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Designing a Solar Fuel Device: Light-Harvesting Materials and Catalytic Modules for Artificial Leaf

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ABSTRACT

Solar energy driven catalytic water splitting process using efficient light-harvesting system and catalytic materials can be exploited to generate electrons and protons that can be utilized to make clean hydrogen as a simple renewable fuel. This scheme can also be combined with a CO_2 reduction module to convert it into nonfossil and easily storable liquid energy carriers. This approach is very appropriate and attractive but the major obstacle in this pursuit is to develop state-of-the art catalytic modules (both for water oxidation and proton/CO_2 reduction) and their synergistic interfacing with light-harvesting materials. Recently, there is a tremendous progress in the field of visible light responsive inorganic-oxide semiconductors and water oxidation electrocatalysts, aiming to build up a stand-alone solar to fuel conversion device, "The Artificial Leaf". Many molecular catalysts and nanoscale materials functionalized on the photoelectrode surfaces have been investigated to drive solar water oxidation reaction. Here we give a miniature account of the development of structural designs of solar fuel devices, and assembling of solar to chemical energy conversion system.

1. Introduction

World current energy demand of 14 TW is expected to get doubled by the mid of this century. This has spurred both political and scientific communities to come along with some working idea to develop renewable and clean energy technologies to be obtained from cheap and earth-abundant system [1, 2]. Water splitting process driven by photoelectrochemical means using efficient light-harvesting materials and active catalytic materials can be utilized to make clean hydrogen in an "Artificial Leaf" type solar energy conversion assembly [3]. This approach looks very attractive and electrons and protons released from water splitting process can also be combined with a CO_2 reduction system to convert it directly into nonfossil carbon based easily storable energy carriers like alkanol or formic acid [4]. Therefore, this scheme gives an alternative way to produce renewable energy supplies to be obtained from wide spread water and enormous sun light that is easily accessible on earth [5]. In this scenario, the development of catalytic systems (for water oxidation and proton/CO_2 reduction) and their interfacing with state-of-the-art light-harvesting materials is crucial.

An artificial leaf is a model light-harvesting device, with self-assembled catalytic modules, operating with solar energy, feeding on simple water and releasing protons and electrons to be used to make hydrogen or other renewable energy carriers [1]. There are two main components of this stand-alone device, light-harvesting (LH) systems and catalytic modules that are combined for anodic and cathodic reactions (Fig. 1). The LH II captures the solar light and charge separation triggered by donor-acceptor pair facilitating the electron transfer to the anode from catalytic sites where water acts as electrons donor. These electrons transfer to the reduction site where LH I and donor-acceptor combination enables the reduction reaction [6]. The anodic reaction is the water oxidation that takes up two water molecules to make one molecule of O_2 releasing four electrons and four protons simultaneously. The protons and electron travel to cathode site to get reduced into hydrogen gas [2]. The catalytic modules may be derived from molecular complexes and inorganic materials [7, 8]. The light-harvesting systems, in most cases, are visible-light responsive inorganic oxide based semiconductor materials although there are reports using molecular organic systems for solar energy capturing [1]. Next step is to blend these components together to assemble the device.

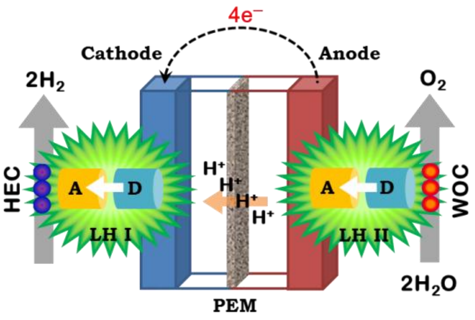


Fig. 1: Schematic presentation of a solar-fuel device showing light-harvesting (LH), water oxidation (WOC) and H_2 evolution catalyst (HEC). The anode and cathode are separated by proton exchange membrane (PEM). (A and D represent donor-acceptor pair)

