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Artificial Leaf Goes Simpler and More Efficient for Solar Fuel Generation

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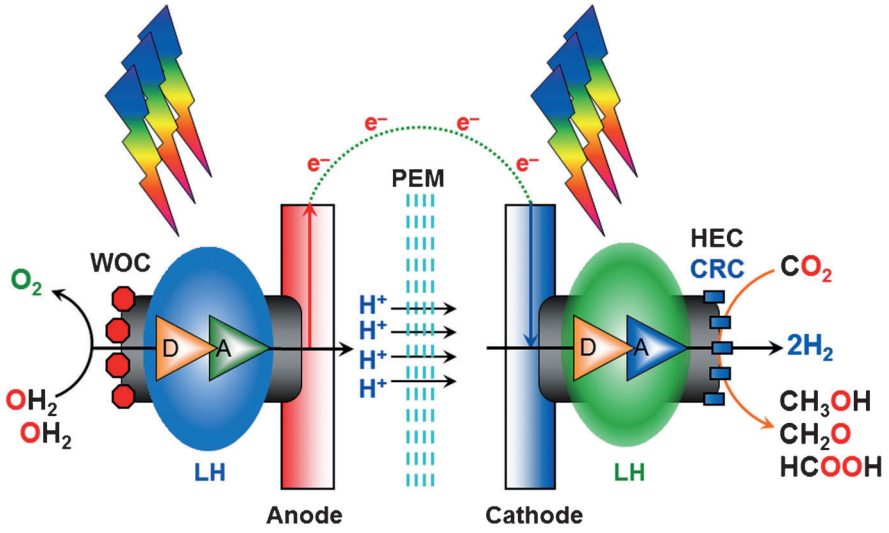
Renewable and clean energy carriers obtained by utilizing unlimited sunlight and from inexpensive and widely available earth-abundant materials have strong prospects to serve as future sustainable energy supplies.[1] Solar-to-fuel conversion through water splitting is an attractive and accessible way to proceed for a light-driven water splitting process using an artificial leaf to produce renewable fuels.[1,2] An artificial leaf is a light-driven stand-alone device, with H_2 and O_2 catalysts, that takes up water and splits it into protons and electrons to generate hydrogen. In combination with a suitable CO_2 reduction module, it may generate liquid fuels such as formic acid or methanol as well (Scheme 1).[2] A modular solar-to-fuel conversion device requires a robust four-electron-transfer water oxidation catalyst (WOC) and a stable proton reduction system, an efficient light harvesting antennae system and a pair of long-living charge-separating donor–acceptor components. It is highly desirable that the WOC is a self-assembling and self-healing oxygen evolution complex or material. To avoid high-energy intermediates that are generated during water oxidation and O–O bond formation, the WOC should operate through a consecutive four-step proton-coupled electron-transfer pathway.[3]

A major part of recent research in catalysis science and energy materials focused on the development of molecular complexes and robust inorganic materials for catalytic water oxidation. Recent breakthroughs in the development of WOCs made this approach more attractive as H_2/O_2 can be generated at near-neutral pH conditions.[4] To drive the full water splitting reaction and generate H_2 and O_2, the electrochemical driving force required to run the process needs to overcome the thermodynamic limit for the reaction $H_2O \rightarrow H_2 + O_2$, which has a standard chemical potential of 1.23 V (vs. standard hydrogen electrode, pH 0).[3] Photocatalytically speaking, it is not possible for a simple light-harvesting system or a solar cell to fulfill the energy demand owing to a high electrochemical overpotential of the water oxidation reaction, especially the oxygen evolution reaction (OER).[5] One simple route is to combine the photochemical approach with an electrochemical bias to sustain the evolution of H_2 and O_2 at the respective electrodes photoelectrochemically.[6] A very attractive approach developed in recent years is the deployment of a stand-alone photochemical device, where two or more solar cells are assembled on top of each other to increase the open circuit voltage, which can then supply a sufficient boost for water oxidation reaction.[3,7]



Scheme 1. Representation of a photoelectrochemical water oxidation assembly showing a WOC/complex at the anode and a H_2 evolution catalyst (HEC) at the cathodic side separated by a proton exchange membrane (PEM). The system can be modified with a carbon dioxide reduction catalyst (CRC) module for the direct conversion of water and sunlight into liquid energy carriers.

