Angewandte
Minireviews

DOI: 10.1002/anie.201300136

Artificial Photosynthesis

Water-Splitting Catalysis and Solar Fuel Devices: Artificial Leaves on the Move

Khurram Saleem Joya, Yasir F. Joya, Kasim Ocakoglu, and Roel van de Krol**

artificial leaves · electrocatalysis · molecular catalysts ·
solar fuels · water splitting

The development of new energy materials that can be utilized to make renewable and clean fuels from abundant and easily accessible resources is among the most challenging and demanding tasks in science today. Solar-powered catalytic water-splitting processes can be exploited as a source of electrons and protons to make clean renewable fuels, such as hydrogen, and in the sequestration of CO_2 *and its conversion into low-carbon energy carriers. Recently, there have been tremendous efforts to build up a stand-alone solar-to-fuel conversion device, the "artificial leaf", using light and water as raw materials. An overview of the recent progress in electrochemical and photo-electrocatalytic water splitting devices is presented, using both molecular water oxidation complexes (WOCs) and nano-structured assemblies to develop an artificial photosynthetic system.*

1. Introduction

Water-splitting catalysis and artificial photosynthesis are hot topics in present-day science research that aims to construct a solar-to-fuel conversion system, the "artificial leaf".[1–3] An artificial leaf is a light-harvesting device, with self-assembled and auto-healing catalysts, that runs with solar energy, consuming water as food, splitting it, and releasing protons and electrons that can be used to make hydrogen or other renewable fuels for a sustainable future (Figure 1).[4] Using light-driven water-splitting reaction, the product(s) can

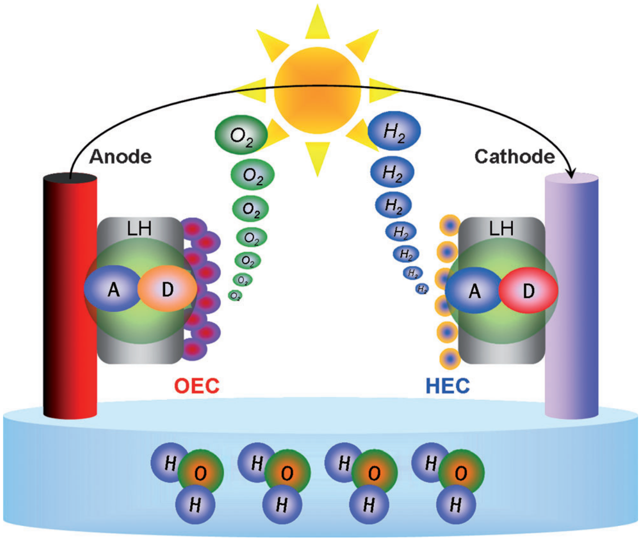

Figure 1. Representation of a stand-alone light-driven solar-fuel device using water to generate protons and electrons. LH = light harvesting systems, OEC = O_2-evolving catalyst, HEC = H_2-generation catalyst; A and D stand for acceptor and donor, respectively.

---

[*] Dr. K. S. Joya
Leiden Institute of Chemistry, Leiden University
P.O. Box 9502, 2300 RA Leiden (The Netherlands)
E-mail: khurramsj@chem.leidenuniv.nl

Dr. K. S. Joya
Max Planck Institute for Chemical Energy Conversion
Stiftstrasse 34–36, 45470/Mülheim an der Ruhr (Germany)

Dr. K. S. Joya
Department of Chemistry, University of Engineering and Technology
GT Road, Lahore, Punjab 54890 (Pakistan)

Prof. R. van de Krol
Helmholtz-Zentrum Berlin für Materialien und Energie GmbH
14109 Berlin (Germany)
E-mail: roel.vandekrol@helmholtz-berlin.de

Dr. Y. F. Joya
Faculty of Materials Science and Engineering, Ghulam Ishaq Khan
Institute of Engineering Sciences and Technology
Topi 23640, Khyber Pakhtunkhaw (Pakistan)

Prof. K. Ocakoglu
Advanced Technology Research & Application Center
Mersin University, Yenisehir, Mersin (Turkey)

also be exploited for carbon dioxide capture and conversion into chemical feedstock and environmentally friendly energy sources.[5,6] The major obstacle in pursuing a solar-to-fuel-conversion water-splitting device is the development of a robust and long-living water-oxidation catalyst. In the artificial leaf, the WOC is required to produce molecular oxygen at a high rate with tremendous efficiency and a turnover number exceeding millions. The protons generated during the water-splitting process can be utilized at the cathodic side for the reduction reaction to make fuel.[7]

The light capture and energy conversion components of the solar-fuel device comprise: 1) an efficient light-harvesting antennae system; 2) long-lived charge-separating units, and 3) a compatible donor–acceptor combination.[8] On the other hand, the catalytic part of the solar-fuel system has to be a stable water-oxidation molecular complex or material sustaining the four-electron water-oxidation process for numerous cycles; it should facilitate the O–O bond formation and dioxygen release from the catalytic sites at a high rate.[9] An ideal WOC would be a self-assembling, and self-healing material exhibiting a consecutive four-step proton-coupled electron transfer (PCET) pathway to circumvent the high-energy intermediates during the four-electron abstracting process of water oxidation.[10]

During past two decades, much progress has been made in the field of light-harvesting systems and charge-separation modules.[11] Since 2000, many attempts have also been made in designing a biomimetic model of the water-splitting catalyst, resembling the Mn cluster in natural photosystem II in efficiency and activity.[12–14] In surface-immobilized electro- or photocatalytic processes, the WOCs tested had neither low activation barriers and small oxygen onset overpotential, nor did they exhibit high current densities for oxygen evolution. This greatly hampered their applications in practical devices for fuel generation.[15] Mono-site as well as binuclear molecular catalytic systems have been studied, both in homogeneous solutions and on anodes under electrochemical conditions. However, these systems were not able to show a four-step proton-coupled electron-transfer regime and good proton management facilitating their locomotion to the reduction site.[15–17] On the other hand, inorganic materials derived from cheap and abundant metals are interesting candidates for oxidation catalysis. However, they are normally required in bulk amounts on the conducting surfaces, which can easily decrease the light-capturing efficiency of the solar device.[18] The catalytic performance of these inorganic materials for oxygen evolution reaction is also not superior compared to the molecular water-oxidation complexes.[18,19]

Apart from focusing on water oxidation chemistry and multi-electron catalysis, solar photovoltaic cells have also been employed in the stand-alone light-driven assemblies to make fuel from water.[4,8] Thus there is a whole variety of topics dealing with water oxidation and hydrogen evolution using molecular catalysts, inorganic materials and transition metal complexes, studied both in solution and electrochemically on anodic surfaces.[15–21] Herein we attempt to review and analyze the electrochemical and photo-electrocatalytic water oxidation systems that were developed during last 15 years as artificial photosynthetic models to make H_2 and O_2 from catalytic water oxidation. Starting from solution-phase catalysis with organometallic complexes and going on to electrochemical assemblies with molecular catalysts and nanostructured systems, we also try to give an overview of the various concepts developed over time for the integration of water-oxidation catalysts and proton-reduction sites with photo-electrochemically and photovoltaically powered systems for solar fuels. We conclude with an outlook regarding solar-fuel research.

2. Molecular Approaches to Water-Oxidation Catalysis

Catalytic water oxidation systems can be derived from heterogeneous inorganic oxide materials, metal and metal oxide nanoparticles, or they can be homogeneous molecular complexes and organometallics of transition metals.[18,22] Simple transition-metal oxides (Co, Mn, Ni, or Fe oxides), oxides of precious metals (such as IrO_2, RuO_2), and other mixed inorganic matrices have been studied broadly for water oxidation both in solution and in electrochemical assemblies; however, the modest catalytic turnover frequencies and relatively low number of active sites are still limiting wide-scale application in catalytic systems to make fuel.[8,22,23] Water-oxidation catalysts in the solution phase can be studied for oxygen generation using an external driving force from a (sacrificial) chemical oxidant or a dye molecule. The most tested chemical oxidant for water oxidation catalysis in aqueous solution is the well-known orange compound ammonium cerium(IV) nitrate $(NH_4)_2[Ce(NO_3)_6]$ [CAN; see Equation (1)]; however, there are also reports on sodium iodate ($NaIO_4$) or Ce^{III}. As light-absorbing dye, tris(bipyr-

Khurram Saleem Joya is a senior lecturer at the Chemistry Department, University of Engineering and Technology, Lahore (Pakistan). After his PhD from Leiden University (Netherlands) and short stay at UNT (USA), he joined the Max Planck Institute for Chemical Energy Conversion (Mülheim, Germany). Currently, he is an independent researcher at Leiden University and also involved in Solar to Liquid Fuel via Water Splitting, a 3M EUR project funded by the Punjab Government (Pakistan).

