from a serious limitation. Both are intermittent. To replace conventional power plants, methods for storing the output of both will need to be developed, for use at night for solar and when the wind isn't blowing. Driven by the need for load leveling and, increasingly to support wind and solar, the field of energy storage is rapidly growing. It includes a diverse range of technologies based on chemical or mechanical storage methods. Examples of chemical storage include batteries and thermal energy storage in materials with high thermal capacitance. Compressed air, flywheels, and pumped hydro, are examples of mechanical energy storage. Figure 1 summarizes other energy storage examples and their current stages of development. In a Grid Energy Storage Report published at the end of 2013, the United States Department of Energy reported that 202 storage systems had been deployed with a cumulative operational capability of 24.6 GW.¹⁰ The vast majority of this stored power (~95%) was sourced from pumped hydro plants operated by major utility companies (Figure 2). Despite its large presence as a source for energy storage, it is unlikely that pumped hydro will become a predominant energy storage medium. In addition to being limited to areas proximal to a large body of water, the energy density as a function of weight is comparatively low (Figure 3). In a recent report, Energy Storage Update reported that the number of existing and planned energy storage projects in the US is dominated by Li-ion batteries (~32%). This is followed by thermal storage (~20%) and pumped hydro (~9%).¹²

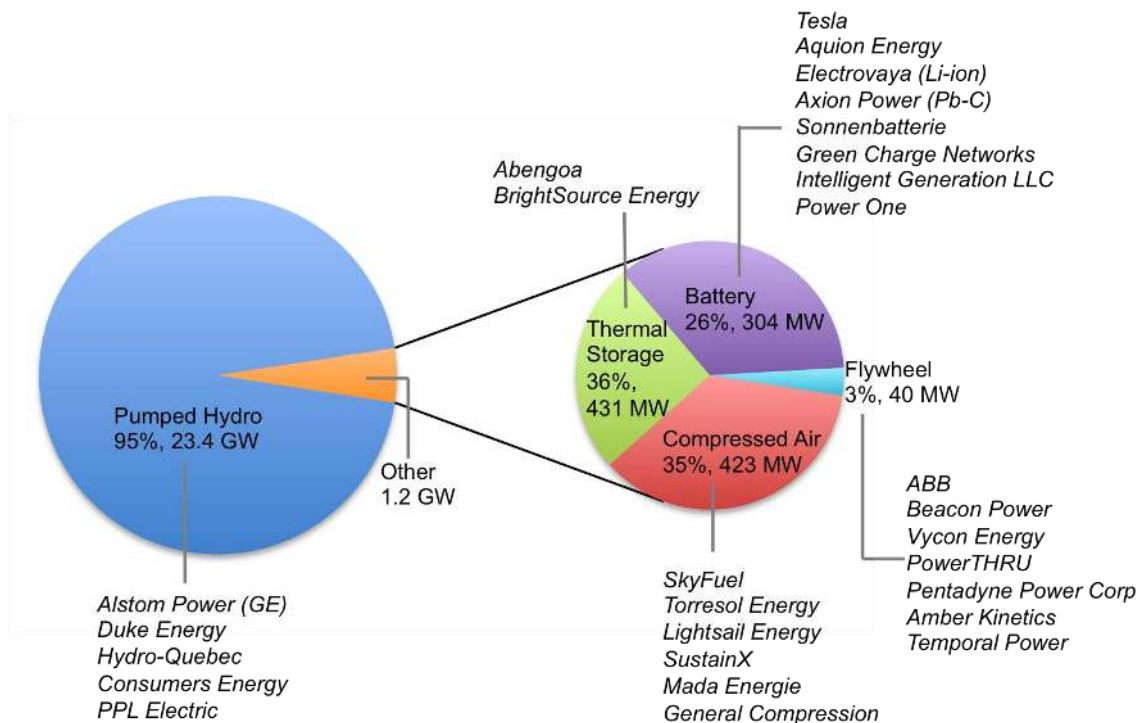


Figure 2. Energy storage technologies currently in use based on market share in the United States at the end of 2013. Examples of companies involved in each sector are shown. Adapted from Department of Energy “Grid Energy Storage”¹⁰

A number of companies, both established and early-stage ventures, with examples shown in Figure 2, have begun to develop alternatives. In all of these schemes, the energy density of the storage medium pales in comparison to the energy density in chemical bonds (Figure 3). Hydrogen gas is the most energy dense and the advantages of switching to a hydrogen-based economy are many. The cost of storing energy as hydrogen is cheaper than storing it as electricity.¹¹ However, the infrastructure for dealing with this gaseous fuel is still nascent because of the considerable infrastructure required to support a hydrogen economy. Carbon-based fuels are relatively inexpensive with a pre-existing infrastructure in place for storage and energy extraction. However, to use them in solar energy conversion and storage schemes will require the evolution of new technologies that mimic plants by integrating light absorption, energy conversion, and catalysis of chemical reactions by artificial photosynthesis.

Photosynthesis in green plants evolved billions of years ago and is extraordinarily complex. It consists of 5 membrane-compartmentalized functional units in the thylakoid membrane of the chloroplast with the external rubisco enzyme for CO₂ reduction. It is a remarkable feat of biological engineering but, given its complexity, it is an inspiration for artificial photosynthesis, not a model.

2. A Brief Review of Photoelectrochemical Cells and Artificial Photosynthesis:

The initial publication by Honda and Fujishima on light-driven water splitting by direct bandgap excitation of TiO₂^{13,14} led to a new area of research. Since their initial study, many publications have appeared on photoelectrochemical water splitting and solar fuels production

based on semiconductors in a variety of liquid junction cell configurations and designs. A summary of water splitting cells is shown in Table 1 based on the criteria developed by Lewis et al.¹⁵ and of Newman et al.¹¹ It has been updated based on an extensive literature survey. Except for a few recent examples, with cell configurations worth noting, the entries selected are for devices with solar hydrogen efficiencies of > 2%.

Solar-to-hydrogen conversion efficiencies in semiconductor photoelectrochemical cells (PEC) improved in performance from less than 1% to 12% from 1975 to 1980.¹⁶ In 1982, Aharon-Shalom and Heller¹⁷ reported efficiencies of 11.4 and 13.3% in cells based on single p-type p-InP photocathodes, coated with either rhenium or rhodium, respectively. Periodic cycling of the photocathodes to the open circuit potential, V_{OC} , was required to maintain cell efficiencies by restoring passivating oxide layers to minimize recombination.