A promising practical example of such a stand-alone solar-to-hydrogen (STH) conversion system through water splitting was demonstrated 15 years ago using a triple-junction amorphous silicon (a-Si) solar cell. A STH efficiency of 7.8% was achieved for a 0.27 cm^2 device using $NiFeO_x$ and CoMo films as

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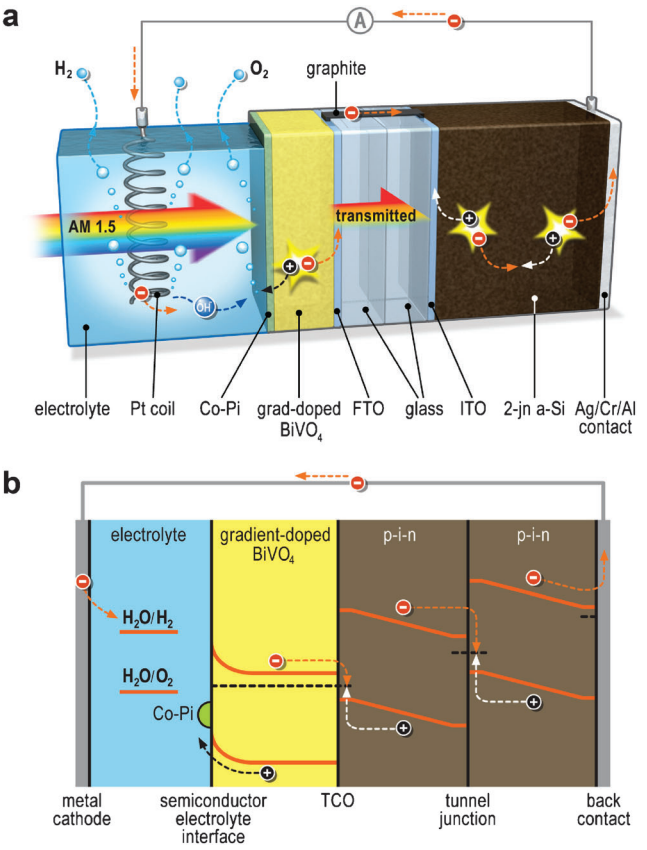
oxygen and hydrogen evolution catalysts, respectively. However, the system operated at a very high pH (1 N KOH) to stabilize the $NiFeO_x$ film for water oxidation; the stability data for the entire device beyond a few hours operating time was not reported.[8] Recently, Nocera and co-workers demonstrated a stand-alone artificial leaf using a similar type of a-Si triple-junction solar cells with a cobalt-based electrocatalyst for water oxidation. The entire device runs efficiently in a neutral phosphate solution, and a solar-to-fuel conversion efficiency of 4.7% was obtained with a wired configuration whereas a wireless design achieved up to 2.8% STH generation.[9] The major advantage of this system is the operating conditions, that is, the whole stand-alone device system operates at neutral pH in a phosphate buffer and uses a simple self-assembling cobalt-oxide based catalyst for electrochemical water oxidation and oxygen evolution.

The hydrogen evolution catalyst in Nocera's device was a thin film of NiMoZn. One of the major limitations that render the large-scale implementation of such stand-alone devices difficult is the use of an expensive triple-junction silicon-based photovoltaic (PV) system and its protection against corrosion and harsh oxidative reaction conditions. It is also noteworthy to mention here the AlGaAs/Si/RuO_2/Pt_{black}-based device reported by Licht et al.[10] They built a rather complicated 11-layer AlGaAs/Si tandem device with an active area of 0.2 cm^2 that was glued on top of a 10 cm^2 RuO_2/Pt_{black} electrode assembly. During the operation, the device was partially immersed in water and revealed an unprecedented STH efficiency of 18.3%. However, the entire system was very expensive and was based on a prohibitively intricate construction that rendered its practical application difficult and expensive.

Currently, many efforts concentrate on demonstrating a more efficient and practically applicable solar-to-fuels conversion system through a water splitting process. Van de Krol and co-workers successfully developed a less expensive and efficient solar-to-fuel conversion assembly that utilizes a simple and low-cost nonporous tungsten-doped bismuth vanadate (W/$BiVO_4$) layer on top of single- or double-junction amorphous silicon solar cells in a tandem or triple junction configuration (Scheme 2).[11] This work is worth highlighting as it uses a simple and easily accessible approach for the development of an efficient working model of an artificial leaf to produce "solar" hydrogen. This device achieved an overall device efficiency of 5% for the first time by using a metal oxide photoanode. This may lead to a practical implementation and commercialization of such a device in the near future as the system operates with a stable short-circuit current density of about 4 mA cm^{-2} under 1 sun illumination using the easily accessible cobalt-phosphate (Co–Pi) system as a simple and self-assembling water oxidation electrocatalyst.[4]

