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Artificial photosynthesis: biomimetic approaches to solar energy conversion and storage

K Kalyanasundaram and M Graetzel

Using sun as the energy source, natural photosynthesis carries out a number of useful reactions such as oxidation of water to molecular oxygen and fixation of CO_2 in the form of sugars. These are achieved through a series of light-induced multi-electron-transfer reactions involving chlorophylls in a special arrangement and several other species including specific enzymes. Artificial photosynthesis attempts to reconstruct these key processes in simpler model systems such that solar energy and abundant natural resources can be used to generate high energy fuels and restrict the amount of CO_2 in the atmosphere. Details of few model catalytic systems that lead to clean oxidation of water to H_2 and O_2, photoelectrochemical solar cells for the direct conversion of sunlight to electricity, solar cells for total decomposition of water and catalytic systems for fixation of CO_2 to fuels such as methanol and methane are reviewed here.

Address
Laboratoire de Photonique et Interfaces (LPI), Ecole Polytechnique
Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Corresponding authors: Kalyanasundaram, K
(k.kalyanasundaram@epfl.ch) and Graetzel, M
(michael.graetzel@epfl.ch)

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Introduction

Natural photosynthesis is an amazing machinery perfected by mother nature over many centuries. It is the process by which plants, some bacteria, and some protistas use sunlight as the energy source, CO_2 of the atmosphere, and water as chemicals to carry out two important reactions required for survival and growth of humanity: decomposition of water to molecular oxygen, accompanied by reduction of CO_2 to carbohydrates and other carbon-rich products [1–4]:

$$6H_2O + 6CO_2\,(\text{sunlight}) \rightarrow C_6H_{12}O_6 + 6O_2 \qquad (1)$$

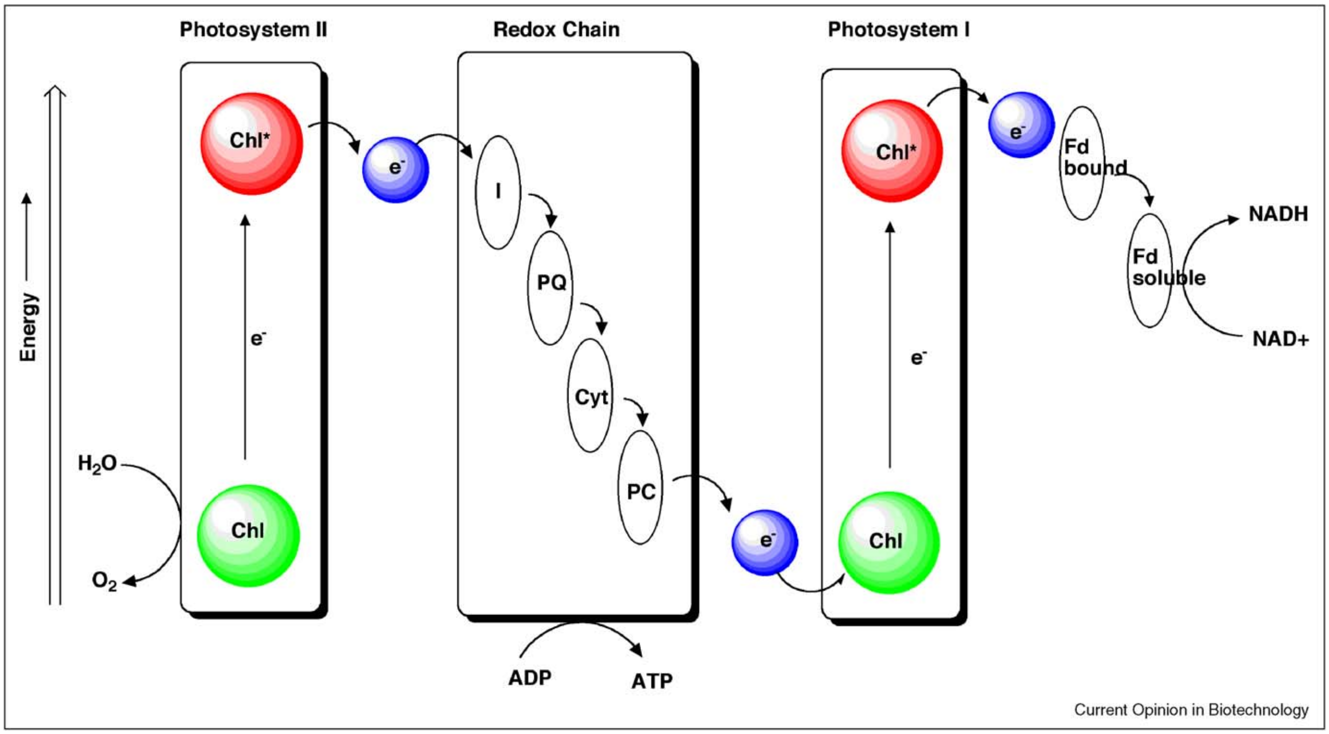
Large scale burning of fossil fuels and extensive pollution arising from industrialization have upset the natural balance of CO_2 levels in the atmosphere. Significant absorption of the infra-red part of the solar radiation and longevity of atmospheric CO_2 are causing the green house effect. The two biggest challenges facing mankind in the 21st century are the increasing global demand for energy (since fossil fuel reserves are getting fast depleted) and control of the level of CO_2 emission regulating the green house effect (level of CO_2 emission). Emphasis is therefore on the development of alternative or additional energy sources via renewable energy pathways ensuring environmental protection and harmony.

In energy terms the solar radiation reaching the earth's surface every day is phenomenal, in the range of terawatts. If we can convert and store even a few percent of this abundant and free resource, our energy needs will be met. Since sunlight is available only for a limited time during the day, it has to be converted and stored for use. Two major approaches are taken for the photochemical conversion and storage of solar energy: direct conversion of solar energy to 'electricity' which then can be used for various needs or go for direct generation of high energy fuels such as molecular hydrogen from water. *Artificial Photosynthesis* is a biomimetic approach [5–7] wherein the important structural elements and reaction features of '*natural photosynthesis*' are used in conceptually simpler systems to achieve results of natural photosynthesis. Since the solar energy conversion efficiency of natural photosynthesis is only a few percent, hope is to do better with artitificial systems. Different approaches are being explored by chemists worldwide and breakthroughs have been obtained in some key areas. Here we shall review some of the recent and exciting developments in the area of artificial photosynthesis.

Features of natural photosynthesis

It is useful to start with a review of some of the key elements and processes of natural photosynthesis that are to be reproduced functionally. Figure 1 shows schematically all the key processes that we shall be concerned with. Photosynthesis reactions occur in two distinct stages. Light absorption by chlorophyll followed by a series of electron-transfer reactions constitutes the 'light-induced reactions' part. Water oxidation to molecular oxygen is an important process in the 'photosystem II' reactions. The electrons are taken through a series of uphill and downhill steps to generate energy-rich intermediates in the part known as 'photosystem I' reactions. Subsequently a series of light-independent ('dark') reactions occur where the products of the light-induced

Figure 1



Schematic presentation of the key components and processes of natural photosynthesis.

reactions (ATP and NADPH) are used to form C–C covalent bonds of carbohydrates. Artificial photosynthetic systems can stop at several intermediate steps, for example, with formation of H_2 or can include reduction of CO_2 to carbon-based fuels (methanol, methane, formate). Hydrogen is a key solar fuel because it permits energy storage and can be used directly in combustion engines or fuel cells.

