

ARTIFICIAL PHOTOSYNTHESIS

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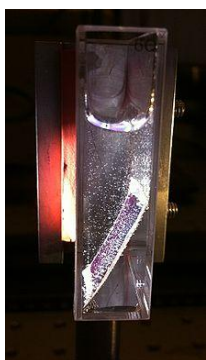
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ABSTRACT

Artificial photosynthesis is a chemical process that replicates the natural process of photosynthesis, a process that converts sunlight, water, and carbon dioxide into carbohydrates and oxygen; as an imitation of a natural process it is biomimetic. The term, artificial photosynthesis, is commonly used to refer to any scheme for capturing and storing the energy from sunlight in the chemical bonds of a fuel (a solar fuel). Photocatalytic water splitting converts water into hydrogen ions and oxygen, and is a major research topic of artificial photosynthesis. Light-driven carbon dioxide reduction is another process studied, that replicates natural carbon fixation. Research of this topic includes the design and assembly of devices for the direct production of solar fuels, photo electrochemistry and its application in fuel cells, and the engineering of enzymes and photo autotrophic microorganisms for microbial biofuel and biohydrogen production from sunlight. The photosynthetic reaction can be divided into two half-reactions of oxidation and reduction, both of which are essential to producing fuel. In plant photosynthesis, water molecules are photo-oxidized to release oxygen and protons. The second phase of plant photosynthesis (also known as the Calvin-Benson cycle) is a light-independent reaction that converts carbon dioxide into glucose (fuel). Researchers of artificial photosynthesis are developing photo catalysts that are able to perform both of these reactions. Furthermore, the protons resulting from water splitting can be used for hydrogen production. These catalysts must be able to react quickly and absorb a large percentage of the incident solar photons. Whereas photovoltaics can provide energy directly from sunlight, the inefficiency of fuel production from photovoltaic electricity (indirect process) and the fact that sunshine is not constant throughout the day sets a limit to its use. One way of using natural photosynthesis is for the production of a biofuel, which is an indirect process that suffers from low energy conversion efficiency (due to photosynthesis' own low efficiency in converting sunlight to biomass), the cost of harvesting and transporting the fuel, and conflicts due to the increasing need of land mass for food production. The purpose of artificial photosynthesis is to produce a fuel from sunlight that can be stored conveniently and used when sunlight is not available, by using direct processes, that is, to produce a solar fuel. With the development of catalysts able to reproduce the major parts of photosynthesis, water and sunlight would ultimately be the only needed sources for clean energy production. The only by-product would be oxygen, and production of a solar fuel has the potential to be cheaper than gasoline.

KEYWORDS: Artificial photosynthesis, photovoltaics, photovoltaics.



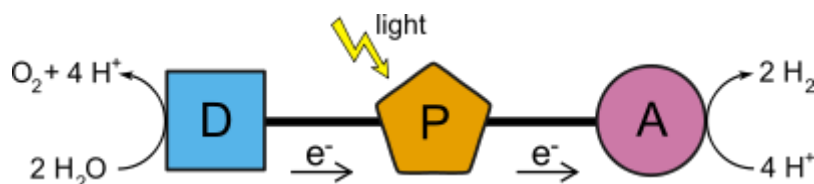
One process for the creation of a clean and affordable energy supply is the development of photocatalytic water

splitting under solar light. This method of sustainable hydrogen production is a major objective for the development of alternative energy systems. It is also predicted to be one of the more, if not the most, efficient ways of obtaining hydrogen from water. The conversion of solar energy into hydrogen via a water-splitting process assisted by photo semiconductor catalysts is one of the most promising technologies in development. This process has the potential for large quantities of hydrogen to be generated in an ecologically sound manner. The conversion of solar energy into a clean fuel (H₂) under ambient conditions is one of the greatest challenges facing scientists in the twenty-first century.

Two methods are generally recognized for the construction of solar fuel cells for hydrogen production:

- A homogeneous system is one such that catalysts are not compartmentalized, that is, components are present in the same compartment. This means that hydrogen and oxygen are produced in the same location. This can be a drawback, since they compose an explosive mixture, demanding gas product separation. Also, all components must be active in approximately the same conditions (e.g., pH).
- A heterogeneous system has two separate electrodes, an anode and a cathode, making possible the separation of oxygen and hydrogen production. Furthermore, different components do not necessarily need to work in the same conditions. However, the increased complexity of these systems makes them harder to develop and more expensive.

