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Review Article Photocatalytic fuel production

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The conversion of carbon dioxide and water to fuel in artificial systems requires efficient coupling of light absorbers and catalysts, and assembly of the components into hierarchical structures to close the photocatalytic cycle. Recent breakthroughs in the embodiment of molecular photoactive components in ultrathin oxide layers, and the introduction of new materials approaches for interfacial charge transfer have led to substantially improved coupling of chromophores and catalysts. These advances are accelerating the exploration of novel architectures for reducing CO₂ by H₂O in scalable, single integrated photosystems to reach the high power efficiencies recently demonstrated with photovoltaic-assisted approaches.

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Introduction

Research in photocatalytic fuel generation from carbon dioxide and water has recently experienced substantial leaps forward in the development of robust, efficient light absorbers, and the discovery of novel catalysts made of Earth abundant materials. This progress brings into focus the challenge of integrating the components into complete artificial photosystems for closing the photosynthetic cycle of CO₂ reduction by H₂O. Critical tasks for meeting this challenge are the efficient coupling of light absorbers with multi-electron oxidation or reduction catalysts in order to maximize the fraction of the energy of the solar photon converted to chemical energy of the product, and achieving high quantum efficiency. A particularly important gap to bridge is the efficient coupling of the oxidation and reduction half reactions without the need for electrical or chemical bias while avoiding cross-over of in-

termediates and products between the incompatible catalytic environments. Furthermore, impact on global fuel consumption demands scalability of artificial photosystems on the unprecedented scale of terawatts. Therefore, consideration of manufacturability and minimization of balance of systems requirements gain critical importance.

In the past few years, novel approaches have emerged for the coupling of molecular light absorbers to water oxidation or fuel forming catalysts that have resulted in substantially improved stability while maintaining or even enhancing activity. Molecular light absorbers offer the distinct advantage of the precise matching of their redox potential and that of the catalyst for maximum conversion of solar photon energy into chemical energy of the reduced fuel product. While H₂ production by solar water splitting continues to be an intense research focus, the first complete systems for visible light-driven reduction of CO₂ by H₂O to CO or formic acid have emerged. Here, progress consists of demonstrating very high sunlight to chemical energy conversion efficiencies for photovoltaic-assisted electrochemical cells, and exploration of concepts for developing single integrated (monolithic) artificial photosystems. This article highlights recent advances in the coupling of light absorbers and solar fuel catalysts, and in the exploration of complete integrated photosynthetic systems for carbon dioxide reduction by water to fuel.

Ultrathin oxide layers for improved light absorber–catalysts coupling

Early studies by the groups of Hupp, Gordon, and Korppi-Tommola on casting of surface anchored organic molecules into ultrathin amorphous wide bandgap oxide layers [1*,2,3], combined with the advent of commercially available atomic layer deposition equipment (ALD), have substantially accelerated progress toward robust and efficient coupling of molecular light absorbers to catalysts for artificial photosynthesis. The ALD technique enables deposition of oxide layers of nanometer thickness with Angstrom accuracy onto open surface areas of solid oxides in between anchored organics. Because the thickness of oxide layers generated by ALD is self-limiting, the coverage is conformal even for highly nanostructured supports, which is critical given the need for high surface area photoelectrodes in order to achieve adequate current densities for solar fuel generation. The result is that the spaces between anchored light absorber molecules are selectively covered by insulating oxide thereby preventing undesired charge transfer or side reactions at the solid–aqueous interface. Furthermore, ALD layers prevent molecular light absorbers from desorbing and

degrading during photocatalysis, thereby improving the durability of light absorber–catalyst assemblies by orders of magnitude [4^{••},7,8].

Kamire *et al.* observed substantial enhancement of both quantum efficiency and stability of the versatile molecular chromophore perylene-3,4-dicarboximide (PMI) anchored via dicarboxylate moieties on a nanostructured nickel oxide cathode after casting into 2 nm of alumina and exposure to molecular cobaloxime or $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{R}}_2)_2]^{2+}$ catalysts for hydrogen generation [4^{••},5]. Static and ultrafast optical spectra show that the alumina cast around the adsorbed PMI molecules imposes structural rigidity while at the same time causing disaggregation and blocking of excimer formation of the dye molecules, thereby substantially enhancing the quantum efficiency of hole transfer from the light absorber to NiO (Figure 1a). Transient absorption spectra show that photo-induced charge separation to yield reduced PMI is extremely fast and complete in 0.5 ps. While the majority of PMI radical anions recombine with holes on NiO within hundreds of ps in the electrically unbiased mode, forward electron transfer is observed by linear sweep voltammetry under acidic conditions and H_2 detected when interacting with cobaloxime or Ni phosphine catalysts [4^{••}]. For example, at an applied potential of -0.4 V vs. Ag/AgCl, H_2 evolution proceeds with 100% Faradaic efficiency for a system with the PMI chromophore embedded in 2 nm alumina and Ni phosphine as catalyst. Without the alumina layer, four times less H_2 is produced at reduced Faradaic efficiency of 80%. The much higher product yield in the presence of alumina is due to diminished back electron transfer between reduced catalyst and injected holes on NiO due to the insulating Al_2O_3 nanolayer. Furthermore, the stabilizing effect of the alumina layer is manifested by the observation that the light absorber was completely degraded after 2 h of photolysis in the absence of the Al_2O_3 nanolayer, while no diminishment was noted in its presence.

