



Leopoldina
Nationale Akademie
der Wissenschaften

2012

Statement

Bioenergy – Chances and Limits

German National Academy of Sciences Leopoldina

www.leopoldina.org

3. BIOLOGICAL AND BIO-INSPIRED SOLAR DIHYDROGEN PRODUCTION

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Dihydrogen (H_2) is a uniquely clean renewable energy carrier; its oxidation for production of heat or electricity yields water (H_2O) as the only product. Furthermore, H_2 is highly important for many industrial processes, e.g. the production of ammonia (for fertilizers) by the “Haber-Bosch” process. Free H_2 occurs only in trace amounts on our planet. Thus, more than 90 % of the H_2 is currently generated from natural gas by steam-reforming with an efficiency of approximately 80 %.

To develop a viable H_2 -based economy, production of H_2 has to be significantly increased while employing renewable non-fossil resources. Carbon-neutral routes to H_2 are mainly based on the electrolysis of water. Large-scale production usually relies on costly high-pressure and high-temperature systems that improve the efficiency of electrolysis. Photovoltaic hydrogen generation is expected to have a promising future but is currently limited by costs that are about ten times higher than those for conventional H_2 production.¹ Additional options for biomass-related H_2 production are discussed in Chapter 2 (p. 43).

The exploitation of solar energy for either chemical or biological generation of H_2 is an attractive and environmentally friendly technological endeavor; yet it is highly challenging and still at the level of basic research. It is still an open question whether these strategies will ever lead to processes that may be used in practice on a large scale. A rapidly expanding research field is focussed on direct H_2 production by artificial photosynthetic systems, which do not rely on intermediate energy carriers such as electricity, biomass or

energy-rich metabolites. Since these processes integrate fewer energy transduction steps, they offer the potential to improve the overall efficiency and to lower the costs of capital investment.²

One option for biological H_2 generation is the photosynthetic conversion of sunlight and water directly to H_2 and di-oxygen (O_2): both water and light are available to an almost unlimited extent and because only H_2 and O_2 are formed in this reaction, no greenhouse gases are generated. The total solar energy that reaches the Earth’s surface and is absorbed there is about $2.7 \times 10^{24} \text{ J yr}^{-1}$ (170 W m^{-2} ; year’s average). This is 5,400 times the primary energy consumed by the world’s population in a whole year ($500 \times 10^{18} \text{ J}$ in 2010).³ Biological conversion of solar energy to H_2 requires efficient, stable, selective, O_2 -tolerant and highly active catalytic systems. Extensive molecular, biochemical and biophysical investigations have contributed to a deeper understanding of the structure and function of the biological catalysts that are involved in photosynthesis and H_2 activation.⁴⁻⁶ This wealth of information has inspired chemists to develop synthetic catalysts for renewable fuel production.⁷

Chapter 3 presents an overview on the current state of research regarding biological and bio-inspired solar H_2 production, addressing the following issues:

- a) technical routes to hydrogen production using solar energy;
- b) biological routes to hydrogen production based on water and sunlight;
- c) bio-inspired catalysts for solar water-splitting and H_2 production.

3.1. Technical routes to hydrogen production using solar energy

Two technical routes of solar hydrogen production have been established: One method makes use of biomass gasification, i.e., processing of renewable biological resources instead of natural gas and coal (see Chapter 2; p. 43). The second route does not involve photosynthetic biomass production but instead produces H₂

through electrolysis of water, applying electricity generated from solar energy by photovoltaic cells or by thermal conversion (Figure 3.1). A third approach, which is the subject of ongoing research and development, is focused on direct production of H₂ from sunlight and water. Each of these methods is directed at producing hydrogen with zero overall emission of greenhouse gases.

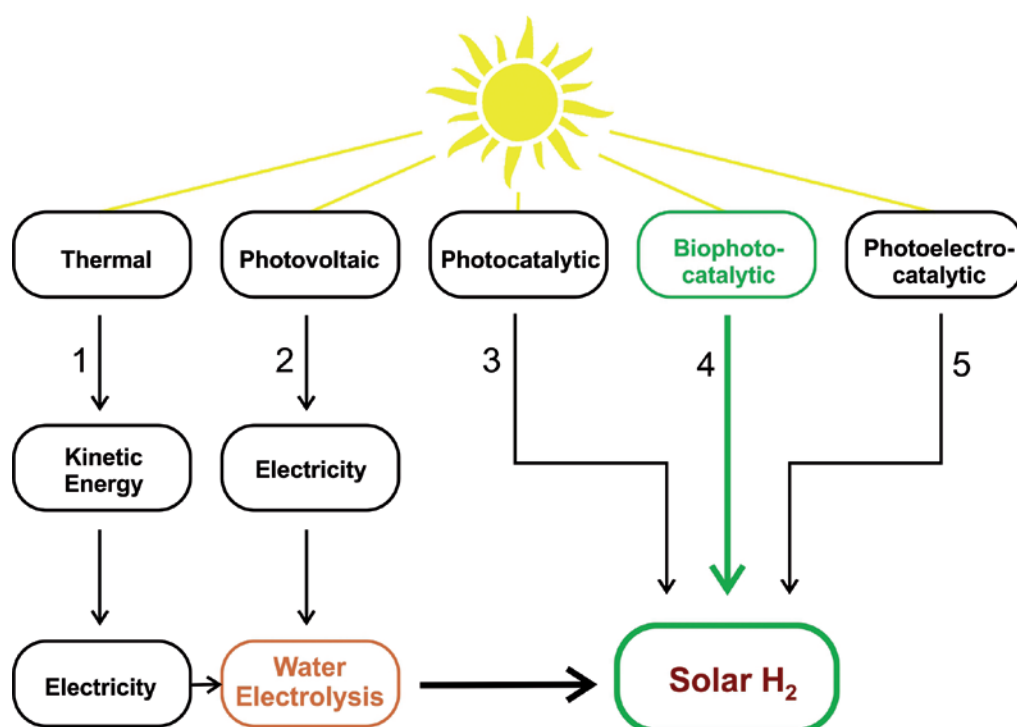


Figure 3.1: Various pathways of H₂ production from water using sunlight as the energy source. Pathways 1 and 2 are established (wind energy, which provides electricity like photovoltaic cells, is not listed in this scheme). Routes 3, 4 and 5 are subject of ongoing research and development.