The terms artificial leaf and related artificial photosynthesis are derived from the mechanistic machinery of natural photosystem (PS) performing photosynthesis using water, CO_2 and sun [2]. In natural PS-II, there present chlorophyll derived light-harvesting systems and Ca-manganese based water oxidation catalyst. The electrons and protons released from water splitting are transferred to the reduction site PS-I, and reacted with CO_2 to form glucose and all types of carbon based energy storage substances [9]. Like the natural photosystems, a modular solar fuel machine must have an excellent mechanism of electron transfer and proton management overcoming the kinetic barriers to make hydrogen or carbon-based liquid fuels [1, 5]. Here we give a brief overview of the structural design of solar fuel devices developed during last few years for solar to chemical energy conversion.

2. Visible-Light Responsive Materials

To drive a photo-electrocatalytic water oxidation and proton reduction, acquisition of efficient and stable light-harvesting assemblies is a prerequisite. In nature, chlorophyll assembly is a state-of-the-art system capable of trapping solar energy that runs all the important processes for the existence of the flora [10]. In photosynthetic systems, the chlorophyll units are self-assembled into ordered supramolecular nanostructures to form light-harvesting antenna complex, known as chlorosome. In chlorosomes, the chlorophyll molecules are self-aggregated via non-covalent interaction to make three dimensional tubular assemblies to facilitate maximum light capturing and energy transfer and work even under low light conditions [11]. This supramolecular organization can be mimicked by synthetic modules and nano templates to make self-aggregated biomimetic light-harvesting architectures. In order to mimic a chlorosomal antenna complex, self-aggregates of synthetic derivatives in functionalized nanotemplates have been proposed.

We recently show the first example of solid-state biomimetic light-harvesting unit based on supramolecular zinc chlorine (ZnChl) aggregate inside anodic aluminum oxide (AAO) nanochannels (Fig. 2). After pore widening of the 40 µm thick AAO discs, the inner walls are decorated with a sol–gel matrix of titanium (IV) propoxide and annealed to make TiO_2 layer (AAO-Ti). They are then functionalized with long alkyl myristic acid (C_{13} acid) to make AAO-Ti-C_{13} where the carboxylic-groups serve as surface anchoring units [12]. This hydrophobic alkyl coating facilitates the supramolecular aggregation in polar environment. Finally the nanoscale self-aggregates of three ZnChl derivatives with different side chain lengths (ZnChl-C_6, ZnChl-C_{12} and ZnChl-C_{18}) are grown inside the AAO-Ti-C_{13}.UV-Vis absorption and steady-state fluorescence emission measurements reveal excellent supramolecular scaffolds of the nanotubular ZnChl aggregate inside AAO nanochannels. Inspired by our study of beautifully biomimicking the natural chlorosomal antenna complex, supramolecular self-assembly of a perylenemonoimide amphiphile are also reported recently in AAO templates connected with a nickel-based molecular catalyst to generate hydrogen [6].

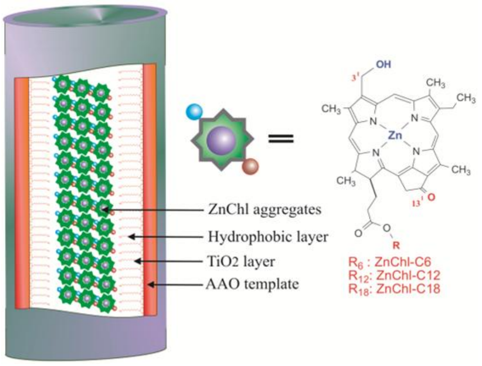


Fig. 2: Schematic view of alkyl-TiO_2coated AAO nanochannel templates (AAO-Ti-C_{13}) and imprinting of self-assembled zinc chlorine aggregates (AAO-Ti-C_{13}ZnChl)