Chlorophyll molecules and other reactants taking part in the absorption of sunlight ('antenna') and electron-transfer processes ('reaction center') are organized in special assemblies called 'thylakoids'. How various components of photosynthesis are organized at the microscopic level is very important for the whole sequence of reactions to take place with good efficiency. We shall now review each of the key steps and see how they can be reproduced in artificial systems.

To use the entire visible-light part of the solar radiation (350–700 nm), green plants use chlorophyll a as the main light absorber along with a number of accessory pigments such as xanthophylls, carotenoids, and a modified form of chlorophyll, called chlorophyll b. Chlorophyll-a absorbs in the blue-violet, orange-red spectral regions while the accessory pigments cover the intermediate yellow-green-orange part. Second important feature is the special arrangement (antenna array) of chlorophyll molecules for efficient light capturing and relay to the reaction center, even when the light flux varies significantly. Photosynthesis occurs at comparable efficiency under bright and diffuse light conditions.

Artificial systems must mimic both these features: use of several dye molecules in tandem to absorb the entire visible part of sunlight and retain high efficiency for energy transfer and electron transfer under conditions where the local concentration of the dye molecules is fairly high. In homogeneous solutions of chlorophyll at concentration comparable to that of the plants, the excited states of the dyes are efficiently quenched via non-productive channels. In the antenna, plants use lipids and lipoproteins to organize chlorophyll molecules in optimal arrangement. A wide variety of artificial systems based on surfactant micelles, lipid monolayers, vesicles and cage compounds have been examined, but with limited success.

The following biomimetic approaches to solar energy conversion and storage have been addressed: i) finding suitable template/substrate architectures that can mimic antennal chlorophyll function; ii) finding suitable molecular redox catalysts that permit formation of molecular/diatomic forms of hydrogen (H_2) and oxygen (O_2) in the presence of suitable oxidants and reductants; iii) total decomposition of water to H_2 and O_2 using sunlight; iv) direct conversion of sunlight to electricity, which then can be used for production of various chemicals and other needs; and v) reduction of CO_2 to various C1 compounds that can be used as fuels or raw materials for industry.

Decomposition of water to its constituents in gaseous form (reactions (2) and (3)) is a challenging problem because i) the reaction is thermo-dynamically uphill; ii) requires the use of strong oxidants and reductants; and iii) involve multi-electron-transfer processes to yield molecular gases:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \quad (E^o{}_{ox} = -1.23\,V) \tag{2}$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad (E^o{}_{red} = 0.00\,V) \tag{3}$$

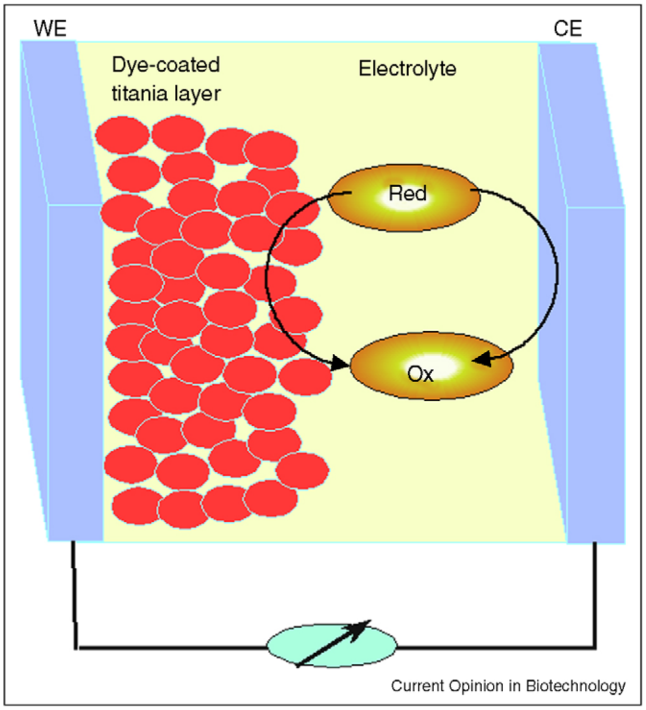
Natural photosynthesis uses a series of electron-transport chains and appropriate enzymes to achieve these processes at moderate efficiencies. Artificial systems need to avoid passage through one-electron oxidation or reduction intermediates, because such species tend to be very reactive and undergo side reactions that can destroy the light absorbing dye molecules.

One of the important breakthroughs in the search for suitable architecture occurred when mesoporous films made out of nano-sized colloidal particles were selected as potential substrate for solar cells [8•,9,10•]. Using different sol–gel hydrolysis routes, it is possible to make monodisperse colloids of titania (TiO_2) and other semiconducting oxides with different particle size. The colloids are subsequently deposited onto glass substrates using doctor-blading or screen printing techniques followed by high temperature sintering. With control of colloid preparation and film deposition, it is possible to make high surface mesoporous thin films of varying porosity and optical transparency. Such nanocrystalline film structures permit efficient distribution of dyes so that locally high concentration of the dyes can be achieved without any side effects. For many inorganic and organic dye molecules, it is possible to have absorbances of >3 in films of few micron thickness and thus to ensure total solar light absorption. Photovoltaic solar cells and rechargeable batteries based on Li-insertion are notable examples.

Dye-sensitized solar cells for direct conversion of sunlight to electricity

Direct conversion of sunlight energy to electricity can be achieved through the use of solar cells. Most popular and widely used solar cells are those based on semiconducting Si as single crystal, multicrystalline or amorphous forms. Solar-to-electrical conversion efficiency, as high as 24% can be obtained, but the requirement of pure single crystalline form renders them very expensive. Thin film solar cells made of CdTe and CIGS (Copper-Indium-Galium-Sulfide) also allow light energy conversion of around 15–18%, but with lower costs [11,12,13•]. Chemists have been working during the past decade on yet another form of photovoltaic solar cell based on the concept of 'dye sensitization' [14•,15–22,23••,24]. Dye-sensitized solar cells are fast emerging as a promising potentially low-cost polyvalent system for solar energy conversion to electricity.

Figure 2



Schematic representation of the composition of a dye-sensitized solar cell (DSC).

