

Finding the Way to Solar Fuels with Dye-Sensitized Photoelectrosynthesis Cells

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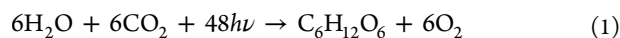
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ABSTRACT: The dye-sensitized photoelectrosynthesis cell (DSPEC) integrates high bandgap, nanoparticle oxide semiconductors with the light-absorbing and catalytic properties of designed chromophore–catalyst assemblies. The goals are photoelectrochemical water splitting into hydrogen and oxygen and reduction of CO₂ by water to give oxygen and carbon-based fuels. Solar-driven water oxidation occurs at a photoanode and water or CO₂ reduction at a cathode or photocathode initiated by molecular-level light absorption. Light absorption is followed by electron or hole injection, catalyst activation, and catalytic water oxidation or water/CO₂ reduction. The DSPEC is of recent origin but significant progress has been made. It has the potential to play an important role in our energy future.

1. INTRODUCTION

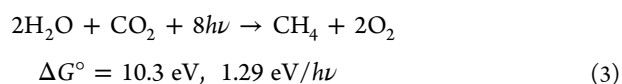
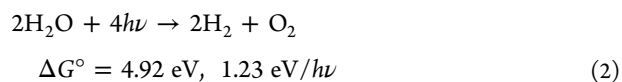
The sun may be the ultimate energy source, but it comes with strings attached. The energy input from the sun is 3×10^{24} joules per year, 10 000 times current global consumption, but it is diffuse and requires large collection areas. To meet current U.S. energy needs with a 10% device would require a collection area of ~60 000 square miles, roughly the size of the state of North Carolina. The sun is also an intermittent light source providing, on the average globally, only 6 h of useful input per day. If it is to become a primary energy source, it will have to be integrated with energy storage on unprecedented scales, well beyond those available with current battery technologies, for example.¹

Energy conversion and storage occur during natural photosynthesis, the solar-driven reduction of CO₂ by water. As shown in eq 1, in green plants, the products are carbohydrates and oxygen.



Photosynthesis takes place on a massive scale with ~10¹¹ tons of carbon stored annually as plant biomass. With oxygen as a co-product and the use of respiration to produce ATP, photosynthesis is the fundamental solar energy conversion process supporting higher life forms on the planet. Nonetheless, as a way to keep pace with increasing energy demands, natural photosynthesis is an inspiration, not a model. It is far too complex to duplicate, and its ~1% efficiency² for biomass production is too low to power the world's large urban centers.

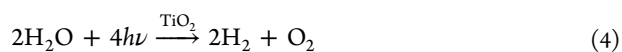
Artificial photosynthesis has the same goal as natural photosynthesis: conversion of solar energy by driving high-energy chemical reactions that convert and store energy. Water splitting is shown as the example in eq 2, and CO₂ reduction to the carbon-based fuel methane is shown in eq 3.



In artificial photosynthesis, the goal is to transform the Earth's energy future by producing "solar fuels", hydrogen from water splitting or reduced forms of carbon. As fuels, they are fully compatible with existing technologies for energy utilization and storage.

2. CHEMICAL APPROACHES TO ARTIFICIAL PHOTOSYNTHESIS

In the 1970s, Honda and Fujishima reported water splitting by ultraviolet bandgap excitation of anatase TiO₂ in a photoelectrochemical cell with a Pt cathode and a small pH gradient, eq 4.³

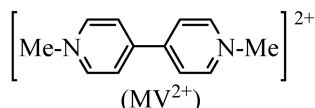
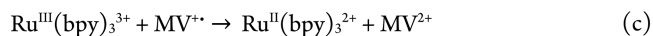
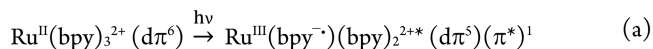


Since then, significant progress has been made by using semiconductors and photoelectrochemical cells to carry out water splitting, although practical devices have yet to emerge.^{4–11} There are significant challenges in this approach, including photocorrosion in water and rapid electron–hole recombination which reduce efficiencies.^{12–16}

A hybrid molecular–semiconductor approach to water splitting is shown in the next section in Figure 1. The underlying chemistry also emerged in the 1970s. It was based on visible light excitation of the dπ⁶ Ru(II) polypyridyl complex Ru(bpy)₃²⁺, with bpy = 2,2'-bipyridine, to give its ¹(dπ⁵π*) metal-to-ligand charge-transfer (MLCT) excited-state Ru^{III}(bpy^{•+})(bpy)₂^{2+*}.^{17,18} In solutions containing both Ru complex and methyl viologen (MV) dication, added as an oxidative quencher, diffusional excited-state electron-transfer quenching occurred, Scheme 1. Electron-transfer quenching of the excited state resulted in conversion of the ~2.1 eV of transiently stored energy in the excited state into redox energy

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Scheme 1. Oxidative Quenching of Ru(bpy)₃^{2+*}

as Ru(bpy)₃³⁺ and MV^{•+}. The potentials of the Ru(bpy)₃^{3+/2+} (1.26 V vs NHE) and MV^{2+/•+} (−0.4 V vs NHE) couples were sufficient to carry out water oxidation and proton reduction at separate catalysts or at separate electrodes in acidic solution.^{19–22} Yet without an architecture to separate the redox equivalents as they form and use them to drive physically separated half-reactions for water oxidation and reduction, the transiently stored energy is given off as heat to the surroundings as back electron transfer occurs, eq c in Scheme 1.

3. THE DYE-SENSITIZED PHOTOELECTROSYNTHESIS CELL

The dye-sensitized photoelectrosynthesis cell (DSPEC) provides an architecture to overcome the limitations of the solution-based example of Scheme 1. The DSPEC is based on the well-developed dye-sensitized solar cell (DSSC).^{23–25} Like the DSSC, a DSPEC combines the properties of n- or p-type semiconductor oxides with molecular-level light absorption and catalysis by surface-bound molecular assemblies. The assembly absorbs light and carries out the solar fuel half-reactions.

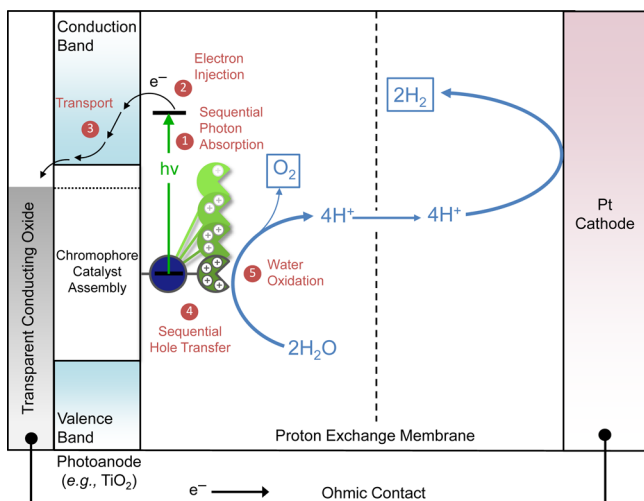


Figure 1. Schematic diagram for a dye-sensitized photoelectrosynthesis cell (DSPEC) for solar-driven water oxidation at an assembly-derivatized TiO₂ photoanode with water or proton reduction to H₂ at a Pt cathode. Reproduced with permission from ref 33. Copyright 2015 American Chemical Society.

Figure 1 illustrates the elements of a photoanode in a DSPEC for water splitting. Solar-driven water oxidation occurs at the photoanode and proton or water reduction at the cathode. A sequence of events occurs at the photoanode: (1) light absorption to give an excited state or states; (2) electron injection from the excited state(s) into the conduction band of an n-type oxide; (3) electron transport to a transparent

conducting oxide (TCO) electrode for ohmic delivery to a cathode or photocathode; (4) electron-transfer activation of a catalyst for water oxidation; and (5) repetition of the activation sequence four times with O₂ evolution, returning the catalyst to its initial state.

The first DSPEC was reported in 1999 for dehydrogenation of iso-propanol to acetone, eq 5, and was based on a Ru(II) polypyridyl chromophore-catalyst assembly.²⁶



A water-splitting DSPEC with nanoparticle IrO_x as the water oxidation catalyst was reported by Mallouk and coworkers in 2009.²⁷ The DSPEC is far less developed than semiconductor-based water splitting, but significant progress has been made in recent years at laboratories worldwide.^{20,26–64}

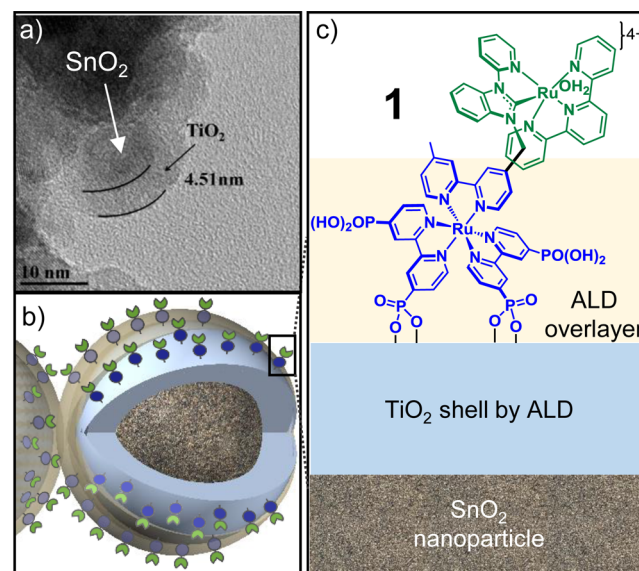


Figure 2. (a) Transmission electron micrograph of SnO₂/TiO₂ core/shell nanostructure. Reproduced with permission from ref 65. (b) Depiction of core/shell nanoparticle along with a surface-stabilizing overlayer of TiO₂ or Al₂O₃ added by atomic layer deposition (ALD). The drawing is based on a 20 nm diameter nanoparticle as the “core” (black/brown speckled pattern), a 5 nm shell (light blue), and a 1.5 nm overlayer (semitransparent tan). A subset of molecular assemblies bound directly to the shell are also depicted with blue circles as chromophores and green, notched circles as catalysts. (c) Zoomed-in view highlighting the structure of assembly 1 on the core/shell surface stabilized by an ALD oxide overlayer. DSPEC photoanodes for solar-driven water oxidation were produced by ALD of a TiO₂ shell, 3–5 nm thick, on the exposed surfaces of a mesoporous SnO₂ nanocrystalline film, 5–15 μm thick, on FTO to give FTO/SnO₂/TiO₂–[Ru^{II}–Ru^{II}–OH₂]⁴⁺, see text. Adapted with permission from ref 65. Copyright 2015 Proceedings of the National Academy of Sciences, USA.

Figure 2 illustrates a DSPEC photoanode based on the chromophore–catalyst assembly, [(4,4′-PO₃H₂)₂bpy)₂Ru(4-Mebpy-4′-bimpy)Ru(tpy)(OH₂)⁴⁺, 1, (4-Mebpy-4′-bimpy = 4-(methylbipyridin-4′-yl)-N-benzimid-N′-pyridine; tpy = 2,2′:6′,2″-terpyridine). It is attached by phosphonate-surface binding to a thin, 3–5 nm, layer of TiO₂ which has been conformally deposited onto the exposed surfaces of a mesoscopic nanoparticle film of SnO₂. Typically, the films consist of ~20–40 nm diameter nanoparticles deposited and annealed as mesoporous, 5–15 μm thin films on the

transparent conducting oxide (TCO) fluorine-doped tin oxide (FTO). The molecular assembly is linked to the shell on the outside of the nanoparticles by a simple solution soaking procedure. In a final step, surface binding is stabilized by adding an inert oxide overlayer of TiO_2 or Al_2O_3 by atomic layer deposition (ALD).⁶⁵

Photocurrent and gas detection measurements of O_2 in the photoanode compartment and H_2 in the cathode compartment were made for DSPECs incorporating the photoanode illustrated in Figure 2. The cell was operated at pH 7 at room temperature in 0.5 M NaClO_4 , 0.1 M phosphate buffer, with an applied bias of 600 mV vs NHE to maximize the photocurrent with reduction of the buffer component H_2PO_4^- to H_2 at a Pt cathode. With monochromatic 445 nm light, the absorbed photocurrent efficiency (APCE) for the assembly in Figure 2 reached ~20% for the cell, less than 1% of that for solar production of H_2 , but a beginning nonetheless.⁶⁵

4. DSPEC COMPONENTS

4.1. Chromophore–Catalyst Assembly. Assembly 1 is a typical covalently bonded chromophore–catalyst assembly, one of many that have been investigated which differ in linking strategies. Other strategies that have been explored used derivatized polymers⁶⁶ and polyproline oligomers.^{67,68} The latter are prepared by stepwise peptide synthesis;⁶⁹ an example,^{67,68} 2, is illustrated below in Figure 3.

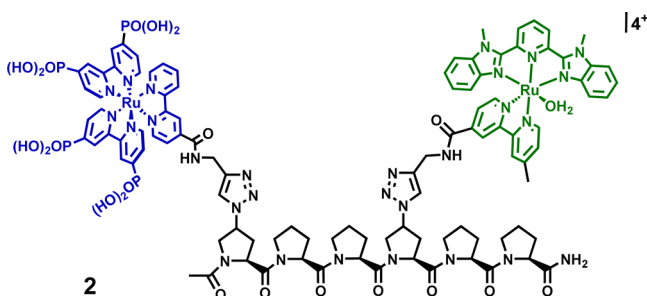


Figure 3. Assembly 2, an oligoproline functionalized with both a Ru(II) chromophore and catalyst.^{33,68} Adapted with permission from ref 33. Copyright 2015 American Chemical Society.

Preformed, covalently linked assemblies have been useful in fundamental studies but require tedious, multistep procedures and complex chromatographic separations which often result in low yields. With the motto “keep it simple”, much of our current effort is on assemblies prepared directly on oxide surfaces. In the simplest “co-loaded” strategy, with an example shown in Figure 4a, chromophore and catalyst are added directly to the oxide surface by sequential or co-loading procedures. In the “layer-by-layer” strategy shown in Figure 4b,

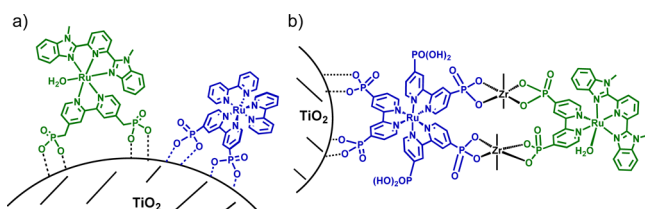


Figure 4. (a) Co-loaded assembly on TiO_2 . (b) Bilayer assembly with Zr(IV) bridging on TiO_2 . Adapted with permission from ref 33. Copyright 2015 American Chemical Society.

based on earlier work by Mallouk and Haga and their co-workers,^{70–72} Zr(IV) or another metal cation is used as a bridge to link phosphonate- or phosphate-derivatized substituents.^{73–80}

Examples of electro-assembly structures are illustrated in Figure 5.^{81–86} They are prepared by vinyl-bpy-based reduction

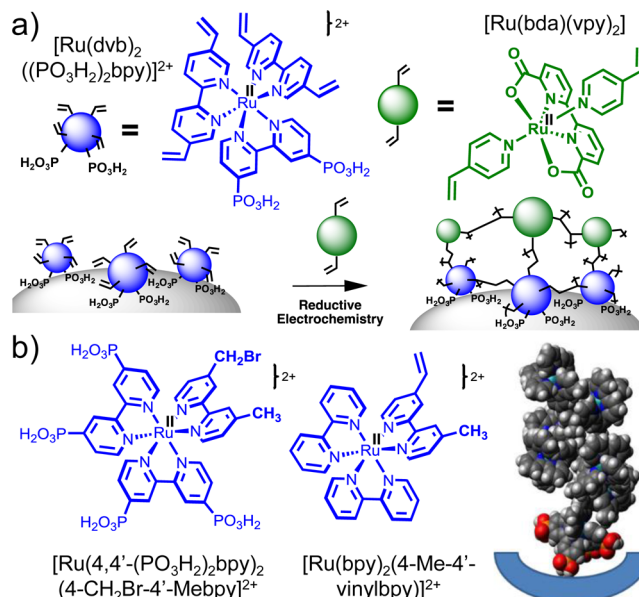


Figure 5. (a) Formation of an assembly by electropolymerization of the vinyl-derivatized, surface-bound phosphonate chromophore $[\text{Ru}(\text{dvb})_2((\text{PO}_3\text{H}_2)_2\text{bpy})]^{2+}$ (blue spheres) by C–C coupling with the water oxidation catalyst $\text{Ru}(\text{bda})(\text{vpy})_2$ (green spheres) in the external solution. Reprinted with permission from ref 85. Copyright 2015 Wiley-VCH Verlag. (b) Structures of the two chromophore building blocks along with a depiction of the resulting 7-member chromophore assembly in a cavity of a TiO_2 nanoparticle film prepared by prior surface binding of $[\text{Ru}(4,4'-(\text{PO}_3\text{H}_2)_2\text{bpy})_2(4\text{-CH}_2\text{Br-4'-Me})\text{bpy}]^{2+}$ ($4\text{-CH}_2\text{Br-4'-Me})\text{bpy} = 4\text{-(bromomethyl)-4'-methyl-2,2'-bipyridine}$) and stepwise reductive C–C bond coupling with $[\text{Ru}(\text{bpy})_2(4\text{-Me-4'-vinylbpy})]^{2+}$ ($4\text{-Me-4'-vinylbpy} = 4\text{-methyl-4'-vinyl-2,2'-bipyridine}$) in the external solution. Reprinted with permission from ref 86. Copyright 2014 Wiley-VCH Verlag.

of Ru(II)–polypyridyl complexes with both vinyl- and phosphonate-functionalized 2,2'-bipyridine ligands, e.g., $[\text{Ru}(\text{dvb})_2(4,4'-(\text{PO}_3\text{H}_2)_2\text{bpy})]^{2+}$, where $\text{dvb} = 4,4'\text{-divinyl-2,2'-bipyridine}$. Reduction at ligand-based π^* levels induces C–C coupling with the vinyl-derivatized water oxidation catalyst in the external solution. In the example shown in Figure 5a, the water oxidation catalyst is $[\text{Ru}(\text{bda})(\text{vpy})_2]$ ($\text{bda} = 6,6'\text{-dicarboxylato-2,2'-bipyridine}$ dianion; $\text{vpy} = 4\text{-vinylpyridine}$). Water oxidation by this class of catalysts is discussed in section 5.4. Figure 5b illustrates the structure of a multichromophore assembly prepared within the cavities of a TiO_2 nanoparticle film. It was prepared by a stepwise procedure with initial surface binding of $[\text{Ru}(4,4'-(\text{PO}_3\text{H}_2)_2\text{bpy})_2(4\text{-CH}_2\text{Br-4'-Me})\text{bpy}]^{2+}$ ($4\text{-CH}_2\text{Br-4'-Me})\text{bpy} = 4\text{-(bromomethyl)-4'-methyl-2,2'-bipyridine}$) followed by electrochemical reduction and Br^- loss with $[\text{Ru}(\text{bpy})_2(4\text{-Me-4'-vinylbpy})]^{2+}$ ($4\text{-Me-4'-vinylbpy} = 4\text{-methyl-4'-vinyl-2,2'-bipyridine}$) in the external solution.⁸⁶

4.2. Semiconductor Oxide. To be useful, a DSPEC semiconductor oxide has to be stable in aqueous solutions over an extended pH range and optically transparent in the visible with a bandgap ≥ 3.2 eV, and it is to have conduction or valence

band potentials, E_{CB} or E_{VB} , that are accessible for excited-state electron or hole injection.³² Mesoporous nanocrystalline films, typically 5–15 μm thick, are used with sufficient surface areas for chromophore binding to maximize light absorption. Thin films are advantageous in minimizing the distance to the inner electrode by decreasing competition from back electron transfer following injection.

