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Photosynthetic energy conversion: hydrogen photoproduction by natural and biomimetic systems

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"I believe that water will one day be used as a fuel, because the hydrogen and oxygen which constitute it, used separately or together, will furnish an inexhaustible source of heat and light. I therefore believe that, when coal deposits are oxidized, we will heat ourselves be means of water. Water is the coal of the future"

Jules Verne, 1875

Abstract

The main function of the photosynthetic process is to capture solar energy and to store it in the form of chemical fuels. Many fuel forms such as coal, oil and gas have been intensively used and are becoming limited. Hydrogen could become an important clean fuel for the future. Among different technologies for hydrogen production, oxygenic natural and artificial photosynthesis using direct photochemistry in synthetic complexes have a great

potential to produce hydrogen as both use clean and cheap sources - water and solar energy. Photosynthetic organisms capture sunlight very efficiently and convert it into organic molecules. Artificial photosynthesis is one way to produce hydrogen from water using sunlight by employing biomimetic complexes. However, splitting of water into protons and oxygen is energetically demanding and chemically difficult. In oxygenic photosynthetic microorganisms water is splitted into electrons and protons during primary photosynthetic processes. The electrons and protons are redirected through the photosynthetic electron transport chain to the hydrogen-producing enzymes-hydrogenase or nitrogenase. By these enzymes, e^- and H^+ recombine and form gaseous hydrogen. Biohydrogen activity of hydrogenase can be very high but it is extremely sensitive to photosynthetic O_2. At the moment, the efficiency of biohydrogen production is low. However, theoretical expectations suggest that the rates of photon conversion efficiency for H_2 bioproduction can be high enough (> 10%). Our review examines the main pathways of H_2 photoproduction using photosynthetic organisms and biomimetic photosynthetic systems and focuses on developing new technologies based on the effective principles of photosynthesis.

1. Introduction

More than 3 billion years ago living organisms developed the capacity to efficiently capture solar energy and use it to power the synthesis of organic molecules. This photosynthetic process set into motion an unprecedented explosion in biological activity, allowing life to prosper and diversify on an enormous scale as witnessed by the fossil records and by the extent and diversity of living organisms on our planet today (Barber, 2007). It is estimated that photosynthesis produces more than 100 billion tons of dry biomass annually, which would be equivalent to a hundred times the weight of the total human population on our planet at the present time and equivalent to a mean annual rate of energy storage of approximately 100 TW. The success of this energy generating and storage system stems from the fact that the raw materials and energy needed to drive the synthesis of biomass are available in almost unlimited amounts, i.e. sunlight, water and carbon dioxide (Barber, 2007). Indeed, solar energy is the most abundant and accessible renewable energy source available for future sustainable production of fuel and, finally, electricity. For effective use of solar energy it is important to develop more cost-effective systems with improved ability to convert solar energy into chemical energy conserved in fuel, such as H_2. Hydrogen is one of the most promising clean fuels for the future (Abraham, 2002). The combustion of the evolved H_2 yields only H_2O and thereby completes a clean energy cycle. A variety of process technologies have been employed for H_2 production, including splitting of water by water-electrolysis, photoelectrolysis and photo-biological production. However, for all H_2 production processes there is a need for significant improvement in efficiencies, reduced capital costs, and enhanced reliability and operating flexibility (Riis et al., 2005). For instance, the photo-electrolysis is at an early stage of development and material cost and much practical issues have to be solved for application. Photo-biological H_2 production may be one of the alternatives to chemical and electrochemical technologies. Photosynthesis is a base for all biological solar-driving methods of H_2 production. Therefore, these approaches examine a link between photosynthetic efficiency, photosynthetic products and H_2 production.

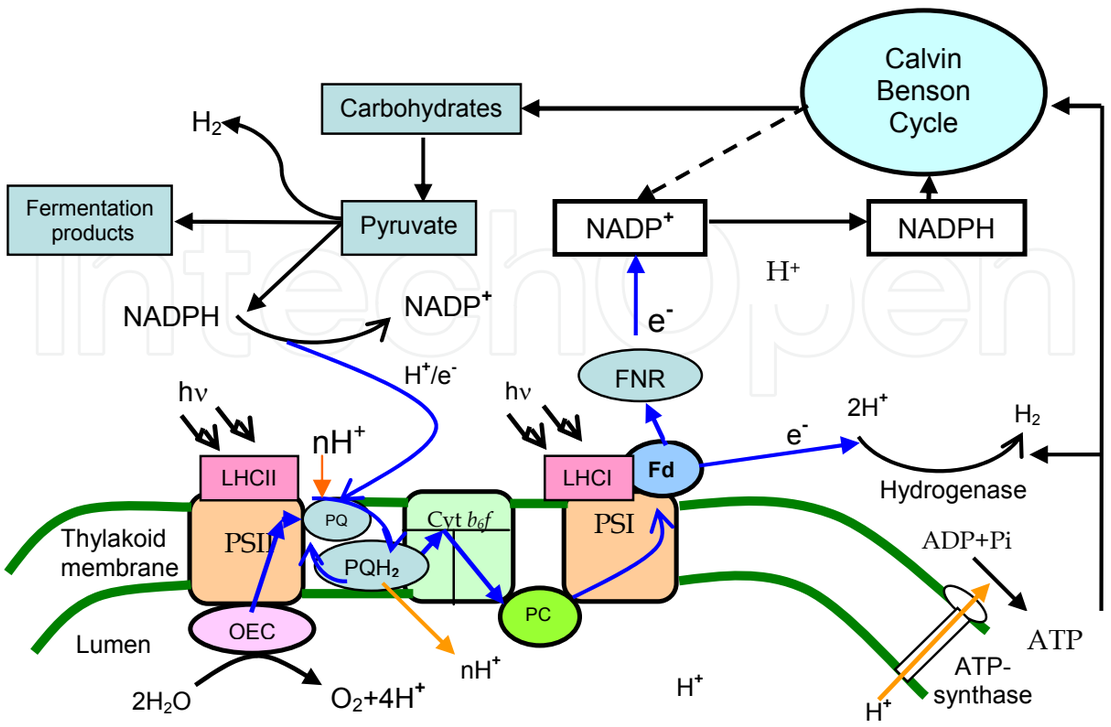

Fig. 1. The scheme of solar-powered H_2 production during oxygenic photosynthesis and subsequent formation of carbohydrates in microalgae. The oxygenic "light reactions" of photosynthesis are driven by the solar energy captured by the light-harvesting complexes of PSI and PSII. Electrons extracted from H_2O by the oxygen-evolving complex of PSII are passed along to the photosynthetic electron transport chain via plastoquinone (PQ), the cytochrome b_6f complex (Cyt b_6f), plastocyanin (PC), photosystem I (PSI), and ferredoxin (Fd), then by ferredoxin-$NADP^+$ oxidoreductase to $NADP^+$ with final production of NADPH. H^+ are released into the thylakoid lumen by PSII and the PQ/PQH_2 cycle and used for ATP production via ATP synthase. The ATP and NADPH generated during primary photosynthetic processes are consumed for CO_2 fixation in the Calvin-Benson cycle, which produces sugars and ultimately starch. Under anaerobic conditions, hydrogenase can accept electrons from reduced Fd molecules and use them to reduce protons to H_2. Certain algae under anaerobic conditions can use starch as a source of H^+ and e^- for H_2 production (via NADPH, PQ, cyt b_6f, and PSI) using the hydrogenase. In cyanobacteria the H^+ and e^- derived from H_2O can be converted to H_2 via a nitrogenase or fermentation. During fermentation process carbohydrate stores such as starch can be converted to sugars and subsequently pyruvate via glycolysis, before producing H_2 and organic acids (e.g., formate, acetate, and butyrate). Thylakoid membrane is denoted with green color. Electron transfer is shown with blue color and protons with brown color. Adapted from (refs. Blankenship, 2002; Kruse et al., 2005b; Rupprecht et al., 2006; Melis et al., 2007; Allakhverdiev et al., 2009).