Figure 2 shows schematically the structure of a dye-sensitized solar cell (DSC). It is a sandwich structure composed of two transparent conducting oxide (TCO) electrodes. On the main working electrode (indicated as WE in the figure) a few micron thick wide-bandgap semiconducting oxide such as TiO_2 is deposited. The material of choice has been TiO_2 (anatase) although alternative wide-bandgap oxides such as ZnO and SnO_2 have also been investigated. The oxide layer is subsequently coated with an organic or inorganic dye. Before the deposition of the dye, the titania layer is heated for 15 min at 450–500 °C so that nanometer-sized particles sinter together to allow for electric conduction to take place. The counter-electrode (marked as CE in the figure) has islands of Pt catalyst deposited. The two electrodes are put together with a spacer and the intermediate space is filled with an organic electrolyte containing iodide/triiodide mixture.

Photo excitation of the dye results in the injection of an electron into the conduction band of the semiconducting oxide TiO_2:

$$S \rightarrow (h\nu)\, S^{+} + e^{-}{}_{cb}(TiO_2) \quad \text{(charge injection)} \qquad (4)$$

The original state of the dye is subsequently restored by electron donation from the electrolyte, usually an organic solvent containing redox system, such as the iodide/triiodide couple:

$$S^{+} + I_3{}^{-} \rightarrow S + I_2 + I \quad \text{(dye regeneration)} \qquad (5)$$

The regeneration of the sensitizer dye by iodide intercepts the recapture of the conduction band electron by the oxidized dye:

$$S^{+} + e^{-}(cb) \rightarrow S \quad \text{(recombination)} \qquad (6)$$

The iodide is regenerated in turn by the reduction of triiodide at the counter-electrode the circuit being completed via electron migration through the external load.

$$I + e^{-}\,(\text{cathode}) \rightarrow 3I^{-} \quad \text{(regeneration of mediator)} \qquad (7)$$

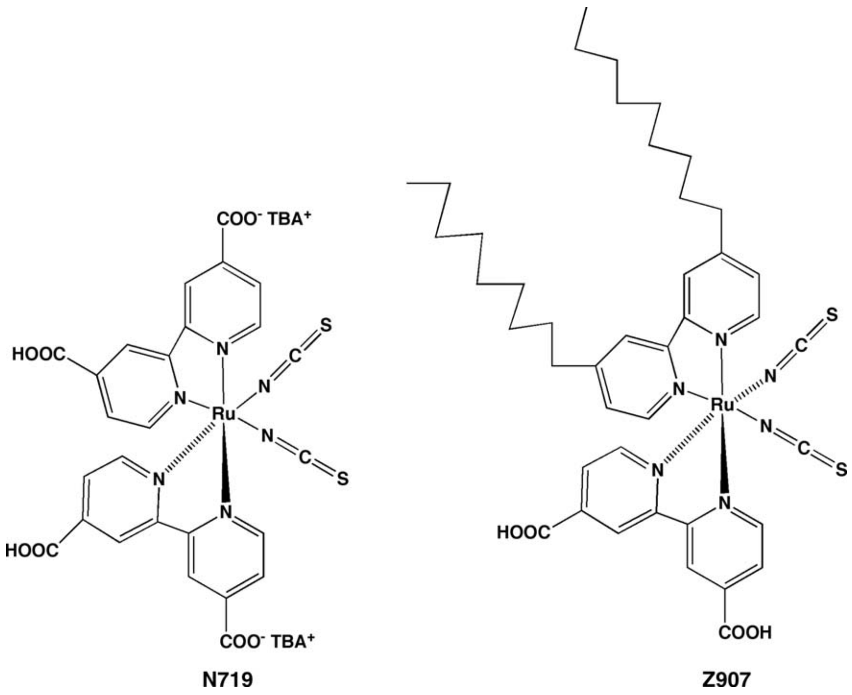
The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. Overall the device generates electric power from light without suffering any permanent chemical transformation. The solar-to-electrical conversion efficiency of these DSCs has reached over 11.5% for lab-size cells ($<$1 cm^2 active area) and about 8% for larger area modules (25–100 cm^2).

A variant of the above is one where an inorganic or organic hole transporter is used to transport charges between the cathode and the dye. The hole transporter is spin-coated after the deposition of the dye on the oxide layers and the solar cell is thus devoid of any organic electrolytes. Conversion efficiencies for such solid-state DSSCs are as yet limited to ~6%. Attention is increasingly focusing on alternative quasi-solid state versions based on ionic liquids, gelled electrolytes and polymer electrolytes.

The high surface area of the mesoporous metal oxide film is crucial for efficient device performance as it allows strong absorption of solar irradiation to be achieved by only a monolayer of adsorbed sensitizer dye. The use of a mesoporous film dramatically enhances the interfacial surface area over the geometric surface area, by up to 1000-fold for a 10 μm thick film, leading to high visible-light absorbance from the many successive monolayers of adsorbed dye in the optical path. Another advantage of the use of a dye monolayers is that there is no requirement for exciton diffusion to the dye/metal oxide interface, and also the non-radiative quenching of excited states often associated with thicker molecular films is avoided.

In order to obtain maximal solar-to-electrical conversion efficiency, all key components (mesoporous oxide layer, dye, redox mediator, electrolyte, and counter-electrode) have to be optimized. Herein we focus on the photosensitizer. The classic sensitizer dye employed in DSSCs

Scheme 1



Standard Ru-dyes for dye-sensitized solar cells N-719 (left) and Z907 (right).

is a ruthenium(II) bipyridyl dye, cis-bis(isothiocyanato)-bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II), which is usually referred to as 'N3', or in its partially deprotonated form (a di-tetra butylammonium salt) as 'N719'. Adsorption of the dye to the mesoporous film is achieved by simple immersion of the TiO_2 film in a solution of dye, which results in the conformal adsorption of a dye monolayer to the film surface. The incorporation of carboxylate groups allows ligation to the film surface via the formation of bidendate and ester linkages, while the (–NCS) groups enhance the absorption of visible light. Highest solar-to-electrical conversion efficiency till date (about 12%) has been obtained with the combination of polypyridine complexes of Ru such as N-719 and the iodide–triiodide mixture dissolved in a low viscosity solvent such as 3-methoxypropionitrile (MPN). Addition of long alkyl units to the bipyridine ring of the Ru-dye, as in the dye Z907 increases significantly the hydrophobicity of the bound titania surface. This in turn reduces the amount of water adsorption and better stability of the solar cells. Scheme 1 shows the structures of these two prototype dyes.

The choice of suitable sensitizer dye is determined by the amount of light absorption in the visible-light region and suitable location of dye redox potentials for one-electron oxidation in the ground and lowest excited state. The excited-state oxidation potential ($E^0(S^+/S^*)$) must be sufficiently negative to achieve efficient electron injection into the TiO_2 conduction band, while the ground-state oxidation potential must be sufficiently positive to oxidize the redox couple. Efficient sunlight harvesting ideally requires a black dye with strong absorption in the entire visible-near IR region. Typical dye redox energies empirically found to be compatible with efficient device function are $E^0(S^+/S) > 0.6$ V vs. normal Hydrogen electrode NHE (H^+/H_2). The ideal sensitizer for a single-junction photovoltaic cell converting standard global AM1.5 sunlight to electricity should absorb all light below a threshold wavelength of about 920 nm.