Roel van de Krol is head of the Institute for Solar Fuels at the Helmholtz-Zentrum Berlin (HZB), and is professor at the Chemistry Department of the TU Berlin. After earning his PhD from TU Delft (Netherlands) and a short postdoctoral stay at MIT (USA), he was an assistant professor at TU Delft until 2012. His main research interests are on thin-film and nanostructured metal oxide semiconductors for solar hydrogen production.

idine)ruthenium(II) $[Ru(bpy)_3]^{2+}$ is most often used for triggering catalytic water oxidation in solution.[24]

$$\mathrm{Cat} + 2\,\mathrm{OH_2(l)} + 4\,\mathrm{Ce^{IV}(aq)} \rightarrow 4\,\mathrm{H^+(aq)} + \mathrm{O_2(g)} + 4\,\mathrm{Ce^{III}(aq)} \qquad (1)$$

There has always been a debate concerning the nature and integrity of homogeneous water oxidation complexes in solution, as the molecular catalysts can be readily oxidized or decomposed by the (sacrificial) chemical oxidants, and may form corresponding metal oxide species.[25] Therefore, the safer side is to put the catalyst on a clean anodic surface to drive water splitting catalysis with an external electron source rather than a chemical species. By immobilizing the catalyst on an anode surface, the water oxidation reaction can be controlled by the applied potential and largely avoid these complications.

2.1. Solution-Phase Water Splitting with Molecular Complexes

The quest for the development of bio-inspired water oxidation catalysts started in the later stage of the 19th century with the advent of a few Mn- and Ru-based complexes using nitrogen-derived ligands; however, the catalytic efficiency was very low.[3,15] Subsequently, metal complexes with iridium and iron have also been investigated in homogeneous water oxidation catalysis.[3,24] Very recently, a few interesting examples have been reported with more stable ligand architecture and efficient catalysis performance.[15–18]

2.1.1. A Dimeric Manganese Complex for Water Oxidation

A bio-inspired dinuclear manganese catalyst, $[Mn_2(mcbpen)_2(OH_2)_2]^{2+}$, with a tetranitrogen carboxy ligand N-methyl-*N′*-carboxymethyl-*N,N′*-bis(2-pyridylmethyl)ethane-1,2-diamine (mcbpen) catalyzes the oxidation of water to dioxygen by using *tert*-butylhydrogenperoxide (TBHP) or ammonium cerium(IV) nitrate as a sacrificial electron acceptor (Figure 2a).[26] Membrane inlet mass spectrometry (MIMS) analysis indicates that each of two oxygen atoms in the evolved O_2 is contributed both from water and TBHP. A turnover number (TON) of 20 was reported for $[Mn_2(mcbpen)_2(OH_2)_2]^{2+}$ using TBHP at pH 4–5. Styring and coworkers studied several monomeric as well as dimeric manganese catalysts, and their results indicate that the known Mn complexes that catalyze oxygen formation from water operate only if oxygen-transfer oxidants are used.[27] Recently, a dinuclear Mn catalyst has been studied in homogeneous solution and is claimed to be the most stable molecular system based on two manganese sites.[28] The complex contains a central 4-methylphenol with an extended oxygen ligand and two benzimidazole units having carboxylate arms bridging two manganese centers (Figure 2b). The complex was prepared from commercially available starting materials and was tested both for homogeneous chemical catalysis as well as photochemically in a phosphate buffer (pH 7.2) solution. Using 480-fold excess of $[Ru(bpy)_3]^{2+}$ as single-electron oxidant, the catalyst operated with an initial turnover rate (TOF) of 0.027 s^{-1} lasting for an hour with a TON of <30.

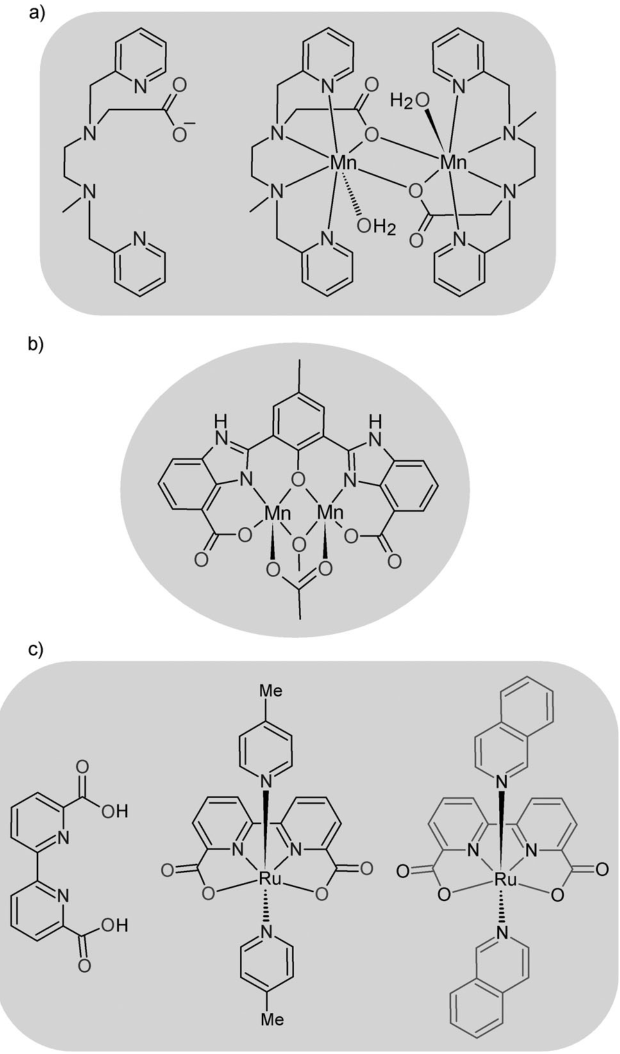

Figure 2. a,b) Dinuclear Mn-derived complexes and c) a single-site $[Ru(dcabpy)(isq)_2]$ complex for homogeneous water oxidation.

2.1.2. A Rapid Homogeneous Ruthenium Catalyst

As mentioned before, several ruthenium derived molecular catalytic systems have been scrutinized for water oxidation, but poor stabilities and low efficiencies limit their application in practical devices.[12,15] Recently, Sun et al. reported several Ru complexes that perform very rapid oxygen evolution in homogeneous solutions using a chemical oxidant. In a solution containing an excess of Ce(IV) under acidic conditions, the single-site ruthenium catalyst, $[Ru(dcabpy)(isq)_2]$ (dcabpy = 6,6′-dicarboxylic acid-2,2′-bipyridine, isq = isoquinoline), shows an unprecedented oxygen generation rate greater than 300 s^{-1} (Figure 2c).[29] Sun's catalyst is the best water oxidation complex reported to date. The complex also has a TON of more than 8000, showing its good stability in aqueous acids.

2.2. Electro-driven Water Oxidation on Conducting Surfaces

To develop an artificial leaf for solar-fuel generation, the molecular bio-inspired catalytic system needs to be tested on an electrode surface in an electrochemical setup.[8] During last decade, several molecular Ru complexes have been studied on anodes in an electrolytic cell, but the oxygen-evolution current densities (J) were very low.[30,31] Furthermore, in full-cell electrolysis operation, molecular-catalyst-based assemblies operate at high electrode potential, the overpotential, which is usually 500–700 mV above the thermodynamic electrochemical potential for water splitting; that is, $E = 1.23$ V (vs. NHE, pH 0).[3] Incorporation of a Ru-tris(bpy)-type redox mediator with the [(bpm)Ru^{II}(Mebimpy)(OH$_2$)] complex (Mebimpy = 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine) yielded a TON of 28000 at a potential of 1.80 V (vs. NHE, pH 0) in an acidic medium, but at low current density, $J < 50\ \mu\text{A cm}^{-2}$.[32] A low current density for O_2 generation is indicative of a low performance for the electrochemical water oxidation. The presence of photosensitizer also had no effect on the water oxidation overpotential.

It is also thought that bio-inspired metal complex with a single catalytic site cannot carry out efficient water oxidation, but very recently we have reported an efficient electrodriven water oxidation system with a Cp*-ligated mono-iridium catalyst (Cp* = pentamethylcyclopentadienyl) anchored to an ITO (indium tin oxide) surface by COOH or PO_3H_2 linkers. The electrocatalytic assembly produced a TON of more than 200000 for molecular oxygen with a TOF of more than 6.7 s^{-1}.[33] This is the first instance when a molecular catalyst shows a current density of more than 1.75 mA cm^{-2} in a pH 4 solution (Figure 3). A pyrene-modified [Ru(dcabpy)(py-pic)$_2$] complex, (py = pyrene; pic = 4-picoline), was also studied on a multiwalled carbon nanotube/ITO system in neutral solution. At 1.4 V (vs. NHE), it generated a TON of 11000 TON for O_2 with $J = 0.22$ mA cm^{-2}.[34] Another interesting report describes a copper bipyridine (Cu-bpy) hydroxo complex, [Cu(bpy)(μ-OH)]$_2^{2+}$, for alkaline water electrolysis. The Cu hydroxo complex self-assembles in a pH > 11 solution and shows a turnover frequency up to 100 s^{-1}.[35] However, the system operates at a high overpotential, 700–900 mV in alkaline electrolyte, which may limit its large-scale application for the H_2/O_2 evolution by water electrolysis, especially when used for liquid fuel production.