None of the techniques exploiting renewable energy sources for H₂ production are currently competitive with fossil resources based on market prices. As a reference figure, the price for H₂ generation from natural gas reforming (the cheapest way to produce H₂) is about € 1 per kg of H₂. From biomass, H₂ is currently obtained at a price of about € 7 per kg of H₂ by gasification in a midsize plant.⁸ This price reflects higher feedstock, distribution, and fixed and capital costs, but does not take into account fertilizer costs and the environmental impact associated with the production, harvest, and transport of biomass.

Of all the greenhouse-gas free methods for H₂ production, alkaline electrolysis is current-

ly the most economically viable, with a cost of about € 3 per kg of H₂. The cost consists of 50 % capital investment in the electrolysis and storage devices and 50 % for electrical power. Alkaline water electrolysis is carried out from concentrated potassium hydroxide solutions (30 to 60 % by weight) at low-cost electrodes fabricated from nickel (Ni) and iron (Fe). The overall yield depends on the current flowing through the device but is optimistically around 70 % for bipolar devices.⁹

Electrolyzers working under acidic conditions are the most promising and adaptable, due to the use of potentially low cost organic materials, operating at low ambient temperatures. Such devices are efficient over a wide

range of power supply (0.1 W to 100 kW) with an overall yield of 50 to 80 %. However, manufacture of proton exchange membrane devices is still expensive due to the high cost of materials like fluorinated acid polymer membranes of the Nafion® type and especially the precious metal catalysts required at both anode and cathode (at least 1 mg of platinum per Watt of nominal power; iridium oxide can also be used at the anode).

The photo-electrochemical approach (Figure 3.1), in which an electrolyzer is coupled directly to a solar photovoltaic device could enable H_2 to be produced at a similar cost to its production from biomass and at a reasonable efficiency (around 10 % overall energy conversion from sunlight to H_2).⁸ This analysis was made in 2004 and is based on the capital investment in an alkaline electrolyzer (€ 125 per kW) with 70 % yield and for solar cells with a module cost of € 1 per W_p – competitive with conventional technologies for electricity production alone. However bipolar alkaline electrolyzers able to display such high yields are sensitive to sudden variations in intensity and require a minimum power level to be maintained. As a result, they are not suitable for coupling with intermittent power sources such as solar panels. For such applications, monopolar alkaline electrolyzers should be used instead; however, they are especially cumbersome and often display a lower yield of 60 % or less. By contrast, coupling a photovoltaic device with a photo-electrochemical electrolyzer operating at 80 % efficiency is much more promising, and could provide an overall solar to hydrogen conversion yield of 10 to 15 %. In both cases, the photovoltaic panel, based on crystalline silicon or composite materials, and the platinum/iridium (Pt/Ir) catalysts account for about 80 % of the costs. Thus alternative, fully integrated photo-electrochemical devices, based on low-cost nanostructured semiconductors or metal oxides and using bio-inspired noble-metal-free catalytic and photocatalytic systems (Figure 3.1) are expected to be economically viable, provided they can be developed into a robust form.

For molecules able to absorb a major fraction of the visible solar spectrum, a lifetime target of 20 years corresponds to about 10^9 pho-

tons absorbed per individual light-harvesting unit. In order to optimize the utilization of these harvested incident solar photons, directly linked catalysts for water oxidation and reduction should combine both high turnover frequencies, exceeding 10 s^{-1} (hydrogen molecules produced per molecular unit of catalyst) and high surface densities, about ten catalytic sites per square nanometer (nm^2).¹⁰ The surface density issue severely restricts the volume or “footprint” of each molecular catalytic unit because even 10 sites per nm^2 correspond to 20 monolayers of a rather small molecule such as ferrocene on a flat surface. Furthermore, if the energy of red and near infrared photons is to be used so that the maximum fraction of the sun’s energy can be converted into chemical energy, these catalysts should operate as close as possible to the thermodynamic potential of the redox reaction. We emphasize, that any existing photo-electrochemical device currently does not meet the above figures. The devices represent targets for future research and development. Sizable research activities are required for assessment of technical feasibility and economic viability.

Once electrical energy is available from solar power, it is important to optimize the rates and efficiencies of the electrode reactions at both cathode (producing H_2) and anode (evolving O_2). The efficiency of electrochemical processes is defined by the current density and by the electrode potential, relative to the thermodynamic potential, at which the current density starts to rise (the overpotential requirement, often called the overvoltage). A large overpotential requirement at either anode or cathode means that energy is wasted. An electrolyzer typically operates at a voltage above 2 V (compared to the reversible, thermodynamic cell potential of 1.2 V) reflecting the sizable overpotential requirements at both anode and cathode. It should be noted that the same principle applies to proton-exchange membrane fuel cells, as their output voltage is typically as low as 0.7 V. Production and oxidation of H_2 is very efficient at Pt metals because the electrode reaction is fully reversible, i.e. requires only a small overpotential in either direction to drive the reactions. On the other

hand, even at Pt (or iridium oxide, IrO_2) water oxidation requires a sizable overpotential, usually above 0.3 V. Although Pt (cathode) and IrO_2 (anode) are the best catalysts, both Pt and Ir are limited, expensive resources. Alternatives must be found if green H_2 technology is to be sustainable and cheap. Replacing noble metals is the “holy grail” for future renewable energy and great efforts are being made to find ways of producing proficient catalysts from abundant metals.

3.2. Biological routes to hydrogen production based on water and sunlight

“Learning from biology” means copying the principles by which enzymes catalyze reactions at rates that are often many orders of magnitude higher than for synthetic catalysts. The metals at the active site of enzymes are indeed abundant, sustainable and cheap. The same principle applies to electro-catalysis because despite their large size, many enzymes are superb electro-catalysts on a per site basis, providing high rates (current density) at small overpotentials and often yielding fully reversible electrochemistry. Thus hydrogenases, enzymes that catalyze the reversible conversion of H_2 into protons and electrons, host active sites containing Fe and in some cases Ni in addition to Fe. They exhibit activities for H_2 production and H_2 oxidation that are comparable, on a per site basis, to Pt. Likewise copper (Cu) enzymes known as ‘blue’ Cu oxidases reduce O_2 to water at smaller overpotentials than Pt and even Pt_3Ni . In photosynthesis, the water-oxidizing manganese (Mn) complex operates at reasonably low overpotential and a rate (turnover frequency) that exceeds typical synthetic catalysts by orders of magnitude. The key enzymes involved in biological H_2 production from water will now be described in more detail.