Numerous studies have shown the need for the dyes to carry attachment groups such as carboxylate or phosphonate to firmly graft it to the semiconductor oxide surface. For reliable performance over long periods the dye should be stable enough to sustain about 100 million oxidation-reduction (turnover) cycles, corresponding to about twenty years of exposure to natural light. A single-junction device with such a sensitizer could reach a maximum conversion efficiency of 32% in global AM 1.5 sunlight.

Porphyrin dyes as sensitizers for dye solar cells

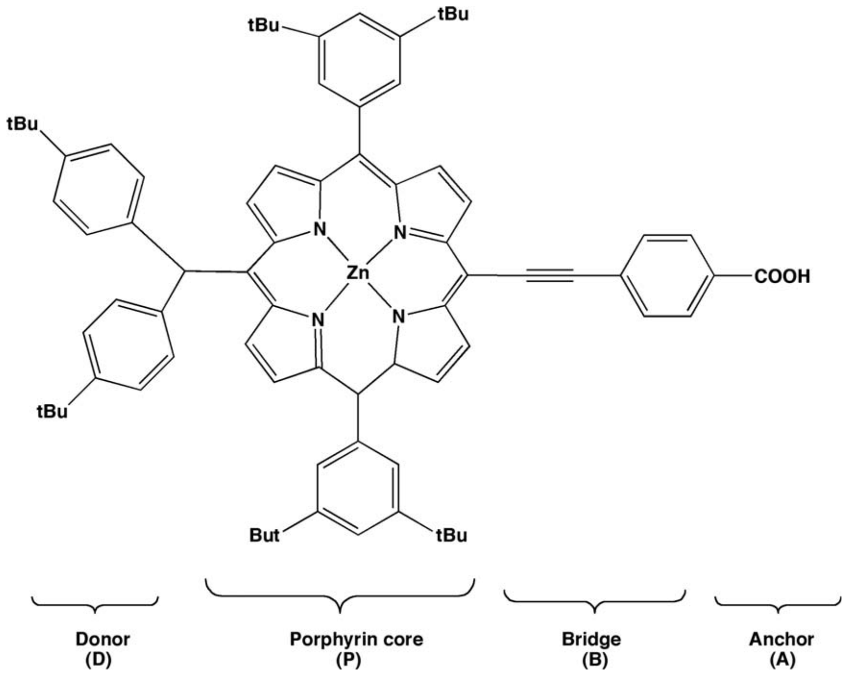
Attractive feature of the DSC is that the system allows to use a wide choice of photosensitizers–transition metal complexes, metal-free organic dyes, metalloporphyrins, and phthalocyanines. Numerous metalloporphyrins have been evaluated as photosensitizers for DSC [25,26,27••,28–45] owing to their strong Soret (400–450 nm) and moderate Q-band (550–600 nm) absorption properties as well as their primary role in natural photosynthesis.

Exploratory studies [46,47,48•] using carboxyphenyl-substituted porphyrin derivatives (such as ZnTPPC) showed that the singlet excited state of porphyrins can efficiently inject charges to the conduction band of TiO_2. In addition, the rate of charge recombination between conduction band electrons and oxidized porphyrins is in the range of several milliseconds, a time that is sufficiently slow to permit the regeneration of the ground state of the porphyrin by the iodide in the electrolyte. Kay and Graetzel [39] examined the sensitization of TiO_2 with a variety of chlorophyll derivatives and related mesoporphyrins. Efficiency of light energy conversion for monochromatic light source is called incident-photon-to-current-conversion efficiency (IPCE). They obtained IPCE values of over 80% for the Soret, Q-band absorption region and overall conversion efficiency η value of 2.6% for a TiO_2 electrode sensitized with copper mesoporphyrin. The kinetic features of key electron-transfer processes for porphyrins are indistinguishable from those of the best performing Ru-complexes. However, owing to poor light absorption in the intermediate region between Soret and Q-bands, overall conversion efficiency is low.

For the best performance in DSCs, porphyrin structures have to be modified suitably as indicated below. For macrocyclic organic dyes such as porphyrins and phthalocyanines, solution aggregation as a result of π-stacking is a serious problem. At the concentrations employed for dye in the stock solutions (>10 μM), aggregation of porphyrins and phthalocyanines is known. Aggregation can be prevented by adding a bulky molecule such as chenodeoxycholic acid to the stock solution of the porphyrin during the dye-coating process. An alternative approach is to hinder π-stacking by introducing bulky 3,5-di-tert-butylphenyl groups at the meso positions of the porphyrin ring.

Though the molar absorbance of the Soret and Q-bands of porphyrins are very high, these dyes still do not absorb much of the sunlight in the intermediate green-orange region. One approach to enhance absorption by porphyrin dyes in the visible region is to expand the π-conjugation system, which causes a red shift and broadening of both Soret and Q bands. Using a number of porphyrin dyes with different substituent groups, David Officer *et al.* have shown that there is a strong interaction between the porphyrin π-system and an olefin-linked electron acceptor substituted at the β-pyrrolic position of the porphyrin ring. A conjugated ethenyl or diethenyl linker in the β-pyrrolic position leads to significant

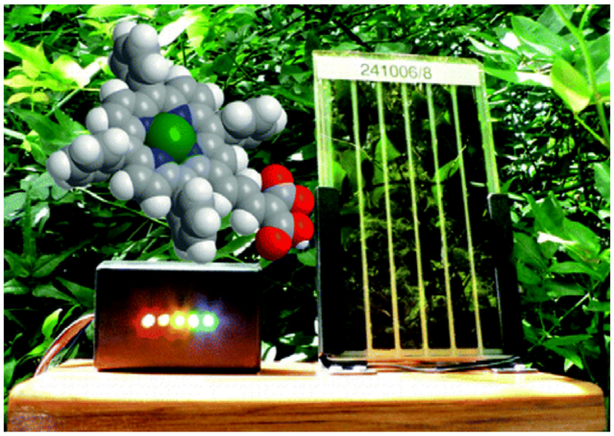
Scheme 2



Extension of the basic porphyrin chromophoric unit for use in dye-sensitized solar cells.

enhancement of light absorption, whereas malonic acid group facilitates stronger binding to the semiconductor surface with a consequent improvement in the electronic coupling of the dye. With these key modifications (malonic acid anchoring groups, extended π-conjugation using ethenyl-type spacer units), a new generation of porphyrin photosensitizers has been designed for DSCs that give record solar-to-electrical conversion efficiencies of over 7%.

Figure 3



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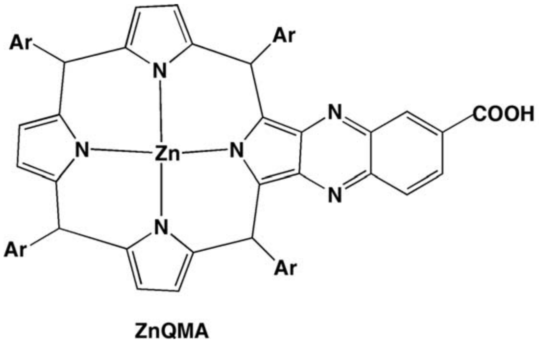
Dye-sensitized solar cell based on metalloporphyrin as the photosensitizer.