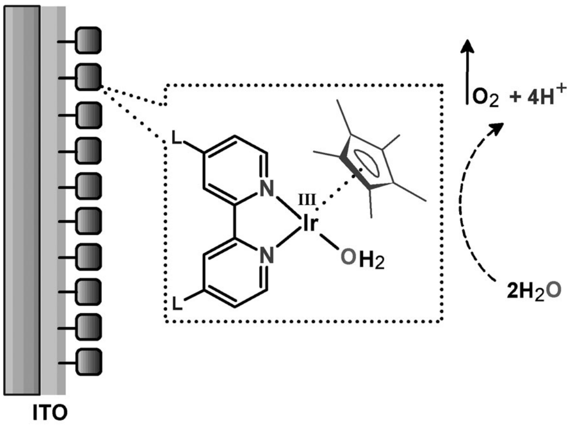

Figure 3. A surface-immobilized electrochemical water oxidation assembly derived from a pentamethylcyclopentadienyl (Cp*) iridium complex (L = PO_3H_2, COOH). ITO = indium tin oxide.

2.3. Photo-electrochemical Water Oxidation and Oxygen Evolution

After testing the molecular catalyst for water oxidation in an electrochemical setup, the next step is to combine the system together with bio-inspired light harvesting units or a semiconductor photovoltaic cell. A simple way of studying visible-light-driven water splitting is to use a dye-sensitized semiconductor oxide material in a photo-electrochemical cell with separate anodic and cathodic compartments to avoid the mixing of H_2 and O_2. Four important components are required to build up a light-induced electrochemical system for fuel generation: 1) an efficient light harvesting material with high molar extinction co-efficient (ε) comparable to $\varepsilon = 90000\ \text{L mol}^{-1}\text{cm}^{-1}$ for natural chlorophylls; 2) a molecular donor–acceptor pair for effective charge separation; 3) a robust and efficient water oxidation catalyst; and 4) a transparent conducting electrode surface or a semiconducting material.[8,36] When a semiconductor is used as a light absorber, molecular donor–acceptor pairs are not required for charge separation as both light absorption and charge separation are taken care of by the semiconductor. However, the chemical architecture of a synergetic blend of a WOC with a light-harvesting unit to trigger high-efficiency photo-electrochemical water oxidation is the major challenge.[15] Various studies have been undertaken in this pursuit to demonstrate a working model of a photo-electrochemical water splitting assembly using synthetic supramolecular dyes as a photosensitizer.

2.3.1. Ruthenium Dye on TiO_2 with a Nanoparticle Catalyst

Mallouk and co-workers described a dye-sensitized photo-electrochemical cell using a circa 2 nm colloidal $IrO_2{\cdot}n\,H_2O$ particles for water oxidation.[36] The [Ru(bpy)$_3$]$^{2+}$ sensitizer was modified with phosphonate linkers for the attachment with TiO_2 on the one side, and other side was substituted with malonate ligands to strongly adhere the iridium oxide nanoparticles (Figure 4). In this way, the TiO_2-dye-IrO_2 combination becomes the photoanode of a dye-sensitized photo-electrochemical cell, and a Pt wire serves as cathode for the reduction of protons to H_2. The whole system was operated with a bias voltage (330 mV) to initiate water oxidation, because the electron potential in trap states below the anatase conduction band is not negative enough to reduce water.[36] Slow electron transfer from the water oxidation catalyst to the oxidized dye limits the internal quantum efficiency to 0.9%, and the turnover number was 16. It is nevertheless an important demonstration and proof-of-principle for a hybrid water-splitting system using a dye-sensitized photoanode with nano-structured water oxidation catalyst.

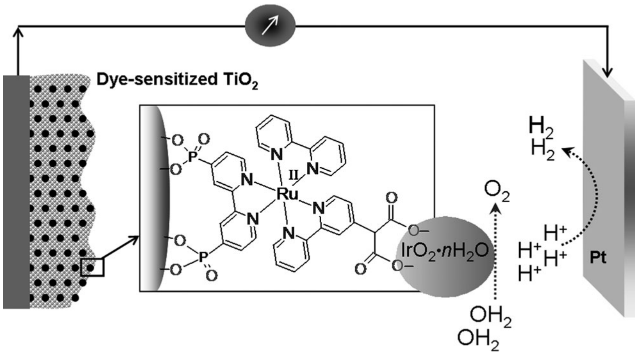

Figure 4. Design of a water-splitting dye-sensitized solar cell with an $IrO_2 \cdot n H_2O$ catalyst particle integrated with a Ru dye on TiO_2 film.

2.3.2. Molecular Catalysts inside Nafion Matrices

The electrochemically studied mononuclear [Ru(dcabpy)-$(pic)_2]^+$ complex, suspended in Nafion on a TiO_2 film sensitized with $[Ru(bpy)_3]^{2+}$, shows photo-electrolysis of water and H_2 generation using a small bias potential of -0.325 V (vs. Ag/AgCl). A rapid decay of the catalytic performance was observed attributed to the high acidity of the Nafion.[37] A bio-inspired Mn cubane complex with a ($2Mn^{III}$-$2Mn^{IV}$) core, $[Mn_4O_4L_6]^+$ (L = bis(*p*-methoxyphenyl)phosphinate, $(MeOC_6H_4)_2PO_2^-$), was also impregnated into a thin Nafion membrane supported on a $[Ru^{II}(bpy)_2\{bpy(COO)_2\}]$-sensitized TiO_2-coated FTO electrode (Figure 5).

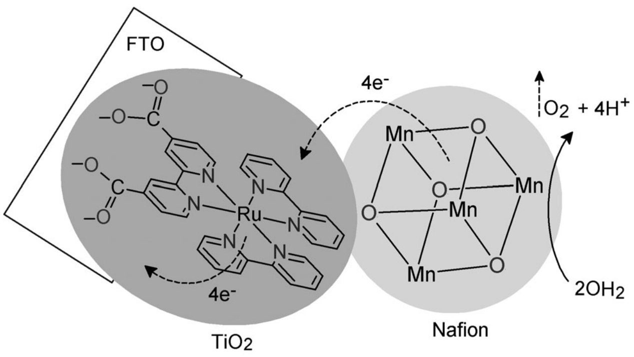

Figure 5. A multilayer photo-electrochemical device with a tetramanganese cubane catalyst impregnated into a Nafion polymer membrane on a $[Ru^{II}(bpy)_2\{(COO)_2bpy\}]$-sensitized TiO_2 film deposited on a fluorine-doped tin oxide (FTO) electrode.

The multilayer photo-electrochemical device has been shown to oxidize water with visible light as driving power without applying any external bias potential.[38] Electrochemical and spectroscopic analyses have revealed the dissociation of the Mn cubane within the Nafion matrices and formation of $Mn^{III/IV}$ type oxides that performed the water oxidation rather than the molecular manganese complex.[39]

3. Distinguishing between Homogeneous Catalysts and Heterogeneous Species for Water Oxidation

3.1. Electrochemical Quartz-Crystal Nanobalance Experiments

Before putting together the solar-fuel device components and transferring the molecular catalytic system to an electrode surface, it is important to have information regarding the molecular homogeneity of the metal complexes during water oxidation catalysis. Under highly oxidative conditions, it is most likely for a molecular system to decompose or disintegrate, and oxidize to heterogeneous metal oxide species that perform the water oxidation rather than the molecular complex.[40] A stable and robust homogeneous catalyst should maintain its integrity during electrocatalysis or photo-electrochemical water oxidation. We have recently reported the effective use of in situ electrochemical quartz-crystal nanobalance (EQCN) measurements for a highly efficient and stable single-site Ir complex during electrocatalytic water oxidation.[33] The EQCN setup was very sensitive to weight change (ng sensitivity) and there was no indication at all for the metal oxide deposition on the surface during potential scanning in the water-oxidation window.

3.2. Spectroscopic and Light-Scattering Measurements

Decomposition of the molecular catalyst to catalytically active metal oxide nanoparticles is often observed for homogeneous solution-phase systems with CAN as the primary oxidant.[40] A combination of UV/Vis and NMR spectroscopy, scanning transmission electron microscopy, and powder X-ray diffraction data revealed that several recently reported molecular-iridium-derived complexes generate metal oxide nanoparticles during water oxidation using CAN as chemical oxidant.[40] In an independent study using sodium periodate ($NaIO_4$) as primary oxidant instead of CAN, it was suggested that the $[Cp^*_2Ir_2(\mu\text{-}OH)_3]OH$ complex generated amorphous metal oxide nanoparticles at room temperature, as monitored with real-time light-scattering measurements and UV/Vis analysis. On the other hand, the incorporation of chelating ligands, such as 2,2′-bipyridine, 2-phenylpyridine, or 2-(2′-pyridyl)-2-propanolate, with Cp*-Ir effectively prevents the formation of nanoparticles, and thus the corresponding complexes of these ligands are ascribed to be truly homogeneous water-oxidation catalysts.[40b] The next challenge is to test these complexes in real-time electrochemical conditions for prolonged full-cell water electrolysis.