Bismuth vanadate is a monoclinic n-type semiconductor with a bandgap of 2.4 eV, and its conduction band is positioned close to the H_2 evolution potential. In a water-splitting setup, the photoanodic performance of $BiVO_4$ is limited by poor carrier separation owing to slow electron transport rather than slow water-oxidation kinetics. Use of donor-type dopants such as tungsten (W) or molybdenum (Mo) may increase $BiVO_4$ conductivity, but the intrinsic mobility remains low.[12] To address this problem, Van de Krol and co-workers used a new strategy to improve carrier separation. Introduction of a gradient in the dopant profile in $BiVO_4$ makes it possible to create a distributed n^+–n homojunction that enhances the charge-separation efficiency similar to the redox-ladder-driven charge separation in natural photosynthesis. The combination of this approach with a silicon-based solar cell in tandem or a triple junction design using an efficient earth-abundant water-oxidation Co–Pi catalyst provides a new concept and a highly effective method to prepare an efficient light-driven water-splitting device for the production of hydrogen.[11]



Scheme 2. Illustration of the a) tandem device for solar fuel generation using a gradient-doped W/$BiVO_4$ layer on top of an a-Si PV and b) the corresponding band diagram of the photocatalytic assembly. ITO and FTO are indium tin oxide and fluorine tin oxides respectively, and TCO stands for transparent conducting oxide. (Adopted from Ref. [11] with author's permission).

In a photoelectrochemical three-electrode system, the gradient-doped W/$BiVO_4$, deposited on a TEC-15 (15 Ω per square; Hartford Glass Co.) FTO-coated glass substrate and coated with a 30 nm thick electrodeposited cobalt phosphate layer, shows an increased photocurrent density of up to 3 mA cm^{-2} at 1.23 V versus reversible hydrogen electrode (RHE) under AM1.5 illumination in comparison to a blank run (1.1 mA cm^{-2}) under similar conditions (Figure 1, solid red and black curves). The replacement of the standard TEC-15 substrate with a textured Asahi VU-type (8 Ω per square; Asahi Glass Co.) conducting glass coated with FTO results in further improvement of the

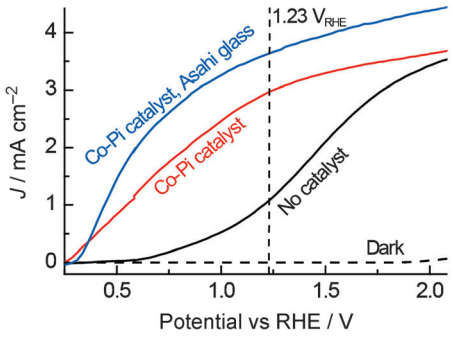


Figure 1. *J–V* curves for a three-electrode system of gradient-doped W/$BiVO_4$ on a TEC-15 surface (black) without catalyst and (red) with Co–Pi-catalyst or (blue) on gradient-doped W/$BiVO_4$ with Co–Pi-catalyst on Asahi conducting glass under AM1.5 illumination. The dashed black curve indicates the dark current density. The electrolyte is 0.1 M potassium phosphate buffer (pH ≈ 7.3). Adopted from Ref. [11] with author's permission.

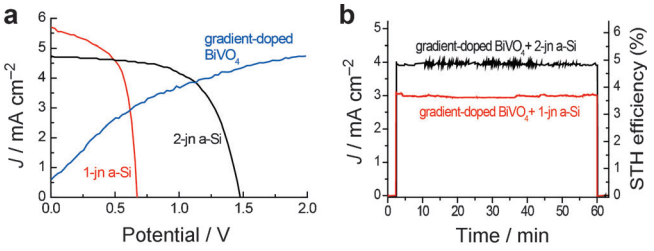


Figure 2. a) *J–V* curve of Co-Pi-catalyzed gradient-doped $BiVO_4$ on Asahi TCO glass (gradient-doped $BiVO_4$, blue curve) in a two-electrode system under AM1.5. Also shown are the *J–V* curves of 2-jn a-Si (black) and single-junction a-Si (red) solar cells placed behind the Co–Pi:W/$BiVO_4$ photoanode. The intersection of the $BiVO_4$ curve with either one of the a-Si curves indicates the operating point of the combined water-splitting device. (b) Current versus time profile for the Co–Pi:W/$BiVO_4$ 2-jn a-Si device and the Co–Pi:W/$BiVO_4$ 1-jn a-Si device in the hybrid photoelectrode configuration under AM1.5 illumination. The electrolyte used is 0.1 M potassium phosphate buffer at pH 7.3. (Adopted from Ref. [11] with author's permission).