Photosynthesis is based on conversion of solar energy into chemical energy by a series of electron transfer steps (Figure 1) (Blankenship, 2002; Chow, 2003; LaVan and Cha, 2006;

Allakhverdiev et al., 2009). Photosynthesis can be divided into oxygenic (O_2 producing) and anoxygenic photosynthesis (LaVan and Cha, 2006; Kruse et al., 2005a,b; Rupprecht et al., 2006; Allakhverdiev et al., 2009). Oxygenic organisms (higher plants, algae and cyanobacteria) use solar energy to extract electron and proton from water mainly for CO_2 assimilation cycle, and to produce oxygen (Figure 1) (Chow, 2003; LaVan and Cha, 2006; Kruse et al., 2005b; Allakhverdiev et al., 2009). Anoxygenic photosynthesis occurs in simpler organisms such as green sulfur and purple non-sulfur bacteria. This review focuses only on oxygenic organisms such as algae and cyanobacteria that are able to split water and evolve H_2.
All oxygenic organisms can extract electrons and protons from water and use them to reduce $NADP^+$ and plastoquinone (or form ATP) for use as energy sources for metabolic processes such as the Calvin cycle (CO_2 fixation) and other pathways. However, oxygenic phototrophs such as cyanobacteria and microalgae can transiently produce H_2 under anaerobic conditions via proton reduction, catalyzed by a hydrogenase (or nitrogenase) in competition with other intracellular processes. In this case the electrons and protons, ultimately produced by water oxidation, are redirected at the level of ferredoxin/NADPH into hydrogenase.
One attractive way to harvest solar energy is to adopt the concept of natural photosynthesis to build artificial systems for H_2 bioproduction. Artificial photosynthesis employs synthetic complexes as photosensitizers (Pn) to harvest solar energy and utilize the energy to produce hydrogen from water (Alstrum-Acevedo et al., 2005). This is an emerging field and the hydrogen generation efficiency of such man-made molecular systems is not however high enough at the moment, but encouraging for researchers.
There are some problems in this field. One or several sensitizers are required for artificial photosynthetic cell (Figure 2). Excited Pn donate electrons to the reductive site of the artificial photosynthetic system and extract electrons from the oxidative site. A catalyst that operates at a very high redox potential is needed for the water-oxidation reaction, performs a four-electron reaction so as to maximize the energetic efficiency, avoid production of reactive intermediates such as hydroxyl radicals, and mediates proton-coupled redox reactions (Figure 2).
To develop active and stable catalysts for water oxidation, it is important to use multinuclear structure, which can accumulate and delocalize four oxidizing equivalents. Di- and tetra-nuclear manganese complexes as well as mono-, di-, and tri-nuclear ruthenium complexes have been reported as molecular catalysts capable of evolving O_2 from water (Allakhverdiev et al., 1999; Yagi and Kaneko, 2001; Lomoth et al., 2006; McEvoy and Brudvig, 2006; Nagata et al., 2007, 2008). The presence of oxygen at the catalytic site for hydrogen production can inactivate or decrease the performance of the many known catalysts. Therefore, biomimetic systems have to be developed to spatially separate the catalytic centers for production of hydrogen and oxygen.
Catalysts such as Co (Hu et al., 2005; Nagasawa and Nagata, 2007) and molecules mimicking hydrogenase structure and possessing hydrogenase activity (Licheng et al., 2005; Ogo et al., 2007; Rauchfuss, 2007) are more favorable for hydrogen production. In any case, whether the devices mimicking photosynthesis are composed of natural biomolecules or organic or inorganic molecules, the architecture and spatial arrangements at multiple length scales play a crucial role (LaVan and Cha, 2006).

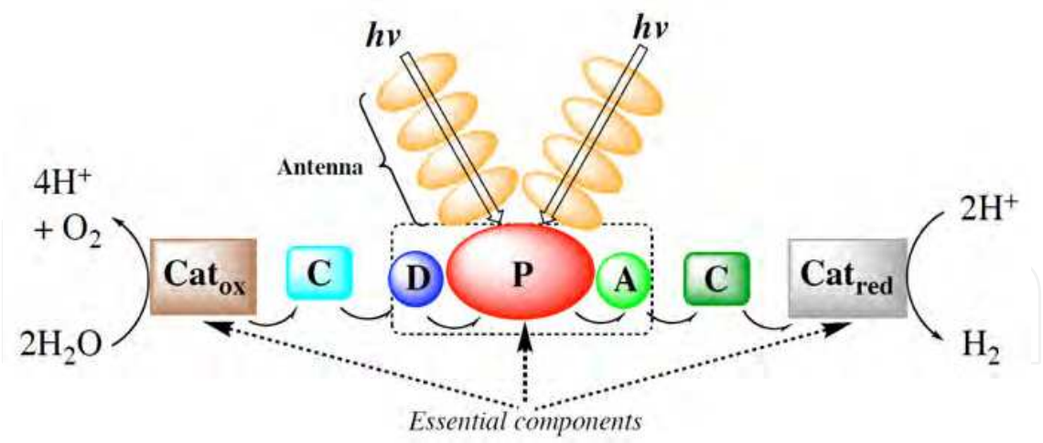

Fig. 2. The schematic view of the artificial photosynthetic system for production of hydrogen. P, photosensitizer; A, electron acceptor; D, electron donor; C, electron carrier; Cat_{ox}, catalyst for oxidation of water; Cat_{red}, catalyst for reduction of H^+.

2. Natural systems

2.1. Oxygenic organisms (cyanobacteria and microalgae)

Photosynthesis involves a sequential chain of reactions that include light absorption, charge separation, water splitting, electron transport, reduction of $NADP^+$, and creation of a proton gradient. Several major complexes are involved in the process of oxygenic photosynthesis: Photosystem II (PSII), including water oxidation complex, Photosystem I (PSI), cytochrome b_6/f, and ATP-synthase complexes (Figure 1). The detailed composition of the photosystems and electron transport intermediates from water to $NADP^+$ are described in a number of papers (see Chow, 2003; Kruse et al., 2005b; McEvoy and Brudvig, 2006; Allakhverdiev et al., 2009).

Electrons are transferred from PSII to ferredoxin (Fd) through PSI. Normally, Fd shuttles electrons to the enzyme ferredoxin-NADP-reductase that reduces $NADP^+$ to NADPH, an important source of electrons needed to convert CO_2 into carbohydrates during the Calvin-Benson cycle. Here, protons (H^+) outside the thylakoids are carried to the inner thylakoid space thus forming a proton gradient across the thylakoid membrane. Under anaerobic conditions, hydrogenase (nitrogenase) can accept electrons from reduced Fd molecules and use them to reduce protons to molecular hydrogen (H_2). In this case, the photosynthetic reducing power can partition between at least two pathways: CO_2 reduction and H_2 production. CO_2 reduction requires ATP for using reductant from water, whereas H_2 production does not use ATP, which is the desired pathway for renewable energy production.

