



'ARTIFICIAL LEAF' COULD POWER COMMUNITIES OF THE FUTURE

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ABSTRACT

It has been estimated that the energy captured in one hour of sunlight that reaches our planet is equivalent to annual energy production by human population globally. To efficiently capture the practically inexhaustible solar energy and convert it into high energy density solar fuels provides an attractive 'green' alternative to running our present day economies on rapidly depleting fossil fuels, especially in the context of ever growing global energy demand. Natural photosynthesis represents one of the most fundamental processes that sustain life on Earth. It provides nearly all the oxygen we breathe, the food we consume and fossil fuels that we so much depend on. Imitating the reactions that occur at the early stages of photosynthesis represents the main challenge in the quest for construction of an efficient, robust, self-renewing and cost-effective 'artificial leaf'. In this review we summarize the main molecular features of the natural solar energy converters, photosystem I and photosystem II, that allow them to operate at high quantum efficiencies, and thus inspire the smart matrix design of the artificial solar-to-fuel devices. We also discuss the main challenges that face the field and overview selected recent technological advances that have tremendously accelerated the race for a fully operational artificial leaf that could serve as a viable alternative to fossil fuels for energy production.

KEYWORDS: Sunlight, equivalent, inexhaustible, solar fuels, tremendously accelerated.

INTRODUCTION



The '**artificial leaf**', a device that can harness sunlight to split water into hydrogen and oxygen without needing any external connections, is seen with some real leaves, which also convert the energy of sunlight directly into storable chemical form.

To convert the energy of sunlight into chemical energy, the leaf splits water via the photosynthetic process to produce molecular oxygen and hydrogen, which is in a form of separated protons and electrons. The primary steps of natural photosynthesis involve the absorption of sunlight and its conversion into spatially separated electron-hole pairs. The holes of this wireless current are captured by the oxygen evolving complex (OEC) of

photosystem II (PSII) to oxidize water to oxygen. The electrons and protons produced as a byproduct of the OEC reaction are captured by ferrodoxin of photosystem I. With the aid of ferrodoxin-NADP⁺ reductase, they are used to produce hydrogen in the form of NADPH. For a synthetic material to realize the solar energy conversion function of the leaf, the light-absorbing material must capture a solar photon to generate a wireless current that is harnessed by catalysts, which drive the four electron/hole fuel-forming water-splitting reaction under benign conditions and under 1 sun (100 mW/cm²) illumination.

This Account describes the construction of an artificial leaf comprising earth-abundant elements by interfacing a triple junction, amorphous silicon photovoltaic with hydrogen- and oxygen-evolving catalysts made from a ternary alloy (NiMoZn) and a cobalt-phosphate cluster (Co-OEC), respectively. The latter captures the structural and functional attributes of the PSII-OEC. Similar to the PSII-OEC, the Co-OEC self-assembles upon oxidation of an earth-abundant metal ion from 2+ to 3+, may operate in natural water at room temperature, and is self-healing. The Co-OEC also activates H₂O by a proton-coupled electron transfer mechanism in which the Co-OEC is increased by four hole equivalents akin to the S-state

pumping of the Kok cycle of PSII. X-ray absorption spectroscopy studies have established that the Co-OEC is a structural relative of Mn_3CaO_4 –Mn cubane of the PSII-OEC, where Co replaces Mn and the cubane is extended in a corner-sharing, head-to-tail dimer.

The ability to perform the oxygen-evolving reaction in water at neutral or near-neutral conditions has several consequences for the construction of the artificial leaf. The NiMoZn alloy may be used in place of Pt to generate hydrogen. To stabilize silicon in water, its surface is coated with a conducting metal oxide onto which the Co-OEC may be deposited. The net result is that immersing a triple-junction Si wafer coated with NiMoZn and Co-OEC in water and holding it up to sunlight can effect direct solar energy conversion via water splitting. By constructing a simple, stand-alone device composed of earth-abundant materials, the artificial leaf provides a means for an inexpensive and highly distributed solar-to-fuels system that employs low-cost systems engineering and manufacturing. Through this type of system, solar energy can become a viable energy supply to those in the non-legacy world.