The Scheme 2 shows a possible extension of the basic porphyrin core in the design of porphyrins for use in DSCs. In principle, modifications of the design of a porphyrin sensitizer are based on a P–B–A structure, in which B represents a π-conjugation bridge serving as a spacer between the porphyrin light-harvesting center P and the carboxyl anchoring group A. A DSC device using porphyrin sensitizers with the B–A unit functionalized at the β-position is reported to give the highest cell performance as great as $\eta = 7.1\%$; the meso-substituted porphyrins gave smaller η values. Liu *et al.* examined [35,36] a series of porphyrin derivatives of the type D-P-B-A structure. YD11, YD12, and YD13 have the same diarylamino substituent as in YD11 but with the phenyl group in B being replaced by naphthalene and anthracene, respectively. Both YD11-sensitized and YD12-sensitized solar cells exhibit excellent cell performances (n = 6.5–6.7%), comparable to that of N719 dye measured under similar conditions.

It was mentioned earlier that, through appropriate sol–gel hydrolysis and sintering procedures it is possible to prepare mesoporous Titania layers that are optically translucent to visible light. With such films it is possible to use different colored dyes to make dye solar cells in different colors—a feature that has potential advantages

Scheme 3



Structures of two quinoxaline-fused porphyrin derivatives for dye solar cells.

for integration as part of building architectures ('building integrated photovoltaics BIPV'). Figure 3 shows a translucent green-colored dye-sensitized solar cell based on a Zn-porphyrin derivative as the photosensitizer, developed by David Officer and co-workers.

Imahori and co-workers [32–34] reported synthesis and the optical, electrochemical, and photovoltaic properties of few porphyrin derivatives with fused quinoxaline moieties for dye-sensitized solar cells. Two such porphyrin derivatives are worth mentioning, mono-carboxyquinoxalino[2,3′]-porphyrins and di-carboxyquinoxalino[2,3′]-porphyrins ZnQMA and ZnQDA (structures shown in Scheme 3). With the introduction of key functional groups, both compounds are expected to have a broader absorption, compared with that of reference porphyrin without the carboxyquinoxalino moiety (ZnP) and changes lead to a high value of short-circuit current (I_{sc}) and overall solar conversion efficiency (η). Four meso-2,4,6-trimethylphenyl groups are introduced to provide oxidative stability of the porphyrins and to reduce the aggregation between the neighboring porphyrins adsorbed onto the TiO_2 surface by the steric hindrance around the porphyrin core. ZnQMA-sensitized TiO_2 solar cell with TiO_2 nanoparticles (P25) reached a power conversion efficiency (η) of 5.2%, whereas ZnQDA-sensitized cell reached 4.0%.

In a recent extension of their work Officer and co-workers explored [31] the utility of Zn-porphyrin [ZnP] derivatives composed of two monoporphyrin dyes linked in different ways, and incorporated them into DSC. The photoexcited ZnP-ZnP dimers show efficient and fast electron injection into TiO_2 indicating that both photoexcited chromophores contribute to current generation. The porphyrin dimer based solar cells showed a 20% increase in the light-harvesting efficiency and a higher photon-to-current conversion efficiency of 70–80%.

Phthalocyanines as sensitizers of DSCs

Phthalocyanines (Pcs) are extentions of porphyrins. They exhibit very high molar absorption coefficients around 300 nm (Soret band) and 700 nm (Q band) and have redox features similar to porphyrins. Unlike porphyrins, however, phthalocyanines are transparent over a large region of the visible spectrum. This leads to poor light harvesting and low solar conversion efficiency η values [49–51].

A novel unsymmetrical zinc phthalocyanine sensitizer [ZnPc] was designed along the lines elaborated earlier [49,51], with three tert-butyl and two carboxylic acid groups that act as 'push' and 'pull' groups, respectively. The Zn-Pc derivative sensitized solar cell produced a modest solar conversion efficiency η of 3.1% under standard AM 1.5 conditions. Interestingly, the solar conversion efficiency of the DSC improved further upon addition of bile acid CDCA that helps suppress aggregation of some of the phthalocyanine dyes. Usage of an organic dye JK-2 that absorbs strongly in the intermediate region of the ZnPc derivative permits a substantial increase to 7.7% in the overall conversion efficiency of this DSC.

Decomposition of water to molecular H_2 and O_2 ('water splitting')

Decomposition of water to its elements as molecular gases H_2 and O_2 has been a big challenge to imitate by chemists.

$$2H_2O \rightarrow 2H_2 + O_2 \quad E^o = 1.23\,V\,vs.\,NHE \tag{8}$$

To oxidize water to O_2 one needs a strong oxidant (with $E^o \geq 1.23$ V at pH 0) and suitable redox catalysts to assist the formation of O2 without going through one-electron intermediates.

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \quad (E^o{}_{ox} = 1.23\,V) \tag{2}$$

The same applies for water reduction to H_2—we need a strong reductant and redox catalysts to reduce protons to H_2

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad (E^o{}_{red} = 0.00\,V) \tag{3}$$

Enzymes-mediated water decomposition

Nature uses a variety of metal-containing and metal-free enzymes to effect complex oxido-reduction processes with high efficiency and in many cases reversibly as well. Reversibility is a requirement to have a proper proton balance for other chemical transformations. Hydrogenases, which occur in both prokaryotic and lower eukaryotic species, catalyze the reversible two-electron interconversion of protons and hydrogen:

$$2H^+ + 2e^- \Leftrightarrow H_2 \qquad (9)$$

Three different classes have been distinguished on the basis of metal content, that is, [NiFe], Fe-only, and metal-free. Hydrogenases have been observed and characterized in many microorganisms, including various algae, trichomonads, anaerobic ciliates and chytrid fungi.

In natural photosynthesis, water oxidation occurs in PS II using Mn-containing enzymes. The oxygen-evolving complex [OEC] is believed to be a metallo-oxo cluster comprising four manganese ions (in oxidation states ranging from +3 to +5) and one divalent calcium ion (Mn_4Ca). Numerous studies have attempted to discover the details of how these enzymes catalyze formation of high energy redox intermediates and coupled oxido-reduction processes. Owing to restrictions of space we will not go into these details.