Lapides *et al.* developed photoanode assemblies consisting of an Al_2O_3 embedded $[\text{Ru}(\text{bpy})_3]^{2+}$ light absorber anchored via phosphonate groups on metal oxide electrodes and a subsequently adsorbed water oxidation catalyst cast by ALD into a second layer of alumina [6[•],7,8]. Efficient electron injection of visible light excited Ru chromophore into nanostructured indium tin oxide (ITO) or TiO_2 support was followed by similarly efficient hole transfer to a Ru catalyst $[\text{Ru}(2,6\text{-bis}(1\text{-methyl-}1H\text{-benzo}[d]\text{imidazole-2-yl})\text{pyridine})(4,4'\text{-((HO)}_2\text{(O)P-CH}_2\text{)}_2\text{-2,2'-bipyridine)}(\text{OH}_2))]^{2+}$ for water oxidation (Figure 1b) despite the fact that the arrangement of the catalyst relative to chromophores was not specifically designed and assumed to be random. Sustained photoelectrocatalytic evolution of O_2 at 17% Faradaic efficiency (limited by organic ligand stability) over 6 h was demonstrated for assemblies attached to nano-

structured TiO_2 . The fact that charge transfer coupling of alumina “mummified” chromophore and molecular water oxidation catalyst is feasible in the absence of a molecularly defined linkage between the components is particularly interesting because it offers flexible routes for the assembly of stable light absorber–catalyst systems on photoelectrodes.

Silica nanolayers with embedded molecular wires for artificial photosynthetic membranes

Coupling of molecular light absorbers with metal oxide nanoparticle catalysts across an ultrathin (2–3 nm) dense phase silica layer with embedded molecular wires affords precise, molecular level control of chromophore–catalyst charge transfer. At the same time, the corrosive water oxidation catalysis is separated from chromophore and reduction chemistry by a proton transmitting, O_2 impermeable membrane (Figure 2a) [9–12]. The permeability of the ultrathin, pinhole-free silica was established by electrochemical methods [11], and the charge transfer properties were evaluated by transient optical spectroscopy and photoelectrochemical measurements [9,10,13[•],14]. Hole transfer from $[\text{Ru}(\text{bpy})_3]^{3+}$, whose redox potential is aligned with the HOMO of embedded *p*-oligo(phenylene vinylene) wires featuring 3 aryl units (abbreviated PV3, Figure 2a), resulted in fast, subnanosecond transfer across the silica layer to the Co oxide catalyst [14]. By contrast, no photocurrent was observed when using a visible light sensitizer with redox properties that do not match the energetics of the wire molecules. For example, reduced Sn porphyrin sensitizer generated in the presence of a donor did not result in electron injection into the wire, consistent with the fact that the reduction potential of the reduced light absorber is not sufficiently negative for electron transfer to the LUMO of the embedded wire molecule (Figure 2b) [13[•]]. The results show that the embedded molecular wires tightly control the charge flow across the silica membrane by their orbital energetics, allowing to exert rectifying properties for properly chosen light absorber–wire combinations. The low temperature ALD (or mild solvothermal) techniques employed for making the silica nanolayers are suitable for any nanoscale morphology thereby opening up the development of nanostructured architectures with built-in membrane separation for a variety of artificial photosystem designs.