Besides the molecular architectured light-harvesting systems, inorganic semiconductors are the most studies materials for photocatalysis regarding solar to fuel conversion scenario. Among the inorganic semiconductor, oxide materials such as titanium dioxide (TiO_2), hematite (α-Fe_2O_3), tungsten trioxide (WO_3) and bismuth vanadate ($BiVO_4$) are most prominent [13]. The photocatalytic properties of TiO_2 for solar to chemical energy conversion were discovered in late 60's and published in 1972. [14] However, direct applications of TiO_2 in water splitting photocatalysis are limited due to its wide band gap of 3.2 eV. Recently, the TiO_2 use in water oxidation was reinvestigated employing dye-sensitization and cocatalyst [15]. The most prominent photo-electrode material is hematite. It has emerged as a promising visible-light responsive oxide due to the significant light absorption in the visible range (300−600 nm) owing to a narrow band gap of ~2.1 eV and a light absorption depth of up to 150 nm. [16]. It is an inexpensive material having good chemical stability and ample availability. Another good feature of α-Fe_2O_3 is its valence band positioning that is aligned at an ideal position for photocatalytic water oxidation [17].

However, the holes mobility (minority carrier) and diffusion length in hematite is very poor (~5 nm) limiting effective charge separation at the interfaces, thus rendering its application in photocatalysis [18]. Solar water oxidation activity of hematite can be improved by bulk doping and using cocatalysts layer on top. This approach improves the charge separation, hole delivery and its effective consumption at the catalytic/electrolyte interface. Besides better charge separation, the photocurrent on catalyst/hematite systems remain low at high driving potentials due to limiting rates of the water oxidation electrocatalysts [18]. Heterogeneous electrocatalysts such as IrO_2, RuO_2, NiO_x or CoOx are tested on hematite thin films [19-21]. Charge transfer kinetics in such assemblies are also impeded by the cocatalyst-hematite contact and the hole migration through the bulk oxide catalyst [16]. The photocatalytic performance of hematite can be further improved by introducing an efficient and molecular featured water oxidation complex. Molecular electrocatalyst can take up hole rapidly and may avoid the charge recombination at photoanode surface. We recently show a unique modification of thin film hematite photoanode with perfluorinated Co-phthalocyanine (CoFPc) for enhanced photoelectrochemical water oxidation [17]. On hematite/CoFPc, the anodic photocurrent has been improved by >90% at all potentials, and a cathodic onset potential shift of about 200 mV is also observed relative to the unmodified hematite sample (Fig. 3).

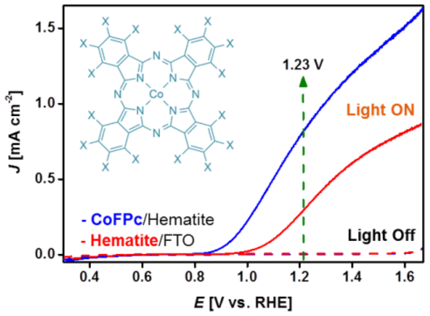


Fig. 3: Linear sweep voltammograms under dark (dashed lines) and full light illumination (solid lines) for hematite (red lines) and hematite/CoFPc (blue lines) systems in 0.1 M NaOH (pH=13; scan rate 10 mV s^{-1})