TiO_2 and SnO_2 have dominated as photoanode materials because of their low conduction band potentials, ease of synthesis, and stability in water. For TiO_2 , $E_{CB} = -0.1$ V vs NHE at pH 0, with E_{CB} decreasing by 59 mV/pH unit, and for SnO_2 , $E_{CB} \approx 0.28$ V vs NHE at pH 0.^{35,43,87,88} A growing number of p-type oxides have been investigated as photocathodes,^{89–99} but their performance characteristics remain far inferior to their n-type counterparts. NiO has been the most commonly studied p-type oxide.^{91,100–113} Its marginal performance has been attributed to slow hole transport and unfavorable interfacial electron-transfer kinetics.^{91,100,114–125}

The lack of appropriate p-type oxides has greatly hindered the development of photocathodes for CO_2 or water/acid reduction in tandem cell configurations.^{89–99} Progress has been made by chemically modifying NiO^{113,126–128} and by using more elaborate chromophore structures to help control interfacial dynamics.^{91,100,101,104,105,107,116–120,129,130} The integration of bandgap excitation with molecular catalysis for other p-type semiconductors has also been reported, including Cu_2O derivatized with a Re(bpy)-based catalyst for CO_2 reduction by Grätzel and co-workers,^{131,132} and TiO_2 -protected p-GaInP₂ for water reduction to H_2 by Turner and co-workers.¹³³

4.3. Surface Binding and Stabilization. A variety of linkage strategies have been used to bind molecules and molecular assemblies to oxide surfaces.^{134–146} Carboxylic acid ($-\text{COOH}$) derivatives have dominated DSSC studies in nonaqueous solvents, but carboxylates typically hydrolyze from the surface in water. Phosphonate-surface binding by phosphonic acid derivatives ($-\text{PO}_3\text{H}_2$) is more robust^{134,147–149} but still suffers from long-term instability.¹⁵⁰ Hydrolysis is catalyzed by added buffer bases such as HPO_4^{2-} and as the pH and concentration of OH^- increase.^{134,147–149,151} Surface instability with added buffer is most unfortunate because water oxidation rates typically increase with buffer base concentration, see section 5.4.

Stabilization of the attachment between molecule and oxide surface has been greatly improved by using hydrophobic polymer overlayers,¹⁵² electro-assembly^{83–85,153} (Figure 5), siloxane surface bindings,^{149,154} silatrane surface bindings,^{155–158} and hydrophobic environments.¹⁵⁹ The most effective stabilization, though, has been achieved by using ALD of oxide overlayers, such as Al_2O_3 or TiO_2 , after surface binding has occurred.^{151,160–169} In the ALD technique, a reactive gas-phase precursor—e.g., $\text{Al}(\text{CH}_3)_3$ for Al_2O_3 , TiCl_4 for TiO_2 —is exposed to a pre-derivatized oxide surface. Reaction of the ALD precursor with the surface followed by hydrolysis yields an atomic layer or sublayer of the oxide. Multilayers of the oxide are then used to “glue” the catalyst or assembly to the surface.

Figure 6a compares the surface stability of the water oxidation catalyst $[\text{Ru}(\text{Mebimpy})(4,4'-(\text{PO}_3\text{H}_2\text{CH}_2)_2\text{bpy})(\text{OH}_2)]^{2+}$ (Mebimpy = 2,6-bis(1-methyl-1H-benzo[*d*]-imidazol-2-yl)pyridine) with and without ALD stabilization on an ITO electrode.¹⁶² For the stabilized electrode at pH 11 with 12 mM added PO_4^{3-} , sustained water oxidation catalysis occurs for >2.8 h at a turnover rate of $\sim 10^4$ s^{-1} .

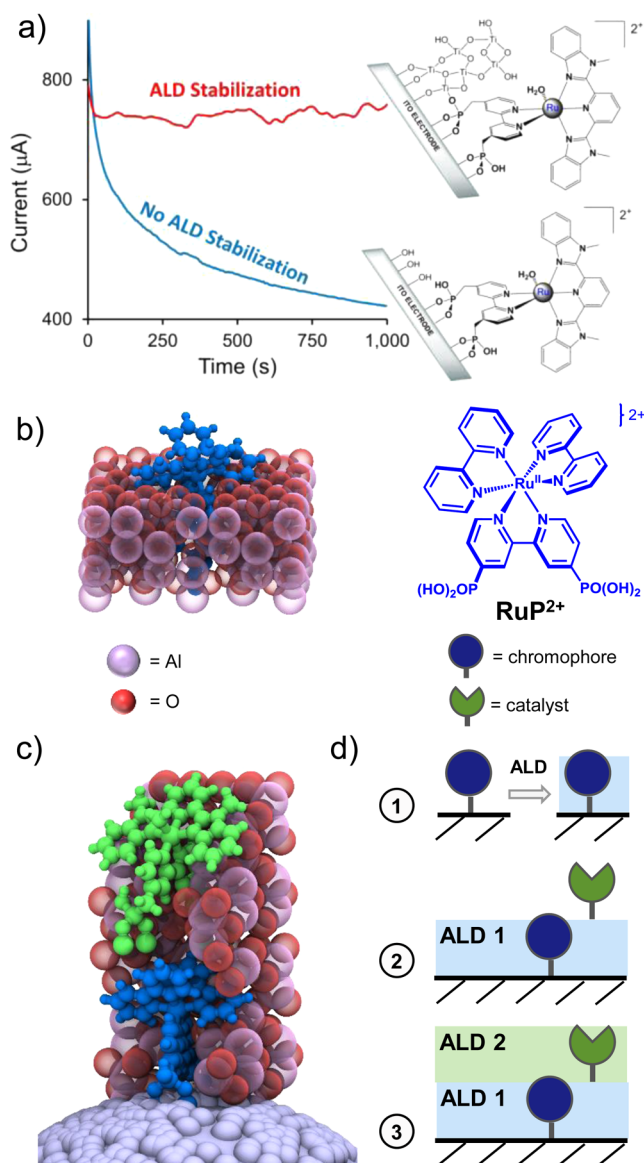


Figure 6. (a) Current–time profiles for water oxidation catalysis by $[\text{Ru}(\text{Mebimpy})(4,4'-(\text{PO}_3\text{H}_2\text{CH}_2)_2\text{bpy})(\text{OH}_2)]^{2+}$ surface-bound to ITO with and without a 1 nm TiO_2 overlayer at pH 11 in 12 mM PO_4^{3-} and 0.25 M LiClO_4 following a potential step to 1.40 V vs NHE. Adapted with permission from ref 162. Copyright 2013 Proceedings of the National Academy of Sciences, USA. (b) Calculated overlayer structure of ALD-deposited TiO_2 (0.76 nm) on surface-bound $[\text{Ru}(4,4'-(\text{PO}_3\text{H}_2)_2(\text{bpy})_2)]^{2+}$ ($-\text{RuP}^{2+}$). (c) Calculated structure of a “mummy” chromophore–catalyst assembly constructed as shown in (d) by (1) ALD overlayer deposition (labeled “ALD 1”) following surface binding of $-\text{RuP}^{2+}$, (2) addition of $[\text{Ru}(\text{Mebimpy})-(4,4'-(\text{PO}_3\text{H}_2\text{CH}_2)_2\text{bpy})(\text{OH}_2)]^{2+}$, and (3) ALD stabilization (labeled “ALD 2”). Panel (c) is adapted with permission from ref 170. Copyright 2015 Royal Society of Chemistry.

ALD has also been extended as a synthesis tool for the direct preparation of stabilized chromophore–catalyst assemblies encased in the oxide by a “mummy” strategy.¹⁷⁰ Figure 6b,c illustrates calculated ALD overlayer structures for surface-bound $-\text{RuP}^{2+}$ and the corresponding “mummy” chromophore–catalyst assembly, with the stepwise “mummy” synthesis protocol outlined in Figure 6d.

5. DSPEC PROCESSES

5.1. Light Absorption. The sun is a relatively low-intensity, wavelength-dependent light source. In a standard AM 1.5G solar flux, a 1 nm dye molecule with a molar absorptivity of $2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ can absorb only ~ 2 photons per second in the visible and near-IR regions and only ~ 0.3 photon per second in the UV.^{23,58,171,172} The maximum efficiency for solar water splitting with an absorption cutoff of 500 nm is $\sim 12\%$, rising to $\sim 18\%$ by 600 nm.

High light absorption by the chromophore is obviously desirable to minimize oxide film thickness and, with it, competition from back electron transfer following injection. For $[\text{Ru}(\text{bpy})_3]^{2+}$ in CH_3CN with $\lambda_{\text{max}} = 449 \text{ nm}$ and $\epsilon = 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, the molar absorptivity decreases to $5.1 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ by 550 nm. In a nanoparticle oxide film of the phosphonate derivative $[\text{Ru}(4,4'-(\text{PO}_3\text{H}_2)_2\text{bpy})(\text{bpy})_2]^{2+}$ (RuP^{2+} , Figure 6b) with a per-micron surface coverage of $\Gamma = 2 \times 10^{-9} \text{ mol}/(\text{cm}^2 \cdot \mu\text{m})$, the film thickness required for an absorbance of 2 OD at 450 nm is $\sim 7 \mu\text{m}$.

The usefulness of a dye is limited not only by its absorption spectrum but also by free energy constraints. Once an excited state is formed, it must be capable of undergoing electron or hole injection. In addition, the oxidized or reduced forms of the chromophore that result must be capable of driving water oxidation or water/ CO_2 reduction to completion.^{35,43,87,88}

An extensive and growing list of chromophores has been investigated for applications in DSSC devices.^{23–25,173–184} Ru(II) polypyridyl chromophores have dominated DSPEC investigations to date, but 3,4:9,10-substituted perylenes,^{182,184} porphyrins,^{174,176,178,181,183} and amine-thiophene-based donor–acceptor dyes^{173,174} have also been used.

Antenna Effect: The Multichromophore Advantage. In the absence of a solar concentrator, the output of a dye-sensitized solar device is limited by the slow, $1\text{--}2 \text{ s}^{-1}$, rate of solar insolation, which poses a major challenge to achieving high DSPEC efficiencies.^{23,58,171,172} In a DSSC, redox equivalents appear and are used one photon at a time. In a DSPEC, multiple redox equivalents have to be *accumulated and stored for seconds*.

In natural photosynthesis, an antenna effect overcomes the slow solar input. In photosystem II, a multichromophore–antenna array absorbs light and rapidly and efficiently transmits excited-state energy to a single terminal acceptor, chlorophyll P_{680} . Oxidative electron-transfer quenching of $^1\text{P}_{680}^*$ and a sequence of five electron-transfer steps deliver oxidative equivalents to the Mn_4Ca cluster in the oxygen-evolving complex separated from photoproduced reductive equivalents, initially in quinone Q_A , by $\sim 50 \text{ \AA}$. The antenna enhances the rate of solar insolation from $(\text{seconds})^{-1}$ to $(\text{milliseconds})^{-1}$, thereby greatly reducing the time scale required for storage of the oxidative equivalents as they appear.^{185–191} Related antenna strategies may be available for DSPEC applications by integration with independent solar concentrators or by using derivatized, polychromophoric polymers. The latter approach is currently under investigation by Kirk Schanze and John Reynolds in the University of North Carolina Energy Frontier Research Center.

5.2. Excited-State Injection. Following light absorption by the chromophore, excited-state injection initiates the series of redox events that ultimately lead to water oxidation or water/ CO_2 reduction. Electron or hole injection depends on an overlap between the energy of the excited state, acting as an

electron or hole donor, and a distribution of unfilled acceptor levels on an n-type oxide, e.g., TiO_2 , or filled donor levels at a p-type oxide, e.g., NiO. Injection is in competition with other excited-state processes: non-radiative decay, emission, and non-productive energy or electron transfer. To be useful, electron or hole injection must occur with high efficiency, with the resulting oxidized or reduced chromophore capable of driving water oxidation or water/ CO_2 reduction through complete multi-electron, multi-proton catalytic cycles.

With the MLCT excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ as the example, the formal potential for the excited-state couple, $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+*}$, with the excited state acting as a reducing agent, $E^\circ(\text{Ru}^{3+/2+*})$, is given by eq 6, with F being Faraday's constant. $E^\circ(\text{Ru}^{3+/2+})$ ($= 1.26 \text{ V}$ vs NHE in water) is the potential of the ground-state couple. ΔG_{ES} ($\sim 2.1 \text{ eV}$) is the free energy of the excited state above the ground state, which is obtained by a Franck–Condon analysis of the emission spectral profile in CH_3CN .^{21,29,192–195} For the excited state acting as an oxidizing agent, $E^\circ(\text{Ru}^{2+*/+})$ for the $[\text{Ru}(\text{bpy})_3]^{2+*}/[\text{Ru}(\text{bpy})_3]^+$ couple is given by eq 7.

$$E^\circ(\text{Ru}^{3+/2+*}) = E^\circ(\text{Ru}^{3+/2+}) - \Delta G_{\text{ES}}^\circ/F \quad (6)$$

$$E^\circ(\text{Ru}^{2+*/+}) = E^\circ(\text{Ru}^{2+*/+}) + \Delta G_{\text{ES}}^\circ/F \quad (7)$$

Electron injection into TiO_2 , extensively studied,^{23,139–141,143,171,196–238} is kinetically complex, a characteristic commonly attributed to heterogeneities in the oxide.^{23,171,172,239} Electron injection can occur by direct light-driven electron transfer from a donor level on the chromophore to an acceptor level in the semiconductor^{139,204,240} or, more commonly, from an excited state or states following light absorption.^{172,196,197,200,202,207,228,231,235–238,241–246} From the experimental data for $-\text{RuP}^{2+}$ and its analogues on TiO_2 , the initial electron injection process or processes occur on the hundreds of femtoseconds to hundreds of picoseconds time scale from the initially formed singlet MLCT state(s), $\text{TiO}_2|^{-1}\{[(4,4'-(\text{PO}_3\text{H}_2)_2\text{bpy})\text{Ru}^{\text{III}}(\text{bpy})_2]^{2+*}\}$, before $^1\text{MLCT} \rightarrow ^3\text{MLCT}$ internal conversion can occur. Electron injection can also take place from non-thermally equilibrated $^3\text{MLCT}$ states before they undergo vibrational relaxation. The remaining injection events occur from lowest-lying, thermally equilibrated $^3\text{MLCT}$ states.^{196,197,199,211,222,223,240} In acidic solution with injection thermodynamically favorable, electron injection into TiO_2 by the MLCT excited states of phosphonate derivatives like $-\text{RuP}^{2+}$ is typically complete in $<1 \text{ ns}$ and highly efficient. These excited states undergo electron injection with low reorganizational barriers into a relatively high density of acceptor levels in the oxide.

In a comprehensive recent study by Zigler and co-workers, based on an extensive series of Ru(II) polypyridyl complexes, electron injection into TiO_2 was found to occur with biphasic kinetics with time constants in the ranges 3–30 and 30–500 ps.²³⁸ The results for the slow component were interpreted by use of the classical Gerischer theory for interfacial electron transfer. On the basis of this analysis, it was concluded that kinetic heterogeneity on longer time scales arises from a competition between excited-state relaxation and injection as the photoexcited dye relaxes through the lower $^3\text{MLCT}$ manifold to the thermally equilibrated excited state.^{247–254}

Although not yet explored in detail, medium effects and variations in pH play a significant role in electron injection. For example, from the Nernstian pH dependence of E_{CB} for

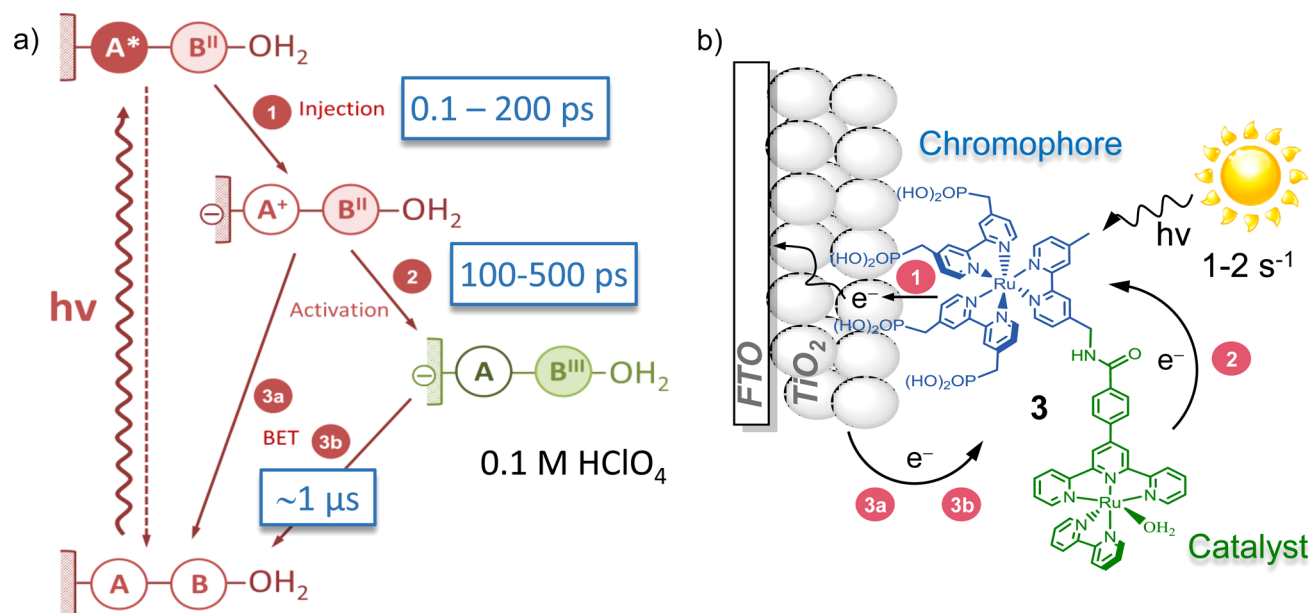


Figure 7. First photoactivation step comprising light absorption/photoinjection/electron-transfer catalyst activation and associated time scales for (a) a generic and (b) an amide-linked Ru(II) polypyridyl chromophore–catalyst assembly **3** on nanoparticle TiO₂. Adapted with permission from refs 33 and 262. Copyright 2015 and 2013, respectively, American Chemical Society.