4. A Standalone Water Splitting Device: The Artificial Leaf

A complete device for solar water splitting involves several key components. Two or more light-absorbing layers (or components) are needed to supply the thermodynamic driving force plus overpotentials required for water splitting (Figure 1). Furthermore, two separate catalysts are needed for the water oxidation and proton reduction reaction. In many cases, Ohmic contact layers or molecular linkers are required to connect the different components.[4,36] Depending on the type of device, an ion-conducting membrane and external wires may also be needed to close the electrical circuit.[8] Combining these elements in an optimal fashion is a challenging task. Most studies therefore concentrate on a specific part of the device, using external bias potential or sacrificial agents in place of the missing parts. As a result, only a handful of complete, standalone photo-electrochemical (PEC) water-splitting systems have been reported to date, and these are based on nanostructured materials rather than molecular components. This section will give an overview of some of the most important examples; a more extensive list can be found in a recent economic perspective on solar fuels.[41]

4.1. Monolithic PV-Driven Electrolysis Systems

While a coupled photovoltaic–electrolysis system is the most obvious and fastest route towards solar hydrogen, the cost of the hydrogen produced (in €kg^{-1}) is prohibitively high. This is largely due to the high balance-of-system (BOS) costs associated with the packaging of the individual devices, the wiring, and the voltage conversion that is generally required. By integrating the PV and electrolysis components into a single, monolithic device, these costs can be significantly reduced. One of the earliest demonstrations was the multijunction amorphous silicon device reported by Miller et al. in 1998.[42] They combined a triple-junction a-Si PV cell having 10 % efficiency with sputtered films of $Co_{0.73}Mo_{0.27}$ and $NiFe_xO_y$ as the hydrogen and oxygen evolution catalysts, respectively. This resulted in a solar-to-hydrogen (STH) efficiency of 7.8 % for a 0.27 cm^2 device immersed in 1 M KOH (Figure 6 a). Stability tests for the individual catalysts showed no degradation for over 7200 h, but stability data for the entire device beyond a few hours was not reported.

A more recent and highly publicized water splitting device was reported by Nocera et al.[43] Similar to the device reported by Miller et al., it consists almost entirely of earth-abundant elements. It is also based on a commercially available triple-junction (3-jn) Si device that is modified with electrodeposited NiMoZn as H_2 and Co-borate as O_2 evolution catalysts (Figure 6). A 4.7 % STH efficiency was achieved for a circa 2 cm^2, two-electrode (wired) device under near-neutral pH conditions (1 M potassium borate, pH 9.2). The catalysts work at modest overpotentials of about 35 mV (H_2) and about 300 mV (O_2). The most remarkable feature is the Co-based water oxidation catalyst,[44] which has a cubane-like structure that resembles the O_2-evolution center in photosystem II. It is formed under illumination by anodic photo-oxidation of dissolved Co^{2+} ions, forming an insoluble $Co^{3+/4+}$-phosphate or -borate complex.[45] This mechanism also offers the intriguing possibility of self-repair of the catalyst, so long as Co^{2+} ions remain present in the solution.[46] For completeness we also briefly mention the $AlGaAs/Si/RuO_2/Pt_{black}$ device reported by Licht et al. in 2000.[47] In this case, a complicated 11-layer AlGaAs/Si tandem device with an active area of 0.2 cm^2 was glued on top of a 10 cm^2 RuO_2/Pt_{black} electrode assembly that is partially immersed in water. While unpractical and prohibitively expensive, it is noteworthy because of its record-high 18.3 % STH efficiency.

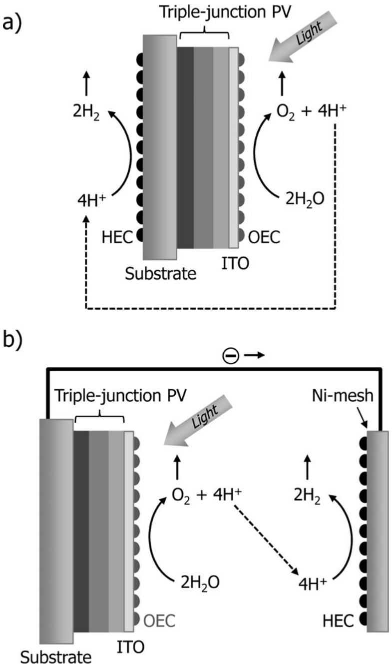

Figure 6. a) A working model of an artificial leaf with a triple-junction amorphous/microcrystalline Si system as reported by Miller and Nocera (using different catalysts).[42,43] b) A wired configuration for the photo-electrochemical water-oxidation device.[4]

4.2. Hybrid Photoelectrodes

The performance of the devices in the previous sections is determined by the current that the PV cell can deliver. Improving this performance will be difficult owing to the complicated multi-junction structures that are necessary to provide the required cell voltage of more than 1.6 V under operating conditions. An alternative approach is to use a single- or double-junction device in combination with a photoelectrode that forms a Schottky junction with the aqueous solution. One of the p-n or p-i-n junctions of the 3-jn device is thus replaced by a single layer, which is a significant simplification. The photoelectrode should have a bandgap between 1.8–2.1 eV, which could lead to conversion efficiencies of up to 16 % in combination with a 1.4 eV bandgap PV cell.[48]

One of the earliest and best known examples of this is the monolithic photovoltaic photo-electrochemical device reported by Turner and Khaselev in 1998.[49] They used a p-type $GaInP_2$ photocathode that was biased with a single GaAs p-n junction (Figure 7). This resulted in an impressive efficiency of 12.4 % (STH). The main problems are the extensive photocorrosion and high cost of the device (\$50 000 m^{-2}).[50] Finding materials with inherently better stabilities, such as $Ga_{1-y}In_yP_{1-x}N_x$, may be a solution. Despite the fact that III-V materials (especially indium) are not earth-abundant, con-

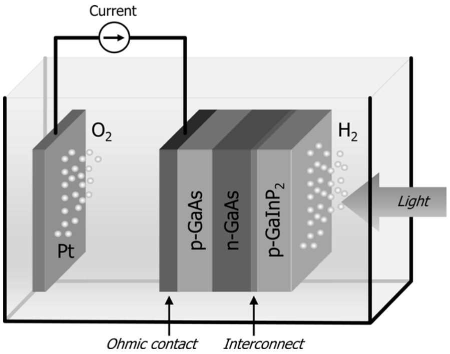

Figure 7. A monolithic photovoltaic photo-electrochemical device for H_2 generation by water splitting as reported by Turner et al.[49]

tinued studies on this class of materials are arguably justified because of their high efficiencies. Recent studies show that device efficiency has a much larger influence on the ultimate price per kg of H_2 than device cost (per m^2) or lifetime.[51] While predictions vary, it appears that the efficiency required to reach the \$2–3 kg^{-1} (H_2) target will be closer to 20% than to 5%.[41,50] At the moment such performance levels can only be reached by inorganic semiconductors used in photovoltaics. However, rapid progress is currently being made in artificial photosynthesis and molecular systems, and it is still much too early to pick a winning approach.

To address the stability and cost issues, Miller et al. also reported a multijunction PEC/PV device based on a Fe_2O_3 or WO_3 photoanode biased by an amorphous SiGe:H tandem cell.[52,53] They coined the term "hybrid photoelectrode" for this particular configuration. Although the efficiency of this early attempt was modest (0.7% STH for WO_3), the stability was promising; no signs of performance degradation were observed after 10 h operation in an acidic electrolyte.[53] A variation on this approach is to combine a metal oxide with a dye-sensitized solar cell (DSSC). The first demonstration was reported in 2001 by Augustynski and Grätzel for a WO_3/DSSC device with a solar-to-chemical conversion efficiency of 4.5%.[54] Later efforts focused on Fe_2O_3 as the photoanode, and more recently these authors reported solar-to-hydrogen efficiencies of 1.17 and 3.1% for nanostructured Fe_2O_3/DSSC and WO_3/DSSC devices, respectively.[55] In general, the performance is limited by the photocurrent that can be delivered by the metal oxide photoelectrode. Many ongoing efforts on metal oxide and oxynitride electrodes are aimed to improve this, and an increasing number of groups is now also starting to revisit the hybrid photoelectrode approach.[56–60]

4.3. Standalone Artificial Leaves versus Wired Systems

4.3.1. Standalone Wireless Devices

Splitting water with a wireless artificial leaf is conceptually attractive for two reasons: 1) The absence of wires and external connections greatly simplifies the design of the device and reduces the costs; and 2) the hydrogen and oxygen evolve at opposite sides of the leaf so that separation of these reaction products is trivial. The main challenge lies in the efficient transport of protons from the anode to the cathode side. Even modest surface areas of a few cm^2 result in significant Ohmic voltage losses and large drops in the overall efficiency. This is illustrated the circa 2 cm^2 triple-junction a-Si device from Nocera et al., which showed STH efficiencies of 4.7% and 2.5% for the wired and wireless configurations, respectively.[43] A possible solution is to incorporate structured photo-electrodes at opposite sides of a proton-conducting membrane (see Section 5.2), but the increased complexity of the device comes at a cost.

4.3.2. Wired Systems for Solar Fuel

A wired device is to some extent similar in layout to an electrolyzer, and similar basic design considerations therefore apply. For example, the distance between the (photo)electrodes must be as small as possible to reduce Ohmic losses, but larger than the size of the bubbles to avoid a reduction in the effective area of the solid–liquid interface. Furthermore, some kind of membrane is required to separate the evolved gases while still providing an efficient conductive pathway for protons. There are, however, crucial differences between photo-electrochemical devices and electrolyzers. Most importantly, typical current densities for PEC devices nearly two orders of magnitude smaller than for electrolyzers (20 mA cm^{-2} vs. 1 A cm^{-2}). This greatly reduces the demands on the ionic conductivity of the membrane. Furthermore, hydrogen crossover is less likely to be an issue in PEC devices, unless they are designed to produce hydrogen and oxygen at high pressures. On the other hand, optical transparency may be an additional and challenging design criterion for certain PEC configurations. Very few chemical engineering studies have yet been carried out on stand-alone PEC devices for water splitting, and we foresee a clear need for such studies to guide efforts in this developing field.