3.2.1. Photosynthetic hydrogen formation from water

In photosynthetic microorganisms such as green algae and cyanobacteria light-induced cleavage of H_2O yields O_2 and biochemically usable energy that under certain physiological conditions is released as H_2 .⁴⁻⁶ This naturally

occurring process involves two photosynthetic protein complexes, the H_2O -splitting photosystem II (PS II) and the electron-delivering photosystem I (PS I). Protons (H^+) and electrons (e^-) released during H_2O oxidation are converted by the enzyme hydrogenase to molecular hydrogen (H_2) as depicted in Figure 3.2. An alternative highly energy-consuming pathway for natural H_2 production by oxygenic photosynthetic microbes is the use of the enzyme nitrogenase, which can produce high levels of H_2 under certain external conditions.¹¹

The key catalysts of biosolar H_2 production, the two photosystems (PS I, PS II) and hydrogenase (Figure 3.2), contain intricate metal cofactors embedded in a network of amino acids that form the protein pocket and providing

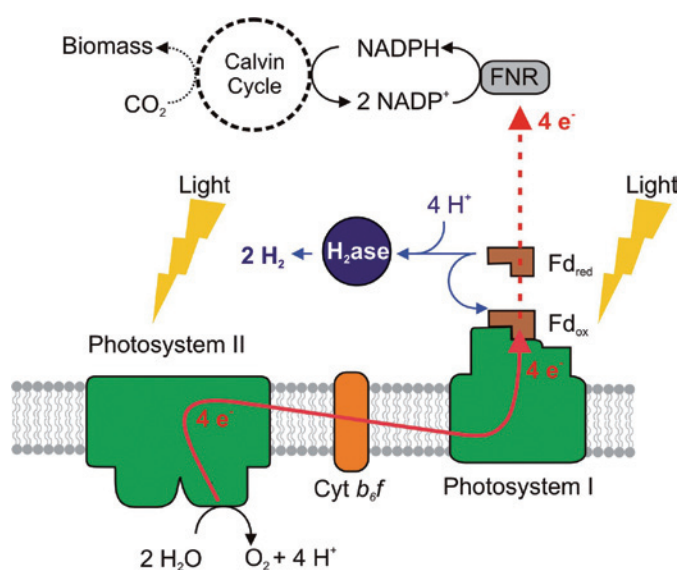


Figure 3.2: Photosynthetic H_2 production from water. Oxygenic photosynthesis is functionally divided into two parts: (i) the light-dependent reactions where light energy is converted to chemical energy and (ii) the light-independent reactions where carbon dioxide is converted into biomass. The light-dependent reactions occur at membranes catalyzed by complexes of proteins, chlorophylls and other cofactors. Photosystem II (PS II, on the left) captures light energy at 680 nm exciting electrons (e^-) that enter the electron transport chain. Electrons are replaced with electrons stripped from water (the water-splitting reaction) creating O_2 as a by-product. The energized electrons are shuttled from PS II via components of the respiratory chain to photosystem I (PS I, on the right) capturing light energy at 700 nm. The e^- transfer releases energy to pump protons (H^+) across the membrane (not shown) forming a reservoir for the synthesis of chemical energy, primarily ATP. In PS I light energy excites electrons, and this time electrons are captured by the electron carrier molecule NADP^+ , which is reduced to NADPH . The reduction process involves ferredoxin (Fd) as electron carrier molecule and the enzyme ferredoxin- NADP^+ reductase (FNR). The product NADPH is used in addition to ATP (not shown) for fixation of carbon dioxide in the light-independent reactions of the Calvin Cycle.

tunnels for the substrate H_2O and the products O_2 , protons (H^+) and electrons (e^-). The electrons released from water in a light-dependent reaction by PS II are shuttled via membrane-associated components (Cyt b_6/f) to PS I, which captures light energy for the reduction of the electron carrier ferredoxin. Reduced ferredoxin can either serve as direct electron donor for the reduction of protons by hydrogenase or for the reduction of NADP^+ by ferredoxin-NADP⁺ reductase (FNR). Reduced NADPH is normally utilized by the cells for autotrophic carbon dioxide fixation via the light independent reactions of the Calvin Cycle yielding biomass.^{5,6}

3.2.2. Photosystem II

A broad inventory of molecular, biochemical and biophysical methods provided the tools to derive detailed insights into the structure and function of the photosynthetic apparatus. In particular, recent progress has been achieved on the water-splitting PS II complex, which constitutes a membrane-spanning protein complex composed of more than 20 polypeptides (Figure 3.2). The molecular structure

was recently analyzed at very high resolution (1.9 Å) with a protein preparation from the thermophilic cyanobacterium *Thermosynechococcus vulcanus*.¹² The central proteins D 1 and D 2 carry several cofactors, including a $\text{Mn}_4\text{O}_5\text{Ca}$ cluster. The Mn cofactor is the site where photolysis of water and the evolution of O_2 take place (Figure 3.3).

Oxidation of H_2O is a four-electron transfer process (Figure 3.3) powered by light-induced charge separation across the photosynthetic membrane. The model predicts that H_2O binds to the Mn cluster in a stepwise cycle (S_0 to S_4). Oxidation occurs by successive subtraction of 4 H^+ accompanied by liberation of O_2 in the last step. Advanced spectroscopic analyses in concert with theoretical calculations¹³⁻¹⁵ contributed to a functional model as depicted in Figure 3.3. The recently published protein structure with considerably improved resolution¹² is considered as a major breakthrough in understanding this elementary process of life. Needless to emphasize that in addition to the metal cofactor the protein matrix of PS II plays an important role in the photosynthetic reaction.

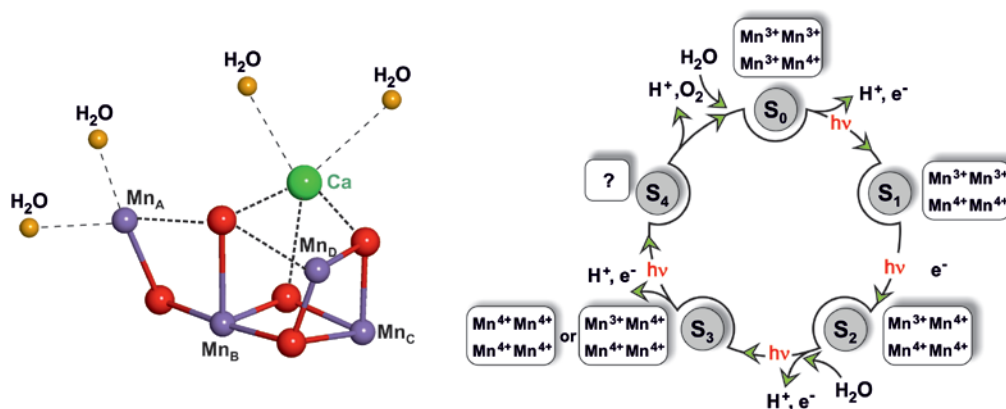


Figure 3.3: The catalytic site of photosystem II. The left site shows the structural model of the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster at which photolysis of H_2O takes place derived from crystal structure analysis.¹² The right site demonstrates the catalytic S-state cycle of H_2O oxidation at the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster of PSII. Proposed oxidation states of the manganese (Mn) ions are given (boxes).