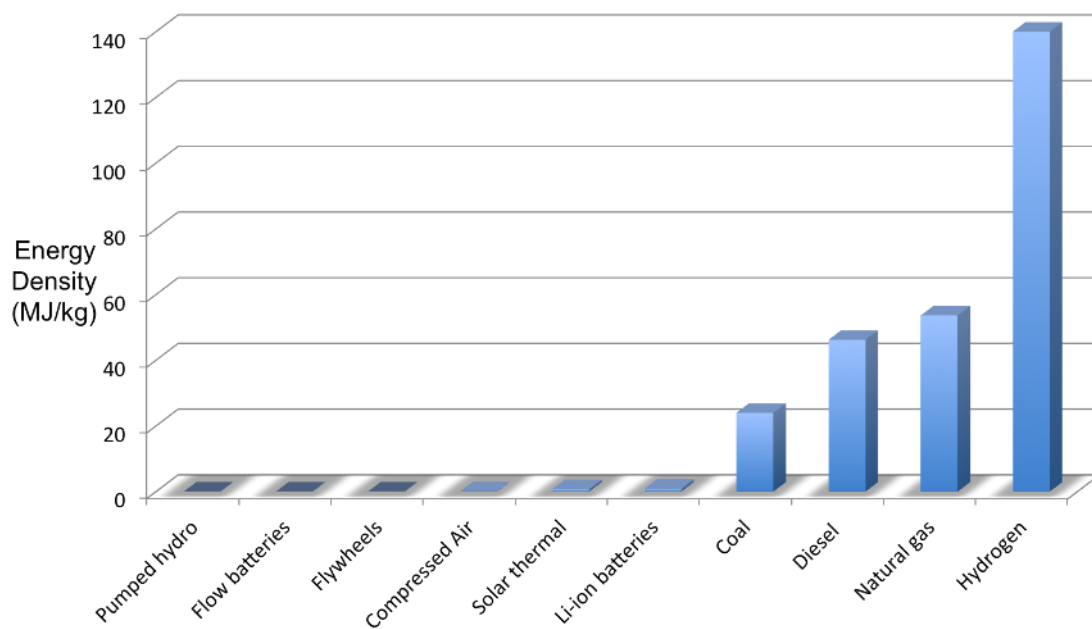


Figure 3. Energy storage media plotted as a function of energy density.

In 1987, Bockris et al.¹⁸ described a tandem photocathode (p-InP with electrodeposited Pt)/photoanode (n-GaAs protected by Mn-oxide) PEC with an efficiency of 8.2% for solar hydrogen conversion with a 10-hour-stability window which decreased in efficiency by 10% after the first hour of operation.

A hydrogen production efficiency of 12.4% was reported for an integrated, monolithic PEC/PV device, with a p-GaInP₂ working photocathode and p/n-GaAs anode by Khaselev and Turner¹⁹ in 1998. In 2001, they improved the efficiency to 16.5% in a multi-junction, monolithic PV/electrolysis cell with a tandem n/pn/p GaInP/GaAs junction in ohmic contact with the external solution.²⁰

A remarkable conversion efficiency of 18.3% was obtained by Licht et al. in 2000²¹ for a device based on p/n-AlGaAs on Si for evolving H₂ and O₂ with RuO₂ and Pt(black) as catalysts. The resulting solar photoelectrolysis cell maintained a steady state photocurrent for over 14 h.

Devices based on triple-junction amorphous silicon or III-V semiconductors have demonstrated fair efficiencies, see Table 1, but with noteworthy stabilities with continuing

performance for up to 31 days achieved by Kelly and Gibson.²² Cost and the complexity of device preparation are major barriers to commercial application.²³

Simpler approaches with Tandem cells for water cleavage based on an oxide photoanode and a dye-sensitized solar cell (DSC), with complementary absorbing layers, first appeared in 1999.²⁴ In one approach, a structured WO_3 photoanode²⁵ was used in series with a DSC^{26,27} or an Fe_2O_3 photoanode²⁸ coupled to a DSC.²⁵ In 2012, results for unassisted water splitting were published for $\text{Fe}_2\text{O}_3/\text{DSC}$ and WO_3/DSC cells, with 1.17% and 3.1% efficiencies, respectively.²³ The use of a trilayer Tandem device, $\text{Fe}_2\text{O}_3/\text{DSC}$ -squareene dye/ DSC -panchromatic dye, achieved an overall conversion efficiency of 1.36% with a AM1.5 solar light source.²⁹

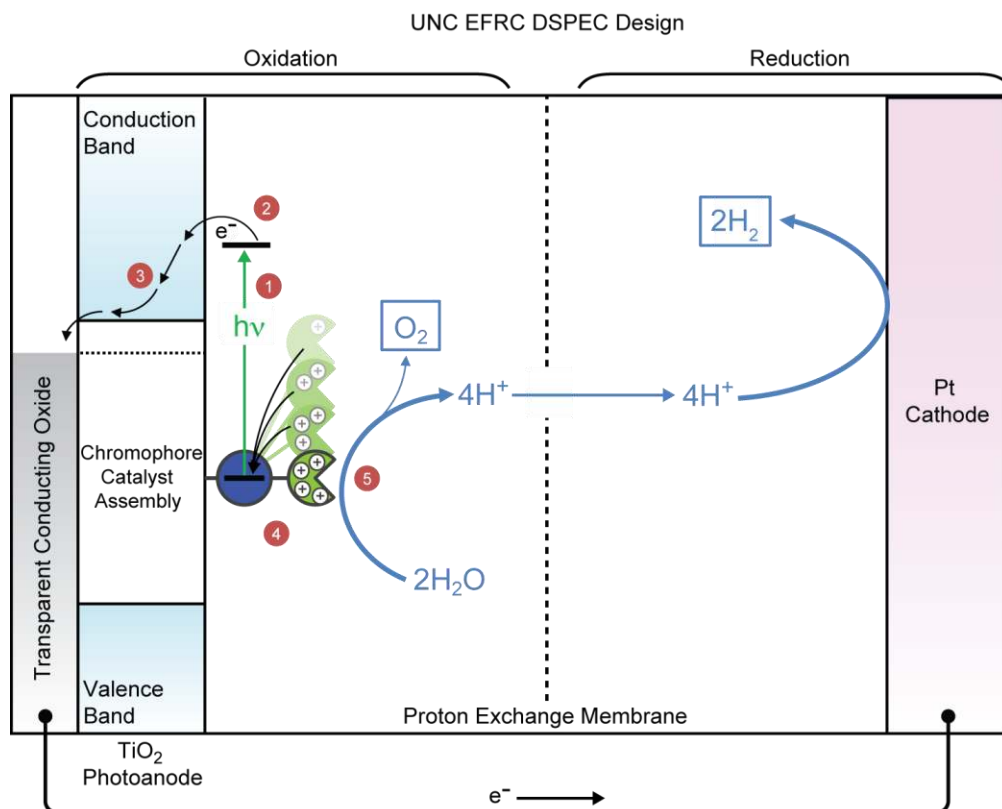


Figure 4. Schematic illustration of a DSPEC for water splitting into hydrogen and oxygen. The steps labeled in the diagram illustrate: (1) Chromophore light absorption to give a surface-bound excited state; (2) Electron injection by the excited state into the conduction band of the semiconductor; (3) Transfer of the injected electron into an external circuit to the cathode. (4) Electron transfer from the catalyst to the chromophore beginning the process of catalyst activation. (5) Steps 1-4 are repeated four times to build up the oxidative equivalents for water oxidation and oxygen evolution at the photoanode. An applied bias of ~ 0.2 V is required to drive $\text{H}_2\text{O}/\text{H}^+$ reduction at the cathode to completion.

The development of a related cell based on a perovskite solar cell resulted in a significant increase in solar-to-electric power conversion efficiency with 12.3% reported for a state of the art $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite tandem solar cell with Ni Fe LDH/Ni foam electrodes for water splitting. Cell lifetime was limited by the stability of the perovskite electrode with improvements possible by passivation.³⁰

Attempts to use less expensive, earth-abundant materials have been reported and significant progress has been made.^{31,32} In 2011, Reece et al.³³ described a fully integrated solar-driven

water-splitting device consisting of a triple junction amorphous silicon photovoltaic cell interfaced to a nanoparticle cobalt oxide anode and NiMoZn cathode. Water splitting was carried out with efficiencies of 4.7% for a wired configuration and 2.5% for a wireless configuration. Further development led to a PV-EC (photovoltaic driven electrochemical cell) device with an efficiency of 10% or higher by using multiple single-junction solar cells connected in series as mini-modules with operating stabilities of over 7 days.³⁴

An interesting approach utilizing modular non-planar semiconductor geometries and advanced photon management strategies and concepts has been described by the Joint Center for Artificial Photosynthesis (JCAP). A complete water splitting system was assembled from three distinct components – photoanode, bipolar membrane,³⁵ and photocathode. With the focus on producing a practical system, JCAP has reported several significant devices, however, all with low conversion efficiencies to date.^{36,37} Various coating strategies have been explored to improve stabilization of semiconductors, including TiO₂ coatings grown by atomic layer deposition (ALD) to prevent corrosion³⁸⁻⁴¹ and produce durable devices.