Along with the higher efficiencies that can be achieved, wired PEC/PV tandem devices also have the advantage that it is possible to switch between electricity-generation and fuel-production modes. The fuel-producing mode is then only used when the solar energy supply exceeds the electricity demand. This is in principle attractive, as direct use of solar-generated electricity involves minimal conversion losses and is therefore always preferred above intermediate storage in the form of a fuel. The question arises however whether the benefits outweigh the costs of such a relatively complicated device, especially when considering that less than 20% of the total energy use is in the form of electricity. A well-chosen mix of photovoltaic modules and fuel-producing devices may provide sufficient flexibility at a lower overall complexity and cost.

5. Nano-architectures for Water Splitting and Solar Fuel Assemblies

5.1. Nanostructured Devices

One of the main challenges for solar fuel devices is to find semiconducting photoelectrodes that combine good visible light absorption with efficient charge separation and high chemical stability.[61] To date, no material has been found that combines these properties to the desired extent. Metal oxides fit the bill with regard to chemical stability, but they often have large bandgaps, modest optical absorption coefficients, low catalytic activities, and poor charge-carrier mobilities and lifetimes.[62] Nanostructuring has proven to be a spectacularly effective approach to address several of these issues at once. Highly porous nanostructures can show up to three orders of magnitude enhanced surface areas that greatly enhance the number of catalytically active sites or anchoring sites, for example for dye molecules.[63] Typical feature sizes can be tuned so that they commensurate with the minority carrier diffusion length, thus reducing recombination. Grätzel et al. have perfected this approach for hematite (α-Fe_2O_3), and the efficiency of their nanostructured electrodes made by atmospheric pressure chemical vapor deposition (APCVD) now exceeds that of hematite single crystals (Figure 8).[56] Augustynski et al. used highly scattering mesoporous morphologies to enhance the optical absorption of WO_3, resulting in impressive AM 1.5 photocurrents of almost 3 mA cm^{-2}, despite the relatively large bandgap of WO_3.[64] A more recent example of a DSSC-inspired water splitting device is reported by Mallouk et al. using colloidal Ir oxide and discussed in the previous section.[65,66]

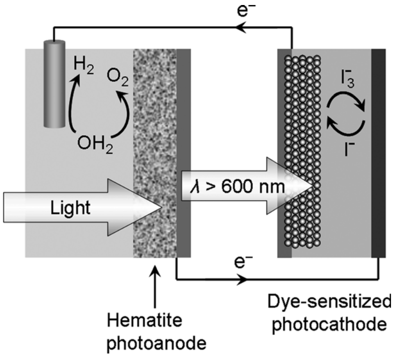

Figure 8. A nanostructured hematite photoanode/PV water-splitting tandem-cell design in combination with a dye-sensitized solar cell.

Along with the advantages mentioned above, nanostructured morphologies also introduce certain complications. Although some surface sites may act as catalytically active centers, others act as charge recombination centers. To suppress surface recombination, defect passivation strategies need to be developed. A recent example is the passivation of surface states in nanostructured hematite by an ultrathin Al_2O_3 coating developed by atomic layer deposition.[67] Another issue is light scattering. Strongly scattering front-electrodes in a tandem cell may prevent the incident light from reaching the junctions below it. A detailed study by Brillet et al. on nanostructured hematite electrodes biased with a nanostructured dye-sensitized solar cell showed that scattering can reduce the overall efficiency by a factor of about 2.5.[55] For this particular example, the highest efficiency (1.36% STH) was found for the tri-level configuration, in which nanostructured hematite and two DSSCs are placed behind one another. Finally, the desired nanostructures actually need to be fabricated. Although some recipes are simple and straightforward, others involve the use of templates and are more complicated. So although nanostructuring is often unavoidable to circumvent intrinsic material limitations (and highly popular amongst researchers), it should be considered a "necessary evil".

5.2. Nanowires and Nanopillar Assemblies

Many of today's efforts are directed towards more advanced nanoarchitectures based on nanowires, nanopillars, and nanotube arrays.[61,68–76] An appealing example is the silicon-based nanowire array concept proposed by the Joint Center for Artificial Photosynthesis (JCAP) in USA (Caltech, Berkeley).[77,78] One of the crucial components is the proton-conducting membrane in which the nanowires have to be embedded (Figure 9).[79,80] Another challenge is the functionalization of these nanowires with suitable catalysts, both for water oxidation and reduction of protons. Putting all these components together into a standalone, cost-effective device for solar water splitting is an enormous challenge, but the potential rewards are high and guaranteed to have a substantial impact in other fields of research. Recently, p-type silicon nanopillars were developed that harvest low-energy photons in the solar spectrum.[81] Modified with molybdenum tetrasulphide (Mo_3S_4) clusters at the surface, this bio-inspired molecular assembly was demonstrated to be a highly efficient photocathode for hydrogen generation. The rate of H_2 evolution is comparable to that of a platinum cathode resulting in more than 10% solar-to-hydrogen conversion efficiency.

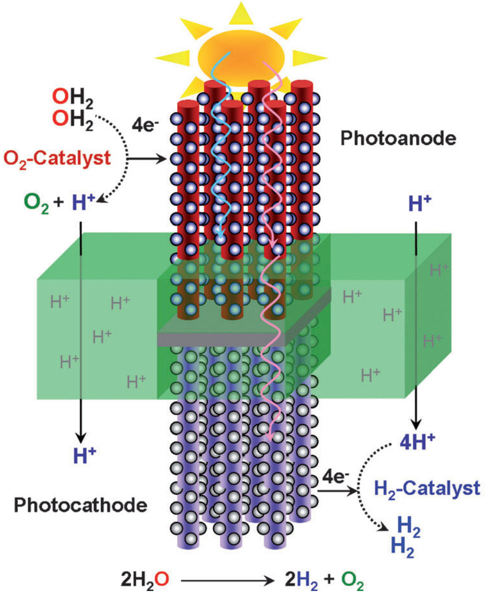

Figure 9. A conceptual design of the artificial leaf proposed by JCAP based on arrays of light harvesting nano-/microwires embedded in a proton-conducting membrane and coated with O_2- and H_2-evolving catalysts from the water splitting reaction.

5.3. TiO_2 Nanotube Arrays

Vertically oriented and highly ordered titania nanotube arrays provide a large-surface-area nanoarchitecture with remarkable properties that can be used in photo-electrochemical H_2 generation systems and photocatalytic CO_2 reduction into hydrocarbon-based liquid fuels.[82] Vertically aligned p-type Cu-Ti-O nanotube arrays on plane FTO-coated glass substrates were developed anodically in an ethylene glycol/NH_4F mixture, and photo-electrochemical water splitting pn-junction diodes were constructed in combination with n-type TiO_2 nanotube array films. Upon illumination in a back-to-back configuration on glass substrates, the UV part is absorbed by n-TiO_2 side, while the visible spectrum passes on to the p-Cu-Ti-O side. In photo-electrochemical reaction, hydrogen is generated from the p-type Cu-Ti-O side and oxygen is evolved at the n-TiO_2 side of the diode. Under global AM 1.5 illumination, such photocorrosion-stable diodes generate photocurrents of about $0.25\,mA\,cm^{-2}$, with a photoconversion efficiency of 0.30% using cheap and abundant materials.[83] The performance of this PEC-device can be significantly improved with further materials optimization, nanostructuring, and electrolyte selection and optimization.[82,83]

Another type of light-driven electrochemical system using vertically oriented carbon-doped titania (TiO_{2}-$_{x}C_{x}$) nanotube arrays was developed by Bard et al. (Figure 10 a).[84] The purpose of carbon doping is that the TiO_2 matrix should absorb a significant fraction of the sunlight, and upon excitation the electron and hole pairs should be located within the space charge layer (5–200 nm) at the electrolyte/semiconductor interface. Under visible-light illumination (> 420 nm), the TiO_2-xCx nanotube arrays displayed higher photocurrent densities than pure TiO_2 nanotube arrays.[84] The efficiency of water splitting was also enhanced and the total photocurrent was 20 times greater than a TiO_2 film developed from TP-25 nanoparticles. Furthermore, there are several research groups working on the use of TiO_2 and other photoactive materials to develop artificial leaves. A modular design of an artificial leaf under progress at the University of Messina (Italy) for solar fuels uses a novel photo-electrocatalytic approach. The concept is to make solar H_2 by photo-electrolysis of water or ethanol photo-reforming at the photoanode, and the gas phase conversion of CO_2, in combination with H_2/protons, to isopropanol at the cathode (Figure 10 b).[85] The photoanode is vertically aligned doped TiO_2 nanotube arrays designed for improved light harvesting, good electron transport, and fast collection and proton diffusion. The cathodic reaction for the electrocatalytic CO_2 reduction is based on iron nanoparticles dispersed over conductive N-doped carbon nanotubes (CNT) that was then deposited over a carbon cloth (CC) acting as electron-transport material. At the Fe/N-CNT-based gas-diffusion CO_2 reduction cathode, the primary reaction product is 2-propanol. Further optimization of design and performance is under development that will use highly ordered TiO_2 nanotube arrays as photoactive membrane to replace the Nafion proton exchange interlayer that significantly quenches the surface process (associated to surface peroxo species), which limits the steady-state performance.[85,86]