The function of other protein-associated components such as chlorophylls, quinones, carotenoids and lipids is only partially understood, they are active in light harvesting, charge separation, electron and proton transfer, and contribute to the stability and protection of the biocatalyst.

3.2.3. Hydrogenases

The second partner in biological hydrogen production is the enzyme hydrogenase. Hydrogenases, microbial metal proteins that catalyse rapid H^+/H_2 inter-conversion, are usually considered as very O_2 -sensitive enzymes.¹⁶ Based on the composition and structure of their active

sites, three classes of hydrogenases are distinguished: the mono-iron [Fe]-, di-iron [FeFe]-, and nickel-iron [NiFe]-hydrogenases.^{17,18} [FeFe]-hydrogenases are highly productive in H₂ evolution (turnover rates up to 10,000 s⁻¹) but are irreversibly inactivated by traces of O₂.¹⁹ [NiFe]-hydrogenases preferentially catalyze H₂ oxidation and are less sensitive to O₂.^{6,20} (Figure 3.4). Typically [NiFe]-hydrogenases and [FeFe]-hydrogenases consist minimally of a large subunit that accommodates the bimetallic active site and at least one electron-transferring iron-sulfur (Fe-S) cluster usually located in a separate subunit as illustrated in Figure 3.4. In both cases the metals are bound to cysteine residues and varying numbers of carbonyl (CO) and cyanide (CN⁻) li-

gands. This fragile environment is a target for O₂ and most of the “standard” hydrogenases, which are instrumental under anaerobic conditions in nature, are inactivated by traces of O₂.¹⁸ However, some [NiFe]-hydrogenases display high catalytic activity for sustained periods under aerobic conditions and are therefore characterized as “O₂-tolerant”.²⁰ An important clue to explain O₂ tolerance is a modified iron-sulfur cluster (4Fe-3S) coordinated by six instead of four cysteine residues (Figure 3.4) that is proximal to the [NiFe] active site.²¹⁻²⁴ Any ability of hydrogenases to remain active in air is important for the design of H₂-producing cellular systems and inspired synthetic catalysts for future H₂ energy technologies.^{6,25}

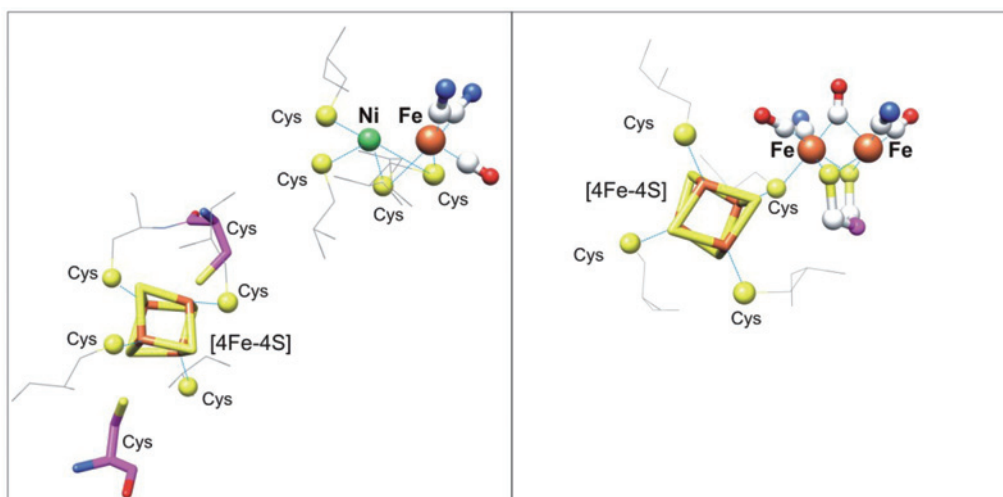


Figure 3.4: The catalytic sites of most common hydrogenases. The [NiFe] active site (left) and the [FeFe] active site (right) are shown in a stick and sphere representation with their carbonyl ligands (red) and cyanide ligands (blue). The cysteine residues that coordinate the proximal Fe-S cluster are shown in yellow. The two supernumerary cysteine residues that are found only in O₂ tolerant [NiFe]-hydrogenases are highlighted in magenta.

3.3. Cellular and semi-artificial systems for H₂ production

Oxygenic photosynthesis evolved in cyanobacteria approximately 2.8 billion years ago. Recruiting PS II enabled the organism to generate organic carbon compounds and cell material from CO₂ and water using sunlight as a source of energy (Figure 3.2). This achievement represents one of the major milestones in the evolution of our planet, yielding all fossil resources and the total amount of currently available biomass. In the course of this process O₂ was liberated and accumulated gradually in the atmosphere providing condi-

tions for the development of the O₂-respiring organisms.