Recent reviews have appeared which cover related aspects in artificial photosynthesis including an evaluation of the challenges in generating solar fuels,⁴²⁻⁴⁵ and on CO₂ reduction.^{46,47}

3. The Dye-Sensitized Photoelectrosynthesis Cell (DSPEC):

The dye-sensitized photoelectrosynthesis cell (DSPEC) is based on molecular level light absorption and excited state electron transfer integrated into the architecture of a dye-sensitized solar cell. Ultimately, the DSPEC offers reasonable costs and simple architectures and materials, but in its development it is still in its infancy. To date, far lower performance metrics have been achieved compared to semiconductor-solution junction-based solar cells. DSPECs combine the electron transport properties of nanocrystalline semiconductor films of TiO₂ or SnO₂⁴⁸⁻⁵⁰ and transparent nanocrystalline conducting oxide films, such as *nano*ITO,^{51,52} on transparent conductive oxide substrates. Molecular level-reactions with chromophore-catalyst assemblies, often Ru(II) polypyridyl based,⁵³ are used to produce oxygen at a photoanode⁵¹ with the assembly attached to the semiconductor oxide surface.^{54,55}

3.1 The University of North Carolina at Chapel Hill Energy Frontier Research Center: Center for Solar Fuels (UNC EFRC):

Solar energy conversion and storage by artificial photosynthesis is the central theme of the UNC EFRC. Established in 2009 and funded by the Department of Energy: Basic Energy Sciences, the UNC EFRC is directed by Dr. Thomas Meyer and includes 17 faculty members including three members of the National Academy of Sciences. Faculty are largely from UNC, but also from Georgia Institute of Technology, the University of Florida, and the University of Colorado Boulder. The UNC EFRC has been a leader in helping to train the next generation of energy scientists with 70 Postdoctoral Fellows, 100 graduate students, and 30 undergraduate students either trained or in training.

Inspired by natural photosynthesis, the UNC EFRC's goal is to develop the concept of the DSPEC for applications in water splitting and reduction of CO₂ to reduced carbon fuels. The DSPEC functions as an artificial leaf utilizing molecular assemblies that both absorb light and catalyze water oxidation at an anode or proton/CO₂ reduction at a cathode. A schematic illustration of a DSPEC for solar water splitting is shown in Figure 4. Given the multidisciplinary

research demands that arise in achieving a working DSPEC, research in the UNC EFRC uses a modular approach. Separate but integrated teams focus on the development of individual research elements – catalysts, assemblies, dynamics, photoanode, photocathode - before integrating them into prototype devices. After four years of research, this approach has led to the development of a first DSPEC prototype for solar hydrogen production.

4. DSPEC Research in the UNC EFRC:

Key elements for solar water splitting with a DSPEC photoanode are illustrated in Figure 5. They include: 1) a nanostructured mesoporous n-type semiconductor oxide electrode that is transparent in the visible region of the spectrum, 2) a light harvesting chromophore, and 3) a water oxidation catalyst (Figure 4).

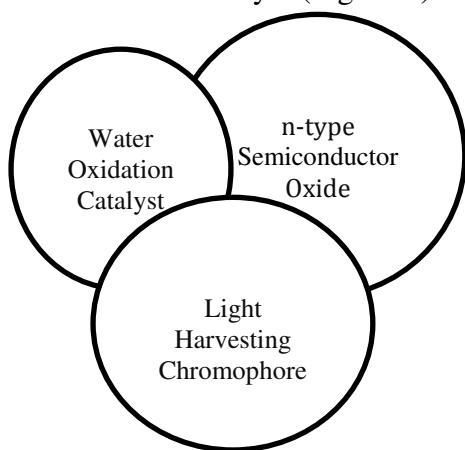


Figure 5. Schematic depiction of key elements in a DSPEC photoanode.

The chromophore and catalyst can be chemically linked or surface assembled on nanocrystalline, nanoparticle films of the semiconductor oxide. Phosphonic or carboxylic acid derivatized ligands on the chromophore are used to tether the assembly to the surface of the oxide. In order to control local interfacial dynamics, and minimize back electron transfer following injection, core/shell oxide structures are used. They consist of a thin (~3-4 nm) external shell of TiO₂ deposited on a nanoparticle film core of either a transparent conducting oxide such as indium tin oxide (ITO) or antimony tin oxide (ATO), or on a semiconducting oxide such as SnO₂.

In water oxidation at a DSPEC photoanode, four excitation-electron transfer cycles are required to meet the $4e^-/4H^+$ demands of the reaction, $2 H_2O - 4 e^- - 4 H^+ \rightarrow O_2$. As illustrated in Figure 4, each activation cycle involves: 1) light absorption, 2) electron injection into the semiconductor, 3) intra-assembly electron transfer activation of the catalyst, and, after four cycles, 4) O₂ evolution. In order to maximize photocurrent efficiencies, an applied bias of ~0.2 V is required when using a TiO₂ based photoanode to drive water splitting.

The efficiency of a water splitting DSPEC is determined by the dynamics of the interfacial processes that occur at the photoanode. Transient absorption measurements show that, if favored energetically and with electronic coupling to the surface, injection occurs on the sub-psec timescale. In assemblies that have been investigated by transient absorption measurements, subsequent electron transfer oxidation of the catalyst is also rapid, typically occurring on the sub-nsec timescale. Following injection, a competition exists between electron migration through the oxide film to the transparent conducting oxide (TCO) and back electron transfer to the oxidized catalyst, surface-bound in the assembly. Even with successful $1e^-$ activation of the catalyst, four excitation-electron transfer activation cycles are required for water oxidation. The accumulated oxidative equivalents have to be long-lived, free from back electron transfer, since the rate of solar insolation in ambient sunlight is only $1-2 s^{-1}$.

Table 1 . Solar-to-fuel efficiencies records.

Research Group	Year	Device Architecture	Surface Catalysts	Materials Systems	Efficiency / %	Lifetime Testing	Ref
Heller <i>et al.</i>	1982	Photocathode	Ru, Re, or Rh @ cathode	p-InP	11.4-13.3	Requires periodic cycling to V_{oc} to maintain high efficiency	¹⁷
Bockris <i>et al.</i>	1985	Tandem PV-PEC	Pt @ cathode RuO ₂ @ anode	Double junction Si	2.6	Not reported	⁵⁶
Kainthla, Zelenay and Bockris	1987	Tandem p/n-PEC	Pt @ cathode MnO/Pt @ anode	p-InP / n-GaAs	8.2	10% efficiency decrease during first hour, then remains constant for 10 h	¹⁸
Tsubomura <i>et al.</i>	1988	PV-PEC	Pt @ cathode RuO ₂ @ anode	Double junction Si	2.93 (Si in solution) 3.23 (Si out of solution)	Not reported	⁵⁷
Bockris <i>et al.</i>	1989	PV-EC	Pt @ cathode RuO ₂ @ anode	Triple junction Si	5	6h; STH > 4%	⁵⁸
Gramaccioni, Selvaggi and Galluzi	1993	PV-EC	Pt @ cathode RuO ₂ @ anode	Triple junction Si	~5	Not reported	⁵⁹
Rocheleau, Miller and Misra	1998	PV-EC	CoMo @ cathode NiFeO @ anode	Triple junction Si	7.5	2h stable current in outdoor test	⁶⁰
Khasalev, Turner	1998	Tandem PV-PEC	Pt @ cathode Pt @ anode	p-GaInP ₂ / p/n-GaAs	12.4	Photocurrent decrease from 120 to 105 mA/cm ² over 20 h	¹⁹
Grätzel <i>et al.</i>	1999	Tandem photoanode/PV	Pt @ cathode	WO ₃ / DSC	4.5	Not reported	²⁴⁻²⁷
Licht <i>et al.</i>	2000	Tandem PV-PEC	Pt @ cathode RuO ₂ @ anode	AlGaAs / p/n-Si	18.3	Stable photocurrent over 14 h	²¹
Khasalev, Bansal and	2001	Tandem PV-PEC	Pt @ cathode	p/n-GaInP ₂ / p/n-GaAs	16.5	9h stable current in outdoor	²⁰