Light-driven cathodic reactions are also very important to generate clean and renewable hydrogen or carbon based nonfossil chemical energy carriers. Low cost Cu_2O photocathodes are very promising materials for photo reduction of protons [22].Cuprous oxide is a p-type semiconductor having a direct bandgap of 2 eV. Cu_2O exhibits a favourable conduction band positioning that is lying 0.7 V negative of the H_2 evolution potential (0.0 V vs. RHE). This corresponds to a theoretical cathodic photocurrent of 14.7 $mAcm^{-2}$ with a solar-to-hydrogen (STH) conversion efficiency of 18% (AM1.5 solar simulation). However, Cu_2O is not a stable under photocatalytic operation and there is a need to stabilize the surface with external coatings [23]. It was shown recently that surface layer of cuprous oxide can be protected against photocathodic decomposition in water using nanolayers of Al-doped ZnO followed by a TiO_2 coating (Fig. 4a). This assembly was activated with electrodeposited Pt nanoparticles for H_2 evolution [24]. Under AM1.5 illumination, an impressive cathodic photocurrent of 7.6 $mAcm^{-2}$ was observed at 0.0 V (vs. RHE) at mild pH (Fig. 4b). The Faradaic efficiency was close to 100% during 1 h of testing and the catalytic system remained stable and intact.

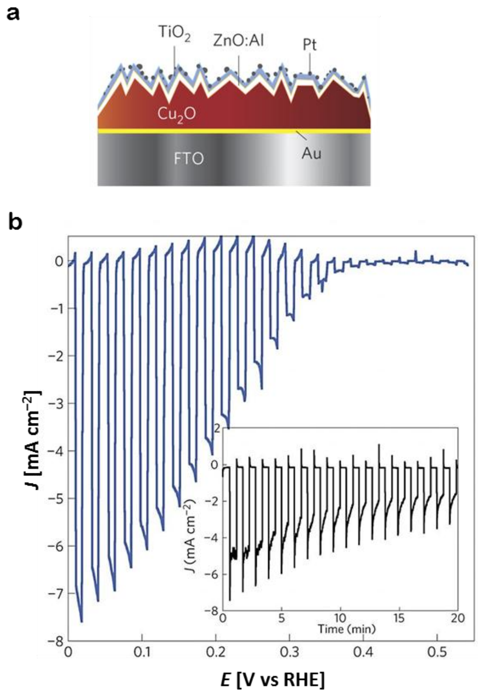


Fig. 4: (a) Schematic structure of the surface-protected Cu_2O electrode showing a top view of the electrode after ALD of 5 × (4nm ZnO / 0.17nm Al_2O_3) with a top layer of 11nm TiO_2that is followed by electrodeposition of Pt nanoparticles. (b) Chopped-light linear sweep voltammogramsin 1M Na_2SO_4 solution at AM1.5 light illumination. The inset shows the respective photocurrent transients for the electrode at constant potential of 0.0 V (vs. RHE) under chopped-light illumination. (Adopted from ref 24 with permission)

In another following example by the same group, an amorphous molybdenum sulphide (MoS_2) film was deposited on top of protected Cu_2O as hydrogen evolution catalyst. This system shows a photocurrent up to 5.7 mA cm^{-m} at 0.0 V (vs. RHE) in a pH 1.0 solution possessing more stability relative to the Pt nanoparticles coated assembly [25]. Besides Cu_2O, Si based photoactive materials, with different catalytic layers on top, have also been employed for the cathodic reactions driven by light [26]. Cadmium derived materials (CdS, CdSe, CdTe) with inorganic and molecular catalytic coatings are also demonstrated to be high efficiency photo-driven hydrogen evolution systems [27-29]. The catalytic layer offers protection against photocorrosion and increase the activity of the hetero-junction assembly in aqueous electrolytes and under illumination condition.

3. Catalytic Modules for Solar Fuel Device

In addition to the evolution of light-responsive semiconductor materials for anodic or cathodic reactions, development of molecular and inorganic catalytic modules (both for water oxidation and proton or CO_2