Biological H₂ conversion in nature is a common metabolic trait. Microorganisms exist that preferentially use H₂ as an energy source and others that produce H₂ to dispose of excess reducing power during anaerobic fermentation of organic biomass as discussed in Chapter 2 (p. 43). Anaerobic H₂ production either occurs in the dark or is powered by a photosynthetic process. Here we focus on H₂ production by photolysis of water carried out by oxygenic phototrophic microbes such as unicellular green algae and cyanobacteria. This process requires

two membrane-bound photosystems, PS I and PS II, which act in series as demonstrated in Figure 3.5. The electron carrier ferredoxin (Fd) functions as a distributor of electrons. It can either reduce [FeFe]-hydrogenases²⁶ present in green algae thereby producing H₂ as a biofuel or

alternatively donate electrons to NADP⁺, which once reduced to NADPH is mainly used for CO₂ fixation, finally yielding biomass (Figure 3.5). It is anticipated that in cyanobacteria NADPH can also feed electrons into [NiFe]-hydrogenases to form H₂.²⁷

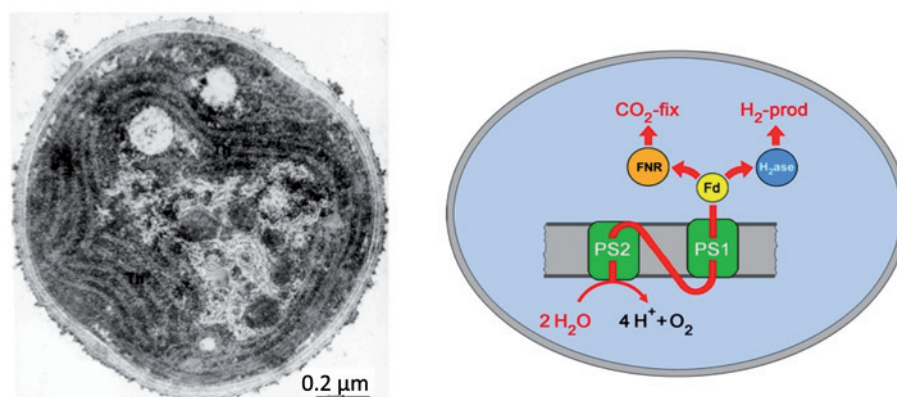


Figure 3.5: Cellular H₂ production from water. A cellular model for designing an H₂-evolving cell is the cyanobacterium *Synechocystis* (left). To increase the efficiency of the system the flow of electrons from the photosystems (PS I and PS II) and the electron carrier ferredoxin (Fd) should be tightly coupled to the enzyme hydrogenase (H₂ase) instead of producing biomass via autotrophic CO₂ fixation.

Bio-photolysis of water is an attractive option for energy generation. To exploit this process as an efficient and economically viable process for H₂ production several requirements have to be met: tight coupling of PS I and hydrogenase,⁶ avoidance of the detrimental effect of the by-product O₂ on hydrogenases,¹⁹ and improvement of the natural repair system to stabilize PS II which is destroyed by light-induced reactive oxygen species.²⁸ These are the most challenging tasks for biosolar H₂ research.

Up to now, protection of H₂ formation against detrimental effects of O₂ has mostly been achieved through indirect bio-photolysis in which H₂ production is spatially or temporally separated from water-splitting photosynthesis. Spatial separation is realized, for instance in cyanobacterial cells, that differentiate into heterocysts, which can fix molecular nitrogen to ammonia.²⁷ These modified cells contain the nitrogen-fixing oxygen-sensitive enzyme nitrogenase that coproduces H₂ in a highly energy-consuming process. The system is protected against O₂ damage due to the lack of PS II and a special morphology of the host cells that guarantees a low O₂ content. Most recently a high potential H₂-producing cyanobacterium has been reported which is even

active in air, producing up to ten times more H₂ than organisms under anaerobic conditions – although not on a continuous basis.¹¹

Temporal separation of H₂ production from oxygenic photosynthesis can experimentally be achieved by anaerobic fermentation of storage compounds such as starch or glycogen accumulated during light-driven CO₂ fixation.²⁶ The most intensively studied form of indirect bio-photolysis is to grow *Chlamydomonas reinhardtii* photosynthetically, i.e. under air, and then expose the cells to a sulfur-limiting medium to decrease PS II activity.²⁹ Under these conditions, the O₂-producing water-splitting reaction is suppressed while respiration proceeds at a high rate, thereby maintaining a low O₂ concentration and allowing for H₂ production discontinuously. Reported H₂ production yields from one liter of algal culture after six days in sulfur-free medium are about 170 ml H₂ using *C. reinhardtii* wild type cells while the light conversion efficiencies are very low (up to 1.6 %).³⁰

3.3.1. Using immobilized enzymes for H₂ production

Several approaches have been initiated to accelerate the photosynthetic electron transport

by coupling the photosystems tightly with hydrogenase and to channel the bulk of electrons to proton reduction rather than CO_2 fixation (Figure 3.5). These approaches were first tested by *in vitro* assays. One device used genetic engineering to construct a protein fusion between a small stromal subunit of PS I from the cyanobacterium *Synechocystis* and the electron-transferring subunit of an O_2 -tolerant [NiFe]-hydrogenase from the aerobic bacterium *Ralstonia eutropha*. This procedure arranged PS I sufficiently close to the hydrogenase to outcompete charge recombination within PS I and direct the electron flow towards the hydrogenase. The recombinant PS I-hydrogenase hybrid complex, immobilized on a gold electrode, evolves H_2 at a fairly high rate of $3,000 \mu\text{mol mg chlorophyll}^{-1} \text{hr}^{-1}$.^{31,32}

Another attempt used a synthetic biological approach by tethering the redox cofactors of both PS I and a [FeFe]-hydrogenase through a chemically synthesized molecular wire to build a direct connection between the electron transfer chains of PS I and hydrogenase. After self-assembly of the modified proteins the complex showed light-induced H_2 evolution.³³ More recently this nano-construct could

be improved yielding an H_2 production rate of $2,200 \mu\text{mol mg chlorophyll}^{-1} \text{hr}^{-1}$, which is equivalent to $105 \text{ e}^- \text{ PS I}^{-1} \text{ s}^{-1}$.³⁴

An alternative design is focused on the immobilization of PS I and PS II using osmium polymers on gold electrodes (Figure 3.6). The photosynthetic electron transport reactions are divided into two compartments, of which one is aerobic (due to water photolysis) and the other one anaerobic as required by O_2 sensitive hydrogenases, all components can then be changed individually aiming at the design of an efficient photosynthetic cellular system. As both half-cells have already been improved considerably the system is now available for attaching various hydrogenases.³⁵

3.3.2. On the way to H_2 producing design cells

To establish an economically viable biosolar H_2 technology the efficiency of the existing cellular systems needs to be increased by a factor of about 100.³⁶ This means that 75 % of the photosynthetic energy derived from water oxidation should be channeled towards H_2 instead of forming biomass. Such an optimized system is expected to produce 250 ml H_2 per liter culture within one hour.³⁷