Under normal conditions, the competition for electron donor favors the CO_2 fixation pathway. However, in the absence or limitation of CO_2, the favorable pathway is the H_2 production, which is down-regulated due to non-dissipation ΔpH caused by the lack of ATP utilization.

There are two major research challenges related to the conversion of protons and electrons by light energy into H_2. 1. The level of solar light intensities that can be efficiently utilized to drive photosynthesis should be optimized for microorganisms. 2. For hydrogenases, there

are kinetic limitations on electron transport to the hydrogenase under H_2-producing conditions. Nitrogenase uses ATP during the production of H_2, therefore, the efficiency of nitrogenase system is lesser than using the hydrogenase.

2.2. Enzymes for biohydrogen production

Terrestrial plants are not capable for the H_2 photoproduction. On the contrary, most of the microalgae and cyanobacteria are able to produce hydrogen (Boichenko et al., 2004; Dutta et al., 2005; Kruse et al., 2005b; Ghirardi et al., 1997, 2000, 2005, 2007).

Cyanobacteria uses two major types of enzymes: nitrogenases that produce H_2 contaminant with N_2 fixation, and NiFe-hydrogenases (Kruse et al., 2005ab; Rupprecht et al., 2006). Nitrogenase is not known to be present in any eukaryote, including the microalgae, whereas hydrogenases are widespread and synthesized in many of the microalgae and cyanobacteria (Ghirardi et al., 2005, 2007; Prince and Kheshgi, 2005). Nitrogenase can be used for H_2 production because it has the advantage of catalyzing the unidirectional production of H_2 in the presence of O_2, thus eliminating the need for a daily anaerobic production-harvesting cycle, although its theoretical maximum energy conversion efficiency is lower than that of hydrogenase (Sakurai and Masukawa, 2007). An additional process to inactivate the up-take hydrogenase is required for completion of the system. Cyanobacteria lacking hydrogenase activity were used in several researches of H_2 production, for instance *A. variabilis* ATCC29413 and its mutant PK84 with lost hydrogenase activity. The light-dependent H_2 production was maximum when the cultures synthesized vanadate-nitrogenase (Tsygankov, 2007; Tsygankov et al., 1997, 2002). A great attention is paid to enzymes participating in these processes occuring in chemotrophs and phototrophs. The basic methods of their isolation and activity determination are presented in details (Kondratieva and Gogotov, 1981).

Among microalgae, many unicellular green algae have the highest rates of H_2 photoproduction. In green algal cells, H_2 production reaction is catalyzed by the [FeFe]-hydrogenase enzyme, as shown by the following reaction equation: $2H^+ + 2Fd^- \rightarrow H_2 + 2Fd$. Green algal hydrogenases that belong to the class of [FeFe]-hydrogenases are involved in much higher specific activities than ones of cyanobacterial NiFe-hydrogenases (Florin et al., 2001).

Hydrogenases are oxygen-labile enzymes, which make them incompatible with the oxygen-evolving photosynthesis present in cyanobacteria. Hence, hydrogenase activity is restricted to cells with anoxic conditions. Based on our current knowledge, various strains of cyanobacteria may have no hydrogenase, only an uptake hydrogenase, only a reversible hydrogenase, or both hydrogenases. Cyanobacterial hydrogenases are Ni-Fe enzymes (Tamagnini et al., 2000, 2002). All cyanobacteria that fix nitrogen appear to have an uptake hydrogenase, whose function is to recover the electrons lost to hydrogen production by nitrogenase (Figure 3) (Tamagnini et al., 2000). The uptake hydrogenase comprises two subunits encoded by *hupS* and *hup*L. The large subunit contains the four cysteines of the active site, two of which is bridge between the Fe and Ni atoms. The small subunit has three Fe-S clusters that pass electrons from the active center to the electron acceptor in the respiratory electron transport chain, thus producing ATP and consuming oxygen, both beneficial for nitrogen fixation. In bacteria that use hydrogen as an energy source, the small subunit of hydrogenase donates electrons to another protein encoded by *hupC* or *hoxZ* that anchors the hydrogenase in the membrane and transfers the electrons to a respiratory

electron transport chain. In cyanobacteria there are no close homologs of *hup*C; thus, the anchoring protein is unknown. The uptake hydrogenase in cyanobacteria is localized on the cytoplasmic side of the cytoplasmic or thylakoid membrane (Tamagnini et al., 2002). [FeFe]-hydrogenases are quite fragile and sensitive to O_2. H_2 production is often limited mainly because of the extreme sensitive nature of hydrogenases to oxygen. A reduced O_2 sensitivity may be obtained by genetic modification of the hydrogenases. Ferredoxin, being the natural electron donor, transports the electrons to the algal [FeFe]-hydrogenase (Figure 1).
As mentioned above, electrons and protons are initially extracted from water ($2H_2O \rightarrow 4H^+ + 4e^- + O_2$) by oxygenic photosynthesis. Here, the hydrogen-producing enzymes act as a H^+/e^- release valve by recombining H^+ (from the medium) and e^- (from the reduced ferredoxin) to produce H_2. The metal clusters of hydrogenases are unique in having CO_2 and CN ligands, but they are sensitive to O_2 and CO. [NiFe]-hydrogenases and [FeFe]-hydrogenases can be inactivated by these inhibitors especially in the latter case, the inactivation by O_2 is irreversible (Ghirardi et al., 2005, 2007). The stoichiometric release of one O_2 and two molecules of H_2 is possible only under the conditions of real anaerobiosis. This is also required for the transcription of the hydrogenase gene and supporting hydrogenase activity (Kruse et al., 2005a). However, very little is known at the moment about regulation of [FeFe]-hydrogenase gene transcription and maturation (Ghirardi et al., 2005, 2007). Such issues as well as structure and function of enzymes – [NiFe]- and [FeFe]-hydrogenases, and nitrogenase are needed to be examined.

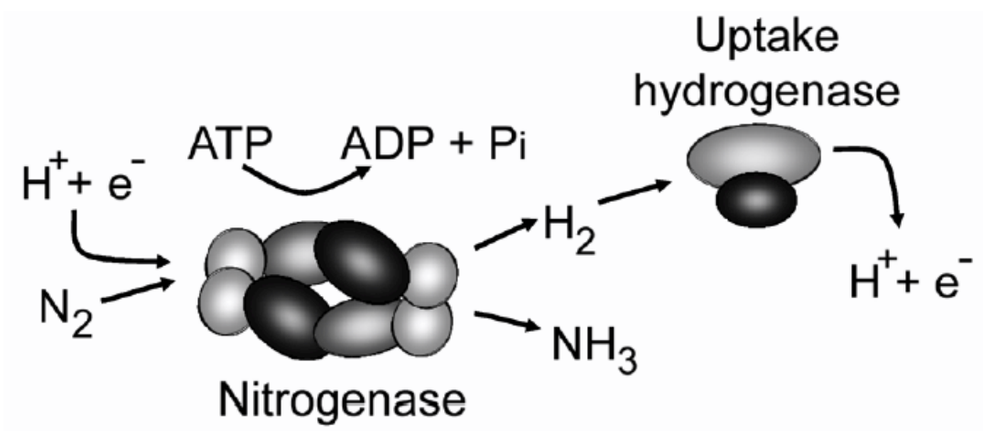

Fig. 3. Hydrogen metabolism by nitrogenase and hydrogenase. Nitrogenase comprises 3 subunits, 2 α -subunits (light gray ovals), 2 β -subunits (dark gray oval) and 4 dinitrogenase reductase subunits (light gray balls). Nitrogenase reduces N_2 to NH_3 and reduces electrons to H_2, consuming ATP. The uptake hydrogenase comprises two subunits, HupL, (the larger light gray oval) and HupS (the smaller dark gray oval), which regenerate electrons from H_2. The actual structure of HupSL has not yet been determined. Adapted from Tamagnini et al., 2002.