reduction) has been a building scenario during last decade or so [2, 30]. There is a big boom in catalytic material innovation during last five years, especially for water splitting reaction ($2H_2O \rightarrow 2H_2 + O_2$) in order to identify the most efficient and stable electrocatalysts for the oxygen evolution reaction (OER). Energetically speaking, water oxidation is more demanding reaction requiring $E° = 1.23$ V (vs. RHE) for its initiation [$E° = 1.23$ V versus normal hydrogen electrode (NHE) at pH=0, and 0.82 V vs. NHE at pH=7]. Inorganic and molecular catalysts for water oxidation generally operate at a potential in excess to the thermodynamic limits of $E° = 1.23$ V vs. NHE, pH=0 [1, 31]. This additional potential is known as overpotential (η) which is usually 500-700 mV extra to that of 1.23 V and a major obstacle in pursuing toward solar fuel device operating at mild voltage. Another important parameter is the benchmark oxygen evolution current densities (J) of 10 mA cm^{-2} that is desired at minimum overpotential [32]. The 10 mA cm^{-2} current density is an optimal requirement to get > 10% efficiency from a standard solar-to-fuel conversion device [33].

The oxygen evolution reaction is kinetically more energy demanding, and to accommodate the redox demand of this reaction water oxidation electrocatalysts are desired to operate over a narrow potential window for high OER current densities. Tafel slope in this scenario is an associative consideration implying current – overpotential (η vs. log i) plot for up to 1 mA cm^{-2} current density during oxygen generation process [34]. A small Tafel slope represents a small potential window in which the oxidation catalytic current operates. In general, a Tafel slope of 60 mV dec^{-1} is considered an optimal indication one electron and one proton oxidation mechanism. However, 30 mV dec^{-1} or less Tafel slope represents the benchmark performance in water oxidation catalysis [35]. Among the list of inorganic heterogeneous phase catalysts for electrochemical water oxidation, RuO_2 and IrO_2 are the best know materials operating at lowest onset overpotentials, $\eta < 300$ mV, and have Tafel slopes in the range of 30-35 mV dec^{-1} [34, 35]. However, limited availability of these materials makes it difficult to use them for large scale applications.

3.1 Molecular Systems

Inspired by natural PS-II and Ca-MnO_x cluster based water oxidation catalyst, several molecular complexes and organometallics have been investigated for oxygen evolution. Mn and Ru derived complexes were among the early developmental investigations [2, 31]. In early 1970, M. Calvin introduced the first example of a molecular catalytic system comprising of a di-μ-oxo-bridged dimanganese (Mn^{III}–Mn^{IV}) bipyridine complex [7]. This work was followed by a series of Mn, Ru and Ir complexes in the next decade using essentially the same ligand architecture [2,7]. Recently there are several examples of non-precious metals (Ni, Co, Fe, Mn, Cu) based molecular catalysts for homogeneous water oxidation using cerium ammonium nitrate $(NH_4)_2[Ce(NO_3)_6]$ (CAN), as primary chemical oxidant to trigger the water oxidation reaction in aqueous solution [7, 31]. However, these catalytic species were not very stable to be employed for long-term applications. In order to build up a half cell device, these catalysts need to be tested on conducting surface. The molecular catalysts were immobilized on electrode surfaces using anchoring units such as carboxylic [−O−(C=O)−], phosphonate $[-(O)_2-(P=O)-]$ or silyl $[-(O_3)-Si-]$ functionalities. These molecular anchoring groups are very good in developing covalent type linkages with conducting substrates like TiO_2, SnO_2 or ITO (indium tin oxide) [1].

We recently demonstrated the surface immobilized mono-site iridium-Cp* complexes that was anchored to an ITO electrode via COOH or PO_3H_2 linkers (Fig. 5). With a moderate overpotential for oxygen onset, the electrocatalytic molecular assembly generated over 250,000 turnovers for O_2 with a turnover frequency of 6.7 s^{-1} [36]. Amazingly, the catalytic system stays stable during long-term controlled-potential electrolysis of water in a pH=4 solution showing a stable oxygen evolution current density of about 1.75 mA cm^{-2}. It is important to note that the water oxidation assembly driven by electrochemical mean is desired to operate under near-neutral pH condition in order to combine with proton reduction or CO_2 conversion systems.