Reducing CO_2 by H_2O in efficient photovoltaic-assisted systems

Photovoltaics-electrochemical cell systems for highly efficient ($\geq 10\%$) conversion of CO_2 to CO or formate using H_2O as electron source were recently demonstrated. Zhou *et al.* reported a photovoltaic-assisted electrosynthetic cell featuring a bipolar separation membrane that allows to conduct O_2 evolution and CO_2 reduction catalysis at widely different pH values, each selected for maximum efficiency of the half reaction, without

Figure 1

Molecular light absorbers embedded in alumina nanolayer driving solar fuels catalyst. (a) Perylene-3,4-dicarboximide chromophore (red) anchored on NiO electrode driving a cobaloxime or Ni phosphine catalyst for H₂ generation (black). From Ref. [4••], with permission. (b) Ru(bpy)₃ light absorber 1 (green) cast into alumina nanolayer on TiO₂ or ITO electrode, overlaid by Ru catalyst for water oxidation 2 (red), also partially embedded in alumina. From Ref. [6•], with permission. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

accompanying chemical bias [15]. The photoanode is a tandem-junction GaAs/InGaP two-photon absorber coated by an amorphous TiO₂-Ni nanolayer for water oxidation catalysis, as previously demonstrated for water splitting systems [16]. It operates in alkaline aqueous solution (1 M KOH, pH 13.7), which is optimal for water oxidation. Carbon dioxide is reduced at a Pd/C-coated Ti mesh cathode in close to neutral solution (2.8 M HCO₃⁻, pH=8.0) exposed to 1 atm of CO₂ gas. The bipolar membrane [17–20] allows to maintain the large pH difference of the cell under continuous operation at a light-limited

photocurrent density of 8.5 mA cm⁻² and >94% Faradaic efficiency for CO₂ reduction to formate [15]. Modest voltage loss of 480 mV at the bipolar membrane and low over-voltages for CO₂ reduction (<100 mV) and O₂ evolution (320 mV) enable a remarkable 10% energy conversion efficiency.

Using 3 perovskite photovoltaic units connected in series for driving electrodes coated with activated Au (cathode) and Ir oxide (anode) co-catalysts in CO₂-saturated aqueous bicarbonate in a single compartment cell shown in

Figure 2

Ultrathin silica layer with embedded molecular wires as separation membrane for artificial photosystems. (a) Graphic representation of construct, and structure of molecular wire. (b) Photoelectrochemical and CV measurements of charge transport across silica membrane with embedded wires. Top: short circuit photocurrent observed for visible light sensitized hole injection into bare Co oxide, Co oxide coated with SiO_2 -PV3 membrane, and Co oxide coated with silica only, using $[Ru(bpy)_3]^{2+}$ -persulfate (blue) and Sn porphyrin-triethylamine (red) systems. Bottom: schematic of experiment. From Ref. [13*], with permission. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Figure 3a, b, Schreier *et al.* achieved 6.5% energy conversion efficiency for the reduction of CO_2 by H_2O to CO at 5.8 mA cm^{-2} current density and 80–90% Faradaic efficiency [21*]. As shown in the current density–voltage curves of Figure 3c, an important advantage of the device is that the operating point is in the flat region of the J–V trace, which provides stability with respect to light intensity or catalytic rate fluctuations. Another single compartment system, by Arai *et al.*, featuring a triple junction photovoltaic unit coated with Ir oxide on the anode side and Ru polymer catalyst on the opposing cathode side of a planar construct achieved conversion of CO_2 to formate at 4.6% power efficiency at 3.3 mA cm^{-2} [22]. The photovoltaic component is a triple junction SiGe element, and the planar design is similar to the one used previously by Nocera for a single compartment cell for high efficiency water splitting [23].

Closing the cycle of CO_2 photoreduction by H_2O on the nanoscale

For addressing the formidable challenge of developing artificial photosynthetic technologies that are scalable on

the unprecedented scale of terawatts, integrated systems designs with minimal balance of systems requirements and negligible side reactions need to be explored. Natural photosynthesis, which is the sole existing technology that produces energy dense chemicals on the terawatt scale, provides a case in point. Main design features of the natural photosystem are the closing of the cycle of water oxidation and formation of the primary reduction product on the shortest possible length scale—the nanometer scale—while separating the incompatible redox environments by a membrane. This poses the task of developing artificial photosystem designs that incorporate these features—complete catalytic cycles on the nanoscale under membrane separation—which might prove critical for realizing the required scalability.

Nanoscale systems in the form wide bandgap semiconductor particles using UV light for photocatalytic reduction of CO_2 by H_2O to CO, methane, methanol, or formaldehyde have been pursued since the earliest reports on aqueous TiO_2 and $SrTiO_3$ particle suspensions almost 40 years ago [24,25]. Continued exploration of the