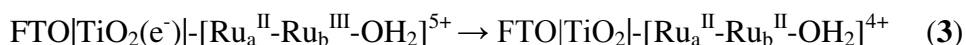
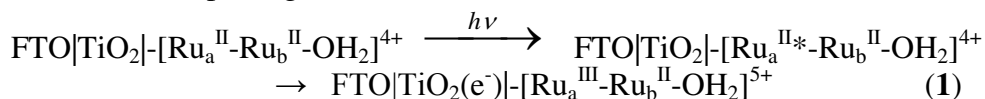
Turner			Pt @ anode	Double junction Si		test	
		PV-EC		Triple junction Si	7.8	Not reported	
Grätzel <i>et al.</i>	2001	Tandem photoanode/PV	Pt @ cathode	Fe ₂ O ₃ / DSC	2.2	Not reported	25, 27, 28
Ohmori <i>et al.</i>	2003	PV-EC	CoMo @ cathode FeNiO @ anode	Triple junction Si	2.8	First 30 min; the efficiency decreased to 2.5% and remained for 18h	61
Park and Bard	2005	PV-EC	Pt @ cathode Pt @ anode	DSC / DSC / DSC	3.7	9mA/cm ² stable current after 20 h	62
Kelly and Gibson	2006	PV-EC	Pt or Ni @ cathode Integrated FTO @ anode	Triple junction Si	5-6	> 31 days of hydrogen production	22
Peharz, Dimroth and Wittstadt	2007	PV-PEC	Pt @ cathode IrO ₂ @ anode	p/n-GaInAs / p/n-GaInP	18	2.3 h stable current outdoor test	63
Imanishi <i>et al.</i>	2009	PV-EC	Pt @ cathode RuO ₂ @ anode	p-CuI / p/n-GaP	2.3	3h constant current	64
Gaillard <i>et al.</i>	2010	Tandem PV-PEC	Pt @ cathode	WO ₃ / Si PV	3.0	Not reported	65
Nocera <i>et al.</i>	2011	PV-EC	NiMoZn @ cathode ITO/amorphous Co @ anode	Triple junction Si	4.7 (wired) 2.5 (wireless)	Stable for 10h in KB _i 1 mol L ⁻¹ , then 20% decrease over next 14h; stable for 30h using FTO instead of ITO	33
Graetzel, Sivula <i>et al.</i>	2012	Tandem photoanode/PV-PEC	Pt @ cathode	WO ₃ / DSC	3.1	-	23
Fujii <i>et al.</i>	2013	PV-EC	Pt @ cathode Pt @ anode	p/n-GaIn/ p/n-InGaAs / p/n-Ge	15 (3 solar cells) 12 (1 PV)	1h constant current and hydrogen production	66

Jacobsson <i>et al.</i>	2013	PV-PEC	Pt @ cathode Pt @ anode	p/n-CuInGaSe / 3 cells	10	27h	⁵³
van de Krol <i>et al.</i>	2013	Tandem PEC	Pt @ cathode Co-P ₁ @ anode	BiVO ₄ Double junction Si	3.6	1h stable photocurrent	⁶⁷
van de Krol <i>et al.</i>	2013	Tandem PEC	Pt @ cathode Co-P ₁ @ anode	BiVO ₄ Triple junction Si	4.9	1h	⁶⁷
Han <i>et al.</i>	2014	PV-PEC	Pt @ cathode Co-P ₁ @ anode	Si:h/Si:H/BiVO ₄	5,2	1 h < 5 % current loss	⁶⁸
Peng, Lee <i>et al.</i>	2014	Tandem PEC-PV	Pt @ cathode Au @ anode	Fe ₂ O ₃ / PV Double junction Si	6.0	40 min measurement of O ₂	⁶⁹
Segalman <i>et al.</i>	2014	PV-EC	Pt @ cathode Pt @ anode	p/n-GaInP ₂ / p/n-GaAs / p/n-Ge	6.2	15h constant current density	⁷⁰
Nocera <i>et al.</i>	2014	PV-EC	NiMoZn @ cathode NiB @ anode	Si minimodules side by side	10	168h constant efficiency	³⁴
Grätzel <i>et al.</i>	2014	Tandem PV	NiFe/Ni foam electrodes	Two CH ₃ NH ₃ PbI ₃ PVs in series	12.3	Decreased photocurrent over 2 hour due to instability of perovskite solar cells	³⁰
Lewis <i>et al.</i>	2014	Tandem PV-PEC	Pt @ cathode	WO ₃ / Si	0.0068	10 min stable photocurrent	³⁶
Hwang, Min <i>et al.</i>	2015	PV-PEC	Au @ cathode Co ₃ O ₄ @ anode	CuInGaSSe / PV	4.23	Efficiency decreased to 2.67% after 5h.	⁷¹
Lewis <i>et al.</i>	2015	PEC	Pt @ cathode Pt @ anode	Si microwires / Nafion	~0.5	2h electrode operation	⁷²
Lewis <i>et al.</i>	2015	PEC	NiO @ anode	NiO _x / Si	2.1 to O ₂ (figure	1200h of O ₂ evolution	⁷³

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PV: Photovoltaics; PEC: Photoelectrochemical; DSC: Dye-Sensitized Solar Cell; ITO: indium tin oxide; KB_i: potassium borate; FTO: fluorine-doped tin oxide. This Table comprises most of the world-records of water-splitting devices with efficiencies > 2%.

A recent article has summarized both chromophore-catalyst assemblies and the interfacial dynamics involved in DSPEC water splitting.⁷⁴ For TiO₂ as the oxide semiconductor, the interfacial dynamics are not favorable. The results of transient absorption measurements on surface-bound assemblies show that back electron transfer following injection and intra-assembly electron transfer, eqs 1-3, occurs on the μ sec timescale. Back electron transfer is typically rate limited by electron diffusion from the nanoparticles back to the interface. On the other hand, electron transfer migration through the microns thick oxide films to the TCO collector electrode in eq 4 occurs on the msec timescale. The unfavorable mismatch in rates ensures low efficiencies for the accumulation of oxidative equivalents at the catalyst and low efficiencies for water splitting.



To overcome this kinetic limitation, core/shell structures were introduced with cores of a nanoparticle TCO, *nano*ITO or *nano*ATO, and a thin, 3-5 nm, external shell of TiO₂. In these structures, with the assembly bound to the TiO₂ shell, injection is followed by rapid transfer through the shell to the conducting core. In the core/shell structure, injection and electron transfer to the core are competitive with back electron transfer resulting in per photon absorbed efficiencies approaching 5% with monochromatic light.⁵¹ In a follow up study, efficiencies were increased by ~5 using a SnO₂ core with back electron transfer from the core through the shell to the oxidized assembly inhibited by the more positive conduction band potential (+0.4 V) for SnO₂ compared to TiO₂.