TiO₂,^{202,255–259} the driving force for electron injection decreases by ~ 420 mV from pH 0 to 7.

Hole injection at a photocathode is significantly less well-studied, with NiO the only oxide investigated in detail. In transient absorption measurements, spectral features for the appearance of reduced chromophores on NiO, an expected product upon successful hole injection, are often not observed. Evaluation of hole injection is typically based on indirect observations, such as loss of stimulated emission features, and not the appearance of reduced chromophores.¹¹⁷ Interpretation of transient absorption results is even more challenging for chromophores with elaborate donor–acceptor structures, such as those used in the most successful p-type DSSC applications.^{124,125} Nevertheless, time constants for hole injection into NiO that vary from hundreds of femtoseconds¹¹⁷ to hundreds of picoseconds¹²⁰ have been reported. As an example, ultrafast transient spectra of [Ru(dceb)₃]²⁺ (dceb = 4,4'-bis(ethylcarboxy)-2,2'-bipyridine) on NiO show that the appearance of the reduced complex occurs with $\tau \approx 20$ ps, but the extent of hole injection is minimal.¹¹⁵

5.3. Assembly Injection and Catalyst Activation. Figure 7 summarizes the results of fs–ms transient absorption measurements on a series of Ru(II) polypyridyl assemblies on TiO₂. The processes observed are illustrated in the figure for chromophore–catalyst assembly **3**, [(4,4'-(PO₃H₂CH₂)bpy)₂-Ru_a(bpy-NH-CO-tpy)Ru_b(bpy)(OH₂)]⁴⁺.^{260–262} Visible-light absorption by the chromophore leads to rapid, sub-nanosecond electron injection followed by intra-assembly electron-transfer activation of the catalyst with $\tau_{\text{intra}} = 145$ ps in 0.1 M HClO₄ at room temperature.²⁶²

In assembly **3**, the catalyst is a competitive, nonproductive light absorber which decreases per-photon-absorbed injection efficiencies for the first injection.²⁶² Competitive light absorption by the catalyst is not a factor after the catalyst is oxidized past Ru(II) as the higher oxidation states of the ruthenium catalyst are only weak light absorbers in the visible.

5.4. Water Oxidation. Semiconductor-based photoelectrochemical cells and commercial water electrolyzers use metal

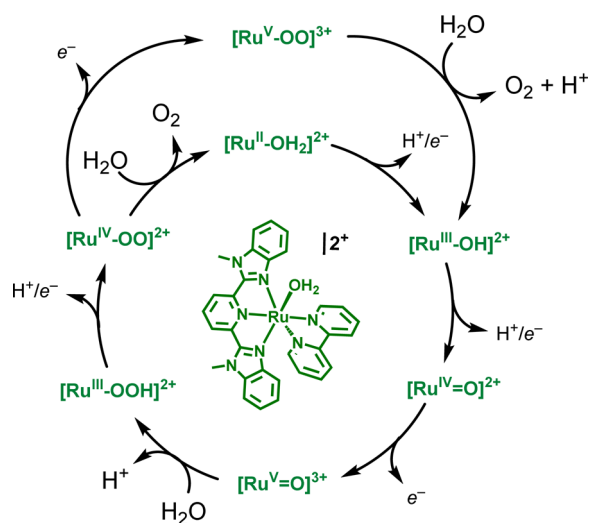
oxide catalysts RuO₂, NiO, and CoO.^{263–271} In a DSPEC, water oxidation occurs at a molecular catalyst. Although less robust than oxides, molecular catalysts have at least two advantages: (1) chemical synthesis can be used to modify structure to affect rates and reactivity, and (2) mechanisms can be evaluated in detail by standard electrochemical and spectroscopic techniques.

Water oxidation catalysis has been reported for molecular complexes²⁷² of Ru(II),^{273–279} Ir(III),^{280–286} Co(III),^{287–290} Cu(II),^{291–293} and Fe(II),^{294–297} with polypyridyl complexes of Ru(II) dominating research in this area.^{276,278,298–305} The underlying synthetic chemistry for these complexes is well developed,^{28,299,306–315} and they offer access to coordinatively stable oxidation states from Ru(II) to Ru(VI), with the higher oxidation states stabilized by oxo and nitrido ligands.^{299,311–313,315–317}

Demands on water oxidation catalysts are high. The catalyst must be integrated with a chromophore or chromophores on a semiconductor oxide surface. Rates of water oxidation need to exceed the 1–2 s⁻¹ rate of solar insolation by 10 or greater, even higher with solar concentration. Long-term performance is also essential. A figure of merit for commercialization of $\geq 10^6$ turnovers per year has been cited,^{32,33,35,43} with turnovers of 10 000s reported for existing catalysts,^{162,276,279,318} as well as one example of >100 000 turnovers for a molecular Ir catalyst.

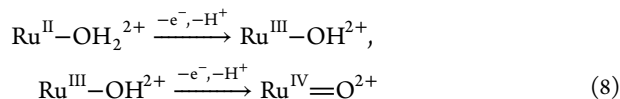
The mechanism of water oxidation by Ru(II) polypyridyl complexes has been investigated by voltammetric techniques and by Ce(IV) oxidation with spectrophotometric monitoring. A general mechanism is shown for [Ru(Mebimpy)(bpy)-(OH₂)]²⁺ in Scheme 2.^{273,301,305} The sequence of reactions in the cycle shown in Scheme 2 add up to meet the 4e⁻/4H⁺ demands of the half-reaction. Mechanisms involving initial 1e⁻ oxidation through the hydroxyl radical are not viable because of the high potential of the OH[•]/H₂O couple, with $E^\circ = 2.32$ V at pH 7.³¹⁹

Depending on conditions and catalyst, the rate-limiting step in water oxidation cycles can occur at the step for oxidative activation of Ru^{III}-OH²⁺ or Ru^{III}-OH₂³⁺ to Ru^{IV}=O²⁺, from

Scheme 2. Mechanism of Water Oxidation by $[\text{Ru}(\text{Mebimpy})(\text{bpy})(\text{OH}_2)]^{2+}$ 

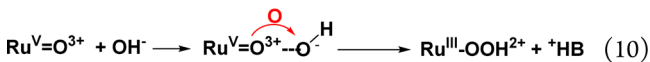
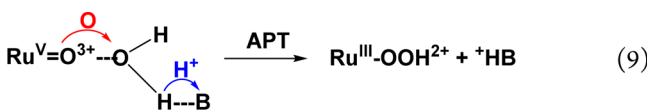
loss of O_2 from the $\text{Ru}^{\text{IV}}(\text{OO})^{2+}$ peroxide intermediate, and most commonly, from O---O bond formation.³²⁰ Evidence has been found for related mechanisms using first-row transition metal complexes of $\text{Cu}(\text{II})$ ^{292,293,321–323} and $\text{Fe}(\text{II})$.³²⁴

In water oxidation cycles, in addition to being the substrate, coordinated water plays a key role mechanistically. Oxidation and proton loss by proton-coupled electron transfer (PCET),



is important in avoiding charge buildup, allowing multiple oxidative equivalents to accumulate at single sites or clusters over a narrow potential range.^{303,325–328} The intermediate oxo complexes have a well-established and extensive reactivity chemistry based on concerted electron–proton transfer (EPT), H-atom transfer, C–H insertion, hydride transfer, and O-atom transfer mechanisms.^{185,273,279,299,301,305,311,329,330} The latter, with O-atom transfer to a water molecule, is the rate-limiting step for the catalyst in Scheme 2.

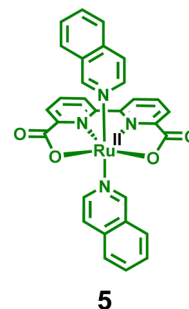
O---O bond formation occurs by concerted atom proton transfer (APT) in which O-atom transfer occurs in concert with loss of a proton to an external base, B. As shown in eq 9, B can



be a water molecule or water cluster, or an added proton acceptor base.^{277,301,304,320,331,332} Although microscopically complex, APT has the advantage of giving the hydroperoxide intermediate $\text{Ru}^{\text{III}}(\text{OOH})^{2+}$ directly while avoiding the higher energy hydrogen peroxide intermediate, $\text{Ru}^{\text{III}}(\text{OOH}_2)^{3+}$, by direct reaction with H_2O .³²⁰ At even higher pH, with the concentration of OH^- kinetically significant, direct reaction between $\text{Ru}^{\text{V}}(\text{O})^{3+}$ and OH^- plays an increasingly important role, eq 9, dominating reactivity in highly basic solutions.¹⁶²

By exploiting APT with added buffer bases, even catalysts that are slow in acidic solution can approach and exceed the 1–2 s^{-1} threshold rate for solar insolation. For surface-bound $[\text{Ru}(\text{Mebimpy})(4,4'-(\text{PO}_3\text{H}_2\text{CH}_2)_2\text{bpy})(\text{OH}_2)]^{2+}$ in Figure 6a, the rate of water oxidation is enhanced by $\sim 10^6$ on going from pH 1 to pH 12, reaching a turnover rate of $\sim 10^4 \text{ s}^{-1}$ with 12 mM added PO_4^{3-} .¹⁶²

Impressive catalytic rates and turnover numbers have been reported for a family of catalysts based on $\text{Ru}(\text{bda})(\text{L})_2$ (L = neutral donor ligand), complexes introduced by Sun and co-workers.^{55,276,333–338} Evidence has been found, from kinetic measurements with $\text{Ce}(\text{IV})$ as the oxidant in acidic solution, for a facile mechanism involving seven-coordinate $\text{Ru}^{\text{V}}(\text{O})^+$ and bimolecular O---O coupling.²⁷⁸ For $\text{Ru}^{\text{II}}(\text{bda})(\text{isoq})_2$, 5 (Figure 8, isoq = isoquinoline), oxidation and chelate ring opening give

Figure 8. Structure of water oxidation catalyst $[\text{Ru}^{\text{II}}(\text{bda})(\text{isoq})_2]$, 5.

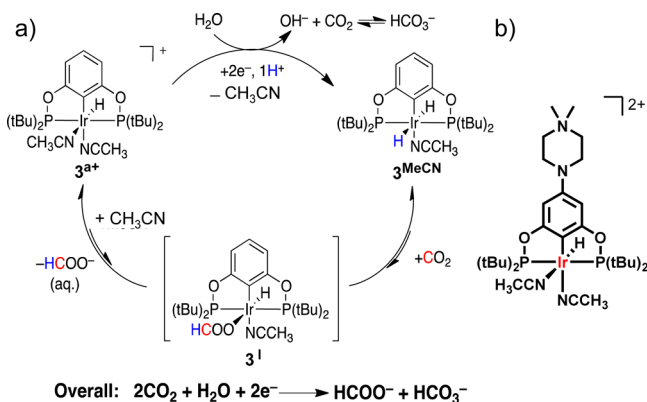
$\text{Ru}^{\text{IV}}=\text{O}$, and further $1e^-$ oxidation gives $\text{Ru}^{\text{V}}(\text{O})^+$. As in the cycle in Scheme 2, $\text{Ru}^{\text{V}}(\text{O})^+$ appears to undergo O-atom transfer to water to give an intermediate hydroperoxide.³³⁷

5.5. CO_2 Reduction. Electrocatalytic reduction of CO_2 ^{339–342} is well advanced at metallic, alloy, and nanoparticle electrodes,^{343–353} by pyridine/pyridinium catalysts as described by Bocarsly and co-workers,^{354–363} and by a variety of transition metal complexes.^{364–370} For the latter, CO_2 reduction in water is typically in competition with proton reduction to H_2 and limited to the $2e^-$ products $\text{HCOO}^-/\text{HCOOH}$ or CO . In a DSPEC with water as the solvent, under conditions appropriate for both DSPEC water oxidation and CO_2 reduction, the limited solubility of CO_2 , 0.034 M at 1 atm pressure and 298 K, is a factor limiting reactivity, as is pH. CO_2 is the reactive form, and with $\text{pK}_a = 6.3$ for the equilibrium $\text{H}_2\text{CO}_3(\text{CO}_2(\text{aq})) \rightleftharpoons \text{HCO}_3^- + \text{H}^+$ (298 K, $I = 0$), the concentration of CO_2 falls rapidly as the pH is increased above 6.3.

The Ir(III) pincer catalyst $[(\text{POCOP})\text{Ir}(\text{CH}_3\text{CN})_2(\text{H})]^+$ ($\text{POCOP} = 2,6-(\text{OP}^t\text{Bu}_2)_2\text{C}_6\text{H}_3$) is a selective electrocatalyst for CO_2 reduction to HCOO^- in CH_3CN with added water. The mechanism is shown in Scheme 3. In this mechanism, the rate-limiting step is CO_2 insertion into the Ir–H bond with $k = 20(2) \text{ M}^{-1} \text{ s}^{-1}$ in CO_2 -saturated solutions.³⁷¹ Catalysis has been extended to water as the solvent with a high selectivity toward formate by using the soluble aminium catalyst,³⁷² shown in Scheme 3, and to a pyrene derivative for CO_2 reduction on high surface area carbon nanotube electrodes.³⁷³

Fischer–Tropsch synthesis converts $\text{H}_2:\text{CO}$ (syngas) mixtures into methanol or hydrocarbons, with the product depending on the $\text{H}_2:\text{CO}$ ratio.^{374–381} In aqueous, CO_2 -saturated solutions with the added weak acid H_2PO_4^- , $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ has been shown to act as an electrocatalyst for syngas formation with the $\text{H}_2:\text{CO}$ ratio

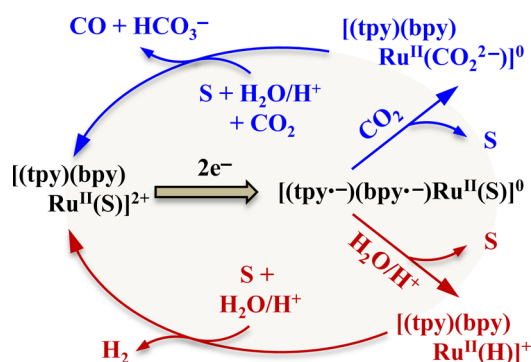
Scheme 3. (a) Catalytic Cycle for CO₂ Reduction to HCOO⁻ by [(POCOP)Ir(CH₃CN)₂(H)]⁺ and (b) Structure of a Water-Soluble Aminium Derivative



^aAdapted with permission from refs 372 and 373. Copyright 2013 Royal Society of Chemistry and 2014 Wiley-VCH Verlag, respectively.

controlled by varying the concentration of added acid. In the mechanism in Scheme 4, reduction at the polypyridyl ligands

Scheme 4. Electrocatalytic Reduction of CO₂ to H₂:CO Mixtures by [Ru(tpy)(bpy)S]²⁺ (S is solvent) with the Added Weak Acid H₂PO₄ as the Proton Source



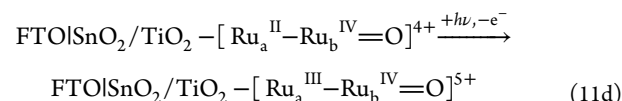
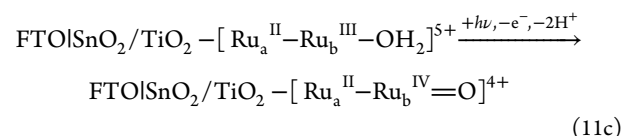
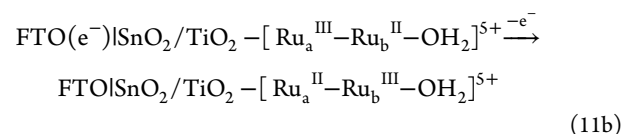
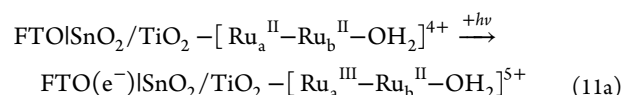
triggers solvent loss to give the 5-coordinate intermediate, [Ru(tpy)(bpy)]⁰, which then reacts with CO₂ to give the metalcarboxylate intermediate, [Ru(tpy)(bpy)(CO₂)]⁰. Formation of the metalcarboxylate is in competition with reaction with water to give the hydride, [Ru(tpy)(bpy)H]⁺. The two intermediates react further under reducing conditions to give CO and H₂, respectively.^{382,383}

The carbene water oxidation catalyst in assembly 1, [Ru(tpy)(Mebimpy)(H₂O)]²⁺, is also a catalyst for CO₂ reduction to syngas in aqueous HCO₃⁻/CO₂ solutions. Remarkably the same complex, in aqueous HCO₃⁻/CO₂, has been used as the sole catalyst for both electrocatalytic water oxidation at the anode and CO₂/HCO₃⁻ reduction to syngas at the cathode in an electrolysis cell. In these experiments, the syngas ratio was quantified and ranged from ~4:1 to ~1:3 by varying the electrolysis potential at a fixed concentration of HCO₃⁻ or, at E_{app} = -1.2 V, from ~4:1 to ~1:2 by varying the concentration of HCO₃⁻.³⁸⁴

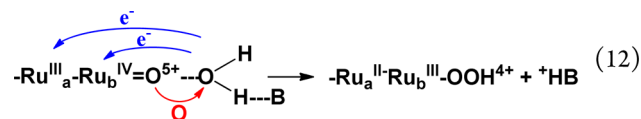
6. DSPEC PHOTOANODES FOR WATER OXIDATION

An assembly oxide interface lies at the heart of a DSPEC photoanode for water oxidation. Many factors interplay to meet

the energetic, time scale, and mechanistic demands for carrying out the overall light-driven reaction:



6.1. Energetics. For assembly 1 in the DSPEC photoanode in Figure 2, water oxidation at the carbene catalyst occurs by a mechanism closely related to the single-site mechanism in Scheme 2, including the requirement of oxidation to Ru^V(O)³⁺ at 1.6–1.7 V.³⁸⁵ For assembly 1 on a SnO₂/TiO₂ core/shell photoanode, the initial electron injection event gives $-\text{[Ru}_a^{\text{III}} - \text{Ru}_b^{\text{II}} - \text{OH}_2]^{5+}$, eq 11a. With E^o(Ru^{III}/II) = 1.36 V vs NHE for the $-\text{Ru}_a^{\text{III}} - \text{Ru}_b^{\text{II}} - \text{OH}_2$ couple, it is capable of oxidizing the catalyst from $-\text{Ru}_b^{\text{II}} - \text{OH}_2$ to $-\text{Ru}_b^{\text{III}} - \text{OH}_2$, eq 11b, and then to $-\text{Ru}_b^{\text{IV}} = \text{O}^{2+}$, eq 11c, with E^o = 1.15 and 0.90 V for the catalyst Ru(III/II) and Ru(IV/III) couples, respectively, at pH 1. Injection and loss of a third electron gives the 3e⁻/2H⁺-activated assembly $-\text{[Ru}_a^{\text{III}} - \text{Ru}_b^{\text{IV}} = \text{O}]^{5+}$, eq 11d. At this stage, access to Ru^V(O)³⁺ by intra-assembly electron transfer, $-\text{[Ru}_a^{\text{III}} - \text{Ru}_b^{\text{IV}} = \text{O}]^{5+} \rightarrow -\text{[Ru}_a^{\text{II}} - \text{Ru}_b^{\text{V}}(\text{O})]^{5+}$, is uphill by ~300 mV. Even with the chromophore oxidized to Ru(III), there is no basis for further photoactivation, and assembly 1 should be incapable of DSPEC water oxidation. Despite this, water oxidation does occur thanks to a previously unknown, assembly-based pathway for O–O bond formation involving concerted electron/O-atom/proton transfer, with both oxidized sites in the assembly acting as electron acceptors, eq 12.³⁸⁵



6.2. Dynamics. With the slow rate of solar input of 1–2 s⁻¹, and the requirement for storing oxidative equivalents for seconds, time scale poses another significant challenge for DSPEC water oxidation.