2.3. Pathways for H_2 production

There are several hydrogenase-dependent pathways available for H_2 production in cyanobacteria and algae (Kruse et al., 2005ab; Rupprecht et al., 2006). The first pathway is

the photo-dependent H_2, in which the electron transport occurs via two photosystems from water to Fd (Figure 1). H^+ that is released from lumen and e^- from reduced ferredoxin are used for H_2 production by hydrogenase. This is an efficient pathway in cyanobacteria, but inefficient in green algae. However, under conditions of low activity of PSII, for instance, upon sulfur deprivation, which significantly eliminates O_2, the rate of H_2 photoproduction can be significant (Melis et al., 2000; Kruse et al., 2005b).

The second pathway for H_2 production is photo-fermentative, which effectively occurs in two temporal stages. During the first stage, the photosynthetic processes produce carbohydrates, providing mitochondrial respiration and cell growth. During the second stage, under anaerobic conditions, hydrogenase expression is induced, and NADPH pumps electrons from stored reductants to the PQ pool.

PSI accepts e^- and H^+ delivered to the PQ pool, which is fully reduced under anaerobic conditions by enzymatic oxidation of intracellular reductants derived from fermentation. Mitochondrial oxidative phosphorylation is largely inhibited. The separation of photosynthetic O2-evolution and carbon accumulation from anaerobic consumption of cellular metabolites and concomitant photosynthetic H_2-evolution is crucial for increasing the efficiency of this pathway (Melis, 2007). Thus, anaerobic conditions force some H_2 producers re-route the energy stored in carbohydrates to chloroplast hydrogenase, likely, using a NADPH–PQ electron transfer mechanism, which presumably facilitates ATP production via photophosphorylation. The two stage pathway seems to be the most effective for H_2 bioproduction (Kruse et al., 2005b).

The third pathway is similar to the second, produces H_2 from water but uses nitrogenase of cyanobacteria. Here, electrons and protons are also delivered from photosynthesis. However, this pathway requires the largest numbers of photons, which results in lower efficiency in comparison with other pathways and hence, makes it economically impractical.

2.4. Oxygen sensitivity of hydrogenases

Like nitrogenases, the majority of hydrogenases are also very sensitive to O_2 (Ghirardi et al., 2000, 2007). It is an important issue, and pathways for suppressing O_2 production and improving H_2 production yield were discussed in several recent reviews (Zhang et al., 2002; Melis, 2005; Kruse et al., 2005b; Rupprecht et al., 2006; Lubitz et al., 2008; Barber, 2007, 2009; Allakhverdiev et al., 2009). Due to the fact that hydrogenases are hypersensitive to oxygen and are located in the chloroplast, where PSII releases O_2, H_2 production rate is usually low. Therefore it is important to decrease the O_2 concentration. Natural mechanisms that could be used for this are: the enhancement of respiration and chemical reduction of O_2 by PSI, and reversible inactivation of O_2 evolution in PSII (Kruse et al., 2005b; Rupprecht et al., 2006; Allakhverdiev et al., 2009). One of the approaches to decline in the rate of oxygenic photosynthesis is sulfur deprivation, which is described in earlier reviews (Ghirardi et al., 2000, 2007).

An effective pathway for generation of H_2 is the indirect biophotolysis that intends to bypass the oxygen sensitivity of the hydrogenases by separating H_2-producing reactions from the oxygen evolving ones (Ghirardi et al., 2000; Laurinavichene et al., 2002; Prince and Kheshgi, 2005). The properties and possible practical applications of hydrogenases of many phototrophic microorganisms are examined earlier in the review of Gogotov (1986) and in recent reviews (Vignais and Colbeau, 2004; Dutta et al, 2005).

2.5. Reduced antenna size and increased PQ pool

The efficiency of light utilization is one of the important factors that determine the H_2 photoproduction yield. Enhanced H_2 production may be achieved by engineering the antenna size to suppress fluorescence and heat dissipation that causes reduction in efficiency (Melis et al., 1999; Kruse et al., 2005b). Genes that regulate the Chl antenna size in the model green alga *Chlamydomonas reinhardtii* were identified and characterized (Melis, 2005). Analysis of the *tla1* and *tlaX* mutants with decreased Chl antenna size in comparison with the wild type demonstrated higher yields of photosynthesis in microalgae with a truncated Chl antenna size.

The increase of PQ pool capacity and strong proton buffer capacity can also be considered for improving light utilization since this leads to an accelerated electron transport to PSI, slows down the back reactions in the PSII, and oxidizes the reducing equivalents stored during CO_2 fixation. Besides, down regulation of competing pathways can redirect the fluxes of electrons via PSI and Fd into hydrogenases (Figure 1).

One additional point might be the regulation of PSI/PSII ratio (Kawamura et al., 1979). It is known that this ratio is variable depending on the light quality and quantity used for growth. The corresponding gene(s) that regulate(s) this ratio has(ve) not yet been identified but selective growth conditions may be favorable for H_2 production.

2.6. Immobilization of microbial cultures

The reported rates of H_2 production by sulfur-deprived cultures are still far below the maximum potential rate of H_2 photoproduction for an algal system (Ghirardi and Amos, 2004) mainly due to the partial inactivation of photosynthetic water oxidation (Laurinavichene et al., 2006). On the other hand, immobilized cyanobacteria produces H_2 at much higher volumetric rates than suspension cultures (Rao and Hall, 1996). The improved and longer-term H_2 photoproduction by immobilized green alga cells was successfully demonstrated (Zhang et al., 2002; Laurinavichene et al., 2002, 2006, 2008). It was shown that sulfur-deprived cultures of *C. reinhardtii* cells can be immobilized by inexpensive matrices and sulfur-deprivation stress can be successfully applied to immobilized algal cells.

Moreover, both natural cultures and future ideal artificial photobiodevise for H_2 photoproduction should be based on two reactions: photosynthetic water splitting to O_2 and H^+ on the donor side and the H^+ reduction on the acceptor side of PSII, using only this photosystem alone. Nevertheless in case of this approach a few problems still exist such as getting H_2 gas separately from other contaminants, first of all O_2, or the inhibition of the catalytic site of water oxidation system by molecular hydrogen. Thus, it is important to separate the processes of O_2 evolution and H_2 photoproduction. The immobilization approach may solve the problem of compartmentalization.