The development of core/shell structures with ultrathin semiconducting shells to control interfacial dynamics was a key in the development of the DSPEC with a first report applied to water splitting in 2013.^{51,54} Significant progress has been made since with a variety of chromophore-catalyst assemblies under active investigation with water splitting as the initial target. An ultimate goal is tandem cells which integrate both photoanodes for water oxidation and photocathodes for CO₂ reduction or bias-free water splitting. The targets for CO₂ reduction are formate/formic acid or H₂:CO synthesis gas ('syngas') mixtures. When combined with Fischer-Tropsch synthesis, syngas is the feedstock for methanol and hydrocarbon production.

4.1 DSPEC Design Strategies for Chromophore-Catalyst Assemblies:

Figure 6 illustrates the structures of two chromophore-catalyst assemblies for water oxidation that have been investigated at the UNC EFRC. The assembly [(4,4'-(PO₃H₂)₂bpy)₂Ru^{II}(bpm)Ru^{II}(tpy)(OH₂)]⁴⁺ (Figure 6A) was notable as a first example of a surface-bound assembly for electrocatalytic water oxidation with sustained water oxidation

catalysis demonstrated in acidic solutions for at least 28,000 turnovers without decomposition at a rate of 0.6 s^{-1} .⁷⁵

A variety of chromophore-catalyst assembly strategies have been investigated. As shown in Figure 7, they include surface assembled structures including a molecular overlayer (Figure 7A),⁷⁶ co-loaded (Figure 7E),⁷⁷ layer-by-layer (Figure 7C),⁷⁸⁻⁸⁰ and electro-assembly structures (Figure 7B)^{81,82}. They also include pre-formed assemblies based on peptide scaffolds (Figure 7D),^{85,86} and polymer scaffolds (Figure 7F),^{83,84} and covalently linked molecular assemblies (Figure 6 A&B).^{75,87-92} In the electro-assembly procedure, a phosphonate derivatized chromophore, also containing a vinyl-2,2'-bpy ligand or ligands, is surface-bound to the oxide. Reductive electrochemical scans with a vinyl-bpy containing water oxidation catalyst in the

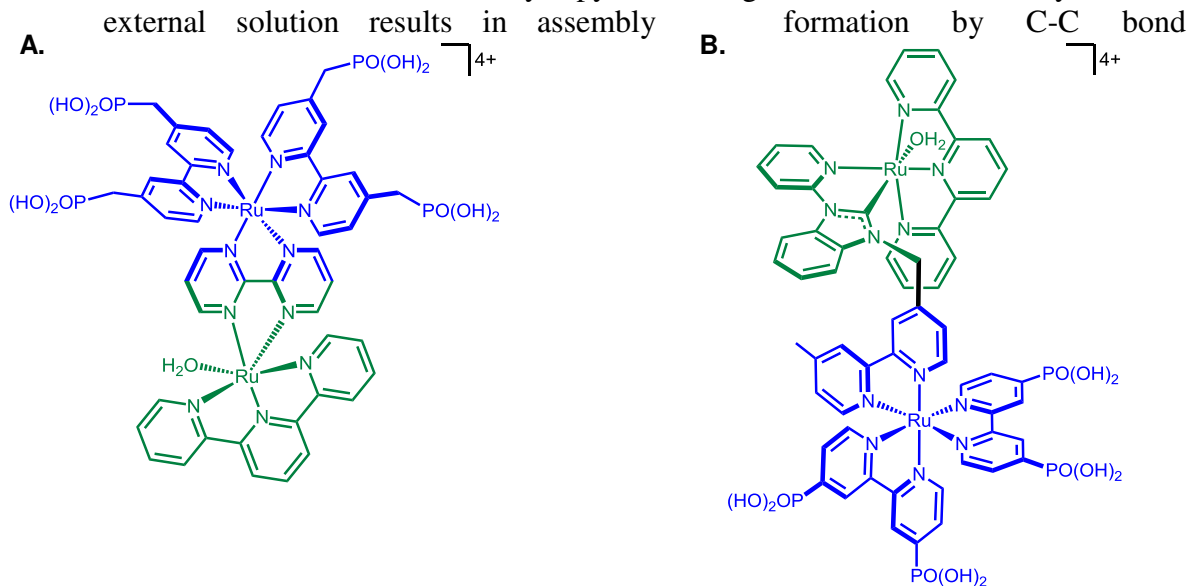
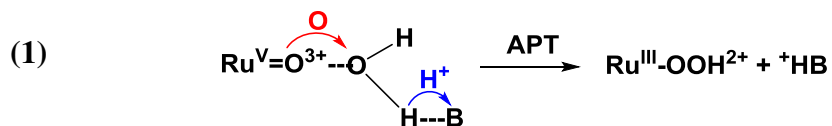


Figure 6. Examples of covalently-linked chromophore-catalyst assemblies: A) “Green Dimer” representing our initial example of a surface-bound assembly for water oxidation catalysis. B) Ru-Carbene chromophore/catalyst assembly for photocatalytic water oxidation. The chromophores are shown in blue and the catalysts in green.

formation.^{93,94}

The electro-assembly, electropolymerization procedure has been applied successfully to the preparation of both electropolymerized films for catalytic water oxidation^{82,95,96} and DSPEC photoanodes for light-driven water splitting in TiO_2 nanoparticle films.⁹⁷ In a recent example, we reported the preparation of electrocatalytically active polymeric films on both oxide and glassy carbon electrodes by electropolymerization of the vinyl-derivatized water oxidation catalyst, $\text{Ru}^{\text{II}}(2,2'$ -bipyridine-6,6'-dicarboxylic acid)(4-vinylpyridine)₂ ($\text{Ru}(\text{bda})(4\text{-vpy})_2$).⁹⁸ Electropolymerization was carried out in acetonitrile solutions of the complex by a sequence of reductive potential scan cycles. The surface coverage of *poly*- $\text{Ru}(\text{bda})(4\text{-vpy})_2$ varied linearly with the number of scan cycles illustrating an advantage of the electropolymerization technique in controlling film thickness and composition. As shown by rotating ring disc experiments (RRDE) with O_2 generation at the disc and detection at the ring, at pH 7 in a $0.1 \text{ M H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffer, water oxidation in the electropolymerized films occurs with a turnover frequency (TOF) of 8.5 mol O_2 per catalyst site per second at an overpotential of 620 mV. Under these conditions, following oxidation of the catalyst to $\text{Ru}^{\text{V}}(\text{O})^+$, rate limiting O---O bond formation is enhanced by the added buffer base by the use of Atom Proton Transfer (APT), eq 1, in which O-

atom transfer to a water molecule occurs in concert with loss of a proton to an added base with $B = \text{Ac}^-$, HPO_4^{2-} , etc.⁹⁹



A chromophore-catalyst electro-assembly was prepared within the cavities of nanoparticle TiO_2 films by reductive scans of surface-bound $[\text{Ru}(5,5'\text{-divinyl-2,2'\text{-bipyridine})}_2(4,4'\text{-}(\text{PO}_3\text{H}_2)_2\text{bpy})_2$ ($\text{RuP}(5,5'\text{-vbpy})_2^{2+}$) with $\text{Ru}(\text{bda})(4\text{-vpy})_2$ in the external solution to give a $\text{FTO}|\text{TiO}_2|\text{-RuP}(5,5'\text{-vbpy})_2^{2+}\text{-Ru}(\text{bda})(4\text{-vpy})_2$ photoanode. Upon 100 mW cm^{-2} white light illumination at pH 7 in a $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffer with a 0.2 V vs. SCE (saturated calomel electrode) bias, sustained photocurrents were observed over a several minute time period with O_2 monitored by using a parallel generator-collector electrode design.⁹⁸⁻¹⁰¹