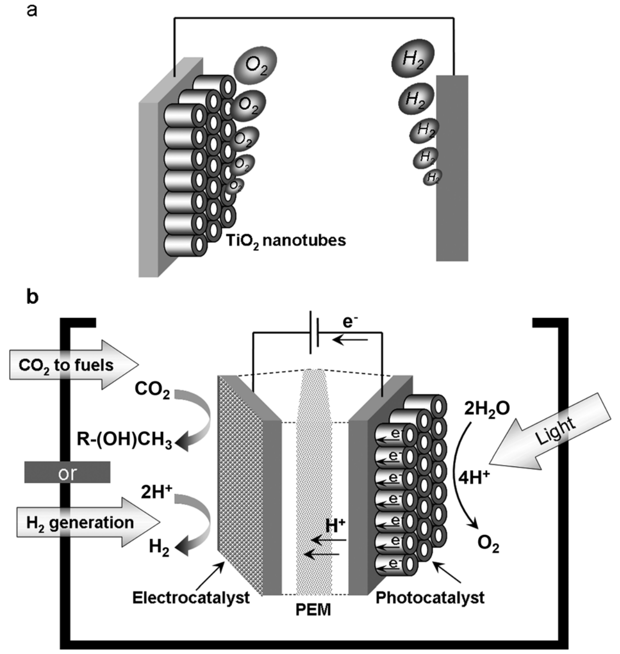

Figure 10. a) Design of the TiO_2 photoanode to optimize its photocatalytic activity for water splitting; b) Solar fuel cell (artificial leaf) under development at the University of Messina (Italy). With the Nafion membrane, the assembly shows the TiO_2 nanotube array electrode with Fe nanoparticles on N-doped carbon nanotubes, which were used as photocatalyst for water oxidation and as electrocatalyst for CO_2 reduction, respectively. PEM = polymer electrolyte membrane. Adopted from Ref. [85].

In a new design, the TiO_2 nanochannels are filled with a polyvinyl alcohol or polyacrylamide hydrogels containing heteropolyacids (HPA) such as $H_{3+n}PV_nMo_{12-n}O_{40}$, which promotes the proton transport and also acts as a sensitizer for injecting electrons (upon visible-photon absorption) into the conduction band of the semiconducting TiO_2 nanotube arrays.[86] Although TiO_2 is an excellent electron transport medium, with good photocatalytic activity and high chemical stability, there is now growing consensus in the PEC community that TiO_2 is in fact not a suitable light absorber for solar energy conversion applications. The high bandgap limits its maximum energy conversion efficiency to 1–2%, and most of the gain in visible light absorption by doping is lost again by increased carrier recombination. One of the main challenges in the PEC field is therefore to find new and stable inorganic light absorbers. Multinary oxides and oxynitride materials, such as $BiVO_4$ and TaON, seem to be promising materials classes.[57,59,60] In particular, oxynitride materials offer reasonable chemical stability at relatively small bandgap values. The small bandgap is due to the mixing of the oxygen 2p orbitals with the higher-energy nitrogen 2p orbitals. β-TaON is one of the best known examples, with a bandgap of 2.4 eV and conduction and valence band edges that straddle the water reduction and oxidation potentials.[87] Domen and Abe have carried out pioneering work on this material,[87–90] and demonstrated photocurrents that exceed

4 mA cm^{-2} when using a CoO_x water oxidation catalyst.[90] The challenges for this material are the high temperature required for nitridation and the narrow range of process conditions under which the phase-pure photoactive β-TaON can be obtained.

5.4. Self-Aggregated Supramolecular Assemblies for Artificial Leaves

The modular units for light harvesting, charge separation, and oxidation/reduction catalysis need to be integrated in a synergized manner to optimize the performance of the desired standalone solar-to-fuel conversion device. An integrated light-driven water-splitting cell for O_2 and hydrogen generation using Ru dye coupled with catalytic modules has been tested, but the efficiency is very low (less than 1 %).[36] Instead of relying only on molecular materials and nanostructured systems for light capture and conversion, self-assembled supramolecular aggregates of biomimetic light-harvesting units and charge separation modules can also be employed in solar fuel devices.[8] Efficient bio-inspired light-harvesting systems obtained from tubular chlorosomes, self-aggregated chlorophylls, or chlorin assemblies (along with a suitable energy trap and donor–acceptor couple) may offer a promising starting point to build a model solar fuel system.[91]

Natural chlorin biomimics that are also self-protected against degradation can be programmed to induce self-assembly for solar fuel devices.[8,91] Such a system has recently been demonstrated to fabricate an artificial supramolecular light harvesting assembly using pheophytin for the energy trap and a fullerene unit as electron-acceptor site (Figure 11). Using a suitable donor material on one side, the H_2 evolving catalyst can be immobilized on the acceptor side to demonstrate a half-cell supramolecular assembly to obtain hydrogen from solar energy. Porphyrin- and chlorin-type self-aggregated systems may be replaced by more robust naphthalenediimide (NDI) and perylenediimide (PDI) dyes for barrierless light harvesting and charge separation in combination with H_2/O_2 catalysts for solar fuel systems.[92,93]

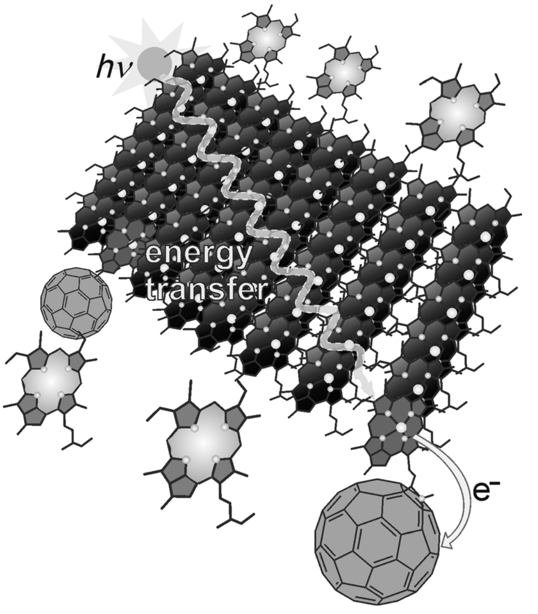

Figure 11. An artificial supramolecular light-harvesting system with pheophytin and a fullerene unit that act as charge separator–acceptor combination.

6. Summary

Abundant water and sunlight can be captured and exploited in an artificial leaf, to produce clean fuels by splitting water. In developing a stable and proficient solar H_2/O_2 generation device, the major task is to combine molecular and/or inorganic components in a way that optimizes the individual light harvesting, charge separation, and catalytic functionalities. The combination of bio-inspired molecular assemblies with nanostructured inorganic materials seems a particularly promising route. The oxidation of water to molecular oxygen is the most difficult step. Once this difficulty is solved, it can also be combined with the reduction of CO_2 to directly form hydrocarbon-based fuels and other feedstock chemicals. In this Minireview, we have discussed some of the recent developments made in the field of electrochemical and photo-electrocatalytic water oxidation systems that were also constructed as artificial photosynthetic models. The next aim is to develop an artificial leaf to make H_2 and O_2 using electrons and protons from water. While pursuing towards bio-inspired water oxidation catalytic devices, various molecular complexes and organometallics have been studied on electrode surfaces electrochemically, with and without the light source. An introduction to nanostructured systems functionalized on the conducting surfaces for water electrolysis cells are also presented. Besides focusing merely on hydrogen as fuel from water splitting, we also exemplify the use of protons from water oxidation to reduce carbon dioxide into useful chemical(s). Finally, we summarized the newly emerging concepts and technologies in solar fuel devices and the design of the supramolecular architecture with self-aggregated biomimics for the artificial leaf.

7. Outlook

There is an overwhelming growth of the scientific and political interest in the conversion of widely available resources, such as CO_2 and water, into clean and renewable fuels using earth-abundant materials. Solar-powered catalytic water splitting can be one of the promising and possible solutions in this quest. Thermodynamically speaking, water oxidation is an energy demanding process, involving high activation barriers and overpotentials, but an intelligent catalyst design in synergy with efficient light-harvesting system could make it possible to split water and produce solar fuel with attractive efficiencies. Recent progress in the area of light-driven water splitting catalysis and artificial leaf is also evident with the current interest of many governments and participation of several research groups across the globe in one way or another. The Swedish consortium for artificial photosynthesis, the BioSolarCells consortium in the Netherlands, the Joint Centre for Artificial Photosynthesis (JCAP) led by Caltech and UC Berkeley, and Korea Centre for artificial photosynthesis (KCAP) are the key players in the solar-to-fuel conversion business funded by heavy budgets and supported by big and efficient scientific research teams. In near future, there is also a strong output expected in the form of many entrepreneurial initiatives and industrial interactions related to energy production, the automotive sector, and catalysis for sustainable materials. This path is steadily heading towards establishing a model sunlight-triggered catalytic system for renewable fuel generation using water as raw material. However, there are still many challenges and open questions in the field, regarding both scientific as well as technological aspects. Strong commitment, rational thinking, and hard-working scientific teams and input from the political sectors could make the demonstration of an efficient practical device for solar fuel a reality.