2.7. The use of mimics of water oxidation system

Another approach to overcome partial inactivation of photosynthetic water oxidation system leading to low efficiency and instability of H_2 photoproduction is the use of mimicks of the natural Mn-cluster. It is well known that the water oxidation complex is composed of a special tetra-manganese cluster with a composition of Mn_4CaCl_2 (Loll et al., 2005; Murray et al., 2008) which is very important in photosynthetic oxygen evolution. However, the oxygen-evolving complex of PSII is not suitable for engineering application such as H_2 photoproduction due to its limited stability.

It is believed that performing a directed molecular design and broad synthesis of different artificial metal-organic complexes with different ligands spheres and matrices that mimic the natural Mn-cluster of PSII might avoid the problems associated with low H_2 photoproduction rates and scale-up of bioreactors. Such systems would have more versatility, and might split water with sun light and produce hydrogen and oxygen, with a high efficiency and long term stability.
Many synthetic Mn complexes with different ligands have been synthesized and were examined with various degree of restoration of the original function of PSII, including oxygen evolution in Mn depleted PSII complexes (Klimov et al., 1982, 1990; Allakhverdiev et al.., 1994ab, 1999; Hotchandani et al., 1999, 2000; Nagata et al., 2007, 2008), and some of them even produced hydrogen peroxide (Nagata et al., 2007). If the protons emerging from the water oxidation complex could be captured and reduced to H_2, such reconstructed photosynthetic systems could provide interesting approaches for future developments. A further approach could be the combination of an artificial Mn-containing water oxidation complex with the hydrogenase system stabilized by inexpensive matrices.

2.8. Enhanced resistance to environmental stress conditions

To increase productivity, algal cells must be maintained in a healthy, active state during H_2 production for a long period of time. The tolerance of cell cultures to environmental stresses, first of all, to photoinhibition, salt stress and high temperatures, is necessary for sustainable photosynthesis and, hence, H_2 production (Kruse et al., 2005b; Rupprecht et al., 2006; Allakhverdiev et al., 2008, 2009). The efficiency of the recovery of PSII, from a damage induced by high light or environmental stress is one of the key factors in photosynthetic resistance (Kreslavski et al., 2007; Allakhverdiev and Murata, 2008; Allakhverdiev et al., 2008).

2.9. The use of mutants

An alternative approach for improving H_2 production in photosynthetic organisms is the systematic genetic screening for mutants with an increased ability for effective production of H_2. Genetic engineering has shown significant promise for increasing H_2 production both in algae and cyanobacteria (Kruse et al., 2005b; Melis, 2005, 2007; Prince and Kheshgi, 2005; Ghirardi et al., 2007; Sakurai and Masukawa, 2007).
Molecular engineering that tunes the algal hydrogenase enzyme insensitive to the presence of O_2 was suggested (Ghirardi et al., 2005, 2007). Besides, replacing the algal hydrogenase with strong oxygen tolerant, or at least reversibly inactivated, bacterial enzyme may be possible (Jones et al., 2003).
It is difficult to judge, which organisms comprise the most promising systems for H_2 production. The NiFe-hydrogenases of cyanobacteria have an advantage compared to Fe-hydrogenases of algae: they have much higher tolerance to O_2 and are resistant to various unfavorable environments (Ghirardi et al., 1997). On the other hand, algal hydrogenases can reach very high specific activities that are much higher that those of cyanobacterial hydrogenases but they are very oxygen sensitive (Ghirardi et al., 2007).
Therefore it is important to develop strategies for reducing the O_2 sensitivity. For example, it is possible to engineer an algal [FeFe]-hydrogenase resistant to O_2 inactivation or introduce a gene encoding for a [NiFe]-hydrogenase with increased resistance into photosynthetic

cyanobacterial cells. The processes of H_2 photoproduction based on using cyanobacteria and other cell cultures demonstrated relatively low conversion efficiencies (Riis et al., 2005).
Besides, as mentioned, H_2 production can be improved with mutants having a reduced antenna size that decreases heat losses and fluorescence (Melis et al., 1999; Melis, 2005) and effectively redirect H^+ and electron fluxes to their corresponding H_2-producing enzymes (Figure 1). The theory predicts that a solar light to H_2 photon conversion efficiency of 10% can be reached (Kruse et al., 2005b).
Biodiversity in cyanobacterial species is well known, therefore it is not rare to find organisms that show unique properties. In terms of H_2 production, the Chl *d*-dominated cyanobacterium, *Acaryochloris marina*, can be an interesting target. This organism contains a *hypABCDEF* gene for a full complement of bidirectional hydrogenase subunits on a plasmid (pREB4) (Swingley et al. 2007). Due to the red-shifted absorption maximum of Chl *d,* this organism can utilize the light up to a near infra-red region. Due to the unique redox potentials of its electron transfer components in photosynthesis (Tomo et al., 2007, 2008) this species might be referred to as a natural mutant in this aspect.

2.10. Role of photosystems in H_2 photoproduction

Besides the activity of PSI, at least some activity of PSII is required to sustain the H_2-photoproduction. This is in line with recent observations obtained with the use of inhibitors (Kosourov et al., 2003). This last study indicated that the vast majority of the electrons driving H_2 production originates from water oxidation. The effect of progressive impairment of PSII photochemical activity in sulfur-deprived *C. reinhardtii* D1-R323 also demonstrated the progressive decrease in O_2-evolution (Makarova et al., 2007). The mutants exhibited lower H_2 yield compared to the wild type.
An interesting problem is the direct evolution of H_2 by PSII. Earlier studies have shown that H_2 can be produced from PSII under certain conditions, both in mutants lacking PSI (Boichenko et al., 1986), and in preparations of PSII (Mal`tsev et al., 1988). The wild type and mutants, lacking PSII, of green alga of *Chlamydomonas reinhardtii,* produced H_2 with high enough efficiency, but the mutant lacking PSI demonstrated low efficiency in H_2 evolution (Boichenko et al., 1986). Conversely, subchloroplast preparations enriched in PSII in the presence of the electron donor TMPD exhibited higher H_2-evolution rates (up to 30 nmol/mg Chl per h) than preparations enriched in PSI under the same conditions (Mal`tsev et al., 1988). Interestingly, $H_2$ photoproduction was stimulated by 10-fold after the removal of manganese (by tris-treatment) from PSII and this reaction was suppressed by DCMU (5 μM), dinoseb (10 μM), atrazine (10 μM) *o*-phenanthroline (10 μM) or CO (0.4%) (Mal`tsev et al., 1988). The data on the suppression of H_2 evolution by well-known inhibitors of PSII (DCMU, dinoseb, atrazine) prove that the H_2 photoproduction is sensitized by the reaction center of PSII. Moreover, it has been shown that the mid-point redox-potential of the intermediate electron acceptor of PSII, pheophytin (Pheo), is –0.61 V (Klimov et al., 1979). Theoretically, this potential is sufficient to allow PSII to photoreduce electron acceptors with redox-potential ca. –0.4 V (ferredoxin, $NADP^+$, methylviologen, benzylviologen, NO_2^-, NO_3^-, SO_4^{2-}, etc.) typical for PSI, and photoreduction of H_2 (–0.42V) (Allakhverdiev and Klimov, 1992).
These results demonstrate that theoretically, isolated PSII can produce H_2 under sun light. However, the detailed characterization and application of this unique approach of H_2 photoproduction by PSII should be a subject of research in the near future.