photocurrent density to 3.6 mA cm^{-2} at 1.23 V versus RHE that is attributed to the higher absorption efficiency and effective surface area of the system (Figure 1, blue curve). These photocurrents are the highest reported for $BiVO_4$-based catalytic devices for light-induced electrochemical water splitting and represents an approximately 1.6-fold improvement in the efficiency of the photocatalytic system compared with the best Co–Pi-catalyzed tungsten-doped bismuth vanadate photoanode.[12c] Under AM1.5 at 1.53 V (vs. RHE), a nanostructured hematite film on a FTO substrate showed a photocurrent density of 4.0 mA cm^{-2}. However, at 1.23 V (vs. RHE), the photocurrents reported by Van de Krol et al. are well in excess of those reported for α-Fe_2O_3 and WO_3.[13] This confirms that $BiVO_4$ is a leading performer among oxide photoanode materials.

Next, a hybrid photoelectrode stand-alone device was established on a 2-jn amorphous Si PV in a tandem arrangement as shown in Scheme 2 by using the Co–Pi:W/$BiVO_4$ system. In this tandem combination, photons with energies less than the bandgap of the $BiVO_4$ layer are absorbed by the a-Si/a-Si PV system. The photocurrent density–voltage (*J–V*) curve for a 2-jn a-Si solar cell (black curve) optimized by tuning the thickness of the individual absorber layers to match the two-electrode *J–V* curve of the state-of-the-art $BiVO_4$ photoanode (blue curve) is shown in Figure 2a. A plot for the AM1.5 photocurrent and STH efficiency of the tandem PEC/PV device as a function of time is presented in Figure 2b. A stable photocurrent density of approximately 4 mA cm^{-2} is obtained with no sign of degradation of the system performance for oxygen and hydrogen evolution during 60 min of device operation. The Faradaic efficiency of this system is 100%,[14] which corresponds to a STH conversion efficiency of 4.9%. This indicates a 60% increase compared to the 2-jn a-Si/WO_3-based device reported earlier by Miller et al.[15] Moreover, the remarkable efficiency of a $BiVO_4$-derived a-Si/a-Si PV system is also superior to the 4.7% efficiency reported by Nocera and co-workers, who used a triple-junction a-Si PV with a Co–Pi catalyst under pH-neutral conditions.[9] It is important to mention here that a 2-jn a-Si cell is considerably easier to manufacture than a triple-junction a-Si PV device. An important contribution was also made by Grätzel and Sivula, who used an assembly for photochemical water oxidation and H_2 generation based on a dual-absorber and hematite in a dye-sensitized-solar-cell (DSC) tandem configuration. This device achieved a STH efficiency of up to 3.1% for unassisted water splitting with simple processing of the device components.[16] A comparative analysis of the solar-to-hydrogen conversion efficiencies by different devices is also provided in Table 1.

Table 1. A comparative analysis of the efficiencies of the water oxidation devices for solar fuel generation.

Device[a]	Conditions	WOC[b]	STH efficiency[c] [%]	Ref
3-jn a-Si	1 M KOH (pH ≈ 13)	$NiFeO_x$	7.8	[8]
3-jn a-Si	0.1 M PO_4 buffer (pH 7)	Co–Pi	4.7	[9]
$BiVO_4$/2-jn a-Si	0.1 M PO_4 buffer (pH 7)	Co–Pi	4.9	[11]
Fe_2O_3/DSC	1 M NaOH (pH ≈ 13.6)		3.1	[16]

[a] PV system used for device fabrication. [b] Co–Pi-based catalyst is electrodeposited on the anode.

In summary, the stand-alone device for the production of solar fuels proposed by Van de Krol et al. using the Co–Pi:W/$BiVO_4$ system on a 2-jn amorphous silicon PV is the simplest form of an efficient water*splitting system to prepare solar hydrogen from water. In their system, a $BiVO_4$ layer on a-Si provides an additional electromotive driving force for the water electrolysis reaction, and the Co–Pi:W/$BiVO_4$ 2-jn a-Si device is effectively a triple-junction system. Besides its simple and easily accessible approach, an overall STH efficiency of the device of 5% is achieved by using a simple metal-oxide photoanode. This scientific contribution may lead to the practical implementation and commercialization of such systems in the near future as the device operates at a stable short-circuit current density of about 4 mA cm^{-2} under 1 sun (AM1.5) illumination using a simple self-assembling cobalt-based water oxidation catalyst. Successful deployment of such systems will help

not only in solving future energy/fuel demands, but also aid in the reduction of CO_2 emissions.[17]

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Keywords: artificial leaf · oxygen evolution · photochemistry · solar fuel · water splitting

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