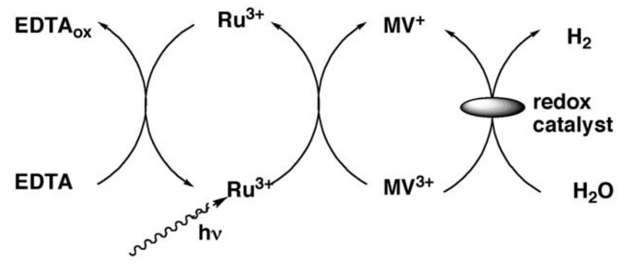
Reduction of water to hydrogen

Total decomposition of water to H_2 and O_2 in artificial systems can be considered into two parts: first, a photochemical or electrochemical component where the required oxidizing or reducing equivalents are generated and a second stage where suitable redox catalysts assist formation of the molecular gases. Most of the efforts till date still revolve around this second component, identifying suitable redox catalysts. For artificial systems, noble metals such as Pt are known as good catalysts for H_2 evolution but not for O_2. Electrolysis of water, for example is best achieved using a Pt electrode as cathode and a metal oxide such as RuO_2 or IrO_2 as the anode [5–7,52–54]. Latter materials show very low overvoltage for water oxidation to molecular O_2.

In photochemical and electrochemical studies of H_2 evolution, a popular and widely used procedure is to use a one-electron redox reagent like Methyl viologen (4,4′-dimethyl-bipyridinium chloride, MV^{2+}) as a key intermediate. MV^{2+} is very soluble in water and has a redox potential slightly more negative than that of normal potential of Hydrogen ($E^0 = -0.44$ V). In its oxidized form, the reagent is colorless but turns deep blue in singly reduced form (MV^{+}.). In the presence of suitable redox catalysts, the reduced form is reoxidized readily with concomittant evolution of H_2 from water:

$$MV^{2+} + e^- \rightarrow MV^+. \qquad (10)$$

Scheme 4



Coupled electron-transfer processes that occur during photolysis of Ru-bpy complex in the presence of Methyl viologen, EDTA and a redox catalyst.

$$2MV^+ + 2H^+ \rightarrow 2MV^{2+} + H_2 \qquad (11)$$

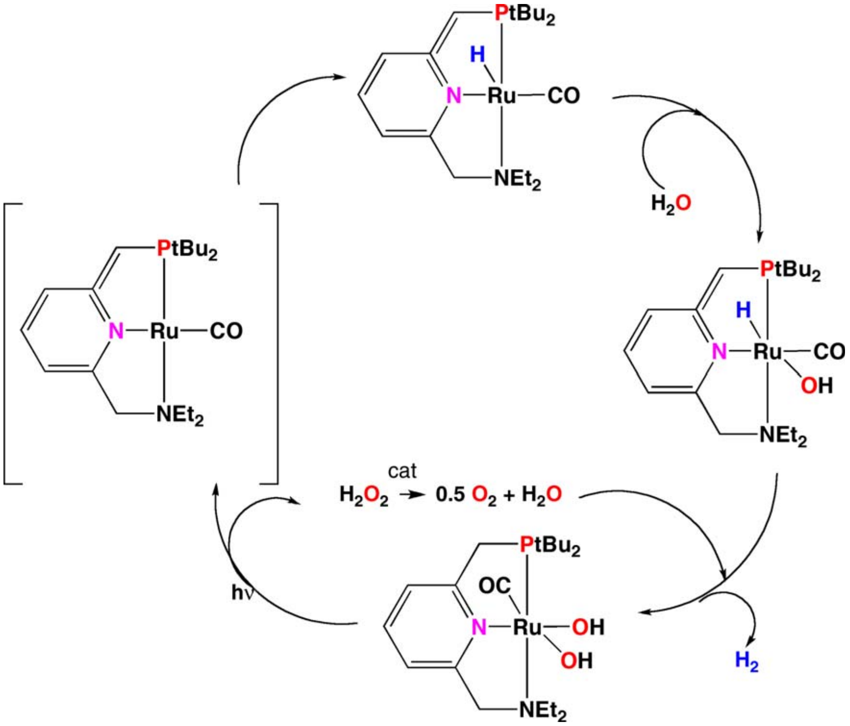
Photolysis of a $Ru(bpy)_3/^{2+}$ complex with visible light in the presence of MV^{2+} e-acceptor, a sacrificial donor like EDTA disodium salt and a redox catalyst leads to sustained evolution of H_2 from water (cf. Scheme 4). In biomimetic systems, enzymes such as hydrogenases can also be used since the photolysis can be carried out in neutral aqueous solutions.

Redox catalysts for oxygen evolution from water

Oxygen evolution can be achieved using either bulk electrodes or homogeneous redox catalysts. It was mentioned earlier that metal oxides such RuO_2 are known as best electrocatalytic material for use as anodes for water oxidation. Finely divided particles of these materials have been used to test oxygen evolution using electrochemical oxidation or using strong chemical oxidants such as Ce(IV) or $Ru(bpy)_3/^{3+}$ produced via light-induced electron-transfer reactions [5–7,52–54]. Mallouk *et al.* [55–57] have shown that nanocrystals of catalytic metal oxides such as Ir-oxide or Nb-oxide work efficiently as catalysts for water oxidation. They have also shown that Potassium hexaniobate nanoscrolls (NS-$K_4Nb_6O_{17}$) formed by exfoliation of lamellar $K_4Nb_6O_{17}$ can be used as redox catalysts for visible-light-driven H_2 production ($\lambda > 420$ nm) from water when $Ru(bpy)_3/^{2+}$ is photolyzed in the presence of EDTA as a sacrificial electron donor.

Frei *et al.* [58] recently demonstrated that nano-sized crystals of Co_3O_4 impregnated on mesoporous silica work efficiently as oxygen-evolving catalysts. A wet-impregnation procedure was used to grow Co clusters within the mesoporous Si as template. The yield for clusters of cobalt oxide (Co_3O_4) nano-sized crystals was about 1600 times higher than for micron-sized particles and the turnover frequency (speed) was about 1140 oxygen molecules per second per cluster. Earlier these authors showed that nanocrystals of Ir-oxide also worked as redox catalysts. Iridium oxide was efficient and fast enough, but

Scheme 5



Sequence of electron-transfer reactions on Ru-complex leading to water splitting.

iridium is the least abundant metal on earth and not suitable for use on a very large scale.

Recently Nocera and co-workers demonstrated [59,60•] the functioning of an efficient water-oxidation catalyst formed *in situ*. Electrolysis of water using an indium tin oxide electrode was examined in aqueous solution in the presence of cobalt and potassium phosphate. Upon applying a voltage to the electrode, cobalt, potassium, and phosphate accumulated on the electrode, forming the catalyst. The catalyst oxidizes water to form oxygen gas and free hydrogen ions.