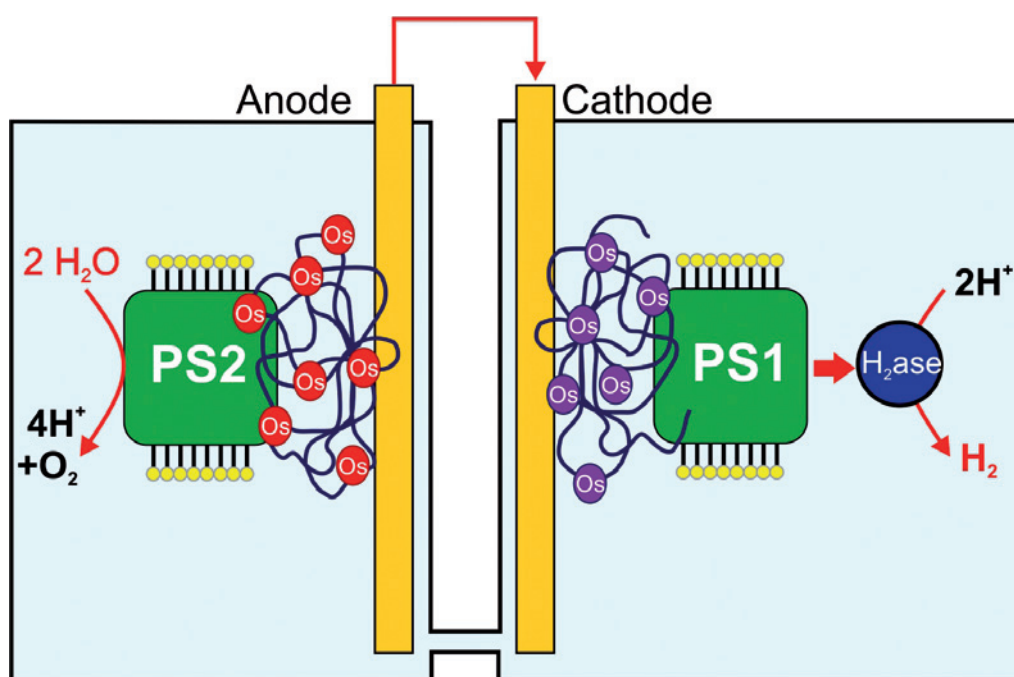


Figure 3.6: An immobilized enzymatic H_2 producing system. The “biobattery” consists of a H_2O -splitting, electron-generating aerobic compartment (left) and a H_2 -producing anaerobic compartment (right). Both photosystems are immobilized to gold electrodes via conducting osmium (Os) polymers, which have been optimized for high photocurrents. Illumination is provided by LEDs.

Two cellular targets are amenable to optimization using genetic engineering techniques. Considerable improvement has been achieved by reduction of the antenna size for decreasing the light sensitivity.³⁸ Systems employed in practice should take advantage of living cells which are capable of self-repair by replacing the D1 protein of PS II, which has a half-life of 20 minutes, by an intact possibly even more stable component.²⁸ Current research is therefore directed at: (i) Systematic screening for novel phototrophic organisms (cyanobacteria and green algae, especially marine systems) with thus far unprecedented H₂-producing capacity. However, the outcome of such an approach is difficult to estimate. (ii) Genetic engineering of existing microbes to design super H₂-producing cells taking into account the progress of scientific knowledge in this field. This approach is expected to lead to an acceleration of H₂ production rates. However, it remains elusive whether the resulting capacity can compete with other technologies. (iii) Both natural and design cells need to be cultivated more efficiently under low-operational costs. This implies the application of new materials for the construction of photo-bioreactors especially in view of the transmission of light and maintenance of homogeneous cell suspensions. Investigations on continuous cell cultivation using specifically designed flat-bed reactors are currently in progress.

3.4 Bio-inspired systems for solar water splitting and hydrogen production

“Learning from biology” means replacing enzymes by small molecular counterparts, not necessarily by analogues that mimic the structures of the active sites, but rather by “functional” analogues that conform to the same mechanistic principles, i.e. abilities to carry out multiple proton-electron transfers at potentials not too different from the thermodynamic potentials of the reactions being driven. In the long term, the new catalysts that are functional analogues of the enzyme active sites must be robust and inexpensive to produce, but at the current stage of research and development the priorities are to ascertain what is possible and identify any special principles of mechanism or synthesis that have not so far been obvious. Two examples of functional

analogues are a nickel (Ni)-based system for production and oxidation of H₂ and a cobalt (Co)-based system for photolysis of water.³⁹⁻⁴¹

Bio-inspired systems for H₂ production are still at a relatively early stage of mostly basic research, whereas research on biological H₂ production using self-reproducing photosynthetic microorganisms has been investigated for longer. The maximum solar-energy conversion efficiency is limited and a photo-bioreactor is unlikely to become a stand-alone system with low operational costs. The concept of *artificial photosynthesis* has been developed to go beyond *natural photosynthesis* by utilization of photosynthetic microorganisms (cyanobacteria, algae) for H₂ production. Researchers in this field also aim at systems for transformation of solar energy into chemical energy. However, instead of using organisms, they copy key processes of natural photosynthesis and H₂ cycling systems. In artificial photosynthesis, systems are built up from synthetic modules, without involvement of photosynthetic organisms or biomass. These modules never represent a direct copy of the photosystems and hydrogenases found in microorganisms. It is merely the function and frequently also the elemental composition and structure of the active site in proteins that is copied – never the natural protein itself. Depending on the level of similarity to the biological paragon, a synthetic module or technological system is considered to be *biomimetic* or *bio-inspired*. Crucial points that characterize a bio-inspired system (Figure 3.7) of artificial photosynthesis are:

- Energetically the overall process is driven by solar energy. The final synthesized product is not electricity but a fuel, that is, an energy-rich chemical.
- The system can cope with a fluctuating solar energy supply.
- Water is the only feedstock if molecular hydrogen (H₂) is to be produced as a fuel. For the synthesis of carbon-based fuels, both water and atmospheric carbon dioxide are used as starting material.
- Reactions proceed at “physiological” temperatures (<100 °C). Moreover extreme pressures and pH-regimes as well as aggressive solvents are largely avoided.

- For the catalytic entities, abundant first-row transition metals (V, Mn, Fe, Co, Ni) are the primary choice as in biological redox catalysis where these metals also constitute the active sites of metalloproteins. The use of rare and/or expensive elements like platinum group metals is avoided.