Figure 7 provides a time scale summary for the first of the four light-driven activation steps for a typical assembly. Injection and electron-transfer activation of the catalyst are rapid, but a competition exists for the injected electron between back electron transfer to the assembly and electron diffusion through the nanoparticle film to the FTO electrode. On TiO₂, back electron transfer occurs on the microsecond to millisecond time scale, with highly non-exponential kinetics attributed to electron diffusion dynamics within and across the oxide. The diffusion rate varies with applied bias, light intensity, and other factors but typically occurs on the

millisecond time scale. Distance-dependent, chemically rate-limiting, back electron transfer has been observed for assemblies with molecular spacers between chromophore and catalyst.^{73–75,77,78} In an ongoing study on the assembly $[(4,4'-\text{PO}_3\text{H}_2)_2\text{bpy}]_2\text{Ru}(4,4'-\text{CH}_3\text{bpyCH}_2\text{CH}_2\text{bpy}-4,4'-\text{CH}_3)\text{Ru}(\text{Mebimpy})(\text{OH}_2)]^{4+}$, **4** (Figure 9), with a $-\text{CH}_2-\text{CH}_2-$ spacer,

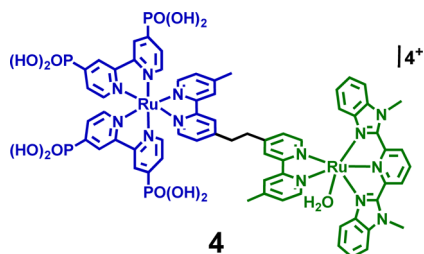


Figure 9. Chromophore–catalyst assembly $[(4,4'-\text{PO}_3\text{H}_2)_2\text{bpy}]_2\text{Ru}(4,4'-\text{CH}_3\text{bpyCH}_2\text{CH}_2\text{bpy}-4,4'-\text{CH}_3)\text{Ru}(\text{Mebimpy})(\text{OH}_2)]^{4+}$, **4**.

back electron transfer was decreased in rate by a factor of ~ 6 compared to that with $-\text{RuP}^{2+}$. With the data fit to the Williams–Watts–Kohlrausch stretched exponential function, the average rate constant for back electron transfer was $k = 3.3 \times 10^3 \text{ s}^{-1}$.³⁸⁶ Because back electron transfer occurs on the microsecond to millisecond time scale, there is a significant and deleterious mismatch in rates, even for the first photoactivation step. From the dynamics of diffusion and back electron transfer, the efficiency for building up multiple oxidative equivalents at the catalyst should be negligible.

Core/Shell Advantage. In a DSSC, an ensemble of single excitation events is sufficient to produce a photopotential and photocurrent. Nevertheless, in both DSSCs and DSPECs, back electron transfer is a major rate-limiting pathway to be overcome, and many strategies have been investigated to slow it.^{163,166–168,387–398} In DSPEC photoanodes, core/shell oxide structures have proven to be sufficiently effective in controlling back electron transfer.^{32,43,65,237,387,399–404} They are produced by ALD of conformal oxide shells on exposed nanoparticle surfaces. A transmission electron micrograph (TEM) of a *nano*ITO/ TiO_2 core/shell structure is shown in Figure 10. Typically, they consist of thin, 3–5 nm, shells of TiO_2 on nanoparticle films of either SnO_2 or a TCO.^{32,65,387,399–402} On a TCO core, photoinjection is followed by rapid transfer to and through the core to the FTO electrode for transmission to a cathode or photocathode for water/acid reduction to H_2 . With the $\text{SnO}_2/\text{TiO}_2$ core/shell in Figure 2, the per-photon-absorbed efficiency is further increased above that observed for TCO core/shells by a factor of 3–5. The increase is attributed to the $\sim 0.4 \text{ V}$ potential offset between the conduction band edge potentials for the two oxides, which creates a barrier to back electron transfer from core to shell.^{65,387}

6.3. DSPEC Photoanodes. The DSPEC concept is relatively new and still evolving, with a growing literature from a number of research groups worldwide.^{20,26–64,91,237,272,277,279,311,405–410}

As an example from our own work, sustained DSPEC water splitting was demonstrated for covalently linked assembly **1** in Figure 2 on *nano*ITO/ TiO_2 and $\text{SnO}_2/\text{TiO}_2$ core/shell electrodes. In an initial set of experiments on *nano*ITO/ TiO_2 , an absorbed-photon-to-current efficiency (APCE) of 4.4% with 445 nm irradiation was obtained in a pH 4.6 acetate buffer with an applied bias of 200 mV vs NHE. The photocurrent decreased from $185 \mu\text{A}/\text{cm}^2$ to $20 \mu\text{A}/\text{cm}^2$ over an extended

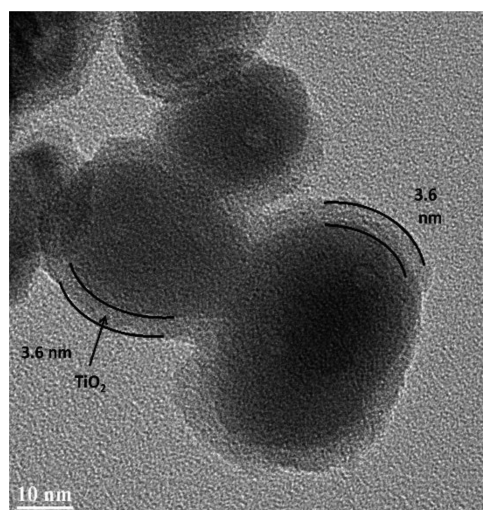


Figure 10. Transmission electron micrograph of a *nano*ITO/ TiO_2 core/shell with a 3.6 nm thick outer shell of TiO_2 . Adapted with permission from ref 387. Copyright 2013 Proceedings of the National Academy of Sciences, USA.

photolysis period because of desorption of the assembly and decomposition of the chromophore.³⁸⁷ For assembly **1** on $\text{SnO}_2/\text{TiO}_2$ with ALD overlayer stabilization of assembly binding to the surface, the APCE for water splitting increased to $\sim 20\%$, with maximum photocurrents of $1.97 \text{ mA}/\text{cm}^2$. There was still long-term loss of photocurrent caused by decomposition of the chromophore.¹⁵⁰

For the vinyl-linked assembly in Figure 11 on a $\text{SnO}_2/\text{TiO}_2$ core/shell electrode, 1 sun ($100 \text{ mW}/\text{cm}^2$) illumination in 0.1

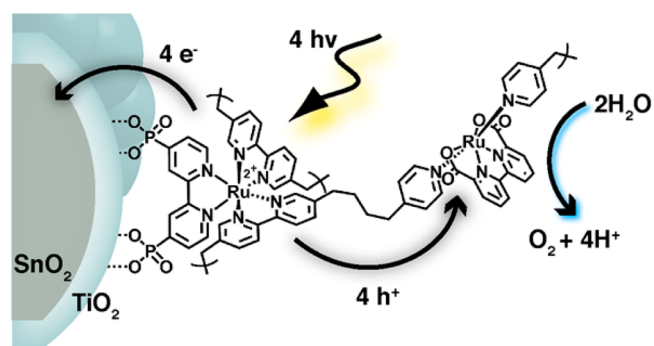


Figure 11. Vinyl-linked electro-assembly on a $\text{SnO}_2/\text{TiO}_2$ core/shell electrode. Reproduced with permission from ref 402. Copyright 2015 American Chemical Society.

$\text{M H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ with an applied bias of 0.4 V vs SCE led to sustained water splitting, with O_2 produced with a Faradaic efficiency of 22%, as measured by a collector-generator method.⁴¹¹ With 450 nm ($14 \text{ mW}/\text{cm}^2$) LED illumination, the solar efficiency for hydrogen production was $\sim 0.3\%$.⁴⁰²

The phosphonate-derivatized donor–acceptor dye, P-A- π -D in Figure 12, undergoes rapid, efficient injection on $\text{SnO}_2/\text{TiO}_2$ core/shell electrodes.⁴⁰¹ With 1 sun excitation in a phosphate buffer at pH 7 and with 20 mM hydroquinone (H_2Q) added as a reductive scavenger, sustained photocurrents of $\sim 2.5 \text{ mA}/\text{cm}^2$ were observed for $>15 \text{ min}$, with a DSPEC solar efficiency for dehydrogenation of H_2Q , $\text{H}_2\text{Q} + 2h\nu \rightarrow \text{Q} + \text{H}_2$, of $\sim 6\%$. On surfaces co-loaded with [P-A- π -D] and the water oxidation catalyst $\text{Ru}(\text{bda})(\text{pyP})_2$ (pyP = pyridin-4-methylphosphonic

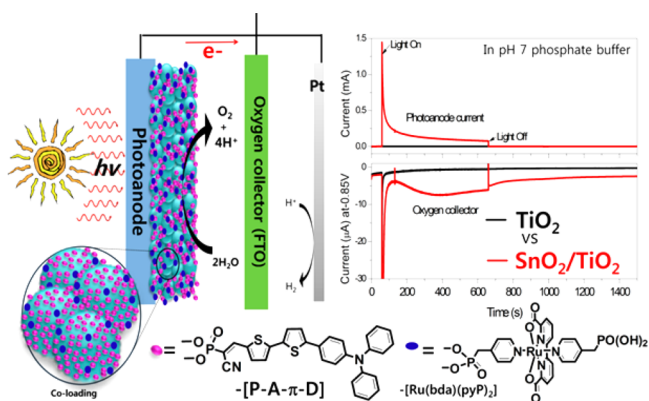


Figure 12. Co-loaded donor-acceptor/catalyst assembly [P-A- π -D]/[Ru(bda)(pyP)₂] (5:1 ratio) on a DSPEC photoanode in a collector-generator configuration for *in situ* O₂ measurements.⁴⁰¹ Upper plot: current–time trace with 1 sun illumination (100 mW/cm²; 400 nm long-pass filter; 60–600 s) on FTO/TiO₂ (black line) and FTO/SnO₂/TiO₂(3 nm) core/shell (red line) electrodes in 0.1 M phosphate buffer at pH 7 with an applied bias of 0.2 V vs SCE. Lower plot: current–time traces at the FTO collector electrode of a collector-generator cell for monitoring O₂ at –0.85 V vs SCE. Reproduced with permission from ref 401. Copyright 2016 Royal Society of Chemistry.

acid), maximum photocurrents of 1.4 mA/cm² were obtained which decreased with time to 0.1 mA/cm² because of decomposition of the dye, giving a Faradaic efficiency for O₂ of only 8.2%.⁴⁰¹

7. DSPEC PHOTOCATHODES AND THE TANDEM DSPEC

Our ultimate DSPEC goals are efficient bias-free water splitting and reduction of CO₂ to carbon-based fuels. Our research focus to date has been on photoanodes for water oxidation. However, a significant research effort is focused on DSPEC photocathodes, bias-free water splitting, and integration of photoanodes and photocathodes in tandem cells for CO₂ reduction.

An extended version of Figure 1, showing a DSPEC for CO₂ splitting into CO and O₂, is presented in Figure 13. It combines two photoelectrodes—the photoanode in Figure 1 and a photocathode for light-driven reduction of CO₂ to CO—both integrated into a single device.

The sequence of events shown at the *photocathode* in Figure 13 is as follows:^{130,412} (1) light absorption; (2) electron transfer from the conduction band of a p-type oxide to the excited state or states (hole transfer from the excited state(s) to the electrode); (3) hole diffusion through the oxide to an inner TCO electrode; (4) 1e[−] activation of a catalyst for CO₂ reduction; and (5) repetition of the cycle for reduction of CO₂ to CO.

In a tandem cell for water splitting, there are two photoreactions, which requires twice as many photons as water splitting at a single photoelectrode. However, properly designed tandem cells offer much broader coverage of the solar spectrum and higher solar efficiencies. They are also advantageous energetically. As an example, at a single TiO₂ photoanode with [Ru(4,4′-(PO₃H₂)₂bpy)(bpy)₂]²⁺ (–RuP²⁺) as the light absorber, excitation and electron injection give –RuP³⁺ with $E^{o'}$ = 1.3 V for the –RuP^{3+/2+} couple, but the injected electron in the conduction band of TiO₂ is weakly reducing, with E_{CB} ≈ –0.1 V vs NHE at pH 0.^{202,255–259} It is insufficiently reducing to convert CO₂ to CO or HCOOH, with

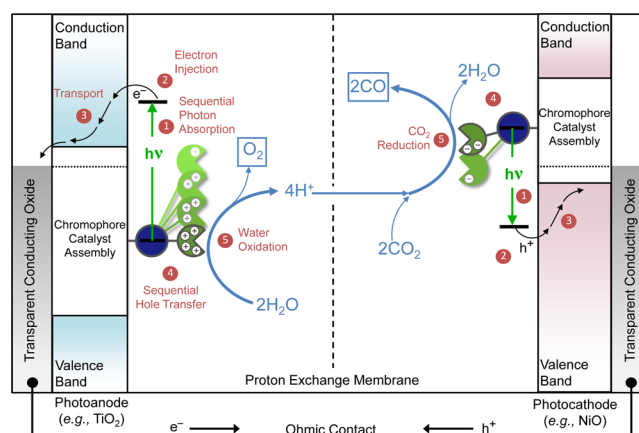


Figure 13. Schematic diagram of a tandem DSPEC for solar-driven CO₂ splitting into CO and O₂ by the net reaction, 2CO₂ + 4hν → 2CO + O₂. Reproduced with permission from ref 33. Copyright 2015 American Chemical Society.

$E^{o'} = -0.2$ V for the CO₂/HCOOH couple under the same conditions.^{63,413–416} By contrast, reduction of RuP^{2+*} by hole injection at a p-type oxide photocathode gives –RuP⁺, which is a powerful reducing agent, with $E^{o'} = -1.2$ V for the RuP^{2+/+} couple. In this example, a tandem cell configuration could provide a boost of more than 1 V in reducing power compared to that produced by a single electrode.

A tandem cell for water splitting based on an organic dye on NiO with a transition metal catalyst for H₂ evolution at the photocathode has been reported by Sun and co-workers.⁴⁷ We are currently exploring other approaches based on bias-free electrodes and other electrode configurations. An important issue in these cells is maximizing efficiencies by balancing current–potential output and wavelength of light between the electrodes.^{35,408,409,417,418}

8. LOOKING AHEAD: CHALLENGES FOR THE FUTURE

The DSPEC offers one approach to artificial photosynthesis and solar energy conversion. Key elements and principles are emerging, and the concept has been substantiated by early experimental results. Progress has been made in integrating light absorption and interfacial electron-transfer dynamics with multi-electron, multi-proton catalysis of water oxidation and CO₂ reduction. Much has been learned about interfacial dynamics and the role of surface structure, with the twin goals of achieving higher solar efficiencies and long-term stabilities.

However, the DSPEC is still an ongoing research project. Basic research challenges remain, and additional challenges are waiting in device design and evaluation, engineering, and scale-up.

8.1. Research Challenges. The stage is set for future research in this area with significant challenges to be met:

- Enhancing catalytic activity and long-term catalyst stability for key solar fuels half-reactions
- Integrating catalysts in photocathode assemblies for water/acid or CO₂ reduction
- Extending light absorption further into the visible and near-IR regions while maintaining excited-state energetics for injection and catalyst activation
- Stabilizing or avoiding decomposition of oxidized or reduced chromophores and other components

- Improving interfacial electron-transfer dynamics by modifying interfacial oxide and assembly structures
- Uncovering and implementing efficient designs for bias-free water splitting, photocathodes for CO₂ reduction, and tandem cells for the integration of water oxidation and CO₂ reduction
- Exploring cell design and scale-up including proton exchange membranes, zero gap configurations, gas collection designs, and application of full cell modeling
- Achieving long-term stability under DSPEC operating conditions

8.2. Target Metrics. It is also useful to summarize long-term target metrics for a working DSPEC device:

- Converting solar photons into redox equivalents in chromophore–catalyst assembly photoelectrodes with >90% efficiency
- Accumulating multiple redox equivalents at catalyst sites for water oxidation or CO₂ reduction with efficiencies >95% on the time scale of the light source, seconds for ambient sunlight, less with solar concentration
- Achieving catalytic rates of >10 s⁻¹ for the target half-reactions, higher with solar concentration
- Achieving overall device efficiencies of 15% with 10⁷ cycles/year and a 95% retention in photoreactivity