4.2 DSPEC Photoanode Design and Construction:

TiO_2 is an n-type semiconductor oxide and the most commonly used oxide in photoanode applications. It has a pH-dependent conduction band potential in an appropriate range, 200 mV vs. NHE at pH 1, well developed methods of synthesis for mesoporous nanoparticle films are available, and the films are stable. Semiconductor/liquid junctions are at the heart of a DSPEC,⁵⁴ and with water as the solvent, semiconductor photoelectrodes must be stable under aqueous conditions. The need for aqueous stability limits the range of useful semiconductors with Cu_2O , InP , and ZnO , for example, unstable at the highly oxidative potentials required for water oxidation.^{38,102-105}

In an initial, preliminary DSPEC study, the photoelectrochemical response of the chromophore, $[\text{Ru}(\text{bpy})_2(4,4\text{-}(\text{PO}_3\text{H}_2)_2\text{bpy})_2]^{2+}$ (RuP^{2+}) on TiO_2 was investigated with triethanolamine or deprotonated EDTA (EDTA^{4-}) added as irreversible reductive scavengers in the external solution. Following excitation and injection by the chromophore, $\text{FTO}|\text{TiO}_2|\text{-RuP}^{2+} + h\nu \rightarrow \text{FTO}|\text{TiO}_2(\text{e}^-)|\text{-RuP}^{3+}$, reduction of -RuP^{3+} by the reductive scavengers freed the injected electron for transfer to a cathode for H^+ reduction to H_2 . With an applied bias to maximize photocurrents, photocurrents and H_2 production at the cathode were observed with efficiencies approaching 14.7% under steady-state irradiation.^{49,106}

Nb_2O_5 nanocrystalline films functionalized with RuP^{2+} were also used as the photoanode in DSPECs for hydrogen generation.¹⁰⁷ For a T-phase orthorhombic Nb_2O_5 nanocrystalline film, the conduction band potential is slightly positive (<0.1 eV) relative to anatase TiO_2 . Anatase TiO_2 has a wide distribution of trap states including deep trap and band-tail trap states. Orthorhombic Nb_2O_5 is dominated by shallow band-tail trap states. Trap state distributions, conduction band energies, and interfacial barriers all appear to contribute to a slower back electron transfer rate, lower injection yield on the nanosecond time scale, and a lower open-circuit voltage (V_{oc}), for Nb_2O_5 compared to anatase TiO_2 . In an operating DSPEC, with EDTA^{4-} added as a reductive scavenger, H_2 quantum yield and photostability measurements show that Nb_2O_5 is comparable, but not superior, to TiO_2 as a photoanode material.¹⁰⁷

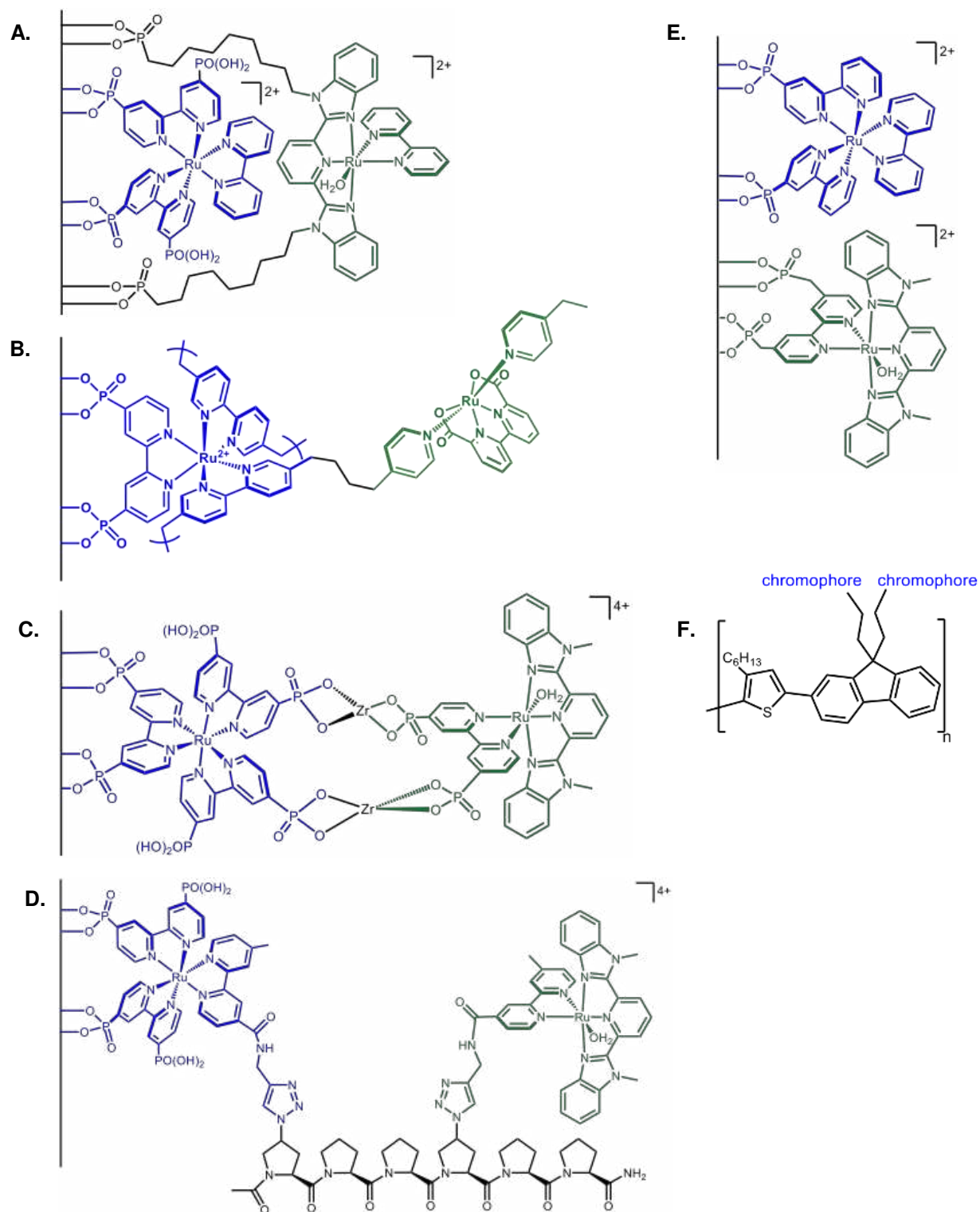


Figure 7. Examples of different strategies for bringing together chromophores and catalysts in close proximity on a surface: A) molecular overlayer strategy⁷⁶; B) electro-assembly structures⁹⁸; C) layer-by-layer strategy⁷⁸⁻⁸⁰; D) peptide scaffold^{85,86}; E) co-loaded assemblies⁷⁷ and F) polymer scaffolds^{83,84}.