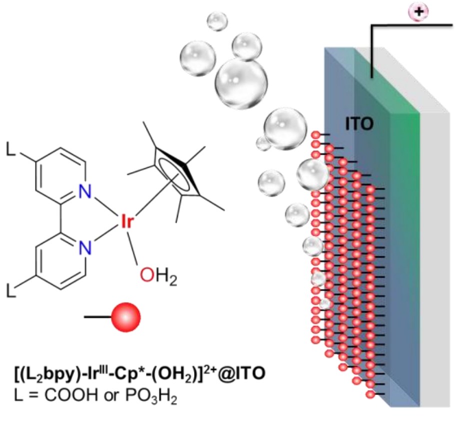


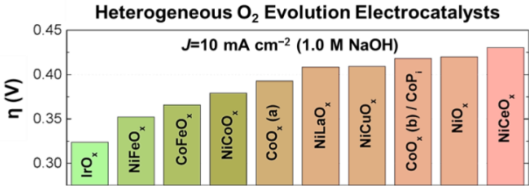
Fig. 5: A surface immobilized electrochemical water oxidation assembly showing Cp*-Iridium derived complexes with L_2bpy (L=COOH, PO_3H_2) ligands for electro-driven oxygen evolution

3.2 Inorganic Materials for Catalysis

In the list of inorganic and heterogeneous phase water oxidation electrocatalysts, there is an evolution of highly stable and efficient oxygen generation catalytic materials. As stated earlier, the main target is to achieve state-of-the-art material having low OER onset overpotential and small Tafel slope [35]. When comparing the catalytic performance of different electrocatalysts, it is important to employ the similar electrochemical condition for their testing, i.e. solution pH, temperatures and electrolyte compositions and concentrations [37]. Ru and Ir oxides are the best known water oxidation electrocatalysts, but they cannot be implemented in commercial devices due to high cost and limited availability. Recently, NiO_x, CoO_x, CuO_x and MnO_x and their blends with other metals have emerged as promising alternative to expensive RuO_2 and IrO_2 [4, 34, 38, 39]. NiO_x, CoO_x and MnO_x are synthesized by electrodeposition and hydrothermal methods. However, the transition metal oxides are not very stable in acidic conditions. The most favourable situation for operating these catalytic systems is at pH 7 or above. There are also reports of preparation and catalytic activity performance of these simple oxides in phosphate, borate or carbonate buffers [34, 38].

Recently, a series of simple inorganic and mixed oxide materials, synthesized via electrodeposition, are investigated for anodic water oxidation in highly alkaline conditions [35]. IrO_2 was found to be the best catalyst for OER reaching 10 mA cm^{-2} current density at η ~325 mV (Table 1). Simple Ni- and Co-oxides have much higher onset overpotential compared to several other mixed-metal oxides. The details are presented in Table 1 showing that $NiFeO_x$ and $CoFeO_x$ outperform all the known non-precious metals OER catalysts. These catalytic systems show promising activities in alkaline condition, but this impose stability constrains to the catalytic system. A near-neural situation is considered a mild operating system to perform long-term water oxidation experiments [34]. We presented that neutral or near-neutral HCO_3^-/CO_2 system is new emerging electrolyte combination for the deposition and activities of NiO_x (Ni-C$_i$) and CoO_x (Co-C$_i$) derived OER catalyst. With moderate overpotential and small Tafel slopes, they exhibit amazing performance for long-term catalytic testing in many electrolytes systems [40, 41].