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Sapunkov, O.; Pande, V.; Khetan, A.; Choomwattana, C.; Viswanathan, V. *Transl. Mater. Res.* **2015**, *2*, 045002.
- (2) Blankenship, R. E.; Tiede, D. M.; Barber, J.; Brudvig, G. W.; Fleming, G.; Ghirardi, M.; Gunner, M. R.; Junge, W.; Kramer, D. M.; Melis, A.; Moore, T. A.; Moser, C. C.; Nocera, D. G.; Nozik, A. J.; Ort, D. R.; Parson, W. W.; Prince, R. C.; Sayre, R. T. *Science* **2011**, *332*, 805–809.
- (3) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37–38.
- (4) Butler, M. A. *J. Appl. Phys.* **1977**, *48*, 1914–1920.
- (5) Kudo, A.; Kato, H.; Tsuji, I. *Chem. Lett.* **2004**, *33*, 1534–1539.
- (6) Kay, A.; Cesar, I.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 15714–15721.
- (7) Chen, X.; Shen, S.; Guo, L.; Mao, S. S. *Chem. Rev.* **2010**, *110*, 6503–6570.
- (8) Hong, S. J.; Lee, S.; Jang, J. S.; Lee, J. S. *Energy Environ. Sci.* **2011**, *4*, 1781–1787.
- (9) Ling, Y.; Wang, G.; Wheeler, D. A.; Zhang, J. Z.; Li, Y. *Nano Lett.* **2011**, *11*, 2119–2125.
- (10) Katz, M. J.; Riha, S. C.; Jeong, N. C.; Martinson, A. B. F.; Farha, O. K.; Hupp, J. T. *Coord. Chem. Rev.* **2012**, *256*, 2521–2529.
- (11) Young, K. M. H.; Klahr, B. M.; Zandi, O.; Hamann, T. W. *Catal. Sci. Technol.* **2013**, *3*, 1660–1671.
- (12) Alexander, B. D.; Kulesza, P. J.; Rutkowska, I.; Solarska, R.; Augustynski, J. *J. Mater. Chem.* **2008**, *18*, 2298–2303.
- (13) Guo, L.; Hung, D.; Wang, W.; Shen, W.; Zhu, L.; Chien, C.-L.; Searson, P. C. *Appl. Phys. Lett.* **2010**, *97*, 063111.
- (14) Kochuveedu, S. T.; Jang, Y. H.; Kim, D. H. *Chem. Soc. Rev.* **2013**, *42*, 8467–8493.
- (15) Zhang, Z.; Dua, R.; Zhang, L.; Zhu, H.; Zhang, H.; Wang, P. *ACS Nano* **2013**, *7*, 1709–1717.
- (16) Albero, J.; Clifford, J. N.; Palomares, E. *Coord. Chem. Rev.* **2014**, *263–264*, 53–64.
- (17) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710–4712.
- (18) Durham, B.; Dressick, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1979**, 381–382.
- (19) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta, Rev. Bioenerg.* **1985**, *811*, 265–322.
- (20) Balzani, V.; Credi, A.; Venturi, M. *ChemSusChem* **2008**, *1*, 26–58.
- (21) Juris, A.; Balzani, V.; Barigelli, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.
- (22) Ghosh, P. K.; Brunschwig, B. S.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1984**, *106*, 4772–4783.
- (23) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595–6663.
- (24) Albero, J.; Atienzar, P.; Corma, A.; Garcia, H. *Chem. Rec.* **2015**, *15*, 803–828.
- (25) Bella, F.; Gerbaldi, C.; Barolo, C.; Grätzel, M. *Chem. Soc. Rev.* **2015**, *44*, 3431–3473.
- (26) Treadway, J. A.; Moss, J. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 4386–4387.
- (27) Youngblood, W. J.; Lee, S.-H. A.; Kobayashi, Y.; Hernandez-Pagan, E. A.; Hoertz, P. G.; Moore, T. A.; Moore, A. L.; Gust, D.; Mallouk, T. E. *J. Am. Chem. Soc.* **2009**, *131*, 926–927.
- (28) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163–170.
- (29) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. *Inorg. Chem.* **2005**, *44*, 6802–6827.
- (30) Song, W.; Chen, Z.; Brennaman, M. K.; Concepcion, J. J.; Patrocinio, A. O. T.; Iha, N. Y. M.; Meyer, T. J. *Pure Appl. Chem.* **2011**, *83*, 749–768.
- (31) Concepcion, J. J.; House, R. L.; Papanikolas, J. M.; Meyer, T. J. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15560–15564.
- (32) Alibabaei, L.; Luo, H. L.; House, R. L.; Hoertz, P. G.; Lopez, R.; Meyer, T. J. *J. Mater. Chem. A* **2013**, *1*, 4133–4145.
- (33) Ashford, D. L.; Gish, M. K.; Vannucci, A. K.; Brennaman, M. K.; Templeton, J. L.; Papanikolas, J. M.; Meyer, T. J. *Chem. Rev.* **2015**, *115*, 13006–13049.
- (34) House, R. L.; Iha, N. Y. M.; Coppo, R. L.; Alibabaei, L.; Sherman, B. D.; Kang, P.; Brennaman, M. K.; Hoertz, P. G.; Meyer, T. J. *J. Photochem. Photobiol., C* **2015**, *25*, 32–45.
- (35) Grätzel, M. *Nature* **2001**, *414*, 338–344.
- (36) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2009**, *42*, 1890–1898.
- (37) Gust, D.; Moore, T. A.; Moore, A. L. *Theor. Exp. Plant Physiol.* **2013**, *25*, 182–185.
- (38) Swierk, J. R.; Mendez-Hernandez, D. D.; McCool, N. S.; Liddell, P.; Terazono, Y.; Pahk, I.; Tomlin, J. J.; Oster, N. V.; Moore, T. A.; Moore, A. L.; Gust, D.; Mallouk, T. E. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 1681–1686.
- (39) Sherman, B. D.; Bergkamp, J. J.; Brown, C. L.; Moore, A. L.; Gust, D.; Moore, T. A. *Energy Environ. Sci.* **2016**, *9*, 1812–1817.
- (40) Moore, G. F.; Blakemore, J. D.; Milot, R. L.; Hull, J. F.; Song, H.-e.; Cai, L.; Schmuttenmaer, C. A.; Crabtree, R. H.; Brudvig, G. W. *Energy Environ. Sci.* **2011**, *4*, 2389–2392.
- (41) Young, K. J.; Martini, L. A.; Milot, R. L.; Snoeberger, R. C., III; Batista, V. S.; Schmuttenmaer, C. A.; Crabtree, R. H.; Brudvig, G. W. *Coord. Chem. Rev.* **2012**, *256*, 2503–2520.
- (42) Zhao, Y.; Swierk, J. R.; Megiatto, J. D., Jr.; Sherman, B.; Youngblood, W. J.; Qin, D.; Lentz, D. M.; Moore, A. L.; Moore, T. A.; Gust, D.; Mallouk, T. E. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15612–15618.
- (43) Swierk, J. R.; Mallouk, T. E. *Chem. Soc. Rev.* **2013**, *42*, 2357–2387.

- (44) Lindquist, R. J.; Phelan, B. T.; Reynal, A.; Margulies, E. A.; Shoer, L. E.; Durrant, J. R.; Wasielewski, M. R. *J. Mater. Chem. A* **2016**, *4*, 2880–2893.
- (45) Hagfeldt, A.; Cappel, U. B.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H.; Gibson, E. A. Dye-Sensitized Photoelectrochemical Cells. In *Practical Handbook of Photovoltaics: Fundamentals and Applications*, 2nd ed.; McEvoy, A., Markvart, T., Castañer, L., Eds.; McEvoy, A., Markvart, T., Castañer, L., Eds.; Academic Press: Boston, 2012; pp 479–542.
- (46) Hagfeldt, A.; Cappel, U. B.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H.; Gibson, E. A. Dye-Sensitized Photoelectrochemical Cells. In *Solar Cells: Materials, Manufacture and Operation*, 2nd ed.; McEvoy, A., Markvart, T., Castañer, L., Eds.; Elsevier: Waltham, MA, 2013; pp 385–441.
- (47) Li, F.; Fan, K.; Xu, B.; Gabrielsson, E.; Daniel, Q.; Li, L.; Sun, L. *J. Am. Chem. Soc.* **2015**, *137*, 9153–9159.
- (48) Wasielewski, M. R. *Acc. Chem. Res.* **2009**, *42*, 1910–1921.
- (49) Tachibana, Y.; Vayssieres, L.; Durrant, J. R. *Nat. Photonics* **2012**, *6*, 511–518.
- (50) Hammarström, L. *Acc. Chem. Res.* **2015**, *48*, 840–850.
- (51) Brimblecombe, R.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L. *Dalton Trans.* **2009**, 9374–9384.
- (52) Singh, A.; Spiccia, L. *Coord. Chem. Rev.* **2013**, *257*, 2607–2622.
- (53) Brimblecombe, R.; Koo, A.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L. *J. Am. Chem. Soc.* **2010**, *132*, 2892–2894.
- (54) Fielden, J.; Sunliner, J. M.; Han, N.; Geletii, Y. V.; Xiang, X.; Musaev, D. G.; Lian, T.; Hill, C. L. *Chem. Sci.* **2015**, *6*, 5531–5543.
- (55) Yu, Z.; Li, F.; Sun, L. *Energy Environ. Sci.* **2015**, *8*, 760–775.
- (56) Yamamoto, M.; Wang, L.; Li, F.; Fukushima, T.; Tanaka, K.; Sun, L.; Imahori, H. *Chem. Sci.* **2016**, *7*, 1430–1439.
- (57) Xiang, X.; Fielden, J.; Rodríguez-Córdoba, W.; Huang, Z.; Zhang, N.; Luo, Z.; Musaev, D. G.; Lian, T.; Hill, C. L. *J. Phys. Chem. C* **2013**, *117*, 918–926.
- (58) Kärkäs, M. D.; Verho, O.; Johnston, E. V.; Åkermark, B. *Chem. Rev.* **2014**, *114*, 11863–12001.
- (59) Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W. *Chem. Rev.* **2015**, *115*, 12974–13005.
- (60) Kirner, J. T.; Stracke, J. J.; Gregg, B. A.; Finke, R. G. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13367–13377.
- (61) Click, K. A.; Beauchamp, D. R.; Huang, Z.; Chen, W.; Wu, Y. J. *J. Am. Chem. Soc.* **2016**, *138*, 1174–1179.
- (62) Wydrzynski, T. J.; Hillier, W. *Molecular Solar Fuels*; RSC Energy and Environment Series 5; Frei, H., Schüth, F., Zhao, T. S., Eds.; The Royal Society of Chemistry: Cambridge, UK, 2012.
- (63) Morris, A. J.; Meyer, G. J.; Fujita, E. *Acc. Chem. Res.* **2009**, *42*, 1983–1994.
- (64) Concepcion, J. J.; Zhong, D. K.; Szalda, D. J.; Muckerman, J. T.; Fujita, E. *Chem. Commun.* **2015**, *51*, 4105–4108.
- (65) Alibabaei, L.; Sherman, B. D.; Norris, M. R.; Brennaman, M. K.; Meyer, T. J. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 5899–5902.
- (66) Fang, Z.; Ito, A.; Luo, H.; Ashford, D. L.; Concepcion, J. J.; Alibabaei, L.; Meyer, T. J. *Dalton Trans.* **2015**, *44*, 8640–8648.
- (67) Bettis, S. E.; Ryan, D. M.; Gish, M. K.; Alibabaei, L.; Meyer, T. J.; Waters, M. L.; Papanikolas, J. M. *J. Phys. Chem. C* **2014**, *118*, 6029–6037.
- (68) Ryan, D. M.; Coggins, M. K.; Concepcion, J. J.; Ashford, D. L.; Fang, Z.; Alibabaei, L.; Ma, D.; Meyer, T. J.; Waters, M. L. *Inorg. Chem.* **2014**, *53*, 8120–8128.
- (69) Vairaprakash, P.; Ueki, H.; Tashiro, K.; Yaghi, O. M. *J. Am. Chem. Soc.* **2011**, *133*, 759–761.
- (70) Lee, H.; Kepley, L. J.; Hong, H. G.; Akhter, S.; Mallouk, T. E. *J. Phys. Chem.* **1988**, *92*, 2597–2601.
- (71) Lee, H.; Kepley, L. J.; Hong, H. G.; Mallouk, T. E. *J. Am. Chem. Soc.* **1988**, *110*, 618–620.
- (72) Ishida, T.; Terada, K.-i.; Hasegawa, K.; Kuwahata, H.; Kusama, K.; Sato, R.; Nakano, M.; Naitoh, Y.; Haga, M.-a. *Appl. Surf. Sci.* **2009**, *255*, 8824–8830.
- (73) Hanson, K.; Torelli, D. A.; Vannucci, A. K.; Brennaman, M. K.; Luo, H.; Alibabaei, L.; Song, W.; Ashford, D. L.; Norris, M. R.; Glasson, C. R. K.; Concepcion, J. J.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 12782–12785.
- (74) Bettis, S. E.; Hanson, K.; Wang, L.; Gish, M. K.; Concepcion, J. J.; Fang, Z.; Meyer, T. J.; Papanikolas, J. M. *J. Phys. Chem. A* **2014**, *118*, 10301–10308.
- (75) Nayak, A.; Knauf, R. R.; Hanson, K.; Alibabaei, L.; Concepcion, J. J.; Ashford, D. L.; Dempsey, J. L.; Meyer, T. J. *Chem. Sci.* **2014**, *5*, 3115–3119.
- (76) Hill, S. P.; Banerjee, T.; Dilbeck, T.; Hanson, K. *J. Phys. Chem. Lett.* **2015**, *6*, 4510–4517.
- (77) Ogunolu, O. O.; Wang, J. C.; Hanson, K. *ACS Appl. Mater. Interfaces* **2015**, *7*, 27730–27734.
- (78) Wang, J. C.; Murphy, I. A.; Hanson, K. *J. Phys. Chem. C* **2015**, *119*, 3502–3508.
- (79) Glasson, C. R. K.; Song, W.; Ashford, D. L.; Vannucci, A.; Chen, Z.; Concepcion, J. J.; Holland, P. L.; Meyer, T. J. *Inorg. Chem.* **2012**, *51*, 8637–8639.
- (80) Ding, X.; Gao, Y.; Zhang, L.; Yu, Z.; Liu, J.; Sun, L. *ACS Catal.* **2014**, *4*, 2347–2350.
- (81) Abruña, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1–5.
- (82) Calvert, J. M.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1983**, *22*, 2151–2162.
- (83) Lapiques, A. M.; Ashford, D. L.; Hanson, K.; Torelli, D. A.; Templeton, J. L.; Meyer, T. J. *J. Am. Chem. Soc.* **2013**, *135*, 15450–15458.
- (84) Ashford, D. L.; Lapiques, A. M.; Vannucci, A. K.; Hanson, K.; Torelli, D. A.; Harrison, D. P.; Templeton, J. L.; Meyer, T. J. *J. Am. Chem. Soc.* **2014**, *136*, 6578–6581.
- (85) Ashford, D. L.; Sherman, B. D.; Binstead, R. A.; Templeton, J. L.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 4778–4781.
- (86) Fang, Z.; Keinan, S.; Alibabaei, L.; Luo, H.; Ito, A.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 4872–4876.
- (87) Green, A. N. M.; Palomares, E.; Haque, S. A.; Kroon, J. M.; Durrant, J. R. *J. Phys. Chem. B* **2005**, *109*, 12525–12533.
- (88) Ashford, D. L.; Glasson, C. R. K.; Norris, M. R.; Concepcion, J. J.; Keinan, S.; Brennaman, M. K.; Templeton, J. L.; Meyer, T. J. *Inorg. Chem.* **2014**, *53*, 5637–5646.
- (89) Odobel, F.; Pellegrin, Y. *J. Phys. Chem. Lett.* **2013**, *4*, 2551–2564.
- (90) Jiang, T.; Bujoli-Doeuff, M.; Farré, Y.; Blart, E.; Pellegrin, Y.; Gautron, E.; Boujtita, M.; Cario, L.; Odobel, F.; Jobic, S. *RSC Adv.* **2016**, *6*, 1549–1553.
- (91) Wood, C. J.; Summers, G. H.; Clark, C. A.; Kaeffer, N.; Braeutigam, M.; Carbone, L. R.; D’Amario, L.; Fan, K.; Farré, Y.; Narbey, S.; Oswald, F.; Stevens, L. A.; Parmenter, C. D. J.; Fay, M. W.; La Torre, A.; Snape, C. E.; Dietzek, B.; Dini, D.; Hammarström, L.; Pellegrin, Y.; Odobel, F.; Sun, L.; Artero, V.; Gibson, E. A. *Phys. Chem. Chem. Phys.* **2016**, *18*, 10727–10738.
- (92) Yu, M.; Draskovic, T. I.; Wu, Y. *Phys. Chem. Chem. Phys.* **2014**, *16*, 5026–5033.
- (93) Huang, Z. J.; He, M. F.; Yu, M. Z.; Click, K.; Beauchamp, D.; Wu, Y. Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 6857–6861.
- (94) Bai, J.; Xu, X.; Xu, L.; Cui, J.; Huang, D.; Chen, W.; Cheng, Y.; Shen, Y.; Wang, M. *ChemSusChem* **2013**, *6*, 622–629.
- (95) Renaud, A.; Cario, L.; Pellegrin, Y.; Blart, E.; Boujtita, M.; Odobel, F.; Jobic, S. *RSC Adv.* **2015**, *5*, 60148–60151.
- (96) McCullough, S. M.; Flynn, C. J.; Mercado, C. C.; Nozik, A. J.; Cahoon, J. F. *J. Mater. Chem. A* **2015**, *3*, 21990–21994.
- (97) Mercado, C. C.; Zakutayev, A.; Zhu, K.; Flynn, C. J.; Cahoon, J. F.; Nozik, A. J. *J. Phys. Chem. C* **2014**, *118*, 25340–25349.
- (98) Sullivan, I.; Brown, C. L.; Llansola-Portoles, M. J.; Gervaldó, M.; Kodis, G.; Moore, T. A.; Gust, D.; Moore, A. L.; Magsgard, P. A. *J. Phys. Chem. C* **2015**, *119*, 21294–21303.
- (99) Du, S.; Cheng, P.; Sun, P.; Wang, B.; Cai, Y.; Liu, F.; Zheng, J.; Lu, G. *Chem. Res. Chin. Univ.* **2014**, *30*, 661–665.
- (100) Morandeira, A.; Fortage, J.; Edvinsson, T.; Le Pleux, L.; Blart, E.; Boschloo, G.; Hagfeldt, A.; Hammarström, L.; Odobel, F. *J. Phys. Chem. C* **2008**, *112*, 1721–1728.