Construction

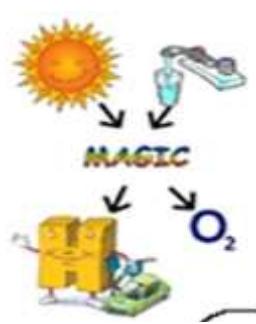
- Si semiconductor: Acts as a harvesting catalyst. It captures solar light.
- Co-OEC: cobalt oxygen evolving complex, it deposits oxygen at anode side.
- NiMoZn: produces H and combine H^+ and e^- made available from the semiconductor at cathode side
- ITO (Indium tin oxide): A conducting metal oxide layer to stabilize silicon in water
- Stainless Steel: Used for support. Si is deposited on it.

Working

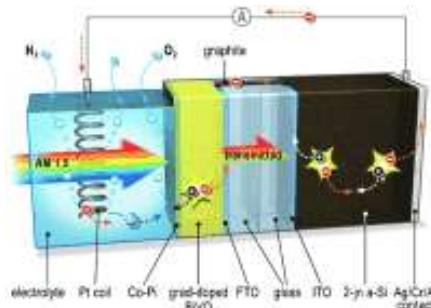
When artificial leaf is placed on the container of water and exposed to sunlight it quickly begins to generate streams of bubbles: oxygen bubbles from one side and hydrogen bubbles from other side, the two streams of bubbles can be collected and stored and used later to deliver power. The device is made entirely of earth-abundant, inexpensive materials mostly silicon, cobalt and nickel and works in ordinary water.

Advantages

- It can store energy in the chemical form i.e., the great advantage of this device over the solar panels which we use now a days.
- Inexpensive.
- By products are eco-friendly.



Artificial Leaf Goes Simpler and More Efficient for Solar Fuel Generation

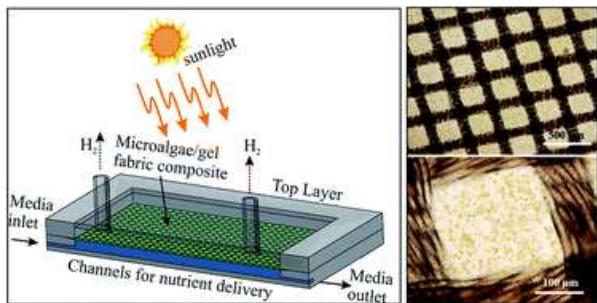


Artificial leaf device for hydrogen generation

Layer upon layer: Solar-to-fuel conversion through water splitting is among the most challenging and growing fields in present day science. Herein, a report is highlighted that successfully demonstrates an efficient photoanodic system utilizing simple and low-cost tungsten-doped bismuth vanadate on single- or double-junction amorphous silicon photovoltaic in a tandem configuration.

A fully biomimetic leaf-like device for hydrogen production which allows incorporated fabric-immobilised microalgae culture to be simultaneously hydrated with media and harvested from the produced hydrogen in a continuous flow regime without the need to replace the algal culture. Our leaf device produces hydrogen by direct photolysis of water resulting from redirecting the photosynthetic pathways in immobilised microalgae due to the lack of oxygen. In contrast to the many other reports in the literature on batch photobioreactors producing hydrogen from suspension culture of microalgae, we present the first report where this is done in a continuous manner from a fabric-immobilised microalgae culture. The reported artificial leaf device maximises the sunlight energy utilisation per gram of algae and can be upscaled cheaply and easily to cover large areas. We compared the production of hydrogen from both immobilised and suspended cultures of *C. reinhardtii* microalgae under sulphur, phosphorus and oxygen deprived conditions. The viability and potential of this approach is clearly demonstrated. Even though this is a first prototype, the hydrogen yield of our artificial leaf device is twenty times higher per gram of algae than in previously the reported batch reactors. Such leaf-like devices could potentially be made from flexible plastic sheets and installed on roofs and other sun-exposed surfaces that are inaccessible by photovoltaic cells. The ability to continuously produce

inexpensive hydrogen by positioning inexpensive sheets onto any surface could have an enormous importance in the field of biofuels. The proposed new concept can provide a cleaner and very inexpensive way of bio-hydrogen generation by flexible sheet-like devices.



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