Table 1. Benchmarking inorganic water oxidation electrocatalysts showing overpotentials required to achieve 10 mA cm^{-2} current density. (Adopted from ref 35 with permission)



Protons reduction is another important scenario in pursuing towards solar to chemical energy conversion system. Pt is the standard material allows reducing protons at 0.0 V (vs. RHE) in acidic solutions. But it cannot be used in commercial electrolyzers due to very high cost [42]. As most of the overpotential and kinetic barriers are arisen due to oxidation of water, proton reduction catalysis is not as much in the limelight relative to water splitting reaction. Many new materials have emerged in recent time to replace Pt with cheap and widespread catalysts [42, 43]. Along with the advent of OER catalysts, many promising molecular systems have been presented from time to time showing excellent performance for hydrogen evolution reaction [44]. Besides proton reduction, many groups are considering the option of going for easily storable liquid energy carriers that can be obtained from CO_2 reduction schemes [5]. At present, water oxidation and carbon dioxide reduction reactions remain major challenges, although many new materials are proposed in the meantime and have potential to be implemented on small commercial scale [45].

4. Interfacing and Device Assembly for Solar Fuel

After the development of catalytic modules, for water oxidation and reduction reactions, one of the most important steps is to interface light-harvesting systems and catalytic materials to assemble a half cell or a complete light-driven device for solar energy conversion [1, 32]. A synergistic combination of various components is required in an optimal fashion to set up a solar water splitting device. The ultimate system may require an ion conducting membrane between two reaction compartments [2]. Although it's a challenging task to glue all parts together to be operated at high efficiency, there are few instances for the demonstration of complete stand-alone photo-electrochemical (PEC) water splitting assemblies. Here we provide an overview of some of the most interesting examples. A more extensive list of other examples can be found in recently publish literature on solar fuels [46]. Another important thing is the final cost of hydrogen per kg which is targeted to be \$2-3/kg H_2 with a device having solar-to-hydrogen (STH) efficiency up to 10% [46, 47].

Miller et al. in 1998 proposed a first working module of a multijunction amorphous silicon based device achieving 7.8% solar-to-hydrogen (STH) efficiency using $NiFe_xO_y$ and $Co_{0.73}Mo_{0.27}$as O_2 and H_2 evolution catalysts, respectively [48]. However, the system was only stable in high pH solution. Recently, the WOE on this 3-junction (3-jn) Si device was replaced with a Co-Pi and system while working under near-neutral conditions using electrodeposited NiMoZn as H_2 generation catalyst (Fig. 6). This system shows a 4.7% STH efficiency for a wired configuration [49]. Licht et al. reported a complicated and very expensive 11-layer AlGaAs/Si tandem device $AlGaAs/Si/RuO_2/Pt_{black}$ showing a record-high STH of 18.3% [50]. Earlier in 1998, a monolithic PEC device comprising a p-type $GaInP_2$ photocathode was proposed using biased with a single GaAs p-n junction [51]. This system showed an impressive STH efficiency of 12.4% but the device was way too expensive and prone to photo-corrosion [47]. Recently, STH efficiency of 12.3 % is achieved using perovskite photovoltaics and cheap layered double hydroxide NiFe type catalyst. However, the device experienced instability due to limitation offered by the perovskite lifetime [52].

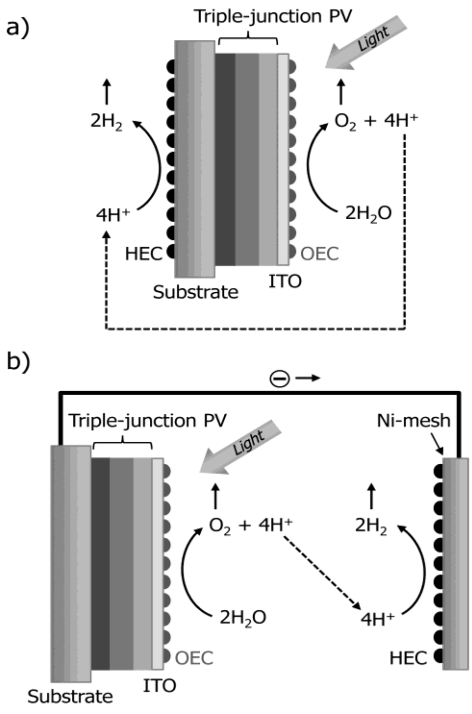


Fig. 6: (a) A working model of an artificial leaf with a triple-junction amorphous/microcrystalline Si system as reported by Miller and Nocera; (b) A wired-configuration for the PEC based water oxidation system