- (101) Gibson, E. A.; Smeigh, A. L.; Le Pleux, L.; Fortage, J.; Boschloo, G.; Blart, E.; Pellegrin, Y.; Odobel, F.; Hagfeldt, A.; Hammarström, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 4402–4405.
- (102) He, J.; Lindström, H.; Hagfeldt, A.; Lindquist, S.-E. *J. Phys. Chem. B* **1999**, *103*, 8940–8943.
- (103) Gibson, E. A.; Smeigh, A. L.; Le Pleux, L.; Hammarström, L.; Odobel, F.; Boschloo, G.; Hagfeldt, A. *J. Phys. Chem. C* **2011**, *115*, 9772–9779.
- (104) Le Pleux, L.; Smeigh, A. L.; Gibson, E.; Pellegrin, Y.; Blart, E.; Boschloo, G.; Hagfeldt, A.; Hammarström, L.; Odobel, F. *Energy Environ. Sci.* **2011**, *4*, 2075–2084.
- (105) Li, L.; Duan, L.; Wen, F.; Li, C.; Wang, M.; Hagfeldt, A.; Sun, L. *Chem. Commun.* **2012**, *48*, 988–990.
- (106) van den Bosch, B.; Rombouts, J. A.; Orru, R. V. A.; Reek, J. N. H.; Detz, R. *J. ChemCatChem* **2016**, *8*, 1392–1398.
- (107) Lyu, S.; Farre, Y.; Ducasse, L.; Pellegrin, Y.; Toupance, T.; Olivier, C.; Odobel, F. *RSC Adv.* **2016**, *6*, 19928–19936.
- (108) Perera, I. R.; Daeneke, T.; Makuta, S.; Yu, Z.; Tachibana, Y.; Mishra, A.; Bäuerle, P.; Ohlin, C. A.; Bach, U.; Spiccia, L. *Angew. Chem., Int. Ed.* **2015**, *54*, 3758–3762.
- (109) Nattestad, A.; Ferguson, M.; Kerr, R.; Cheng, Y.-B.; Bach, U. *Nanotechnology* **2008**, *19*, 295304.
- (110) Powar, S.; Daeneke, T.; Ma, M. T.; Fu, D.; Duffy, N. W.; Götz, G.; Weidener, M.; Mishra, A.; Bäuerle, P.; Spiccia, L.; Bach, U. *Angew. Chem., Int. Ed.* **2013**, *52*, 602–605.
- (111) Gardner, J. M.; Beyler, M.; Karnahl, M.; Tschierlei, S.; Ott, S.; Hammarström, L. *J. Am. Chem. Soc.* **2012**, *134*, 19322–19325.
- (112) Li, L.; Gibson, E. A.; Qin, P.; Boschloo, G.; Gorlov, M.; Hagfeldt, A.; Sun, L. *Adv. Mater.* **2010**, *22*, 1759–1762.
- (113) Dini, D.; Halpin, Y.; Vos, J. G.; Gibson, E. A. *Coord. Chem. Rev.* **2015**, *304–305*, 179–201.
- (114) Morandeira, A.; Boschloo, G.; Hagfeldt, A.; Hammarström, L. *J. Phys. Chem. B* **2005**, *109*, 19403–19410.
- (115) Bräutigam, M.; Kübel, J.; Schulz, M.; Vos, J. G.; Dietzek, B. *Phys. Chem. Chem. Phys.* **2015**, *17*, 7823–7830.
- (116) Wood, C. J.; Cheng, M.; Clark, C. A.; Horvath, R.; Clark, I. P.; Hamilton, M. L.; Towrie, M.; George, M. W.; Sun, L.; Yang, X.; Gibson, E. A. *J. Phys. Chem. C* **2014**, *118*, 16536–16546.
- (117) Warnan, J.; Gardner, J.; Le Pleux, L.; Petersson, J.; Pellegrin, Y.; Blart, E.; Hammarström, L.; Odobel, F. *J. Phys. Chem. C* **2014**, *118*, 103–113.
- (118) He, M.; Ji, Z.; Huang, Z.; Wu, Y. *J. Phys. Chem. C* **2014**, *118*, 16518–16525.
- (119) Ji, Z.; Wu, Y. *J. Phys. Chem. C* **2013**, *117*, 18315–18324.
- (120) Ji, Z.; Natu, G.; Huang, Z.; Kokhan, O.; Zhang, X.; Wu, Y. *J. Phys. Chem. C* **2012**, *116*, 16854–16863.
- (121) Bian, Z.; Tachikawa, T.; Cui, S.-C.; Fujitsuka, M.; Majima, T. *Chem. Sci.* **2012**, *3*, 370–379.
- (122) Odobel, F.; Pellegrin, Y.; Gibson, E. A.; Hagfeldt, A.; Smeigh, A. L.; Hammarström, L. *Coord. Chem. Rev.* **2012**, *256*, 2414–2423.
- (123) D'Amario, L.; Boschloo, G.; Hagfeldt, A.; Hammarström, L. *J. Phys. Chem. C* **2014**, *118*, 19556–19564.
- (124) D'Amario, L.; Antila, L. J.; Rimgard, B. P.; Boschloo, G.; Hammarström, L. *J. Phys. Chem. Lett.* **2015**, *6*, 779–783.
- (125) Daeneke, T.; Yu, Z.; Lee, G. P.; Fu, D.; Duffy, N. W.; Makuta, S.; Tachibana, Y.; Spiccia, L.; Mishra, A.; Bäuerle, P.; Bach, U. *Adv. Energy Mater.* **2015**, *5*, 1401387.
- (126) Uehara, S.; Sumikura, S.; Suzuki, E.; Mori, S. *Energy Environ. Sci.* **2010**, *3*, 641–644.
- (127) Flynn, C. J.; McCullough, S. M.; Oh, E.; Li, L.; Mercado, C. C.; Farnum, B. H.; Li, W.; Donley, C. L.; You, W.; Nozik, A. J.; McBride, J. R.; Meyer, T. J.; Kanai, Y.; Cahoon, J. F. *ACS Appl. Mater. Interfaces* **2016**, *8*, 4754–4761.
- (128) Liu, Q.; Wei, L.; Yuan, S.; Ren, X.; Zhao, Y.; Wang, Z.; Zhang, M.; Shi, L.; Li, D.; Li, A. *RSC Adv.* **2015**, *5*, 71778–71784.
- (129) Click, K. A.; Beauchamp, D. R.; Garrett, B. R.; Huang, Z.; Hadad, C. M.; Wu, Y. *Phys. Chem. Chem. Phys.* **2014**, *16*, 26103–26111.
- (130) Tian, H. *ChemSusChem* **2015**, *8*, 3746–3759.
- (131) Schreier, M.; Luo, J.; Gao, P.; Moehl, T.; Mayer, M. T.; Grätzel, M. *J. Am. Chem. Soc.* **2016**, *138*, 1938–1946.
- (132) Luo, J.; Steier, L.; Son, M.-K.; Schreier, M.; Mayer, M. T.; Grätzel, M. *Nano Lett.* **2016**, *16*, 1848–1857.
- (133) Gu, J.; Yan, Y.; Young, J. L.; Steirer, K. X.; Neale, N. R.; Turner, J. A. *Nat. Mater.* **2016**, *15*, 456–460.
- (134) Gillaizeau-Gauthier, I.; Odobel, F.; Alebbi, M.; Argazzi, R.; Costa, E.; Bignozzi, C. A.; Qu, P.; Meyer, G. J. *Inorg. Chem.* **2001**, *40*, 6073–6079.
- (135) Zou, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7578–7584.
- (136) McNamara, W. R.; Milot, R. L.; Song, H.-e.; Snoeberger, R. C., III; Batista, V. S.; Schmuttenmaer, C. A.; Brudvig, G. W.; Crabtree, R. H. *Energy Environ. Sci.* **2010**, *3*, 917–923.
- (137) Haller, I. *J. Am. Chem. Soc.* **1978**, *100*, 8050–8055.
- (138) McNamara, W. R.; Snoeberger, R. C.; Li, G.; Schleicher, J. M.; Cady, C. W.; Poyatos, M.; Schmuttenmaer, C. A.; Crabtree, R. H.; Brudvig, G. W.; Batista, V. S. *J. Am. Chem. Soc.* **2008**, *130*, 14329–14338.
- (139) Banerjee, T.; Kaniyankandy, S.; Das, A.; Ghosh, H. N. *J. Phys. Chem. C* **2013**, *117*, 3084–3092.
- (140) Banerjee, T.; Kaniyankandy, S.; Das, A.; Ghosh, H. N. *Inorg. Chem.* **2013**, *52*, 5366–5377.
- (141) Banerjee, T.; Biswas, A. K.; Sahu, T. S.; Ganguly, B.; Das, A.; Ghosh, H. N. *Dalton Trans.* **2014**, *43*, 13601–13611.
- (142) Zhang, L.; Cole, J. M. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3427–3455.
- (143) Ernstorfer, R.; Gundlach, L.; Felber, S.; Storck, W.; Eichberger, R.; Willig, F. *J. Phys. Chem. B* **2006**, *110*, 25383–25391.
- (144) Zhang, L.; Cole, J. M.; Waddell, P. G.; Low, K. S.; Liu, X. *ACS Sustainable Chem. Eng.* **2013**, *1*, 1440–1452.
- (145) Wang, D.; Mendelsohn, R.; Galoppini, E.; Hoertz, P. G.; Carlisle, R. A.; Meyer, G. J. *J. Phys. Chem. B* **2004**, *108*, 16642–16653.
- (146) Galoppini, E. *Coord. Chem. Rev.* **2004**, *248*, 1283–1297.
- (147) Hanson, K.; Brennaman, M. K.; Ito, A.; Luo, H.; Song, W.; Parker, K. A.; Ghosh, R.; Norris, M. R.; Glasson, C. R. K.; Concepcion, J. J.; Lopez, R.; Meyer, T. J. *J. Phys. Chem. C* **2012**, *116*, 14837–14847.
- (148) Hanson, K.; Brennaman, M. K.; Luo, H.; Glasson, C. R. K.; Concepcion, J. J.; Song, W.; Meyer, T. J. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1462–1469.
- (149) Brown, D. G.; Schauer, P. A.; Borau-Garcia, J.; Fancy, B. R.; Berlinguette, C. P. *J. Am. Chem. Soc.* **2013**, *135*, 1692–1695.
- (150) Hyde, J. T.; Hanson, K.; Vannucci, A. K.; Lapides, A. M.; Alibabaei, L.; Norris, M. R.; Meyer, T. J.; Harrison, D. P. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9554–9562.
- (151) Kim, D. H.; Losego, M. D.; Hanson, K.; Alibabaei, L.; Lee, K.; Meyer, T. J.; Parsons, G. N. *Phys. Chem. Chem. Phys.* **2014**, *16*, 8615–8622.
- (152) Wee, K.-R.; Brennaman, M. K.; Alibabaei, L.; Farnum, B. H.; Sherman, B.; Lapides, A. M.; Meyer, T. J. *J. Am. Chem. Soc.* **2014**, *136*, 13514–13517.
- (153) Moss, J. A.; Yang, J. C.; Stipkala, J. M.; Wen, X.; Bignozzi, C. A.; Meyer, G. J.; Meyer, T. J. *Inorg. Chem.* **2004**, *43*, 1784–1792.
- (154) Szapkowski, K.; Latham, K.; Rix, C.; Rani, R. A.; Kalantar-zadeh, K. *Polyhedron* **2013**, *52*, 719–732.
- (155) Materna, K. L.; Rudsteyn, B.; Brennan, B. J.; Kane, M. H.; Bloomfield, A. J.; Huang, D. L.; Shopov, D. Y.; Batista, V. S.; Crabtree, R. H.; Brudvig, G. W. *ACS Catal.* **2016**, *6*, 5371–5377.
- (156) Puri, J. K.; Singh, R.; Chahal, V. K. *Chem. Soc. Rev.* **2011**, *40*, 1791–1840.
- (157) Materna, K. L.; Brennan, B. J.; Brudvig, G. W. *Dalton Trans.* **2015**, *44*, 20312–20315.
- (158) Brennan, B. J.; Llansola Portoles, M. J.; Liddell, P. A.; Moore, T. A.; Moore, A. L.; Gust, D. *Phys. Chem. Chem. Phys.* **2013**, *15*, 16605–16614.
- (159) Zakeeruddin, S. M.; Nazeeruddin, M. K.; Humphry-Baker, R.; Péchy, P.; Quagliotto, P.; Barolo, C.; Viscardi, G.; Grätzel, M. *Langmuir* **2002**, *18*, 952–954.

- (160) Hanson, K.; Losego, M. D.; Kalanyan, B.; Ashford, D. L.; Parsons, G. N.; Meyer, T. J. *Chem. Mater.* **2013**, *25*, 3–5.
- (161) Hanson, K.; Losego, M. D.; Kalanyan, B.; Parsons, G. N.; Meyer, T. J. *Nano Lett.* **2013**, *13*, 4802–4809.
- (162) Vannucci, A. K.; Alibabaei, L.; Losego, M. D.; Concepcion, J. J.; Kalanyan, B.; Parsons, G. N.; Meyer, T. J. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 20918–20922.
- (163) Son, H.-J.; Wang, X.; Prasittichai, C.; Jeong, N. C.; Aaltonen, T.; Gordon, R. G.; Hupp, J. T. *J. Am. Chem. Soc.* **2012**, *134*, 9537–9540.
- (164) Losego, M. D.; Hanson, K. *Nano Energy* **2013**, *2*, 1067–1069.
- (165) Son, H.-J.; Prasittichai, C.; Mondloch, J. E.; Luo, L.; Wu, J.; Kim, D. W.; Farha, O. K.; Hupp, J. T. *J. Am. Chem. Soc.* **2013**, *135*, 11529–11532.
- (166) Antila, L. J.; Heikkilä, M. J.; Mäkinen, V.; Humalampi, N.; Laitinen, M.; Linko, V.; Jalkanen, P.; Toppari, J.; Aumanen, V.; Kemell, M.; Myllyperkiö, P.; Honkala, K.; Hakkinen, H.; Leskela, M.; Korppi-Tommola, J. E. I. *J. Phys. Chem. C* **2011**, *115*, 16720–16729.
- (167) Prasittichai, C.; Hupp, J. T. *J. Phys. Chem. Lett.* **2010**, *1*, 1611–1615.
- (168) Hamann, T. W.; Farha, O. K.; Hupp, J. T. *J. Phys. Chem. C* **2008**, *112*, 19756–19764.
- (169) O'Neill, B. J.; Jackson, D. H. K.; Lee, J.; Canlas, C.; Stair, P. C.; Marshall, C. L.; Elam, J. W.; Kuech, T. F.; Dumesic, J. A.; Huber, G. W. *ACS Catal.* **2015**, *5*, 1804–1825.
- (170) Lapides, A. M.; Sherman, B. D.; Brennaman, M. K.; Dares, C. J.; Skinner, K. R.; Templeton, J. L.; Meyer, T. J. *Chem. Sci.* **2015**, *6*, 6398–6406.
- (171) Ardo, S.; Meyer, G. J. *Chem. Soc. Rev.* **2009**, *38*, 115–164.
- (172) Akimov, A. V.; Neukirch, A. J.; Prezhdo, O. V. *Chem. Rev.* **2013**, *113*, 4496–4565.
- (173) Mahmood, A. *Sol. Energy* **2016**, *123*, 127–144.
- (174) Lee, C.-P.; Lin, R. Y.-Y.; Lin, L.-Y.; Li, C.-T.; Chu, T.-C.; Sun, S.-S.; Lin, J. T.; Ho, K.-C. *RSC Adv.* **2015**, *5*, 23810–23825.
- (175) Housecroft, C. E.; Constable, E. C. *Chem. Soc. Rev.* **2015**, *44*, 8386–8398.
- (176) Diau, E. W.-G.; Li, L.-L. Porphyrin-Sensitized Solar Cells. In *Chlorophyll, Photosynthesis and Bio-inspired Energy*; Ferreira, G. C., Ed.; Handbook of Porphyrin Science with Applications to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine, Vol. 28; Kadish, K. M., Smith, K. M., Guillard, R., Vol. Eds.; World Scientific Publishing Co. Pte. Ltd.: Toh Tuck Link, Singapore, 2014; pp 279–317.
- (177) Rees, T. W.; Baranoff, E. *Polyhedron* **2014**, *33*, 37–49.
- (178) Giribabu, L.; Kanaparthi, R. K. *Curr. Sci.* **2013**, *104*, 847–855.
- (179) Shalini, S.; Balasundara Prabhur, R.; Prasanna, S.; Mallick, T. K.; Senthilarasu, S. *Renewable Sustainable Energy Rev.* **2015**, *51*, 1306–1325.
- (180) Jinchu, I.; Sreekala, C. O.; Sreelatha, K. S. *Mater. Sci. Forum* **2014**, *771*, 39–51.
- (181) Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B. F. E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, Md. K.; Grätzel, M. *Nat. Chem.* **2014**, *6*, 242–247.
- (182) Li, C.; Wonneberger, H. *Adv. Mater.* **2012**, *24*, 613–636.
- (183) Li, L.-L.; Diau, E. W.-G. *Chem. Soc. Rev.* **2013**, *42*, 291–304.
- (184) Yao, Z.; Zhang, M.; Li, R.; Yang, L.; Qiao, Y.; Wang, P. *Angew. Chem., Int. Ed.* **2015**, *54*, 5994–5998.
- (185) Meyer, T. J.; Huynh, M. H. V.; Thorp, H. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5284–5304.
- (186) Brudvig, G. W. *Philos. Trans. R. Soc., B* **2008**, *363*, 1211–1218.
- (187) Renger, G.; Renger, T. *Photosynth. Res.* **2008**, *98*, 53–80.
- (188) Dau, H.; Zaharieva, I. *Acc. Chem. Res.* **2009**, *42*, 1861–1870.
- (189) Renger, G. *J. Photochem. Photobiol., B* **2011**, *104*, 35–43.
- (190) Renger, G. *Biochim. Biophys. Acta, Bioenerg.* **2012**, *1817*, 1164–1176.
- (191) Cox, N.; Pantazis, D. A.; Neese, F.; Lubitz, W. *Acc. Chem. Res.* **2013**, *46*, 1588–1596.
- (192) Ito, A.; Meyer, T. J. *J. Phys. Chem. Chem. Phys.* **2012**, *14*, 13731–13745.
- (193) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. Bimolecular Electron Transfer Reactions of the Excited States of Transition Metal Complexes In *Organic Chemistry and Theory*; Boschke, F. L., Ed.; Topics in Current Chemistry 75; Springer: Berlin, 1978; pp 1–64.
- (194) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717–2738.
- (195) Meyer, T. J. Excited-State Electron Transfer. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley & Sons: New York, 1983; Vol. 30, pp 389–440 and references therein.
- (196) Tachibana, Y.; Moser, J. E.; Grätzel, M.; Klug, D. R.; Durrant, J. R. *J. Phys. Chem.* **1996**, *100*, 20056–20062.
- (197) Hannappel, T.; Burfeindt, B.; Storck, W.; Willig, F. *J. Phys. Chem. B* **1997**, *101*, 6799–6802.
- (198) Kelly, C. A.; Farzad, F.; Thompson, D. W.; Stipkala, J. M.; Meyer, G. J. *Langmuir* **1999**, *15*, 7047–7054.
- (199) Tachibana, Y.; Haque, S. A.; Mercer, I. P.; Durrant, J. R.; Klug, D. R. *J. Phys. Chem. B* **2000**, *104*, 1198–1205.
- (200) Benkö, G.; Kallioinen, J.; Korppi-Tommola, J. E. I.; Yartsev, A. P.; Sundström, V. *J. Am. Chem. Soc.* **2002**, *124*, 489–493.
- (201) Ramakrishna, S.; Willig, F.; May, V. *Chem. Phys. Lett.* **2002**, *351*, 242–250.
- (202) Asbury, J. B.; Anderson, N. A.; Hao, E.; Ai, X.; Lian, T. *J. Phys. Chem. B* **2003**, *107*, 7376–7386.
- (203) Ramakrishna, S.; Willig, F.; May, V.; Knorr, A. *J. Phys. Chem. B* **2003**, *107*, 607–611.
- (204) Redfern, P. C.; Zapol, P.; Curtiss, L. A.; Rajh, T.; Thurnauer, M. C. *J. Phys. Chem. B* **2003**, *107*, 11419–11427.
- (205) Benkö, G.; Kallioinen, J.; Myllyperkiö, P.; Trif, F.; Korppi-Tommola, J. E. I.; Yartsev, A. P.; Sundström, V. *J. Phys. Chem. B* **2004**, *108*, 2862–2867.
- (206) Kallioinen, J.; Benkö, G.; Myllyperkiö, P.; Khriachtchev, L.; Skärman, B.; Wallenberg, R.; Tuomikoski, M.; Korppi-Tommola, J.; Sundström, V.; Yartsev, A. P. *J. Phys. Chem. B* **2004**, *108*, 6365–6373.
- (207) Watson, D. F.; Meyer, G. J. *Annu. Rev. Phys. Chem.* **2005**, *56*, 119–156.
- (208) Liu, F.; Meyer, G. J. *Inorg. Chem.* **2005**, *44*, 9305–9313.
- (209) She, C.; Anderson, N. A.; Guo, J.; Liu, F.; Goh, W.-H.; Chen, D.-T.; Mohler, D. L.; Tian, Z.-Q.; Hupp, J. T.; Lian, T. *J. Phys. Chem. B* **2005**, *109*, 19345–19355.
- (210) Guo, J.; She, C.; Lian, T. *J. Phys. Chem. C* **2007**, *111*, 8979–8987.
- (211) Morandeira, A.; López-Duarte, I.; Martínez-Díaz, M. V.; O'Regan, B.; Shuttle, C.; Haji-Zainulabidin, N. A.; Torres, T.; Palomares, E.; Durrant, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 9250–9251.
- (212) She, C.; Guo, J.; Irle, S.; Morokuma, K.; Mohler, D. L.; Zabir, H.; Odobel, F.; Youm, K.-T.; Liu, F.; Hupp, J. T.; Lian, T. *J. Phys. Chem. A* **2007**, *111*, 6832–6842.
- (213) Smeigh, A. L.; Katz, J. E.; Brunschwig, B. S.; Lewis, N. S.; McCusker, J. K. *J. Phys. Chem. C* **2008**, *112*, 12065–12068.
- (214) Jakubikova, E.; Snoberger, R. C., III; Batista, V. S.; Martin, R. L.; Batista, E. R. *J. Phys. Chem. A* **2009**, *113*, 12532–12540.
- (215) Du, L.; Furube, A.; Hara, K.; Katoh, R.; Tachiya, M. *J. Phys. Chem. C* **2010**, *114*, 8135–8143.
- (216) Furube, A.; Wang, Z.-S.; Sunahara, K.; Hara, K.; Katoh, R.; Tachiya, M. *J. Am. Chem. Soc.* **2010**, *132*, 6614–6615.
- (217) Listorti, A.; O'Regan, B.; Durrant, J. R. *Chem. Mater.* **2011**, *23*, 3381–3399.
- (218) Pijpers, J. J. H.; Ulbricht, R.; Derossi, S.; Reek, J. N. H.; Bonn, M. *J. Phys. Chem. C* **2011**, *115*, 2578–2584.
- (219) Sunahara, K.; Furube, A.; Katoh, R.; Mori, S.; Griffith, M. J.; Wallace, G. G.; Wagner, P.; Officer, D. L.; Mozer, A. J. *J. Phys. Chem. C* **2011**, *115*, 22084–22088.
- (220) Mahanta, S.; Furube, A.; Matsuzaki, H.; Murakami, T. N.; Matsumoto, H. *J. Phys. Chem. C* **2012**, *116*, 20213–20219.
- (221) Teuscher, J.; Décoppet, J.-D.; Punzi, A.; Zakeeruddin, S. M.; Moser, J.-E.; Grätzel, M. *J. Phys. Chem. Lett.* **2012**, *3*, 3786–3790.
- (222) Giokas, P. G.; Miller, S. A.; Hanson, K.; Norris, M. R.; Glasson, C. R. K.; Concepcion, J. J.; Bettis, S. E.; Meyer, T. J.; Moran, A. M. *J. Phys. Chem. C* **2013**, *117*, 812–824.