K.S.J. acknowledges the funding from the Higher Education Commission (HEC) Government of Pakistan. The authors would like to thank Scientific and Technological Research Council of Turkey, TUBITAK (Grant: 110M803).

Received: January 8, 2013

[1] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* **2010**, *110*, 6446 – 6473.
[2] R. Cao, W. Laia, P. Du, *Energy Environ. Sci.* **2012**, *5*, 8134 – 8157.
[3] a) K. S. Joya, H. J. M. de Groot, *Int. J. Hydrogen Energy* **2012**, *37*, 8787 – 8799; b) K. S. Joya, *Molecular Catalytic System for Efficient Water Splitting*, PhD thesis, Leiden University (The Netherlands), **2011**.
[4] D. G. Nocera, *Acc. Chem. Res.* **2012**, *45*, 767 – 776.
[5] R. Angamuthu, P. Byers, M. Lutz, A. L. Spek, E. Bouwman, *Science* **2010**, *327*, 313 – 315.
[6] a) M. Halmann, *Nature* **1978**, *275*, 115 – 116; b) H. Li, P. H. Opgenorth, D. G. Wernick, S. Rogers, T.-Y. Wu, W. Higashide, P. Malati, Y.-X. Huo, K. M. Cho, J. C. Liao, *Science* **2012**, *335*, 1596.
[7] D. Gust, T. A. Moore, A. L. Moore, *Faraday Discuss.* **2012**, *155*, 9 – 26.
[8] K. S. Joya, J. L. Vallés-Pardo, Y. F. Joya, T. Eisenmayer, B. Thomas, F. Buda, H. J. M. de Groot, *ChemPlusChem* **2013**, *78*, 35 – 47.
[9] T. J. Meyer, *Nature* **2008**, *451*, 778 – 779.
[10] C. J. Gagliardi, A. K. Vannucci, J. J. Concepcion, Z. Chen, T. J. Meyer, *Energy Environ. Sci.* **2012**, *5*, 7704 – 7717.
[11] D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2009**, *42*, 1890 – 1898.
[12] a) X. Sala, I. Romero, M. Rodŕguez, L. Escriche, A. Llobet, *Angew. Chem.* **2009**, *121*, 2882 – 2893; *Angew. Chem. Int. Ed.* **2009**, *48*, 2842 – 2852; b) M. M. Najafpour, T. Ehrenberg, M. Wiechen, P. Kurz, *Angew. Chem.* **2010**, *122*, 2281 – 2285; *Angew. Chem. Int. Ed.* **2010**, *49*, 2233 – 2237.
[13] H. Yamazaki, A. Shouji, M. Kajita, M. Yagi, *Coord. Chem. Rev.* **2010**, *254*, 2483 – 2491.
[14] a) J. L. Vallés-Pardo, M. C. Guijt, M. Iannuzzi, K. S. Joya, H. J. M. de Groot, F. Buda, *ChemPhysChem* **2012**, *13*, 140 – 146; b) K. S. Joya, H. J. M. de Groot, Proceedings of the 4th ECCLS **2011**, pp. 51 – 54.
[15] L. Duan, L. Tong, Y. Xua, L. Sun, *Energy Environ. Sci.* **2011**, *4*, 3296 – 3313.
[16] P. D. Tran, L. H. Wong, J. Barber, J. S. C. Loo, *Energy Environ. Sci.* **2012**, *5*, 5902 – 5918.
[17] V. Artero, M. Chavarot-Kerlidou, M. Fontecave, *Angew. Chem.* **2011**, *123*, 7376 – 7405; *Angew. Chem. Int. Ed.* **2011**, *50*, 7238 – 7266.
[18] H. Dau, C. Limberg, T, Reier, M. Risch, S. Roggan, P. Strasser, *ChemCatChem* **2010**, *2*, 724 – 761.
[19] A. Kubacka, M. Fernández-García, G. Colón, *Chem. Rev.* **2012**, *112*, 1555 – 1614.
[20] M. Liao, J. Feng, W. Luo, Z, Wang, J. Zhang, Z. Li, T. Yu, Z. Zou, *Adv. Funct. Mater.* **2012**, *22*, 3066 – 3074.
[21] G. Zhu, Y. V. Geletii, P. Kögerler, H. Schilder, J. Song, S. Lense, C. Zhao, K. I. Hardcastle, D. G. Musaev, C. L. Hill, *Dalton Trans.* **2012**, *41*, 2084 – 2090.
[22] a) K. Takanabe, K. Domen, *Green* **2011**, *1*, 313 – 322; b) A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253 – 278.
[23] R. Subbaraman, D. Tripkovic, K.-C. Chang, D. Strmcnik, A. P. Paulikas, P. Hirunsit, M. Chan, J. Greeley, V. Stamenkovic, N. M. Markovic, *Nat. Mater.* **2012**, *11*, 550 – 557.
[24] X. Liu, F. Wang, *Coord. Chem. Rev.* **2012**, *256*, 1115 – 1136.
[25] D. B. Grotjahn, D. B. Brown, J. K. Martin, D. C. Marelius, M.-C. Abadjian, H. N. Tran, G. Kalyuzhny, K. S. Vecchio, Z. G. Specht, S. A. Cortes-Llamas, V. Miranda-Soto, C. van Niekerk, C. E. Moore, A. L. Rheingold, *J. Am. Chem. Soc.* **2011**, *133*, 19024 – 19027.
[26] A. K. Poulsen, A. Rompel, C. J. McKenzie, *Angew. Chem.* **2005**, *117*, 7076 – 7080; *Angew. Chem. Int. Ed.* **2005**, *44*, 6916 – 6920.
[27] P. Kurz, G. Berggren, M. F. Anderlund, S. Styring, *Dalton Trans.* **2007**, 4258 – 4261.
[28] E. A. Karlsson, B.-L. Lee, T. Åkermark, E. V. Johnston, M. D. Kärkäs, J. Sun, Ö. Hansson, J.-E. Bäckvall, B. Åkermark, *Angew. Chem.* **2011**, *123*, 11919 – 11922; *Angew. Chem. Int. Ed.* **2011**, *50*, 11715 – 11718.
[29] L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun, *Nat. Chem.* **2012**, *4*, 418 – 423.
[30] T. Wada, K. Tsuge, K. Tanaka, *Angew. Chem.* **2000**, *112*, 1539 – 1542; *Angew. Chem. Int. Ed.* **2000**, *39*, 1479 – 1482.
[31] J. Mola, E. Mas-Marza, X. Sala, I. Romero, M. Rodríguez, C. Viňas, T. Parella, A. Llobet, *Angew. Chem.* **2008**, *120*, 5914 – 5916; *Angew. Chem. Int. Ed.* **2008**, *47*, 5830 – 5832.
[32] J. J. Concepcion, J. W. Jurss, P. G. Hoertz, T. J. Meyer, *Angew. Chem.* **2009**, *121*, 9637 – 9640; *Angew. Chem. Int. Ed.* **2009**, *48*, 9473 – 9476.
[33] K. S. Joya, N. K. Subbaiyan, F. D'Souza, H. J. M. de Groot, *Angew. Chem.* **2012**, *124*, 9739 – 9743; *Angew. Chem. Int. Ed.* **2012**, *51*, 9601 – 9605.
[34] F. Li, B. Zhang, X. Li, Y. Jiang, L. Chen, Y. Li, L. Sun, *Angew. Chem.* **2011**, *123*, 12484 – 12487; *Angew. Chem. Int. Ed.* **2011**, *50*, 12276 – 12279.
[35] S. M. Barnett, K. I. Goldberg, J. M. Mayer, *Nat. Chem.* **2012**, *4*, 498 – 502.
[36] W. J. Youngblood, S.-H. A. Lee, K. Maeda, T. E. Mallouk, *Acc. Chem. Res.* **2009**, *42*, 1966 – 1973.
[37] L. Li, L. Duan, Y. Xu, M. Gorlov, A. Hagfeldt, L. Sun, *Chem. Commun.* **2010**, *46*, 7307 – 7309.
[38] R. Brimblecombe, A. Koo, G. C. Dismukes, G. F. Swiegers, L. Spiccia, *J. Am. Chem. Soc.* **2010**, *132*, 2892 – 2894.
[39] R. K. Hocking, R. Brimblecombe, L.-Y. Chang, A. Singh, M. H. Cheah, C. Glover, W. H. Casey, H. Spiccia, *Nat. Chem.* **2011**, *3*, 461 – 466.
[40] a) Ref. [25]; b) U. Hintermair, S. M. Hashmi, M. Elimelech, R. H. Crabtree, *J. Am. Chem. Soc.* **2012**, *134*, 9785 – 9795.