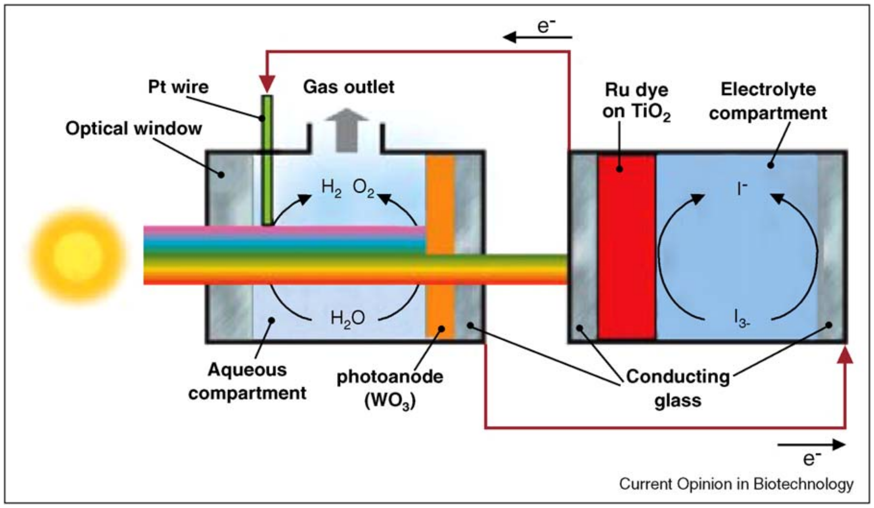
David Milstein and co-workers [61] describe a solution-phase reaction scheme that leads to the stoichiometric liberation of dihydrogen and dioxygen in consecutive thermal-driven and light-driven steps mediated by mononuclear, well-defined ruthenium complexes. The initial reaction of water at 25 °C with a dearomatized ruthenium(II) [Ru(II)] pincer complex yields a monomeric aromatic Ru(II) hydrido-hydroxo complex that, on further reaction with water at 100 °C, releases H_2 and forms a cis-dihydroxo complex. Irradiation of this complex in the 320–420-nanometer range liberates oxygen and regenerates the starting hydrido-hydroxo Ru(II) complex, probably by elimination of hydrogen peroxide, which rapidly disproportionates. Isotopic labeling experiments with $H_2{}^{17}O$ and $H_2{}^{18}O$ show unequivocally that the process of oxygen–oxygen bond formation is intramolecular, establishing a previously elusive fundamental step toward dioxygen-generating homogeneous catalysis (Scheme 5).

Meyer and co-workers [62,63•] have examined possible uses of mononuclear and binuclear mixed ligand complexes of Ru as homogeneous catalysts for oxygen evolution from water. For example, Ru-complexes such as $Ru(tpy)(bpm)(OH_2)^{2+}$ and $Ru(tpy)(bpz)(OH_2)^{2+}$ (bpm is 2,2′-bipyrimidine; tpy is 2,2′:6′,2″-terpyridine) exhibit sustained O_2 evolution from water with Ce(IV) as oxidant with very high turnovers. Detailed mechanistic studies and DFT calculations have revealed a stepwise mechanism: initial $2e^-/2H^+$ oxidation, to $Ru^{IV}{=}O_2{}^+$, $1e^-$ oxidation to $Ru^{V}{=}O_3{}^+$, nucleophilic H_2O attack to give $Ru^{III}{-}OOH_2{}^+$, further oxidation to $Ru^{IV}(O_2)^{2+}$, and, finally, oxygen loss, which is in competition with further oxidation of $RuIV(O_2)^{2+}$ to $RuV(O_2)^{3+}$, which loses O_2 rapidly. An extended family of 10–15 catalysts based on Mebimpy (Mebimpy is 2,6-bis(1-methylbenzimidazol-2-yl)pyridine), tpy, and heterocyclic carbene ligands all appear to share a common mechanism.

Photoelectrolysis of water

Photoelectrochemical solar cells have been designed to achieve total decomposition of water to H_2 and O_2. Fujishima and Honda [64••] were the first to show that water splitting can be achieved using bandgap irradiation

Figure 4



Photoelectrolysis of water using a WO_3 photoanode in a tandem configuration with a dye-sensitized solar cell to provide the voltage bias. Photo on the right shows evolution of H_2 and O_2 gases at the Pt and WO_3 electrodes respectively.

of suitable wide-band oxide n-type semiconductors such as TiO_2 or $SrTiO_3$. When an n-type semiconductor is irradiated with light of energy equal or greater than the bandgap energy, electrons and holes are produced that separate under the influence of the local electric field, and move in the valence and conduction bands of the semiconductor. For many oxide semiconductors, holes of valence band of the semiconductor are strong oxidants ($E > 2.5$ eV) that, in aqueous solutions can oxidize water to oxygen. However, the conduction band energy is barely in the vicinity of the normal hydrogen reduction potential. As a consequence some additional voltage has to be applied to the counter-electrode to evolve H_2.

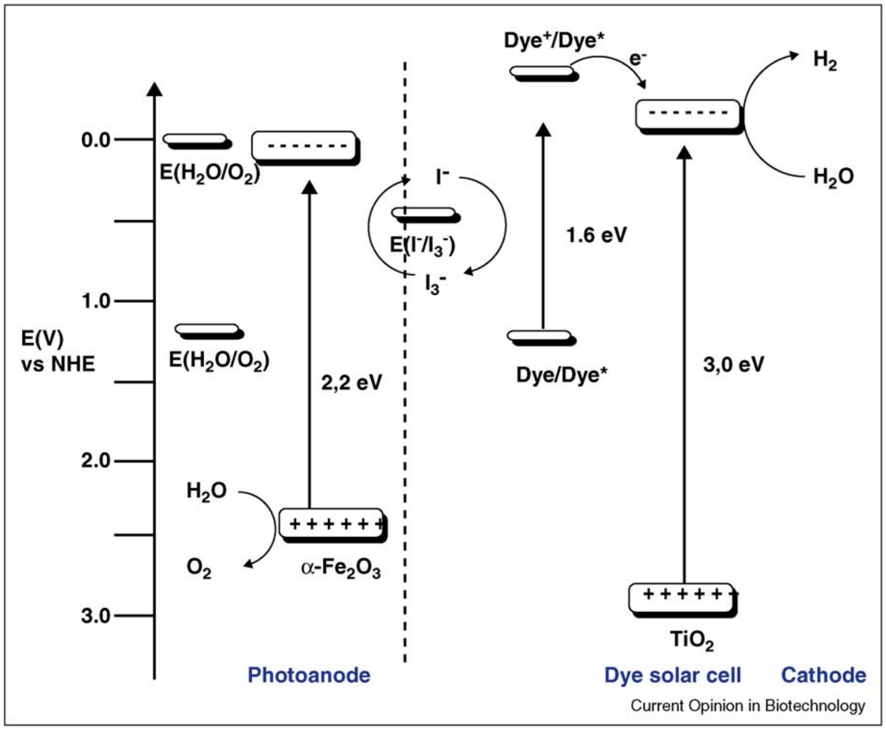
A major limitation of Titania as a semiconductor is that it absorbs less than a few percent of solar radiation in the near-UV region. A better alternative is to use moderate bandgap (E_{bg} in the range of 2–3.0 eV) semiconductors such as WO_3 or Hematite Fe_2O_3. Total electrolysis of water using such materials requires an additional voltage bias of 200–300 mV. Hence they are known as photo-assisted water electrolysis. Studies of photoelectrochemical cells using bulk electrodes however show only very low efficiency. Owing to poor mobility of holes in the bulk of the semiconductors, most of the photogenerated charge carriers recombine before they reach the surface.