- (223) Juozapavicius, M.; Kaucikas, M.; Dimitrov, S. D.; Barnes, P. R. F.; van Thor, J. J.; O'Regan, B. C. *J. Phys. Chem. C* **2013**, *117*, 25317–25324.
- (224) Srimath Kandada, A. R.; Fantacci, S.; Guarnera, S.; Polli, D.; Lanzani, G.; De Angelis, F.; Petrozza, A. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4334–4339.
- (225) Antila, L. J.; Myllyperkiö, P.; Mustalahti, S.; Lehtivuori, H.; Korppi-Tommola, J. *J. Phys. Chem. C* **2014**, *118*, 7772–7780.
- (226) Banerjee, T.; Biswas, A. K.; Reddy, G. U.; Sahu, T. S.; Das, A.; Ganguly, B.; Ghosh, H. N. *J. Phys. Chem. C* **2014**, *118*, 3864–3877.
- (227) Fakis, M.; Hrobárik, P.; Yushchenko, O.; Sigmundová, I.; Koch, M.; Rosspeintner, A.; Stathatos, E.; Vauthey, E. *J. Phys. Chem. C* **2014**, *118*, 28509–28519.
- (228) Furube, A.; Katoh, R.; Hara, K. *Surf. Sci. Rep.* **2014**, *69*, 389–441.
- (229) Hsu, H.-Y.; Cheng, C.-W.; Huang, W.-K.; Lee, Y.-P.; Diau, E. W.-G. *J. Phys. Chem. C* **2014**, *118*, 16904–16911.
- (230) Katoh, R.; Furube, A. *J. Photochem. Photobiol., C* **2014**, *20*, 1–16.
- (231) Rao, V. G.; Dhital, B.; He, Y.; Lu, H. P. *J. Phys. Chem. C* **2014**, *118*, 20209–20221.
- (232) Borgwardt, M.; Wilke, M.; Kampen, T.; Mähl, S.; Xiang, W.; Spiccia, L.; Lange, K. M.; Kiyani, I. Y.; Aziz, E. F. *J. Phys. Chem. C* **2015**, *119*, 9099–9107.
- (233) Brauer, J. C.; Marchioro, A.; Paraecattil, A. A.; Oskouei, A. A.; Moser, J.-E. *J. Phys. Chem. C* **2015**, *119*, 26266–26274.
- (234) Li, R.; Zhang, M.; Yan, C.; Yao, Z.; Zhang, J.; Wang, P. *ChemSusChem* **2015**, *8*, 97–104.
- (235) Milot, R. L.; Schmuttenmaer, C. A. *Acc. Chem. Res.* **2015**, *48*, 1423–1431.
- (236) Martín, C.; Ziólek, M.; Douhal, A. *J. Photochem. Photobiol., C* **2016**, *26*, 1–30.
- (237) Swierk, J. R.; McCool, N. S.; Nemes, C. T.; Mallouk, T. E.; Schmuttenmaer, C. A. *J. Phys. Chem. C* **2016**, *120*, 5940–5948.
- (238) Zigler, D. F.; Morseth, Z. A.; Wang, L.; Ashford, D. L.; Brennaman, M. K.; Grumstrup, E. M.; Brigham, E. C.; Gish, M. K.; Dillon, R. J.; Alibabaei, L.; Meyer, G. J.; Meyer, T. J.; Papanikolas, J. M. *J. Am. Chem. Soc.* **2016**, *138*, 4426–4438.
- (239) Chen, P.-Y.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439–1477.
- (240) Miller, S. A.; West, B. A.; Curtis, A. C.; Papanikolas, J. M.; Moran, A. M. *J. Chem. Phys.* **2011**, *135*, 081101.
- (241) Asbury, J. B.; Hao, E.; Wang, Y.; Ghosh, H. N.; Lian, T. *J. Phys. Chem. B* **2001**, *105*, 4545–4557.
- (242) Anderson, N. A.; Lian, T. *Annu. Rev. Phys. Chem.* **2005**, *56*, 491–519.
- (243) Duncan, W. R.; Prezhdo, O. V. *Annu. Rev. Phys. Chem.* **2007**, *58*, 143–184.
- (244) Tachibana, Y.; Haque, S. A.; Mercer, I. P.; Moser, J. E.; Klug, D. R.; Durrant, J. R. *J. Phys. Chem. B* **2001**, *105*, 7424–7431.
- (245) Katoh, R.; Furube, A.; Barzykin, A. V.; Arakawa, H.; Tachiya, M. *Coord. Chem. Rev.* **2004**, *248*, 1195–1213.
- (246) Anderson, N. A.; Lian, T. *Coord. Chem. Rev.* **2004**, *248*, 1231–1246.
- (247) Farnum, B. H.; Morseth, Z. A.; Brennaman, M. K.; Papanikolas, J. M.; Meyer, T. J. *J. Am. Chem. Soc.* **2014**, *136*, 15869–15872.
- (248) Farnum, B. H.; Morseth, Z. A.; Brennaman, M. K.; Papanikolas, J. M.; Meyer, T. J. *J. Phys. Chem. B* **2015**, *119*, 7698–7711.
- (249) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 962–972.
- (250) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557–580.
- (251) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196.
- (252) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679–701.
- (253) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275–282.
- (254) Hush, N. S. *J. Electroanal. Chem.* **1999**, *470*, 170–195.
- (255) Enright, B.; Redmond, G.; Fitzmaurice, D. *J. Phys. Chem.* **1994**, *98*, 6195–6200.
- (256) O'Regan, B.; Grätzel, M.; Fitzmaurice, D. *J. Phys. Chem.* **1991**, *95*, 10525–10528.
- (257) Rothenberger, G.; Fitzmaurice, D.; Grätzel, M. *J. Phys. Chem.* **1992**, *96*, 5983–5986.
- (258) Boschloo, G.; Fitzmaurice, D. *J. Phys. Chem. B* **1999**, *103*, 7860–7868.
- (259) Lyon, L. A.; Hupp, J. T. *J. Phys. Chem. B* **1999**, *103*, 4623–4628.
- (260) Ashford, D. L.; Song, W. J.; Concepcion, J. J.; Glasson, C. R. K.; Brennaman, M. K.; Norris, M. R.; Fang, Z.; Templeton, J. L.; Meyer, T. J. *J. Am. Chem. Soc.* **2012**, *134*, 19189–19198.
- (261) Ashford, D. L.; Stewart, D. J.; Glasson, C. R.; Binstead, R. A.; Harrison, D. P.; Norris, M. R.; Concepcion, J. J.; Fang, Z.; Templeton, J. L.; Meyer, T. J. *Inorg. Chem.* **2012**, *51*, 6428–6430.
- (262) Wang, L.; Ashford, D. L.; Thompson, D. W.; Meyer, T. J.; Papanikolas, J. M. *J. Phys. Chem. C* **2013**, *117*, 24250–24258.
- (263) Nocera, D. G. *Acc. Chem. Res.* **2012**, *45*, 767–776.
- (264) Doyle, R. L.; Godwin, I. J.; Brandon, M. P.; Lyons, M. E. G. *Phys. Chem. Chem. Phys.* **2013**, *15*, 13737–13783.
- (265) Sivula, K.; van de Krol, R. *Nat. Rev. Mater.* **2016**, *1*, 15010.
- (266) Jiao, F.; Frei, H. *Energy Environ. Sci.* **2010**, *3*, 1018–1027.
- (267) Fang, Y.-H.; Liu, Z.-P. *J. Am. Chem. Soc.* **2010**, *132*, 18214–18222.
- (268) Winther-Jensen, B.; Winther-Jensen, O.; Forsyth, M.; MacFarlane, D. R. *Science* **2008**, *321*, 671–674.
- (269) Da Silva, L. M.; Boodts, J. F. C.; De Faria, L. A. *Electrochim. Acta* **2001**, *46*, 1369–1375.
- (270) Bertocello, R.; Cattarin, S.; Frateur, I.; Musiani, M. *J. Electroanal. Chem.* **2000**, *492*, 145–149.
- (271) Jirkovský, J.; Makarova, M.; Krtíl, P. *Electrochem. Commun.* **2006**, *8*, 1417–1422.
- (272) *Molecular Water Oxidation Catalysis: A Key Topic for New Sustainable Energy Conversion Schemes*. Llobet, A., Eds.; John Wiley & Sons Ltd.: New York, 2014.
- (273) Concepcion, J. J.; Jurss, J. W.; Norris, M. R.; Chen, Z. F.; Templeton, J. L.; Meyer, T. J. *Inorg. Chem.* **2010**, *49*, 1277–1279.
- (274) Wasylenko, D. J.; Ganesamoorthy, C.; Koivisto, B. D.; Henderson, M. A.; Berlinguette, C. P. *Inorg. Chem.* **2010**, *49*, 2202–2209.
- (275) Li, F.; Zhang, B.; Li, X.; Jiang, Y.; Chen, L.; Li, Y.; Sun, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 12276.
- (276) Duan, L.; Bozoglian, F.; Mandal, S.; Stewart, B.; Privalov, T.; Llobet, A.; Sun, L. *Nat. Chem.* **2012**, *4*, 418–423.
- (277) Badiei, Y. M.; Polyansky, D. E.; Muckerman, J. T.; Szalda, D. J.; Haberdar, R.; Zong, R.; Thummel, R. P.; Fujita, E. *Inorg. Chem.* **2013**, *52*, 8845–8850.
- (278) Duan, L.; Wang, L.; Inge, A. K.; Fischer, A.; Zou, X.; Sun, L. *Inorg. Chem.* **2013**, *52*, 7844–7852.
- (279) Sala, X.; Maji, S.; Bofill, R.; Garcia-Anton, J.; Escriche, L.; Llobet, A. *Acc. Chem. Res.* **2014**, *47*, 504–516.
- (280) McDaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S. J. *Am. Chem. Soc.* **2008**, *130*, 210–217.
- (281) Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 8730–8731.
- (282) Blakemore, J. D.; Schley, N. D.; Balcells, D.; Hull, J. F.; Olack, G. W.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2010**, *132*, 16017–16029.
- (283) Savini, A.; Bellachioma, G.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D.; Macchioni, A. *Chem. Commun.* **2010**, *46*, 9218–9219.
- (284) Schley, N. D.; Blakemore, J. D.; Subbaiyan, N. K.; Incarvito, C. D.; D'Souza, F.; Crabtree, R. H.; Brudvig, G. W. *J. Am. Chem. Soc.* **2011**, *133*, 10473–10481.
- (285) Joya, K. S.; Subbaiyan, N. K.; D'Souza, F.; de Groot, H. J. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 9601.
- (286) Blakemore, J. D.; Mara, M. W.; Kushner-Lenhoff, M. N.; Schley, N. D.; Konezny, S. J.; Rivalta, I.; Negre, C. F. A.; Snoberger, R. C.; Kokhan, O.; Huang, J.; Stickrath, A.; Tran, L. A.; Parr, M. L.; Chen, L. X.; Tiede, D. M.; Batista, V. S.; Crabtree, R. H.; Brudvig, G. W. *Inorg. Chem.* **2013**, *52*, 1860–1871.