The light-driven transformation of H_2O into H_2 and O_2 is currently the predominant target of research in artificial photosynthesis. A basic view on the system is illustrated in Figure 3.7. Key processes to be addressed are those discussed in the previous chapter:

- The oxidation of H_2O to O_2 , which in nature is catalyzed by the Mn-Ca complex of PS II in photosynthesizing organisms (see also Chapter 3.3).
- The reduction of protons to H_2 , which in intact organisms is not facilitated by proteins of the photosynthetic apparatus but by hydrogenases, these are enzymes that can use reducing equivalents provided by PS I.
- The coupling of these two catalytic processes to the primary light reactions, where in natural photosynthesis the chlorophyll molecules of PS II and PS I are the key players.

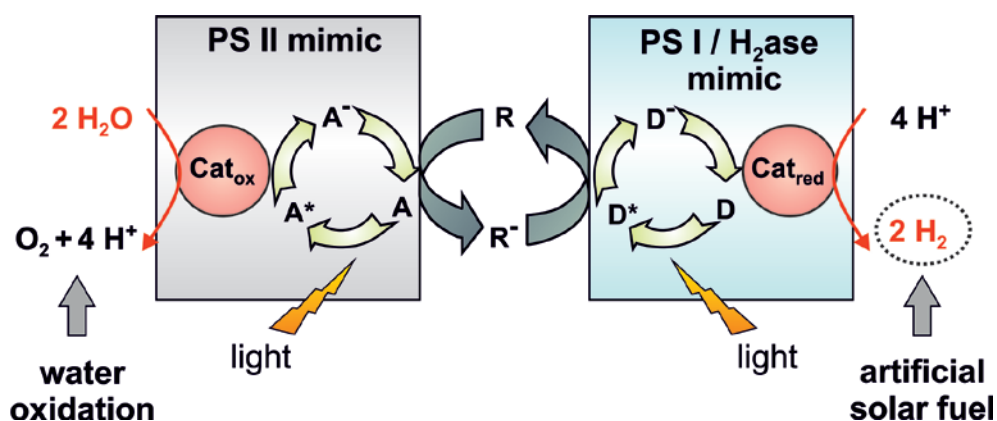


Figure 3.7: A bio-inspired system for H_2 -formation from H_2O . A, electron acceptor; D, electron donor. The gray box labeled, as 'PS II mimic' comprises the reactions for light-driven water oxidation; the box labeled, as 'PS I / H_2 ase mimic' comprises the light-driven reductive reactions resulting in the formation of H_2 . The two boxes are coupled via an electron relay R. Alternatively, electrodes may substitute for the molecular electron relay.⁴²

3.4.1. Light reactions

Coupling the catalytic processes with the primary light reactions can be addressed by employing conventional and new concepts developed in various fields of physical and chemical science. Following the natural example closely, organic or metal-organic pigments (dyes) can be used both as light-absorbing photosensitizers and primary electron acceptors (A) and donors (D) in Figure 3.7. These dye molecules have been coupled to molecular catalysts or semiconducting materials. Alternatively, semiconducting materials themselves can facilitate the primary photo-physical steps, provided that they possess a suitable band structure.^{42,43} The use of charge-transfer transitions in relatively simple, purely inorganic transition-metal compounds represents another promising route that recently came into focus.³⁹ Also other types

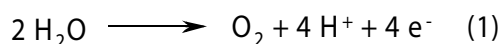
of new inorganic materials, e.g. quantum dots, may replace dye molecules as photosensitizers.

While research on artificial photosynthesis typically is aiming at the direct coupling of light reactions to the catalytic processes, electro-catalytic systems are of interest as well (Figure 3.1). Here, solar energy is first converted into electricity, e.g., by photovoltaic solar cells, and then used, in a second step, for the electro-catalysis of water oxidation and proton reduction. Again, for any large scale use of such systems it is essential that only non-rare elements are used and that the system operates efficiently under largely fluctuating irradiation conditions.

3.4.2. Water oxidation

New catalysts for water oxidation are the topic of a number of current research projects. Many of these have adopted a biomimetic approach,

aiming at copying the very efficient natural catalyst for reaction (1), the “Water Oxidizing Complex” (WOC) of PS II.⁴⁴ This enzyme is able to catalyze water oxidation at high turnover frequency and little energy loss. Moreover, in PS II this is achieved with a catalyst composed of Mn, Ca and O₂, all inexpensive and earth-abundant elements (Figure 3.3).



In recent years, progress has been made especially for two classes of WOC-mimics: oxido-bridged di-nuclear metal complexes and metal oxides. For homogeneous H₂O oxidation catalysis, a large number of complexes containing two (or more) closely linked Mn centers has been synthesized and studied in great detail. Important knowledge about both the architecture and the properties of the WOC could be gained in this way.^{44,45} However, catalysis of reaction (1) in homogeneous solution could not be reached using such Mn compounds, but only by similarly constructed di-ruthenium (Ru₂) complexes. In some cases, these Ru compounds reached very high turnover frequencies and good stability for H₂O oxidation, but the high price and low abundance of Ru leaves doubts whether such compounds will ever become affordable components of artificial photosynthetic systems.

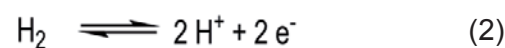
Alternatively, heterogeneous catalysts in the form of oxides could model the active site of PS II. Specific Mn and Co oxides showed promising catalytic performances and were successfully used both as catalysts in light-driven systems (Cat_{ox} in the left half of Figure 3.7) and for electro-catalytic H₂O oxidation. Reaction rates are still slow and a convincing link of the catalysts to photoreactions is so far lacking. If it were possible in the future to improve the catalytic rates of these materials, such oxides would have the potential to play a key role in solar fuel production, as they are easily prepared from both affordable and abundant raw materials. Their discovery thus marks a significant step forward, represents a real milestone in the field of artificial photosynthesis and indicates a potentially rewarding research direction.⁴⁴ The device constructed by Nocera’s group consisting of earth-abundant metals and

a cobalt-borate catalyst allows the solar-driven water-splitting reaction at efficiencies of 4.7 % for a wired configuration and 2.5 % for a wireless configuration when illuminated,⁴¹ which can compete with the basic functional elements of natural photosynthesis.