Atomic layer deposition (ALD) has played a major role in the evolution of the DSPEC in the UNC EFRC. ALD is a conformal, layer-by-layer gas phase technique. It has been used successfully for stabilizing phosphonate surface binding of chromophores,^{50,108} catalysts,¹⁰⁹ and assemblies by depositing overlayers of Al₂O₃ or TiO₂.¹¹⁰

ALD has also been used to fabricate nanostructured core/shell electrodes for both DSC¹¹¹ and DSPEC applications with the core/shell used to control interfacial dynamics.^{51,54,110} Initial results were reported on a dye-sensitized solar cell with the N719 dye with TCO cores and thin shells of TiO₂. Short-circuit current densities, open-circuit voltages, and back electron transfer lifetimes were all found to depend on TiO₂ shell thickness. All increased up to 1.8–2.4 nm and then declined as the shell thickness was increased further. It was suggested that, as the shell layer was increased in thickness, low energy trap states appear with back electron transfer to Ru(III) becoming increasingly competitive with transport to the core, decreasing device efficiencies.⁵¹

Initial DSPEC water splitting experiments were conducted on core/shell structures with transparent conducting oxide cores of antimony-doped tin oxide (Sb(V):SnO₂ – nanoATO) or tin-doped indium oxide (Sn(IV):In₂O₃ – nanoITO) with 3.6 nm TiO₂ shells. The core/shell oxides were derivatized with the assembly shown in Figure 6B to give the photoanode structures,

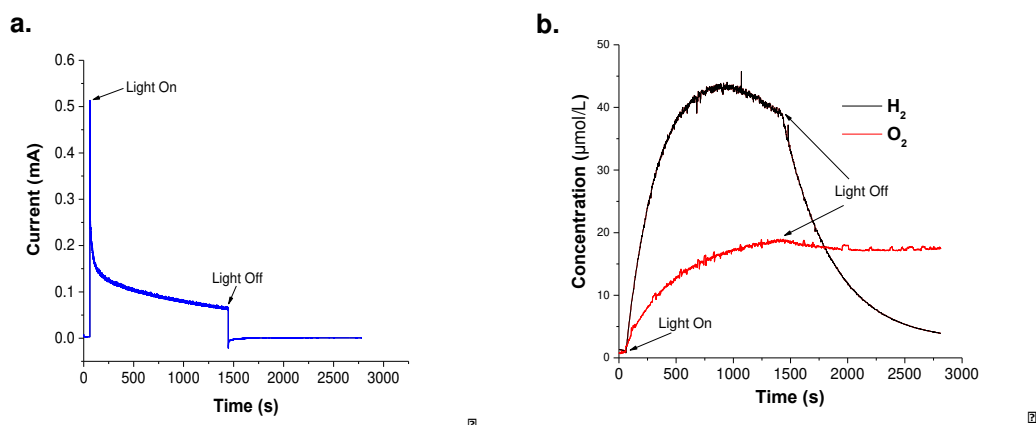


Figure 8. Photoelectrochemical water splitting by FTO|SnO₂/TiO₂(6.6nm)|-[Ru^{II}-Ru^{II}-OH₂]⁴⁺(0.3nmAl₂O₃) with a 600 mV applied bias in a 0.1 M H₂PO₄/HPO₄²⁻ buffer at pH 7 at room temperature. The assembly structure is shown in Figure 6B. A bias was applied across the working and counter electrodes in a two electrode configuration with the counter and reference leads both connected to the Pt counter electrode. The ionic strength was adjusted to 0.5 M with NaClO₄. Illumination was by a 46.2 mW/cm², 455 nm LED: **(a)** Photocurrent-time trace and **(b)** H₂ and O₂ evolution time traces recorded in concert with the photocurrent trace.

FTO|*nano*ITO|TiO₂|- [Ru^{II}-Ru^{II}-OH₂]⁴⁺. Photolysis in a pH 4.6 acetate buffer with a Pt cathode resulted in water splitting with an absorbed photon conversion efficiency of 4.4% at peak photocurrent.⁵⁴

In a follow up study, DSPEC light-driven dehydrogenation of benzyl alcohol (BnOH) to benzaldehyde and hydrogen was investigated on TiO₂ and *nano*ITO/TiO₂ core/shells (*nano*ITO/TiO₂) with co-surface bound chromophore RuP²⁺ and catalyst [Ru(Mebimpy)((4,4'-(OH)₂P(O)CH₂)₂bpy)(OH₂)²⁺ (Mebimpy = 2,6-bis(1-methylbenzimidazol-2-yl) pyridine). On these surfaces, chromophore excitation and electron injection are followed by cross surface electron-transfer activation of the catalyst to –Ru(IV)=O²⁺, which then oxidizes benzyl alcohol to benzaldehyde. At an optimized shell thickness, a sustained absorbed photon to current efficiency of 3.7% was achieved for BnOH dehydrogenation, an increase in efficiency of ~10 compared to n-type TiO₂.⁵²

Follow-up DSPEC experiments have used cores of SnO₂ in mesoporous SnO₂/TiO₂ core/shells derivatized with the assembly in Figure 6B.¹¹⁰ In this structure the ~0.4V more positive conduction band potential for SnO₂ compared to TiO₂ was exploited to create an uphill barrier to back electron transfer. Maximum photocurrents of 1.97 mA/cm² were obtained with 445 nm excitation. Direct monitoring of evolved O₂ at the photoanode and H₂ from the Pt cathode by *in situ* microelectrode analysis is shown in Figure 8. The relative ratios of H₂:O₂ provide direct evidence for water splitting and the enhanced efficiency a promising beginning to the design of future DSPEC prototypes for solar-driven water splitting.

5. Reduction of CO₂ in water to syngas mixtures:

As part of the larger goal of DSPEC water splitting and CO₂ reduction, significant progress has been made in the UNC EFRC on electrocatalyzed CO₂ reduction. One target is synthesis gas or ‘syngas’, mixtures of H₂ and CO that serve as important industrial feedstocks for methanol, acetic acid, ammonia, and hydrocarbons, the latter by Fischer-Tropsch synthesis. Solar driven production of syngas from CO₂ and water could be important in the sustainable production of chemicals and fuels.

Electrochemical investigations into the mechanisms of CO₂ to CO and of water to H₂ by Ru(II) polypyridyl complexes in acetonitrile have provided detailed insight into how these reactions occur.¹¹² For [Ru^{II}(tpy)(bpy)(NCCH₃)]²⁺, **1** in Figure 9, 2e⁻ reduction occurs at the polypyridyl ligands activating the metal toward loss of bound CH₃CN by CO₂ to give the metalcarboxylate, [Ru(tpy)(bpy)(CO₂)]. The twice-reduced complex undergoes further reduction and O²⁻ loss to CO₂ to give the corresponding CO complex. With added weak acids - H₂O, H₂PO₄⁻, HCO₃⁻ - [Ru(tpy)(bpy)(CO₂)] is protonated to give the hydride, [Ru^{II}(tpy)(bpy)(H)]⁺. Following reduction and protonation it releases H₂. Electrolysis in the presence of both CO₂ and added H₂PO₄⁻ gave syngas mixtures of H₂ and CO at ratios from 1:1 to 2:1 depending on the concentration of added acid.

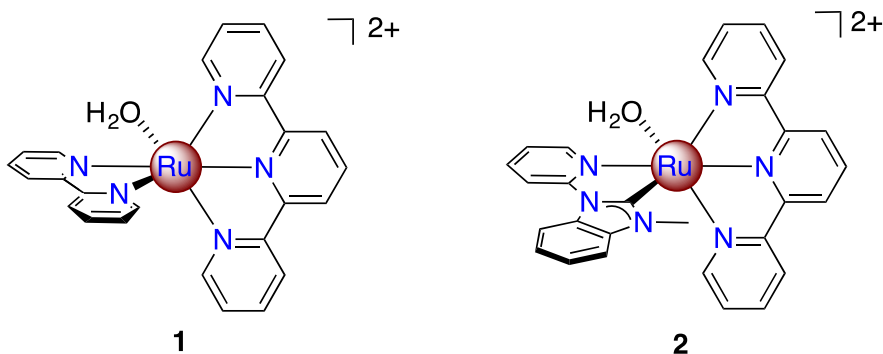


Figure 9. Structures of Ru(II) polypyridyl-aqua complex CO₂ catalyst precursors **1** and **2**.