[41] J. Newman, P. G. Hoertz, C. F. Bonino, J. A. Trainham, *J. Electrochem. Soc.* **2012**, *159*, A1722 – A1729.
[42] R. E. Rocheleau, E. L. Miller, A. Misra, *Energy Fuels* **1998**, *12*, 3 – 10.
[43] S. Y. Reece, J. A. Hamel, K. Sung, T. D. Jarvi, A. J. Esswein, J. J. H. Pijpers, D. G. Nocera, *Science* **2011**, *334*, 645 – 648.
[44] M. W. Kanan, D. G. Nocera, *Science* **2008**, *321*, 1072 – 1075.
[45] Y. Surendranath, M. Dinca, D. G. Nocera, *J. Am. Chem. Soc.* **2009**, *131*, 2615 – 2620.
[46] D. A. Lutterman, Y. Surendranath, D. G. Nocera, *J. Am. Chem. Soc.* **2009**, *131*, 3838 – 3839.
[47] S. Licht, B. Wang, S. Mukerji, T. Soga, M. Umeno, H. Tributsch, *J. Phys. Chem. B* **2000**, *104*, 8920 – 8924.
[48] M. F. Weber, M. J. Dignam, *J. Electrochem. Soc.* **1984**, *131*, 1258 – 1265.
[49] O. Khaselev, J. A. Turner, *Science* **1998**, *280*, 425 – 427.
[50] R. F. Service, *Science* **2011**, *334*, 925 – 927.
[51] Report: B. D. James, G. N. Baum, J. Perez, K. N. Baum, *Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production*, **2009**. Virginia, Directed Technologies Inc.
[52] E. L. Miller, R. E. Rocheleau, S. Khan, *Int. J. Hydrogen Energy* **2004**, *29*, 907 – 914.
[53] E. L. Miller, D. Paluselli, B. Marsen, R. E. Rocheleau, *Sol. Energy Mater. Sol. Cells* **2005**, *88*, 131 – 144.
[54] M. Grätzel, *Nature* **2001**, *414*, 338 – 344.
[55] a) J. Brillet, M. Cornuz, F. Le Formal, J. H. Yum, M. Grätzel, K. Sivula, *J. Mater. Res.* **2010**, *25*, 17 – 24; b) J. Brillet, J. H. Yum, M. Cornuz, T. Hisatomi, R. Solarska, J. Augustynski, M. Grätzel, K. Sivula, *Nat. Photonics* **2012**, *6*, 824 – 828.
[56] a) K. Sivula, F. Le Formal, M. Grätzel, *ChemSusChem* **2011**, *4*, 432 – 449; b) Ref. [55a].
[57] F. F. Abdi, N. Firet, R. van de Krol, *ChemCatChem* **2013**, *5*, 490 – 496.
[58] A. Paracchino, V. Laporte, K. Sivula, M. Grätzel, E. Thimsen, *Nat. Mater.* **2011**, *10*, 456 – 461.
[59] R. Abe, M. Higashi, K. Domen, *J. Am. Chem. Soc.* **2010**, *132*, 11828 – 11829.
[60] S. Banerjee, S. K. Mohapatra, M. Misra, *Chem. Commun.* **2009**, 7137 – 7139.
[61] R. van de Krol, Y. Q. Liang, J. Schoonman, *J. Mater. Chem.* **2008**, *18*, 2311 – 2320.
[62] *Photoelectrochemical Hydrogen Production* (Eds.: R. van de Krol, M. Grätzel), Springer, New York, **2012**.
[63] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737 – 740.
[64] B. D. Alexander, P. J. Kulesza, L. Rutkowska, R. Solarska, J. Augustynski, *J. Mater. Chem.* **2008**, *18*, 2298 – 2303.
[65] W. J. Youngblood, S. H. A. Lee, Y. Kobayashi, E. A. Hernandez-Pagan, P. G. Hoertz, T. A. Moore, A. L. Moore, D. Gust, T. E. Mallouk, *J. Am. Chem. Soc.* **2009**, *131*, 926 – 927.
[66] A. Harriman, I. J. Pickering, J. M. Thomas, P. A. Christensen, *J. Chem. Soc. Faraday Trans. 1* **1988**, *84*, 2795 – 2806.
[67] F. Le Formal, N. Tetreault, M. Cornuz, T. Moehl, M. Gratzel, K. Sivula, *Chem. Sci.* **2011**, *2*, 737 – 743.
[68] I. S. Cho, Z. B. Chen, A. J. Forman, D. R. Kim, P. M. Rao, T. F. Jaramillo, X. L. Zheng, *Nano Lett.* **2011**, *11*, 4978 – 4984.
[69] J. H. Noh, H. S. Han, S. Lee, J. Y. Kim, K. S. Hong, G. S. Han, H. Shin, H. S. Jung, *Adv. Energy Mater.* **2011**, *1*, 829 – 835.
[70] J. R. Maiolo, B. M. Kayes, M. A. Filler, M. C. Putnam, M. D. Kelzenberg, H. A. Atwater, N. S. Lewis, *J. Am. Chem. Soc.* **2007**, *129*, 12346 – 12347.
[71] S. W. Boettcher, J. M. Spurgeon, M. C. Putnam, E. L. Warren, D. B. Turner-Evans, M. D. Kelzenberg, J. R. Maiolo, H. A. Atwater, N. S. Lewis, *Science* **2010**, *327*, 185 – 187.
[72] D. D. Qin, C. L. Tao, S. A. Friesen, T. H. Wang, O. K. Varghese, N. Z. Bao, Z. Y. Yang, T. E. Mallouk, C. A. Grimes, *Chem. Commun.* **2012**, *48*, 729 – 731.
[73] G. K. Mor, H. E. Prakasam, O. K. Varghese, K. Shankar, C. A. Grimes, *Nano Lett.* **2007**, *7*, 2356 – 2364.
[74] M. T. Mayer, C. Du, D. W. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 12406 – 12409.
[75] Y. J. Lin, S. Zhou, S. W. Sheehan, D. W. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 2398 – 2401.
[76] X. J. Feng, T. J. Latempa, J. I. Basham, G. K. Mor, O. K. Varghese, C. A. Grimes, *Nano Lett.* **2010**, *10*, 948 – 952.
[77] http://solarfuelshub.org.
[78] J. M. Spurgeon, M. G. Walter, J. F. Zhou, P. A. Kohl, N. S. Lewis, *Energy Environ. Sci.* **2011**, *4*, 1772 – 1780.
[79] J. M. Spurgeon, S. W. Boettcher, M. D. Kelzenberg, B. S. Brunschwig, H. A. Atwater, N. S. Lewis, *Adv. Mater.* **2010**, *22*, 3277 – 3281.
[80] S. L. McFarlane, B. A. Day, K. McEleney, M. S. Freund, N. S. Lewis, *Energy Environ. Sci.* **2011**, *4*, 1700 – 1703.
[81] Y. Hou, B. L. Abrams, P. C. K. Vesborg, M. E. Bjorketun, K. Herbst, L. Bech, A. M. Setti, C. D. Damsgaard, T. Pedersen, O. Hansen, J. Rossmeisl, S. Dahl, J. K. Nørskov, I. Chorkendorff, *Nat. Mater.* **2011**, *10*, 434 – 438.
[82] S. Rani, S. C. Roy, M. Paulose, O. K. Varghese, G. K. Mor, S. Kim, S. Yoriya, T. J. LaTempa, C. A. Grimes, *Phys. Chem. Chem. Phys.* **2010**, *12*, 2780 – 2800.
[83] G. K. Mor, O. K. Varghese, R. H. T. Wilkie, S. Sharma, K. Shankar, T. J. Latempa, K. S. Choi, C. A. Grimes, *Nano Lett.* **2008**, *8*, 1906 – 1911.
[84] J. H. Park, S. Kim, A. J. Bard, *Nano Lett.* **2006**, *6*, 24 – 28.
[85] C. Ampelli, G. Centi, R. Passalacqua, R. Perathoner, *Energy Environ. Sci.* **2010**, *3*, 292 – 301.
[86] S. Bensaid, G. Centi, E. Garrone, S. Perathoner, G. Saracco, *ChemSusChem* **2012**, *5*, 500 – 521.
[87] W. J. Chun, A. Ishikawa, H. Fujisawa, T. Takata, J. N. Kondo, M. Hara, M. Kawai, Y. Matsumoto, K. Domen, *J. Phys. Chem. B* **2003**, *107*, 1798 – 1803.
[88] R. Abe, T. Takata, H. Sugihara, K. Domen, *Chem. Lett.* **2005**, *34*, 1162 – 1163.
[89] M. Higashi, K. Domen, R. Abe, *Energy Environ. Sci.* **2011**, *4*, 4138 – 4147.
[90] M. Higashi, K. Domen, R. Abe, *J. Am. Chem. Soc.* **2012**, *134*, 6968 – 6971.
[91] M. Katterle, V. Prokhorenko, A. Holzwarth, A. Jesorka, *Chem. Phys. Lett.* **2007**, *447*, 284 – 288.
[92] a) S. V. Bhosale, C. H. Janiab, S. J. Langford, *Chem. Soc. Rev.* **2008**, *37*, 331 – 342; b) N. Sakai, J. Mareda, E. Vauthey, S. Matile, *Chem. Commun.* **2010**, *46*, 4225 – 4237.
[93] S. L. Suraru, U. Zschieschang, H. Klauk, F. Wurthner, *Chem. Commun.* **2011**, *47*, 11504 – 11506.