In conclusion, homogeneous (molecular) and heterogeneous (solid state) approaches are currently being pursued for the development of H₂O-oxidation catalysts. There is no clear dividing line between molecular and solid-state catalysts. The catalytically active oxides formed from first-row transition metals are highly amorphous and exhibit molecular properties. Also recently discovered all-inorganic metal complexes built up from a larger number of metal centers may be considered as an “in-between” with respect to both concepts. Key challenges for all approaches are first-and-foremost to increase the catalytic rates and catalyst stability. For the natural catalyst, nature has developed repair mechanisms to replace the protein subunit D 1 containing the WOC within the PS II enzyme (see Chapter 3.3). Given the very high oxidation potentials needed for water oxidation, it is likely that in long-term applications, also any artificial catalyst will need a mode of “healing” (or self-repair) after oxidative modifications.

3.4.3. Hydrogen formation

The reversible inter-conversion of protons and H₂ is a two-electron process, which also requires catalysts to make it practically useful.



Available technological devices, such as proton exchange membrane (PEM) electrolyzers and fuel cells, integrate rare and expensive metals such as Pt for catalysis. Except for Ni electrodes used in alkaline electrolyzers (a technology associated with strong corrosion)⁴⁶ only few noble-metal-free H₂-evolving systems are known. One of which is molybdenum disulfide, operating under pH 0 conditions with an overpotential of 0.1 – 0.2 V.⁴⁰ Interestingly, this catalyst has a structure close to that found in the H₂-evolving metalloenzyme, nitrogenase.

Again, inspiration for the development of catalysts for reaction (2) comes from nature

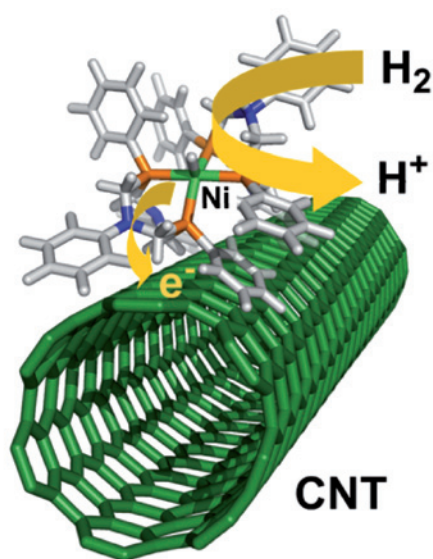


Figure 3.8: Schematic representation of the structure of the bio-inspired H_2 -evolving nickel (Ni) catalyst grafted on a carbon nanotube (CNT). The material catalyzes both H_2 production and oxidation, without overpotential requirement.⁴⁷

where a family of enzymes, the hydrogenases, catalyzes this reaction at active sites containing Fe and Ni centers (Figure 3.4). Starting from the detailed structural information on hydrogenases, a number of chemists succeeded in synthesizing bio-inspired complexes that imitate the active sites of hydrogenases.^{39,48,49} When assayed in non-aqueous solvents, some of these compounds have been shown to display remarkable catalytic properties for both, the electro-reduction of protons to H_2 or the electro-oxidation of H_2 . Alternatively, Co and Ni complexes coordinated with imine or oxime ligands also proved to be efficient and robust catalysts for H_2 -evolution at low overpotentials. Such catalysts have been successfully coupled with photosensitizers to generate light-driven H_2 -evolving systems (they act as Cat_{red} in the right half of Figure 3.7).³⁹

It was an important step forward when recently bio-inspired Ni complexes bearing anchor groups were immobilized onto carbon nanotubes (Figure 3.8).^{39,47} Carbon nanotubes were chosen for their outstanding electron conductivity and also because of their large surface area, optimal for high catalyst loading. Deposition of a thin film of these electro-active Ni-functionalized carbon nanotubes onto a

carbon substrate generated an inexpensive, stable, air-resistant cathode material with remarkable performance especially under the strongly acidic conditions required for the expanding proton exchange membrane technology. In this system, H_2 evolves from aqueous sulfuric acid solution at very low overvoltages and exceptional stability of the catalyst ($> 100,000$ turnovers). Interestingly, this Pt-free catalyst is also very efficient for the reverse reaction, H_2 oxidation under the same conditions with current densities similar to those observed for previously described hydrogenase-based materials ($1\text{--}5 \text{ mA cm}^{-2}$).³⁹ The latter property was completely unexpected from solution studies and shows how a modification of the distant environment of a metal complex, may also allow tuning of its catalytic properties. This has been the first report of a molecular-engineered and noble-metal-free electrode material that is capable of achieving H_2 evolution/oxidation with no or little overpotential. Key challenges now include the improvement of catalytic turnovers and development of new electrode materials for direct photocatalysis of H_2 production.

3.4.4. Perspectives

The concept of artificial photosynthesis offers a highly attractive perspective for sustainable production of molecular H_2 and also for fuels in general. For this concept to be implemented, the development of catalysts based on abundant, low-cost materials will be essential. Insufficient functionality and lack of robustness presently characterize molecular catalysts for homogeneous H_2O oxidation, especially the group of biomimetic Mn complexes. Degradation problems resulting from ligand oxidation may be solved by the development of new ligand systems or the employment of inorganic frameworks instead of organic ligands. Recently, there has been a wealth of new developments relating to heterogeneous water-oxidation catalysts composed of oxides of abundant transition metals (Co, Mn, Fe). These materials achieve catalysis without the need of organic ligands and are therefore highly promising candidates for the development of robust oxidation catalysts.⁵⁰

In the field of H₂-evolving catalysis, recently developed bio-inspired Fe and Ni complexes catalyze the reduction of protons at high rates. As catalyst performance could be increased substantially by the attachment of catalytic units to carbon nanotubes, well-designed nano-structures could generally result in desirable new properties of immobilized molecular catalysts. Metal oxides cannot easily be employed at the reducing potentials needed for proton reduction, but sulfides or other inorganic materials synthesized from abundant elements are of interest.

Today specific rates (per metal ion) for reactions electro-catalyzed by these new bio-inspired materials typically are by more than three orders of magnitude lower than those of the corresponding reactions in enzymes. However, taking into account the catalytic rate (or turnover frequency) per catalyst volume, com-

parable performance levels are within reach.

The development of functional components for artificial photosynthesis appears to be an especially promising concept for replacement of fossil fuels. However, all research and development activities in this area are at an early stage. The foundations for a technologically and economically viable solution are expected to arise from ongoing research on the biological systems, which still provide the basis for bio-inspired solutions. Therefore, most investigators in the field believe that currently any commitment to a specific direction of technological development might be premature; multiple alternatives are therefore currently being explored.⁵⁰ This implies that the timeframe for large-scale implementation of technological systems is highly uncertain and as a consequence neither natural nor artificial photosynthesis can contribute to short-term solutions.

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