Artificial photosynthesis was first anticipated by the Italian chemist Giacomo Ciamician during 1912. In a lecture that was later published in *Science* he proposed a switch from the use of fossil fuels to radiant energy provided by the sun and captured by technical photochemistry devices. In this switch he saw a possibility to lessen the difference between the rich north of Europe and poor south and ventured a guess that this switch from coal to solar energy would "not be harmful to the progress and to human happiness."



A triad assembly, with a photosensitizer (P) linked in tandem to a water oxidation catalyst (D) and a hydrogen evolving catalyst (A). Electrons flow from D to A when catalysis occurs.

Using biomimetic approaches, artificial photosynthesis tries to construct systems doing the same type of processes. Ideally, a triad assembly could oxidize water with one catalyst, reduce protons with another and have a photosensitizer molecule to power the whole system. One of the simplest designs is where the photosensitizer is linked in tandem between a water oxidation catalyst and a hydrogen evolving catalyst:

- The photosensitizer transfers electrons to the hydrogen catalyst when hit by light, becoming oxidized in the process.
- This drives the water splitting catalyst to donate electrons to the photosensitizer. In a triad assembly, such a catalyst is often referred to as a donor. The oxidized donor is able to perform water oxidation.

During the late 1960s, Akira Fujishima discovered the photocatalytic properties of titanium dioxide, the so-called Honda-Fujishima effect, which could be used for hydrolysis.

The Swedish Consortium for Artificial Photosynthesis, the first of its kind, was established during 1994 as a collaboration between groups of three different universities, Lund, Uppsala and Stockholm, being presently active around Lund and the Ångström Laboratories in Uppsala. The consortium was built with a multidisciplinary approach to focus on learning from natural photosynthesis and applying this knowledge in biomimetic systems.

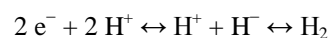
CURRENT RESEARCH

In energy terms, natural photosynthesis can be divided in three steps

- Light-harvesting complexes in bacteria and plants capture photons and transduce them into electrons, injecting them into the photosynthetic chain.
- Proton-coupled electron transfer along several cofactors of the photosynthetic chain, causing local, spatial charge separation.
- Redox catalysis, which uses the aforementioned transferred electrons to oxidize water to dioxygen and protons; these protons can in some species be utilized for dihydrogen production.

Hydrogen catalysts

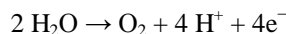
Hydrogen is the simplest solar fuel to synthesize, since it involves only the transference of two electrons to two protons. It must, however, be done stepwise, with formation of an intermediate hydride anion:



The proton-to-hydrogen converting catalysts present in nature are hydrogenases. These are enzymes that can either reduce protons to molecular hydrogen or oxidize hydrogen to protons and electrons. Spectroscopic and crystallographic studies spanning several decades have resulted in a good understanding of both the structure and mechanism of hydrogenase catalysis. Using this information, several molecules mimicking the structure of the active site of both nickel-iron and iron-iron hydrogenases have been synthesized. Other catalysts are not structural mimics of hydrogenase but rather functional ones. Synthesized catalysts include structural H-cluster models, a dirhodium photocatalyst and cobalt catalysts.

Water-oxidizing catalysts

Water oxidation is a more complex chemical reaction than proton reduction. In nature, the oxygen-evolving complex performs this reaction by accumulating reducing equivalents (electrons) in a manganese-calcium cluster within photosystem II (PS II), then delivering them to water molecules, with the resulting production of molecular oxygen and protons:



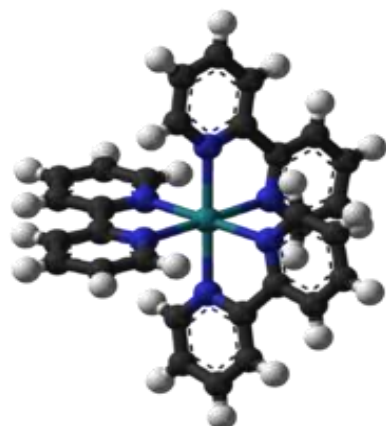
Without a catalyst (natural or artificial), this reaction is very endothermic, requiring high temperatures (at least 2500 K).

The exact structure of the oxygen-evolving complex has been hard to determine experimentally. As of 2011, the most detailed model was from a 1.9 Å resolution crystal structure of photosystem II. The complex is a cluster containing four manganese and one calcium ions, but the exact location and mechanism of water oxidation within the cluster is unknown. Nevertheless, bio-inspired manganese and manganese-calcium complexes have been synthesized, such as $[\text{Mn}_4\text{O}_4]$ cubane-type clusters, some with catalytic activity.