3. H_2 photoproduction in artificial systems

3.1. Principles and molecular units for artificial photosynthetic systems

Production of hydrogen from water by use of solar light energy is an important technology for hydrogen economy. Although there are many approaches towards this goal, we focus here on the "biomimetic" approach based on the mechanism of natural photosynthesis.

Figure 2 shows the conceptual overview of an artificial photosynthetic system that produces H_2 from water. The minimal system consists of three components: photosensitizer (P), oxidation catalyst (Cat_{ox}) and reduction catalyst (Cat_{red}). The photosensitizer is required to produce the photo-excited state that initiates electron transport. Cat_{ox} oxidizes water to O_2, and Cat_{red} reduces H^+ to H_2. At present, however, no artificial systems that contain all three components have been reported. This is mainly due to the difficulty for two redox (reduction/oxidation) catalysts with opposite functions to cooperate within a single system. These catalytic sites should be spatially separated to avoid undesirable interference of each other, which presents a great challenge in the molecular architecture. In practice, the present researches focus on either of the "half" reactions, that is, formation of O_2 or H_2 by use of sacrificial electron acceptor or donors. Systems having both oxidation and reduction sites will be the subject for future study.

In addition to these "minimal" components, an artificial photosynthetic system can have other components with different functions, which are also shown in Figure 2. The light-harvesting antenna molecules will capture the incoming light and deliver the excitation energy to the photosensitizer. The donor (D) and acceptor (A) molecules will give/receive electrons to/from the excited photosensitizer. Owing to the short lifetime of the excited states, these molecules should be located in the vicinity of the photosensitier, as is seen in the natural photosynthetic reaction centers.

Electron carriers (C) will transport electrons from the acceptors (A) to the reductive catalytic site, or from the oxidative catalytic site to the donors (D). These "carriers" act as a temporary storage of electrons, or an electron "buffer", between the photophysical and photochemical parts of the system. This feature will allow the asynchronous operation of the photoinduced electron transfer and the electrocatalytic chemistry.

In the following part, we will discuss each of these functional components. Since we are particularly interested in H_2 production, we will first discuss Cat_{red}, which is responsible for production of H_2 from H^+. Other functional components are described later, with special emphasis on biomimetic standpoints.

3.2. Catalysts for H_2 production

Catalysts for conversion of H^+ into H_2 (or vice versa) will play a key role, not only in artificial photosynthesis, but also for the hydrogen economy in general (Crabtree, 2004). Many essential technologies for hydrogen economy, including fuel cells, storage, and production, depend heavily on the efficiency of H^+/H_2 catalysts, so that the quest for better catalysts is getting more intensive these days.

The platinum metal is the most classical, and still the most efficient, catalyst for hydrogen evolution (Wohrle et al., 2003). It has almost ideal properties required for reduction of H^+ to H_2; low overpotential, high reaction rate, good electron capacity and conductivity, and high chemical and mechanical stability. As such, Pt metal is often the best choice both for laboratory research and for practical applications. However, as the needs for catalysts grow

rapidly, the high cost and limited quantity are the major issues. In order to address this problem, many researchers are actively seeking for reasonable alternatives to Pt metal catalyst.

Particularly interesting from the biomimetic viewpoint are the efforts in the field of coordination chemistry (Koelle, 1992). The known H_2 catalysts based on coordination compounds can be classified roughly into three categories; those based on precious metals (Pt, Rh, Ir), on common metals (Co, Ni, Fe), and those related to (and/or inspired by) the natural enzyme hydrogenase. Since the enzyme hydrogenases use Fe and Ni in the active centers, there are significant overlaps in the latter two categories. Nevertheless, such classification will be beneficial for us to get a quick overview of this fast-growing research area.

3.3. H_2 catalysts with precious metals

In early studies of H_2 production, rhodium(III) polypyridine complexes such as $[Rh(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine) were used as electron carriers together with Pt metal catalysts (Lehn and Sauvage, 1977; Brown et al., 1979a), but later it was found that these complexes were capable of generating hydrogen without Pt (Chou et al, 1982). In this system, a four-coordinate Rh(I) complex $[Rh(bpy)_2]^{+}$ was produced during the course of the reaction (via two-electron reduction of the Rh(III) complex and subsequent departure of one bipyridine ligand), and the rhodium-hydride species such as $[Rh(bpy)_2H]^{2+}$ is the likely intermediate for the hydrogen production. Rhodium porphyrins are also known to catalyze electrochemical generation of H_2 (Lexa et al., 1997). Iridium(III) complexes have also been used for photoproduction of H_2 (Goldsmith et al, 2005). However, in this system the iridium complexes mainly act as the photosensitizers, and the true catalysts for production of hydrogen may be the cobalt complex (used as an electron relay) rather than the iridium complexes.

From the synthetic point of view, one of the advantages of these precious metal complexes is the robustness of the metal-ligand bonds, so that sophisticated compounds with different functional groups can be prepared. One interesting approach is to combine the photosensitizer and catalyst for hydrogen evolution in one molecule; the first successful example of such "combined" photocatalyst was based on Pt for hydrogen evolution and Ru as photosensitizer (Ozawa et al., 2006). Covalent assembly of Rh center and Ru photosensitizer was also prepared, and gave good performance of rhodium-based photoproduction of H_2 (Arachchige et al., 2008; Elvington et al., 2007).

Unfortunately, these precious metal catalysts share with Pt catalyst the problem of high cost and limited availability; both Rh and Ir are even less abundant than Pt in earth crust. Although these catalysts are quite interesting from the viewpoint of coordination chemistry, it is not likely that these catalysts will become of practical importance in real world applications, unless some compounds with extremely high activity are discovered.

3.4. H_2 catalysts with common metals

Among the less precious metals in the first-row transition metal series, iron (Fe), cobalt (Co) and nickel (Ni) have shown promising results as H_2 catalysts. Complexes of cobalt, like its congener rhodium, are often used as electron carriers in photochemical H_2 producing systems (Brown et al., 1979b), but they are also useful for production of H_2 (Kellet and Spiro,

1985ab; Connolly and Espenson, 1986). Although the reaction mechanism has not yet been fully clarified, it is generally accepted that Co(III)-hydride complexes are crucial intermediates (Koelle and Paul, 1986). A BF_2-bridged diglyoxime Co complex produces H_2 electrochemically at potentials of –0.28 V vs. SCE, which presents one of the smallest overpotentials reported for complex catalysts (Figure 4) (Hu et al., 2005). Covalent assembly of ruthenium photosensitizer and cobalt complex is also reported (Fihri et al., 2008).

Fe and Ni are particularly interesting because of their presence in the hydrogenase enzymes. Fe is also attractive because of its high abundance and low cost. Macrocyclic complexes of iron (Bhugun et al., 1996) and nickel (James et al., 1996) have been used for photochemical or electrocatalytic H_2 production. Although the active center of hydrogenase is dinuclear, a simple mononuclear Fe(I) complex can sometimes be active for H_2 production (Kayal and Rauchfuss, 2003).