Figure 3

Photovoltaics powering electrochemical cell for CO_2 reduction by H_2O . (a) Schematic of device. (b) Energy diagram showing the voltage generated by three series-configured perovskite solar components, which exceeds the reaction free energy (ΔE) and the over-potentials (η) at the electrodes. (c) Current-voltage response (J-V curves) of perovskite cells under simulated solar light (red trace) and dark (blue trace). The operating point is represented by the intersection of the electrode and photovoltaic curves (x), which is close to the maximum power point for solar-to-electrical energy conversion (o). From Ref. [21^{*}], with permission. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

photoconversion with wide bandgap particles has focused on functionalization by co-catalysts [26–30] or the introduction of nanoporous structures such as oxometalates [31]. Aqueous mixtures of smaller bandgap semiconductor particles for two-photon tandem photocatalysis mediated by molecular or ion redox shuttles has enabled the use of longer wavelength, visible light [32^{••},33]. Several recent advances in the coupling of photochemical CO_2 reduction and H_2O oxidation half reactions on the nanoscale for both aqueous and vapor phase systems open up opportunities for exploring a variety of different integrated photosystem architectures, with the goal of identifying designs suitable for development on the unprecedented scale that is required.

Li *et al.* demonstrated visible light-driven CO_2 reduction by H_2O to CH_4 in a two-photon tandem system

that consists of $\text{Fe}_2\text{V}_4\text{O}_{13}$ nanoribbons interfaced with CdS nanoparticles across reduced graphene oxide (RGO) sheets as shown in Figure 4a [34[•]]. The graphene layer functions as mediator for efficient electron transfer from the conduction band of photoexcited CdS to the valence band of excited Fe vanadate. While bare CdS is vulnerable to photocorrosion, recent development of TiO_2 nanolayer coating of III–V semiconductors affords dramatic stabilization of the semiconductor surface and opens up the use of these materials as photocatalysts for water oxidation [35]. Also recently, reduced graphene oxide was shown by Iwase *et al.* to afford superior electron transfer coupling of semiconductor nanoparticles in aqueous solution compared to molecular (ion) shuttles. Here, CO_2 reduction to CO was achieved with a tandem system consisting of BiVO_4 nanoparticles coated with Co oxide co-catalyst for water oxidation and CuGaS_2 particles for

Figure 4

(a) TEM image and schematic representation of Fe₂V₄O₁₃/RGO/CdS, and (b) high resolution TEM images and schematic of WO₃/Au/In₂S₃ two-photon tandem heterostructures for CO₂ reduction by H₂O to methane. From Refs. [34[•],37^{••}], with permission. (c) Hetero-binuclear ZrOCo^{II} charge transfer light absorber coupled to Ir oxide nanocluster catalyst for the direct photoreduction of CO₂ to CO by H₂O (vapor phase). Schematic illustration of unit (top) and CO gas product monitored by infrared (bottom). From Ref. [38], with permission.

carbon dioxide reduction using RGO as electron mediator [36]. Furthermore, Li *et al.* reported a WO₃ nanowire array decorated with Au core–In₂S₃ shell nanoparticles in which WO₃ and In₂S₃ form a two-photon tandem system for efficient visible light-induced generation of CH₄ from a CO₂–H₂O vapor phase mixture, with Au nanoparticles serving as electron mediator (Figure 4b) [37^{••}]. Yet another type of all-inorganic nanoscale photocatalytic assembly for the conversion of CO₂ and H₂O vapor, in this case to CO and O₂, consists of a heterobinuclear ZrOCo charge transfer light absorber coupled to an Ir oxide nanocluster catalyst (2 nm) supported on nanoporous silica (Figure 4c) [38,39]. Hierarchical assembly of this photocatalytic unit was achieved by a new photodeposition method that allowed the spatially directed coupling of

the Co donor center to the IrO_x nanocluster catalyst. The photodeposition method has similarly allowed the spatially controlled coupling of a cuprous oxide nanocluster for CO₂ reduction to the Zr acceptor center of the binuclear ZrOCo light absorber [40]. These advances expand the methods available for integrating light absorbers and catalysts, and for coupling CO₂ reduction and H₂O oxidation half reactions on the nanoscale, which provide a basis for developing hierarchical structures for robust, scalable artificial photosystems.

Outlook

New approaches utilizing inorganic nanostructures and spatially controlled assembly of molecular and nanoparticle components have led to substantially improved coupling of molecular light absorbers and catalysts for ar-

tificial photosynthesis. Especially promising is the casting of molecular light absorbers or charge transfer moieties with their precisely tunable electronic properties into ultrathin oxide layers, which results in substantially improved stability and minimizes or even blocks efficiency-degrading charge transfer and catalytic processes. The new materials approaches for nanoscale integration expand the range and type of solid heterostructures that can be explored for developing single integrated artificial photosystems with the required characteristics for implementation on unprecedented large scale. Recent demonstration of very high efficiency for carbon dioxide reduction by water to carbon monoxide or formic acid with photovoltaic-electrochemical cell devices establishes an important marker that serves as target for carbon dioxide to fuel conversion efficiency of scalable artificial photosystems.

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