5. Conclusion and Outlook

Scientific and political interests are growing steadily in pursuit of solar to chemical energy conversion system using widely available resources such as sun light, CO_2 and water and earth-abundant materials [1, 45]. There is already some progress in the field of light-driven water splitting catalysis and to develop the artificial leaf. Several governmental organization and many research groups and universities are now participating in this quest around the world in one way or another. The first established research consortium is the Swedish consortium for artificial photosynthesis (that was established in mid 90s). They are focusing both on artificial photosynthesis and biologically improved systems for solar to fuel conversion. Few years back, the Bio Solar Cells consortium was also established in the Netherlands, again concentrating on bioinspired and natural systems for solar fuels. Recently, the joint centre for artificial photosynthesis (JCAP) has emerged as a leading research fraternity managed by Caltech and UC Berkeley. Their advanced approach is to use nano-architectural designed nanowire and nanopillars based state-of-the-art technology to make solar fuel system [53-55]. An attractive design in this scenario is to use silicon based vertically aligned nanowire array and the two components (anodic and cathodic) will be separated by efficient polymer based proton conducting membrane (Fig. 7) [56, 57]. However, it is very tricky to incorporate such a delicate proton-conducting membrane with the nanowires on both sides [58, 59]. Next step will be to put efficient catalytic modules, both for water oxidation and for protons or CO_2 reduction on each side of the nanowire assembly. This approach looks very interesting and promising and we have to wait and see the outcome of this joint effort.

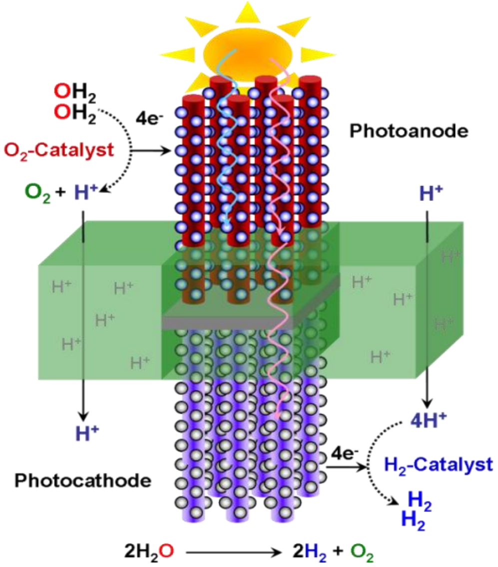


Fig. 7: A conceptual design of the artificial leaf proposed by JCAP based on arrays of light harvesting nano-/micro-wires, embedded in a proton-conducting membrane, coated with O_2 and H_2 evolving catalysts from water splitting reaction

Clean energy supplies based on electrochemical or photoelectrochemical water splitting processes are feasible and attractive schemes to produce renewable fuels from water and solar energy. For an energy sustainable world, the prosperity of humanity greatly depends on the availability of renewable energy sources that are cost-effective and easily accessible. Solar energy conversion systems look to be the ultimate approach to meet the demand of growing economies in the world. Photoelectrochemical water splitting systems can be exploited to directly convert solar energy into storable chemical energy for the domestic and industrial uses. That is why this domain has received tremendous political and scientific attention in recent time. This field is steadily glowing and in near future, a strong output is expected in the form of several entrepreneurial activities and industrial involvements regarding the clean and renewable energy generation technologies. Also the automotive industrial sector seems to be interested to implant these systems to make hybrid automobiles. But many challenges are to be addressed on the road with numerous scientific open questions. Resilient scientific commitments, rational political thinking and brilliance in research methodologies and hardworking efforts are still required that can turn the dream of solar fuel from water into reality.

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