In comparison with the precious metals, the difficulty of handling coordination compounds of first-row transition metals lies in their high susceptibility towards ligand exchange, particularly in aqueous solutions. This is generally due to the weaker metal-to-ligand bonds of these metals than the second- and third-row transition metals. Such characteristics, however, can also provide advantages when catalytic reactions are concerned, because weaker bonds may lead to smaller activation energies (and thus faster reactions). To utilize the inherent power of these elements, it is definitely necessary to design the coordination environment carefully, thereby improving the stability and controlling the reactivity. This is exactly what the natural enzymes do, so that it is worthwhile to see what structural features are found in the enzymes that catalyze hydrogen production (see below).

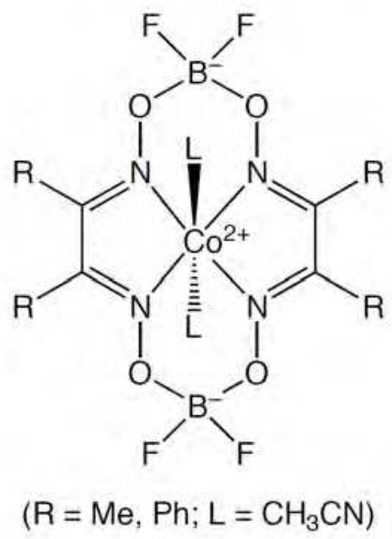

Fig. 4. The cobalt complex that produces hydrogen with small overpotential (Hu et al., 2005).

3.5. Hydrogenase and related synthetic compounds

A hydrogenase is an enzyme which presents in some anaerobic organisms, and catalyzes reversible conversion between H_2 and H^+. In the active center of a hydrogenase enzyme, there are two metal ions (FeFe or NiFe) that cooperate during the catalytic cycle for

production (and consumption) of H_2. Recently much progress was made in researches on the structures and function of the hydrogenases by X-ray analysis, spectroscopic techniques, theoretical methods, and model studies (Artero and Fontecave, 2005; Peters et al., 1998). The schematic view of the active centers of two types of hydrogenases is shown in Figure 5.

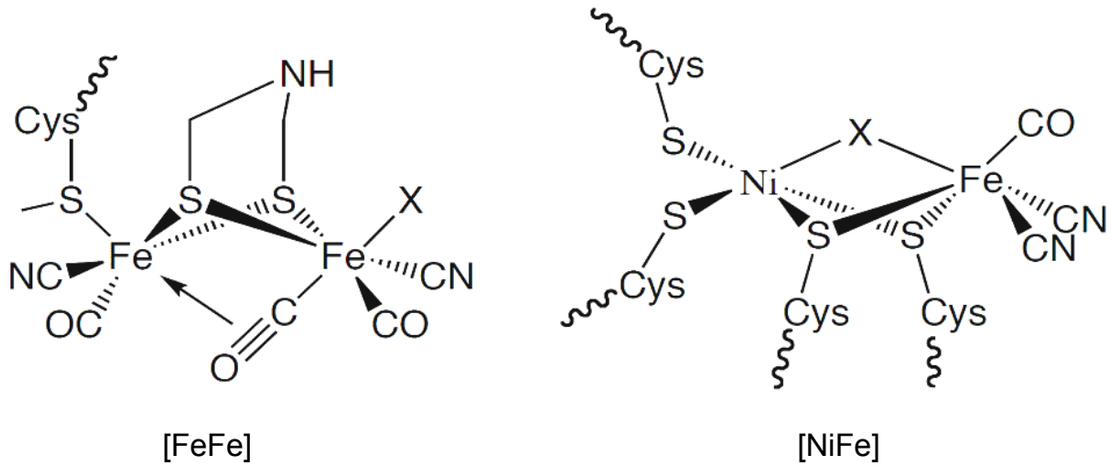

Fig. 5. The active centers of [FeFe] hydrogenase (left) and [NiFe] hydrogenase (right).

As for the synthetic model studies, much attention has been focused on the active sites of the Fe-only hydrogenases, which consist of a bimetallic iron center bridged with a dithiolate, terminal thiolate ligands and CO/CN auxiliary ligands (Rauchfuss, 2004, 2007; Tard et al., 2005). On the other hand, the syntheses of the models of [NiFe]-hydrogenases have been more challenging. By use of Ru in place of Fe (Ru is electronically similar to but more robust than Fe), a Ni-Ru complex with a bridging hydride ligand was successfully isolated (Ogo et al., 2007).

The Fe-only hydrogenases catalyze the reduction of protons to dihydrogen with almost zero overpotential (Holm et al., 1996). On the other hand, the synthetic model compounds still require large negative over-potentials (–0.4 to –1.4 V) (Tard et al., 2005; Gloaguen et al., 2001, 2002; Borg et al., 2004). There are theoretical studies to clarify the detailed mechanism of hydrogenase (Bruschi et al., 2004; Siegbahn, 2004), and zero overpotential of hydrogenase is claimed to be reproducible by computation (Norskov and Christensen, 2006). Such attempts will be helpful for designing new catalysts with better performance (Hinnermann et al., 2005; Norskov et al., 2005).

4. Other Components of Artificial Photosynthesis

4.1. Overview

While the H_2 producing catalysts are the crucial components for photoproduction of hydrogen, there are other important components as well. Obviously the most important is the photosensitizer, which converts light energy into chemical energy. The photosensitizers in photosynthesis (natural or biomimetic) are molecules that acquire light and cause photoinduced charge separation between nearby donor or acceptor molecules. This is in contrast with the semiconductor systems (e.g. solar cells), where the photoinduced charge

separation takes place between the valence and conduction bands of the semiconductor. An interesting hybrid between these systems is dye-sensitized solar cells (O'Regan and Grätzel, 1991), in which inorganic semiconductors act as the electron acceptor from the excited photosensitizers.

For photoinduced charge separation to take place efficiently, it is important that the donors and acceptors are located within short distances from the photosensitizers. This is actually the case in all resolved structures of natural photosynthetic reaction centers (Deisenhofer and Michel, 1989; Jordan et al., 2001; Zouni et al., 2001; Loll et al., 2005; Barber and Murray, 2008). In many artificial systems, donors and acceptors are simply put within the solution containing the photosensitizers, so that the efficiency of the photoinduced electron transfer depends on the random diffusion of these molecules. It is a great challenge for chemists to build the multi-component systems that are specifically designed for photoinduced electron transfer; in fact, many organic chemists were so much attracted in this subject that great progress has been achieved in the area of electron transport (Wasielewski, 2006). However, application of these sophisticated systems for redox chemical conversions is yet to be explored.

The antenna complexes, which collect light energy and transport to the photosensitizer, are also crucial components for efficient use of incident light (Kühlbrandt et al., 1994). In natural photosynthetic reaction centers, the quantum efficiency is very high because of the carefully designed molecular architecture, however the optical density of the reaction centers is very low because only one pigment in the huge reaction center complex is photoactive towards photosynthetic reactions. Antenna complexes have high optical density in the wide range of visible spectral region, and funnel the excitation energy towards the photoactive pigment in the reaction center.