The co-catalysis chemistry was extended to water with the complex [Ru^{II}(tpy)(Mebimpy)(H₂O)](PF₆)₂ (Mebim-py = 3-methyl-1-pyridyl-benzimidazol-2-ylidene, **2** in Figure 9). Electrochemical experiments demonstrated that catalyst **2** catalyzes both CO₂ reduction to CO and water/proton reduction to H₂ in aqueous CO₂/HCO₃⁻ solutions with the product ratio adjustable by controlling the applied potential or the concentration of HCO₃⁻.¹¹³

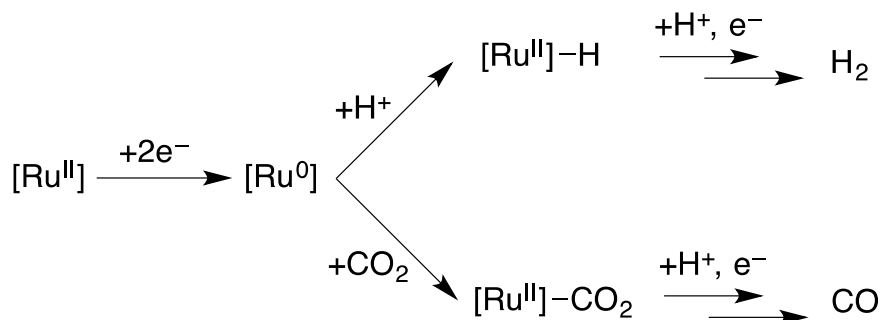


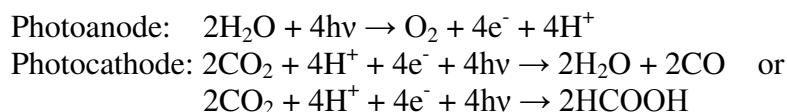
Figure 10. Pathways for syngas generation.

As shown by the mechanism in Figure 10, syngas generation occurs from a common intermediate. The product distribution in a CO₂-saturated solution varies depending on the concentration of added acid and applied potential. Decreasing the potential from -1.2 to -1.5 V increases the H₂:CO ratio from 0.5:1 to 3:1, and decreasing the pH from 7.2 to 6.5 increases the H₂:CO ratio from 0.5:1 to 4:1. Complex **1** is also a water oxidation catalyst^{114,115} and its use as a catalyst for both water oxidation and CO₂ reduction in an O₂/syngas electrochemical cell has been demonstrated.¹¹⁶ An extension to surface-bound, high surface area electrodes is currently under investigation.

6. Next step: Tandem DSPEC designs:

In a tandem DSPEC design, a photoanode for water oxidation and photocathode for CO₂ reduction are integrated in a single cell, separated by a proton exchange membrane. Target reactions for the two half-cells in a tandem DSPEC are water oxidation and CO₂ reduction to either formate/formic acid or syngas, Scheme 1. In this design the two photoelectrodes utilize

Scheme 1.



n-type semiconductor photoanodes (TiO₂, SnO₂) for water oxidation and a p-type photocathode (NiO) for CO₂ reduction.¹¹⁶⁻¹¹⁸ In a light efficient device, chromophore matching will be used to split the solar spectrum with different portions of the incident solar input absorbed by the two photoelectrodes. The most studied p-type semiconductor for DSC and DSPEC applications is NiO but the results of extensive studies have shown that NiO undergoes slow hole transport and unfavorable interfacial kinetics. In current research, core/shell NiO structures are currently under investigation as are the development of other oxide p-type materials.

7. Looking to the Future. Outlook:

The development of the DSPEC is a promising step forward with potential applications to solar fuels. Although likely to be at least a decade away from widespread use, niche markets exist that could benefit from initial prototypes. Because it is a solar-driven electrochemical approach,

DSPEC panels for solar fuels can be deployed under ambient solar conditions anywhere there is sunlight. This concept of decentralized energy storage and production has implications for military forward operating bases, off-grid communities, island nations, and remote regions in the third world. There may even be early markets in the US where there are communities that pay 275% of the national average for their energy (Table 2)¹¹⁹ including island communities in Hawaii and the Virgin Islands and remote communities in Alaska and indigenous communities including parts of the Navajo, Yurok, and Lakota Nations.

Initial results are available which assess the potential for market entry and large-scale development. A study by Newman et al., examines federal government guarantees for the purchase of synthetic diesel fuel to supply the military with the cost of making diesel electrochemically comparable to petroleum as a starting material.¹¹ Demand by the US Air Force and Navy is ~80% of the total demand and equivalent to ~26.8 GW or 395,000 barrels of oil equivalent per day (BOE/day). Although promising as markets, these opportunities will only become viable as the technoeconomics become cost competitive. There are potentially viable strategies on a short timescale. For example, PV or wind turbines could be used to power electrochemical water splitting or CO₂ reduction to syngas, H₂:CO mixtures. CO₂ is available as a byproduct of cement plants and, potentially from power plant flue gas with capture by amine scrubbers. Long distance CO₂ pipelines already exist to supply the oil and gas industry, which could help minimize the need for new infrastructure.¹¹ In the long term, CO₂ capture as it is produced for solar recycling would provide a basis for closed cycles with minimal emissions and environmental impact.

Table 2. Comparison of the cost of energy between the national average and areas that pay up to 275% more than this average.

Fuel	National Average	275% of national average per unit cost benchmark
Electricity	\$0.12 per kWh	\$0.33 per kWh
Natural Gas	\$12.18 per thousand cubic feet	\$30.50 per thousand cubic feet
Fuel Oil	\$2.42 per gallon	\$6.68 per gallon
LPG/Propane	\$2.09 per gallon	\$5.76 per gallon
Total Household Energy cost per BTUs	\$22.59 per million BTUs	\$62.12 per million BTUs

At present, steadily decreasing costs for wind and PV make them less expensive than direct solar-to-fuel conversion in photoelectrochemical cells. In a technoeconomic analysis by Newman et al., the cost of producing H₂ with wind was \$3.64/kg, \$7.62/kg with PV. The cost with existing PEC approaches exceeded \$100/kg. To become cost competitive, the lifetime of a PEC

would have to be extended to 25 years with an energy efficiency of ~15%. Much of the research in PECs is still fundamental and at the lab scale but recent progress augurs well for the future. Further research progress is needed with extension to translation and scale up. Much remains to be done, but significant progress has been made and the path forward is promising.

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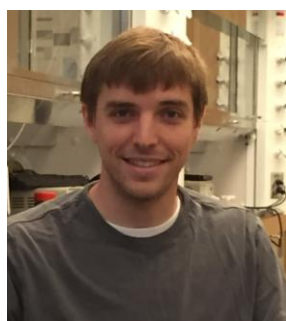
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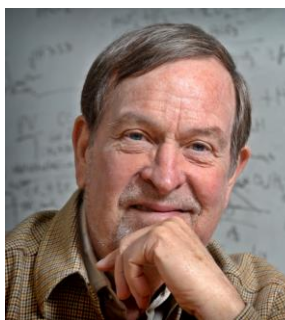
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