- (287) Dogutan, D. K.; McGuire, R.; Nocera, D. G. *J. Am. Chem. Soc.* **2011**, *133*, 9178–9180.
- (288) Wasylenko, D. J.; Ganesamoorthy, C.; Borau-Garcia, J.; Berlinguette, C. P. *Chem. Commun.* **2011**, *47*, 4249–4251.
- (289) Wang, D.; Groves, J. T. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 15579.
- (290) Lopez, A. M.; Natali, M.; Pizzolato, E.; Chiorboli, C.; Bonchio, M.; Sartorel, A.; Scandola, F. *Phys. Chem. Chem. Phys.* **2014**, *16*, 12000–12007.
- (291) Barnett, S. M.; Goldberg, K. I.; Mayer, J. M. *Nat. Chem.* **2012**, *4*, 498–502.
- (292) Chen, Z. F.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 700–703.
- (293) Zhang, M.-T.; Chen, Z.-F.; Kang, P.; Meyer, T. J. *J. Am. Chem. Soc.* **2013**, *135*, 2048–2051.
- (294) Tiago de Oliveira, F.; Chanda, A.; Banerjee, D.; Shan, X.; Mondal, S.; Que, L., Jr.; Bominaar, E. L.; Muenck, E.; Collins, T. J. *Science* **2007**, *315*, 835–838.
- (295) Ellis, W. C.; McDaniel, N. D.; Bernhard, S.; Collins, T. J. *J. Am. Chem. Soc.* **2010**, *132*, 10990–10991.
- (296) Fillol, J. L.; Codolà, Z.; Garcia-Bosch, I.; Gómez, L.; Pla, J. J.; Costas, M. *Nat. Chem.* **2011**, *3*, 807–813.
- (297) Codolà, Z.; Garcia-Bosch, I.; Acuña-Pares, F.; Prat, I.; Luis, J. M.; Costas, M.; Lloret-Fillol, J. *Chem. - Eur. J.* **2013**, *19*, 8042–8047.
- (298) Liu, F.; Concepcion, J. J.; Jurss, J. W.; Cardolaccia, T.; Templeton, J. L.; Meyer, T. J. *Inorg. Chem.* **2008**, *47*, 1727–1752.
- (299) Concepcion, J. J.; Jurss, J. W.; Brennaman, M. K.; Hoertz, P. G.; Patrocínio, A. O. T.; Murakami Iha, N. Y.; Templeton, J. L.; Meyer, T. J. *Acc. Chem. Res.* **2009**, *42*, 1954–1965.
- (300) Duan, L.; Fischer, A.; Xu, Y.; Sun, L. *J. Am. Chem. Soc.* **2009**, *131*, 10397–10399.
- (301) Concepcion, J. J.; Tsai, M.-K.; Muckerman, J. T.; Meyer, T. J. *J. Am. Chem. Soc.* **2010**, *132*, 1545–1557.
- (302) Hughes, T. F.; Friesner, R. A. *J. Phys. Chem. B* **2011**, *115*, 9280–9289.
- (303) Gagliardi, C. J.; Vannucci, A. K.; Concepcion, J. J.; Chen, Z. F.; Meyer, T. J. *Energy Environ. Sci.* **2012**, *5*, 7704–7717.
- (304) Lin, X.; Hu, X.; Concepcion, J. J.; Chen, Z.; Liu, S.; Meyer, T. J.; Yang, W. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15669–15672.
- (305) Concepcion, J. J.; Jurss, J. W.; Templeton, J. L.; Meyer, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 16462–16463.
- (306) Brandt, W. W.; Dwyer, F. P.; Gyarfas, E. D. *Chem. Rev.* **1954**, *54*, 959–1017.
- (307) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334–3341.
- (308) Flamigni, L.; Barigelletti, F.; Armaroli, N.; Collin, J.-P.; Dixon, I. M.; Sauvage, J.-P.; Williams, J. A. G. *Coord. Chem. Rev.* **1999**, *190–192*, 671–682.
- (309) Fanni, S.; Keyes, T. E.; O'Connor, C. M.; Hughes, H.; Wang, R.; Vos, J. G. *Coord. Chem. Rev.* **2000**, *208*, 77–86.
- (310) Spiccia, L.; Deacon, G. B.; Kepert, C. M. *Coord. Chem. Rev.* **2004**, *248*, 1329–1341.
- (311) Zong, R.; Thummel, R. P. *J. Am. Chem. Soc.* **2005**, *127*, 12802–12803.
- (312) Vos, J. G.; Kelly, J. M. *Dalton Trans.* **2006**, 4869–4883.
- (313) Sabo-Etienne, S.; Grellier, M. Ruthenium: Inorganic & Coordination Chemistry. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Ed.; John Wiley & Sons, Ltd: New York, 2006; Vol. 7, pp 4757–4778.
- (314) Constable, E. C. *Coord. Chem. Rev.* **2008**, *252*, 842–855.
- (315) Boyer, J. L.; Rochford, J.; Tsai, M.-K.; Muckerman, J. T.; Fujita, E. *Coord. Chem. Rev.* **2010**, *254*, 309–330.
- (316) Meyer, T. J.; Huynh, M. H. V. *Inorg. Chem.* **2003**, *42*, 8140–8160.
- (317) Winkler, J. R.; Gray, H. B. Electronic Structures of Oxo-Metal Ions. In *Molecular Electronic Structures of Transition Metal Complexes I*; Mingos, P. D. M., Day, P., Dahl, P. J., Eds.; Structure and Bonding **142**; Springer: Berlin/Heidelberg, 2012; pp 17–28.
- (318) Concepcion, J. J.; Jurss, J. W.; Hoertz, P. G.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 9473–9476.
- (319) Wood, P. M. *Biochem. J.* **1988**, *253*, 287–289.
- (320) Chen, Z.; Concepcion, J. J.; Hu, X.; Yang, W.; Hoertz, P. G.; Meyer, T. J. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 7225–7229.
- (321) Chen, Z.; Kang, P.; Zhang, M.-T.; Stoner, B. R.; Meyer, T. J. *Energy Environ. Sci.* **2013**, *6*, 813–817.
- (322) Barnett, S. M.; Goldberg, K. I.; Mayer, J. M. *Nat. Chem.* **2012**, *4*, 498–502.
- (323) Coggins, M. K.; Zhang, M.-T.; Chen, Z.; Song, N.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 12226–12230.
- (324) Coggins, M. K.; Zhang, M.-T.; Vannucci, A. K.; Dares, C. J.; Meyer, T. J. *J. Am. Chem. Soc.* **2014**, *136*, 5531–5534.
- (325) Cukier, R. I.; Nocera, D. G. *Annu. Rev. Phys. Chem.* **1998**, *49*, 337–369.
- (326) Huynh, M. H. V.; Meyer, T. J. *Chem. Rev.* **2007**, *107*, 5004–5064.
- (327) Weinberg, D. R.; Gagliardi, C. J.; Hull, J. F.; Murphy, C. F.; Kent, C. A.; Westlake, B. C.; Paul, A.; Ess, D. H.; McCafferty, D. G.; Meyer, T. J. *Chem. Rev.* **2012**, *112*, 4016–4093.
- (328) Mayer, J. M. *Annu. Rev. Phys. Chem.* **2004**, *55*, 363–390.
- (329) Cady, C. W.; Crabtree, R. H.; Brudvig, G. W. *Coord. Chem. Rev.* **2008**, *252*, 444–455.
- (330) Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P. *ChemCatChem* **2010**, *2*, 724–761.
- (331) Chen, Z.; Concepcion, J. J.; Meyer, T. J. *Dalton Trans.* **2011**, *40*, 3789–3792.
- (332) Chen, Z.; Concepcion, J. J.; Hull, J. F.; Hoertz, P. G.; Meyer, T. J. *Dalton Trans.* **2010**, *39*, 6950–6952.
- (333) Tong, L.; Duan, L.; Xu, Y.; Privalov, T.; Sun, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 445–449.
- (334) Duan, L.; Araujo, C. M.; Ahlquist, M. S. G.; Sun, L. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15584–15588.
- (335) Sheridan, M. V.; Sherman, B. D.; Fang, Z.; Wee, K.-R.; Coggins, M. K.; Meyer, T. J. *ACS Catal.* **2015**, *5*, 4404–4409.
- (336) Sheridan, M. V.; Sherman, B. D.; Marquard, S. L.; Fang, Z.; Ashford, D. L.; Wee, K.-R.; Gold, A. S.; Alibabaei, L.; Rudd, J. A.; Coggins, M. K.; Meyer, T. J. *J. Phys. Chem. C* **2015**, *119*, 25420–25428.
- (337) Song, N.; Concepcion, J. J.; Binstead, R. A.; Rudd, J. A.; Vannucci, A. K.; Dares, C. J.; Coggins, M. K.; Meyer, T. J. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 4935–4940.
- (338) Sheridan, M. V.; Sherman, B. D.; Wee, K.-R.; Marquard, S. L.; Gold, A. S.; Meyer, T. J. *Dalton Trans.* **2016**, *45*, 6324–6328.
- (339) Costentin, C.; Robert, M.; Savéant, J.-M. *Chem. Soc. Rev.* **2013**, *42*, 2423–2436.
- (340) Lim, R. J.; Xie, M.; Sk, M. A.; Lee, J.-M.; Fisher, A.; Wang, X.; Lim, K. H. *Catal. Today* **2014**, *233*, 169–180.
- (341) Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. *Chem. Soc. Rev.* **2014**, *43*, 631–675.
- (342) Fontaine, F.-G.; Courtemanche, M.-A.; Légaré, M.-A. *Chem. - Eur. J.* **2014**, *20*, 2990–2996.
- (343) Hori, Y.; Wakebe, H.; Tsukamoto, T.; Koga, O. *Electrochim. Acta* **1994**, *39*, 1833–1839.
- (344) Gattrell, M.; Gupta, N.; Co, A. *J. Electroanal. Chem.* **2006**, *594*, 1–19.
- (345) Chen, Y.; Li, C. W.; Kanan, M. W. *J. Am. Chem. Soc.* **2012**, *134*, 19969–19972.
- (346) Kumar, B.; Llorente, M.; Froehlich, J.; Dang, T.; Sathrum, A.; Kubiak, C. P. *Annu. Rev. Phys. Chem.* **2012**, *63*, 541–569.
- (347) Detweiler, Z. M.; White, J. L.; Bernasek, S. L.; Bocarsly, A. B. *Langmuir* **2014**, *30*, 7593–7600.
- (348) Zhang, S.; Kang, P.; Meyer, T. J. *J. Am. Chem. Soc.* **2014**, *136*, 1734–1737.
- (349) Zhang, S.; Kang, P.; Ubnoske, S.; Brennaman, M. K.; Song, N.; House, R. L.; Glass, J. T.; Meyer, T. J. *J. Am. Chem. Soc.* **2014**, *136*, 7845–7848.
- (350) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *J. Am. Chem. Soc.* **2015**, *137*, 4606–4609.

- (351) Zhang, S.; Kang, P.; Bakir, M.; Lapidès, A. M.; Dares, C. J.; Meyer, T. J. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 15809–15814.
- (352) Gao, S.; Lin, Y.; Jiao, X.; Sun, Y.; Luo, Q.; Zhang, W.; Li, D.; Yang, J.; Xie, Y. *Nature* **2016**, *529*, 68–71.
- (353) Torelli, D. A.; Francis, S. A.; Crompton, J. C.; Javier, A.; Thompson, J. R.; Brunschwig, B. S.; Soriaga, M. P.; Lewis, N. S. *ACS Catal.* **2016**, *6*, 2100–2104.
- (354) Seshadri, G.; Lin, C.; Bocarsly, A. B. *J. Electroanal. Chem.* **1994**, *372*, 145–150.
- (355) Barton, E. E.; Rampulla, D. M.; Bocarsly, A. B. *J. Am. Chem. Soc.* **2008**, *130*, 6342–6344.
- (356) Windle, C. D.; Perutz, R. N. *Coord. Chem. Rev.* **2012**, *256*, 2562–2570.
- (357) Boston, D. J.; Xu, C.; Armstrong, D. W.; MacDonnell, F. M. *J. Am. Chem. Soc.* **2013**, *135*, 16252–16255.
- (358) Keith, J. A.; Carter, E. A. *Chem. Sci.* **2013**, *4*, 1490–1496.
- (359) Yan, Y.; Zeitler, E. L.; Gu, J.; Hu, Y.; Bocarsly, A. B. *J. Am. Chem. Soc.* **2013**, *135*, 14020–14023.
- (360) Lim, C.-H.; Holder, A. M.; Hynes, J. T.; Musgrave, C. B. *J. Am. Chem. Soc.* **2014**, *136*, 16081–16095.
- (361) Barton Cole, E. E.; Baruch, M. F.; L'Esperance, R. P.; Kelly, M. T.; Lakkaraju, P. S.; Zeitler, E. L.; Bocarsly, A. B. *Top. Catal.* **2015**, *58*, 15–22.
- (362) Lucio, A. J.; Shaw, S. K. *J. Phys. Chem. C* **2015**, *119*, 12523–12530.
- (363) Peroff, A. G.; Weitz, E.; Van Duyne, R. P. *Phys. Chem. Chem. Phys.* **2016**, *18*, 1578–1586.
- (364) Sampson, M. D.; Froehlich, J. D.; Smieja, J. M.; Benson, E. E.; Sharp, I. D.; Kubiak, C. P. *Energy Environ. Sci.* **2013**, *6*, 3748–3755.
- (365) Grice, K. A.; Kubiak, C. P. Recent Studies of Rhenium and Manganese Bipyridine Carbonyl Catalysts for the Electrochemical Reduction of CO₂. In *CO₂ Chemistry*; Aresta, M., van Eldik, R., Eds.; Advances in Inorganic Chemistry 66; Academic Press: San Diego, 2014; Chapter 5, pp 163–188.
- (366) Agarwal, J.; Shaw, T. W.; Schaefer, H. F.; Bocarsly, A. B. *Inorg. Chem.* **2015**, *54*, 5285–5294.
- (367) Franco, F.; Cometto, C.; Garino, C.; Minero, C.; Sordello, F.; Nervi, C.; Gobetto, R. *Eur. J. Inorg. Chem.* **2015**, *2015*, 296–304.
- (368) Kang, P.; Chen, Z.; Brookhart, M.; Meyer, T. J. *Top. Catal.* **2015**, *58*, 30–45.
- (369) Sampson, M. D.; Kubiak, C. P. *J. Am. Chem. Soc.* **2016**, *138*, 1386–1393.
- (370) Weng, Z.; Jiang, J.; Wu, Y.; Wu, Z.; Guo, X.; Materna, K. L.; Liu, W.; Batista, V. S.; Brudvig, G. W.; Wang, H. *J. Am. Chem. Soc.* **2016**, *138*, 8076–8079.
- (371) Kang, P.; Cheng, C.; Chen, Z.; Schauer, C. K.; Meyer, T. J.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134*, 5500–5503.
- (372) Kang, P.; Meyer, T. J.; Brookhart, M. *Chem. Sci.* **2013**, *4*, 3497–3502.
- (373) Kang, P.; Zhang, S.; Meyer, T. J.; Brookhart, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 8709–8713.
- (374) Lee, S. *Methanol Synthesis Technology*; CRC Press, Inc.: Boca Raton, FL, 1989.
- (375) Waugh, K. C. *Catal. Today* **1992**, *15*, 51–75.
- (376) Wender, I. *Fuel Process. Technol.* **1996**, *48*, 189–297.
- (377) Schulz, H. *Appl. Catal., A* **1999**, *186*, 3–12.
- (378) Van Der Laan, G. P.; Beenackers, A. A. C. M. *Catal. Rev.: Sci. Eng.* **1999**, *41*, 255–318.
- (379) Dry, M. E. *Catal. Today* **2002**, *71*, 227–241.
- (380) van de Loosdrecht, J.; Botes, F. G.; Ciobica, I. M.; Ferreira, A.; Gibson, P.; Moodley, D. J.; Saib, A. M.; Visagie, J. L.; Weststrate, C. J.; Niemantsverdriet, J. W. Fischer–Tropsch Synthesis: Catalysts and Chemistry. In *Surface Inorganic Chemistry and Heterogeneous Catalysis*, 2nd ed.; Reedijk, J., Poeppelmeier, K., Eds.; Comprehensive Inorganic Chemistry II: From Elements to Applications, Vol. 7; Elsevier: Amsterdam, 2013; pp 525–557.
- (381) Galadima, A.; Muraza, O. *J. Nat. Gas Sci. Eng.* **2015**, *25*, 303–316.
- (382) Chen, Z.; Chen, C.; Weinberg, D. R.; Kang, P.; Concepcion, J. J.; Harrison, D. P.; Brookhart, M. S.; Meyer, T. J. *Chem. Commun.* **2011**, *47*, 12607–12609.
- (383) Chen, Z.; Concepcion, J. J.; Brennaman, M. K.; Kang, P.; Norris, M. R.; Hoertz, P. G.; Meyer, T. J. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15606–15611.
- (384) Kang, P.; Chen, Z.; Nayak, A.; Zhang, S.; Meyer, T. J. *Energy Environ. Sci.* **2014**, *7*, 4007–4012.
- (385) Norris, M. R.; Concepcion, J. J.; Fang, Z.; Templeton, J. L.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 13580–13583.
- (386) Sampaio, R. N.; Hu, K.; Brennaman, M. K.; Tamaki, Y.; Marquard, S. L.; Lapidès, A. M.; Meyer, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **2016**, manuscript in preparation.
- (387) Alibabaei, L.; Brennaman, M. K.; Norris, M. R.; Kalanyan, B.; Song, W.; Losego, M. D.; Concepcion, J. J.; Binstead, R. A.; Parsons, G. N.; Meyer, T. J. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 20008–20013.
- (388) Ogawa, J.-i.; Agrawal, S.; Koumura, N.; Mori, S. *J. Phys. Chem. C* **2016**, *120*, 3612–3618.
- (389) Lai, H.; Hong, J.; Liu, P.; Yuan, C.; Li, Y.; Fang, Q. *RSC Adv.* **2012**, *2*, 2427–2432.
- (390) Kim, M.-J.; Yu, Y.-J.; Kim, J.-H.; Jung, Y.-S.; Kay, K.-Y.; Ko, S.-B.; Lee, C.-R.; Jang, I.-H.; Kwon, Y.-U.; Park, N.-G. *Dyes Pigm.* **2012**, *95*, 134–141.
- (391) Cowan, A. J.; Durrant, J. R. *Chem. Soc. Rev.* **2013**, *42*, 2281–2293.
- (392) Murakami, T. N.; Koumura, N.; Uchiyama, T.; Uemura, Y.; Obuchi, K.; Masaki, N.; Kimura, M.; Mori, S. *J. Mater. Chem. A* **2013**, *1*, 792–798.
- (393) Lin, C.; Tsai, F.-Y.; Lee, M.-H.; Lee, C.-H.; Tien, T.-C.; Wang, L.-P.; Tsai, S.-Y. *J. Mater. Chem.* **2009**, *19*, 2999–3003.
- (394) Wu, M.; Yang, Z. H.; Jiang, Y. H.; Zhang, J. J.; Liu, S. Q.; Sun, Y. M. *J. Solid State Electrochem.* **2010**, *14*, 857–863.
- (395) Li, X.; Qiu, Y.; Wang, S.; Lu, S.; Gruar, R. I.; Zhang, X.; Darr, J. A.; He, T. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14729–14735.
- (396) Kang, S. H.; Kim, J.-Y.; Kim, Y.; Kim, H. S.; Sung, Y.-E. *J. Phys. Chem. C* **2007**, *111*, 9614–9623.
- (397) Song, J.; Yang, H. B.; Wang, X.; Khoo, S. Y.; Wong, C. C.; Liu, X.-W.; Li, C. M. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3712–3717.
- (398) Clifford, J. N.; Palomares, E.; Nazeeruddin, M. K.; Grätzel, M.; Nelson, J.; Li, X.; Long, N. J.; Durrant, J. R. *J. Am. Chem. Soc.* **2004**, *126*, 5225–5233.
- (399) Alibabaei, L.; Farnum, B. H.; Kalanyan, B.; Brennaman, M. K.; Losego, M. D.; Parsons, G. N.; Meyer, T. J. *Nano Lett.* **2014**, *14*, 3255–3261.
- (400) Michaux, K. E.; Gambardella, A. A.; Alibabaei, L.; Ashford, D. L.; Sherman, B. D.; Binstead, R. A.; Meyer, T. J.; Murray, R. W. *J. Phys. Chem. C* **2015**, *119*, 17023–17027.
- (401) Wee, K.-R.; Sherman, B. D.; Brennaman, M. K.; Sheridan, M. V.; Nayak, A.; Alibabaei, L.; Meyer, T. J. *J. Mater. Chem. A* **2016**, *4*, 2969–2975.
- (402) Sherman, B. D.; Ashford, D. L.; Lapidès, A. M.; Sheridan, M. V.; Wee, K.-R.; Meyer, T. J. *J. Phys. Chem. Lett.* **2015**, *6*, 3213–3217.
- (403) Diamant, Y.; Chappel, S.; Chen, S. G.; Melamed, O.; Zaban, A. *Coord. Chem. Rev.* **2004**, *248*, 1271–1276.
- (404) Grinis, L.; Ofir, A.; Dor, S.; Yahav, S.; Zaban, A. *Isr. J. Chem.* **2008**, *48*, 269–275.
- (405) Rabten, W.; Kärkäs, M. D.; Åkermark, T.; Chen, H.; Liao, R.-Z.; Tinnis, F.; Sun, J.; Siegbahn, P. E. M.; Andersson, P. G.; Åkermark, B. *Inorg. Chem.* **2015**, *54*, 4611–4620.
- (406) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40–48.
- (407) Sherman, B. D.; Vaughn, M. D.; Bergkamp, J. J.; Gust, D.; Moore, A. L.; Moore, T. A. *Photosynth. Res.* **2014**, *120*, 59–70.
- (408) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. *Chem. Rev.* **2010**, *110*, 6446–6473.
- (409) Trainham, J. A.; Newman, J.; Bonino, C. A.; Hoertz, P. G.; Akunuri, N. *Curr. Opin. Chem. Eng.* **2012**, *1*, 204–210.

- (410) McDaniel, N. D.; Bernhard, S. *Dalton Trans.* **2010**, 39, 10021–10030.
- (411) Sherman, B. D.; Sheridan, M. V.; Wee, K.-R.; Song, N.; Dares, C. J.; Fang, Z.; Tamaki, Y.; Nayak, A.; Meyer, T. J. *Inorg. Chem.* **2016**, 55, 512–517.
- (412) Ji, Z.; He, M.; Huang, Z.; Ozkan, U.; Wu, Y. *J. Am. Chem. Soc.* **2013**, 135, 11696–11699.
- (413) Rakowski Dubois, M.; Dubois, D. L. *Acc. Chem. Res.* **2009**, 42, 1974–1982.
- (414) Mikkelsen, M.; Jorgensen, M.; Krebs, F. C. *Energy Environ. Sci.* **2010**, 3, 43–81.
- (415) Takeda, H.; Ishitani, O. *Coord. Chem. Rev.* **2010**, 254, 346–354.
- (416) Schneider, J.; Jia, H.; Muckerman, J. T.; Fujita, E. *Chem. Soc. Rev.* **2012**, 41, 2036–2051.
- (417) Sivula, K.; Grätzel, M. Tandem Photoelectrochemical Cells for Water Splitting. In *Photoelectrochemical Water Splitting: Materials, Processes and Architectures*; Lewerenz, H.-J., Peter, L., Eds.; RSC Energy and Environment Series 9; Peter, L., Frei, H., Schüth, F., Zhao, T. S., Eds.; The Royal Society of Chemistry: Cambridge, UK, 2013; pp 83–108.
- (418) Prévot, M. S.; Sivula, K. *J. Phys. Chem. C* **2013**, 117, 17879–17893.