The electrons for reduction of H^+ must come from somewhere. In many photochemical systems that produce hydrogen, sacrificial donors such as ethylenediaminetetraacetic acid (EDTA) or triethanolamine (TEOA) are used. Apparently, these cannot be practical sources of hydrogen because of their high cost. The ideal source of electrons is water, which is abundant and produces only dioxygen as the byproduct. Consequently, synthetic oxygen-evolving complexes are under active study (Sala et al., 2009). Another interesting approach from the biomimetic viewpoint is to follow the evolutional pathway of natural photosynthetic organisms. Before the appearance of oxygen evolving center, old photosynthetic organisms utilized other substances such as H_2S and alcohols as electron donor. In this context, there are reports of biomimetic photosynthetic systems that utilize thiols and alcohols as electron donors (Nagata and Kikuzawa, 2007; Nagasawa et al., 2009).

4.2. Photosensitizers

The most successful photosensitizers in artificial photosynthetic systems are ruthenium polypyridyl complexes. Photoproduction of H_2 by use of $Ru(bpy)_3^{2+}$ as the photosensitizer was reported as early as 1978 (Moradpour et al., 1978). The big advantage of the ruthenium complexes as the photosensitizers is their long lifetimes of the excited MLCT states (870 μs in CH_3CN) (Jones and Fox, 1994). The strong absorption band in the visible region is also advantageous. Moreover, from the viewpoint of synthetic chemistry, the relatively slow rates of ligand exchange on the ruthenium center is beneficial for constructing elaborated multinuclear structures, as demonstrated by recent examples of "multinuclear molecular devices" for photoproduction of H_2 (Sakai and Ozawa, 2007).

Clear disadvantage of ruthenium complexes is the cost of the element. In this respect, better alternatives are the pigments that are purely organic or organic with some common metals. Inspired by the natural photosynthesis, chlorophylls and porphyrins were used for photoproduction of H_2 (Ngweniform et al., 2007; Amao and Okura, 2002). The weak points of the organic pigments are poor long-term stability and low quantum efficiency. In order to overcome these problems, we may learn from natural photosynthesis and introduce mechanisms of light-protection and/or high efficiency electron transports.

4.3. Donors, acceptors, and electron carriers

Various electron donors and acceptors were examined during the course of mimicking the primary events of photosynthesis (Wasielewski, 2006), but only a few are used in relation to photoproduction of H_2. Early studies use EDTA as the sacrificial donor and viologens as the acceptor (Moradpour et al., 1978). The viologens were also used as electron carriers that transport electrons to the reductive catalytic site. Covalent connections of viologens and photosensitizers were examined with promising results (Amao and Okura, 2002). Natural photosynthesis uses quinones for both the terminal acceptor in the photosystems and the electron carrier in the form of PQ pool. However, it is only recently that the function of the PQ pool was mimicked by use of synthetic molecules (Nagata and Kikuzawa, 2007).
Because of the inherent kinetic mismatch between the (fast) photoinduced electron transfer and (slow) electrochemical processes, it is important to select appropriate use of the electron carriers for successful photoproduction of H_2. Apparently, there are plenty of rooms for improvement in this particular area of artificial photosynthesis.

4.4. Antennas

In spite of the apparent structural complexity of the natural photosynthetic antennas, the synthetic models of photosynthetic antenna have been quite successful. This is partly because the excitation energy transfer by the Förster mechanism (Förster, 1948) has relatively mild dependence on interchromophore distances ($1/r^6$) in contrast with the case in electron transfer (exponential), so that the geometries of the chromophores need not be so rigorously controlled. Self-aggregation of amphiphilic chlorophyll analogues leads to spontaneous formation of artificial antenna (Prokhorenko et al., 2002). As for covalently bonded systems, dendritic molecules can effectively collect excitation energy, which can be used for production of H_2 (Sakamoto et al., 2001). One unique approach is to use a π-conjugated polymer embedded in dendrimer-based protecting shield (Jiang et al., 2004). The polymer acts both as the light absorber (photosensitizer) with a large absorption cross section and as the molecular wire (antenna) that transports the excitation energy to the reactive site.

4.5. Catalysts for water oxidation

The catalyst at the oxidizing side, which performs 4-electron oxidation of water to O_2, is arguably the most difficult part in artificial photosynthesis (Herrero et al., 2008). Although there have been many research works on electrochemical and photochemical production of O_2 from water (Eisenberg and Gray, 2008), it should be stated that all approaches are currently still at the developmental stage.

The natural oxygenic photosynthesis may provide hints to tackle this problem. The oxygen-evolving complex contains four manganese ions and one calcium ion (Barber and Murray, 2008). Although the detail mechanism is still under intense investigation (McEvoy and Brudvig, 2006), it is certain that these metal ions should play central roles during O_2 production.
Along this idea, multinuclear complexes that can accumulate and delocalize four oxidizing equivalents have been developed as functional models of oxygen-evolving complex. Di- and tetranuclear manganese complexes, especially a family of metal-oxo "cubane' complexes as well as mono-, di-, and trinuclear ruthenium complexes have been reported as molecular catalysts capable of evolving O_2 from water (Naruta et al., 1994; Wada et al., 2000; Carrell et al., 2002; Wu et al., 2006). Some of these complexes undergo photocatalytic oxidation of water via direct action of light into the metal core (Brimblecombe et al., 2008).

To summarize, research in artificial biomimetic photosynthesis is in its early stage and has not yet reached to the state that production of integrated and practical systems is feasible. Nevertheless, there has been significant progress in all important aspects in this area. Towards the future, there should be continuous efforts in the development of synthetic catalysts for H_2/O_2 production, photochemical conversion apparatus for controlled electron transfer, and light-harvesting units. Even more important is to integrate these components into functional assemblies, which is likely to be realized with the aid of profound understanding of the structural/functional features of biological systems.

5. Conclusion

Both the natural and biomimetic photosynthetic processes are efficient and cost-effective for water splitting, and H_2 formation. The actual photo-production of hydrogen will have to be carried out in a sealed photobioreactor, and also requires careful reactor designs (Tsygankov et al., 2002) for the substantial improvements of hydrogen production rates and yields. A prerequisite challenge is to improve current systems at the biochemical level so that they can clearly generate hydrogen at a rate and approach the 10% energy efficiency, which has been already surpassed in photoelectrical systems (Shah et al., 1999; Gratzel, 2001).
Currently and in near future, researchers could focus on increasing the O_2-tolerance of [FeFe]-hydrogenases and the use of immobilized microbial cultures to reach this target, as these methods are promising. Reduced antenna size and increased PQ pool, decreased PSI cyclic electron transport as well as enhanced resistance to environmental stress conditions should be considered for the improvement of photohydrogen production. These studies will guide further molecular engineering research aimed at improving the efficiency of hydrogen bioproduction. Thus, research is also needed to understand the diversity and capacity of natural hydrogen production systems and optimize their utilization in H_2 production processes.

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Abbreviations

AP, artificial photosynthesis; DCMU, 3-(3′,4′-dichlorophenyl)-1,1-dimethylurea; Fd, ferredoxin; PQ, plastoquinone; PSII, photosystem II; PSI, photosystem I; TMPD, N,N,N′,N′-tetramethyl-p-phenylenediamine.

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Nature's evolution has led to the introduction of highly efficient biological mechanisms. Imitating these mechanisms offers an enormous potential for the improvement of our day to day life. Ideally, by bio-inspiration we can get a better view of nature's capability while studying its models and adapting it for our benefit. This book takes us into the interesting world of biomimetics and describes various arenas where the technology is applied. The 25 chapters covered in this book disclose recent advances and new ideas in promoting the mechanism and applications of biomimetics.

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