The above problem can be elegantly solved with the use of mesoporous thin film forms of these semiconductors. In mesoporous films composed of nano-sized particles, the charge carrier diffusion length can be much larger as compared to the particle size, allowing all charges to escape recombination. In fact Graetzel and co-workers have demonstrated the feasibility of water splitting using such mesoporous WO_3 or Fe_2O_3 electrodes [65–67]. Figure 4 shows schematically the set up used in the water-splitting experiments using sunlight. Since the semiconductor does not absorb the light in the orange-red region, a dye-sensitized solar cell can be placed at the bottom of the photoelectrochemical cell to generate the required bias voltage. Thus in a tandem cell where the visible light is efficiently partitioned between an electrolysis and sensitized solar cell decomposition of water to H_2 and O_2 can be sustained.

Figure 5 shows schematically various coupled electron-transfer processes that occur in the two photoelectrochemical cells working in tandem. There are advantages in the use of two electrode design. Two gases are evolved at different sites and can be collected separately. Photoelectrolysis using homogeneous redox catalysts can produce a gaseous mixture that is expensive to separate. This two coupled photoelectrochemical cell systems for water splitting possibly is the nearest one can come in the biomimetic approaches to photosynthesis.

Mallouk *et al.* [57,68,69] have designed an elegant photo-induced water oxidation system based on a variant of the dye-sensitized solar cell. A Ru-polypyridine complex was modified with both phosphonate and malonate ligands in the 4-positions of the 2,2′-bipyridyl ligands in order to adsorb strongly to TiO_2 and $IrO_2{\cdot}nH_2O$, respectively. The cathode was a Pt wire electrode. Because the potential of electrons in trap states below the anatase conduction band is not sufficiently negative to reduce water, a bias voltage (≈330 mV) must be applied for water splitting to occur in this cell. Each surface iridium atom can cycle through the water oxidation reaction about 50 times per second, which is about three orders of magnitude faster than the next best synthetic catalysts, and comparable to

Figure 5



Current Opinion in Biotechnology

Schematic representation of coupled electron-transfer processes that occur in the photoelectrochemical solar cell for the decomposition of water.

the turnover rate of Photosystem II in green plant photosynthesis. Through exfoliation of layered metal oxide semiconductors, a multilayer electron donor–acceptor thin films or sensitized colloids is constructed in which individual nanosheets mediate light-driven electron-transfer reactions. When sensitizer molecules are 'wired' to $IrO_2{\cdot}nH_2O$ nanoparticles, a dye-sensitized TiO_2 electrode becomes the photoanode of a water-splitting photoelectrochemical cell.

Photochemical and electrochemical reduction of CO_2

In addition to water splitting, fixation of CO_2 is another important reaction associated with photosynthesis. In addition to photoinduced H_2 production from water, there has been sustained interest to find viable means of reducing CO_2 gas to other C-1 products such as alcohols and aldehydes. Depending on the degree of reduction, formic acid (HCOOH), CO and methanol (CH_3OH) can be obtained as reduction products:

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \quad E^o = -0.61\,V \tag{12}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad E^o = -0.53\,V \tag{13}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad E^o = -0.38\,V \tag{14}$$

The fact that the proton-assisted, multi-electron routes to these products require much less energy than the one-electron process to CO_2/CO_2^- ($E^o = -1.9$ V) has been the motivation to use these multi-electron-transfer routes for CO_2 reduction using transition-metal complexes.

The conversion of carbon dioxide into useable hydrocarbon fuels has been of much industrial interest for over a century. In 1913 Sabatier discovered that CO_2 can be reduced to methane with hydrogen gas in the presence of a Ni catalyst at high temperature and high pressures:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta G = -27\,\mathrm{kcal/mole} \tag{15}$$

The Sabatier reaction is becoming of commercial interest for the manufacture of natural gas from the products of coal gasification. The reverse reaction, is called 'steam reformation' and is a commercial method for hydrogen manufacture. For many years researchers have been trying to find means of catalytic hydrogenation of carbon dioxide to methane at milder conditions. Methane is generated biologically by methanogenic bacteria, largely from acetate dissimilation and carbon dioxide reduction.

There have been a number of studies of photocatalytic CO_2 reduction using Ru-bpy, $Re(CO)_3$bpy, metalloporphyrin complexes with or without additional metal/metal oxide catalysts [70–75,76••]. Photochemical CO_2 reduction is normally carried out in aqueous solutions or organic solvents under 1 atm CO_2 at room temperature. The concentration of dissolved CO_2 is substantially higher in organic solvents as compared to water (e.g. 0.28 M in acetonitrile and 0.03 M in water). These systems produce formate and CO as products, however the formate-to-CO ratio varies from system to system. Metallocarboxylates (and metallocarboxylic acids) are postulated intermediates in photochemical and electrochemical CO_2 reduction and the water–gas-shift reaction.

Despite its favorable thermodynamics, eight electron reduction of CO_2 with H_2 is difficult to achieve. Finely divided Ru has been found to be equally effective for the Sabatier reaction. Photolysis of particulate dispersions of TiO_2 loaded with Ru catalyst in aqueous solutions [70] in the presence of CO_2 leads to selective formation of methane at ambient temperatures. In the absence of CO_2, water reduction giving rise to H_2 gas takes place. Photolysis of aqueous dispersions of Titania loaded with Cu catalyst [71,72] has been found to yield methanol as a major reduction product:

$$CO_2 + 2H_2O \rightarrow (h\nu) \rightarrow CH_3OH + 3/2O_2 \qquad (16)$$

Cobalt and nickel tetraazamacrocyclic complexes ($CoHMD^{2+}$ and $Ni(cyclam)^{+}$, in which HMD and cyclam are more saturated ligands than a porphyrin) have been used as catalysts to produce CO in photochemical and electrochemical CO_2 reduction. Catalytic photoreduction of CO_2 to CO and formate has also been carried out by visible-light irradiation of acetonitrile solutions containing cobalt and iron porphyrins as catalysts and as photosensitizers, and triethylamine as a reductive quencher.

Meyer and co-workers have summarized recently [73–75,76••] results of their studies of CO_2 reduction using four classes of transition-metal catalysts: (a) metal tetraazamacrocyclic compounds; (b) supramolecular complexes; (c) metalloporphyrins and related metallomacrocycles; (d) $Re(CO)_3(bpy)X$-based compounds where bpy = 2,2′-bipyridine. Carbon monoxide and formate were the primary CO_2 reduction products, and we also propose bicarbonate/carbonate production.

Conclusions

In this paper we have attempted to give a broad overview of various attempts that are being made to reproduce key functional processes of natural photosynthesis. The goal of such studies of ‘artificial photosynthesis’ is to find alternate means of producing electric power and high energy fuels from water and abundant and ‘free’ solar energy reaching the earth’s surface everyday. Goals of these studies are not to slavishly reproduce every aspect of natural photosynthesis but to mimic in a simplified manner to achieve better performance. In this regard, recent progress has been very encouraging.

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