Some ruthenium complexes, such as the dinuclear μ -oxo-bridged "blue dimer" (the first of its kind to be synthesized), are capable of light-driven water oxidation, thanks to being able to form high valence states. In this case, the ruthenium complex acts as both photosensitizer and catalyst.

Recently Metal-Organic Framework (MOF)-based materials have been shown to be a highly promising candidate for water oxidation with first row transition metals. The stability and tunability of this system is projected to be highly beneficial for future development.

Photosensitizers



Nature uses pigments, mainly chlorophylls, to absorb a broad part of the visible spectrum. Artificial systems can use either one type of pigment with a broad absorption range or combine several pigments for the same purpose.

Ruthenium polypyridine complexes, in particular tris (bipyridine) ruthenium (II) and its derivatives, have been extensively used in hydrogen photoproduction due to their efficient visible light absorption and long-lived consequent metal-to-ligand charge transfer excited state, which makes the complexes strong reducing agents. Other noble metal-containing complexes used include ones with platinum, rhodium and iridium.

Carbon dioxide reduction catalysts

In nature, carbon fixation is done by green plants using the enzyme RuBisCO as a part of the Calvin cycle. RuBisCO is a rather slow catalyst compared to the vast majority of other enzymes, incorporating only a few molecules of carbon dioxide into ribulose-1,5-bisphosphate per minute, but does so at atmospheric pressure and in mild, biological conditions. The resulting product is further reduced and eventually used in the synthesis of glucose, which in turn is a precursor to more complex carbohydrates, such as cellulose and starch. The process consumes energy in the form of ATP and NADPH.

Artificial CO_2 reduction for fuel production aims mostly at producing reduced carbon compounds from atmospheric CO_2 . Some transition metal polyphosphine complexes have been developed for this end; however, they usually require previous concentration of CO_2 before use, and carriers (molecules that would fixate CO_2) that are both stable in aerobic conditions and able to concentrate CO_2 at atmospheric concentrations haven't been yet developed. The simplest product from CO_2 reduction is carbon monoxide (CO), but for fuel development, further reduction is needed, and a key step also needing further development is the transfer of hydride anions to CO.

LIGHT-DRIVEN METHODOLOGIES UNDER DEVELOPMENT

Photo electrochemical cells

Photo electrochemical cells are a heterogeneous system that use light to produce either electricity or hydrogen. The vast majority of photo electrochemical cells use semiconductors as catalysts. There have been attempts to use synthetic manganese complex-impregnated Nafion as a working electrode, but it has been since shown that the catalytically active species is actually the broken-down complex.

A promising, emerging type of solar cell is the dye-sensitized solar cell. This type of cell still depends on a semiconductor (such as TiO_2) for current conduction on one electrode, but with a coating of an organic or inorganic dye that acts as a photosensitizer; the counter electrode is a platinum catalyst for H_2 production. These cells have a self-repair mechanism and solar-to-electricity conversion efficiencies rivaling those of solid-state semiconductor ones.

Photo catalytic water splitting in homogeneous systems

Direct water oxidation by photo catalysts is a more efficient usage of solar energy than photo electrochemical water splitting because it avoids an intermediate thermal or electrical energy conversion step.

Bio-inspired manganese clusters have been shown to possess water oxidation activity when adsorbed on clays together with ruthenium photosensitizers, although with low turnover numbers.

As mentioned above, some ruthenium complexes are able to oxidize water under solar light irradiation. Although their photostability is still an issue, many can be reactivated by a simple adjustment of the conditions in which they work. Improvement of catalyst stability has been tried resorting to polyoxometalates, in particular ruthenium-based ones.

Whereas a fully functional artificial system is usually intended when constructing a water splitting device, some mixed methods have been tried. One of these involve the use of a gold electrode to which photosystem II is linked; an electric current is detected upon illumination.

Advantages and Disadvantages

- The solar energy can be immediately converted and stored. In photovoltaic cells, sunlight is converted into electricity and then converted again into chemical energy for storage, with some necessary loss of energy associated with the second conversion.
- The byproducts of these reactions are environmentally friendly. Artificially photosynthesized fuel would be a carbon-neutral source of energy, which could be used for transportation or homes.

Disadvantages include

- Materials used for artificial photosynthesis often corrode in water, so they may be less stable than photovoltaics over long periods of time. Most hydrogen catalysts are very sensitive to oxygen, being inactivated or degraded in its presence; also, photodamage may occur over time.
- The cost is not (yet) advantageous enough to compete with fossil fuels as a commercially viable source of energy.

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