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Artificial photosynthetic systems

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Presently endeavors are being undertaken to design systems capable of converting solar radiation into fuels. These efforts are timely and mandatory in order to reduce our dependence on fossil energy reserves. Recently there has been an explosion of information on this subject[1–13] and a multitude of processes are under investigation which attempt to mimic photosynthesis. The present article gives a brief overview over these artificial systems and explains some basic principles of their operation.

Plant photosynthesis serves to convert light into energy-rich compounds such as carbohydrates. This biological device is, however, a rather poor energy converter if the amount of biomass produced by the incident solar flux is considered. Although the primary photoredox reactions that occur in the chloroplasts proceed with high quantum efficiency the overall conversion yield is approximately 5-6% and falls to 1-3% at best when averaged over the whole year[14]. Major losses are due to growth, adaptation and reproduction processes. Thus the photosynthetic machinery could work more efficiently had it been designed mainly for fuel production without any constraints due to evolutionary history[15].

Artificial systems try to overcome this shortcoming of the biological counterpart by simplifying both the energy storing process and the molecular units that accomplish this transformation. Three different approaches are presently being pursued. In the first or hybrid system the thylakoid membranes or individual photosystems are employed as light harvesting units. The objective is to exploit the high efficiency of the primary photosynthetic redox events without attempting to synthesize carbohydrates from CO_2. Instead, hydrogen generation from water is achieved through artificial redox relays and catalysts.

The second approach is to employ synthetic molecular assemblies such as micelles or membranes as reaction systems. These aggregates simulate the microenvironment present in biological systems and serve as a host for hydrophobic entities participating in the photoreactions.

Finally, artificial systems with very little resemblance to their biological counterpart are also under study. Prominent and promising at the same time are here colloidal semiconductor solutions.

None of the presently available model systems will achieve the conversion of carbon dioxide into sugar under illumination with visible light. However, they will perform other more simple endoergic transformations such as the photocleavage of water and the production of methanol from CO_2.

Hybrid systems

Before the recent development of bifunctional catalysts and the design of totally artificial systems, which will be described later, the photolysis of water by visible light was achieved only by the chloroplast and cyanobacteria machinery. The light-induced water decomposition

$$H_2O \xrightarrow{h\nu} H_2 + \frac{1}{2} O_2 \qquad (1)$$

is an attractive means by which to convert solar photon energy into chemical potential. Cell-free hybrid systems, composed of isolated chloroplasts coupled to suitable redox catalysts have been shown to achieve this decomposition[16]. Figure 1 illustrates

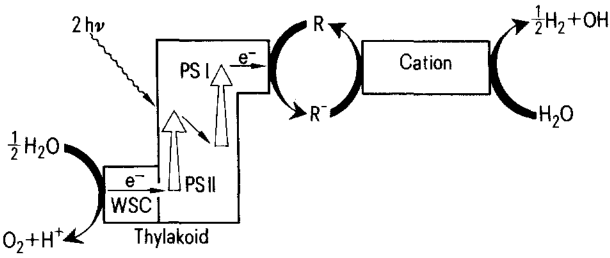

Figure 1. Schematic illustration of a cell-free hybrid system for the biophotolysis of water.

the mechanisms of this biophotolysis where the whole electron transport chain supported by the thylakoidal membrane is involved. Electrons are abstracted from water by the water splitting complex (WSC) at the oxidative end of the chain. The electron relay R is reduced by the terminal PSI acceptor and then transfers electrons to the redox catalyst which evolves hydrogen.

Since the first hydrogen production obtained in such systems with water as the sole electron donor[17] about 10 years ago, great improvements have been obtained and hydrogen yields of 20–50 μmoles per h and mg chlorophyll are now currently measured for several hours.

An oxygen scavenging system is, however, usually needed in these hybrid systems in order to remove oxygen and peroxide radicals which are formed under illumination and which inactivate the chloroplast components and diminish the energy conversion efficiency. Various means have been proposed to enhance the stability and the efficiency of the processes. Longer life-times have been recently obtained by using alginate-immobilized[18] or albumine cross-linked chloroplasts[19]. Oxygen-insensitive hydrogenases still possessing good catalytic activities have also been studied[20]. It is worthwhile to note that synthetic compounds can replace part of the system. Artificial catalysts, such as PtO_2[21], platinum or palladium asbestos[22], or ultrafine platinum colloids developed in our laboratory[18,23] have been used instead of hydrogenases and can evolve hydrogen at comparable rates. Various synthetic relays can also replace the natural electron carriers. Particularly, synthetic iron-sulfur and iron-selenium analogues have been developed to mimic ferredoxin[24].

The low efficiency of the hydrogen evolution compared to the electron transport capacity of the photosynthetic membrane has been shown in recent studies to be due to an important loss of reductive equivalents by reoxidation of methylviologen, a relay commonly employed, between PSII and PSI[22,25]. The electron transfer efficiency between the thylakoidal membrane and the redox catalyst has been shown in our laboratory to depend on the pH and the redox potential of the relay[23]. Our present work in this field is now devoted to the study of new compounds which back react much slower with the membrane.

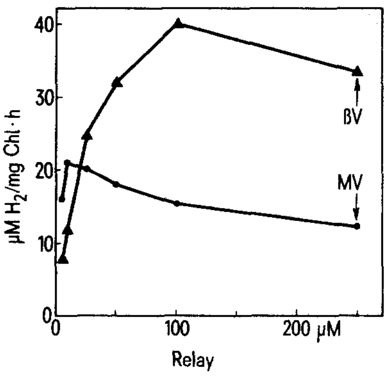

Figure 2. Hydrogen evolution rates as a function of the concentration of 2 electron relays in a hybrid system composed of broken spinach chloroplasts, platinum colloids and oxygen scavengers.

As an example, figure 2 shows the hydrogen evolution rates obtained in a system containing broken spinach chloroplasts, platinum colloids, O_2 scavengers and methylviologen (MV) or betaine-viologen (βV) as electron relays. This last compound, although thermodynamically less favorable because of its higher redox potential, mediates a two times higher hydrogen production rate. This is attributed to the negative charge of its reduced form which produces electrostatic repulsion from the membrane leading to smaller extent of back reaction with the electron transport chain than in the case of the positive analogue methyl viologen.

Great improvements, particularly in the stabilization of the water splitting complex and the pigment system will certainly be achieved in the future. This will lead to a better understanding of the natural photosynthetic energy converter and could help in the design of more efficient biomimetic photoredox devices for the photolysis of water.

Biomimetic systems

These devices make use of the effect of self-assembly of surfactant agents in aqueous solution to produce molecular assemblies mimicking the microenvironment present in the biological systems. Examples are given in figure 3 which illustrates structural features of micelles, microemulsions and vesicles. These aggregates are distinguished by a charged lipid water interphase that may be exploited to control kinetically the electron transfer events. In the light-induced redox reaction

$$S + R \overset{h\nu}{\rightleftarrows} S^{+} + R^{-} \qquad (2)$$

the goal is to enhance the rate of the forward reaction and at the same time retard that of the backward electron transfer. A micellar system that achieves this goal is now discussed in detail.

Consider an artificial system where chlorophyll a (Chla) is used as a sensitizer and duroquinone (DQ) as an electron relay[26]. Such a system is reminiscent of the redox species involved in photosystem II. Both Chla and DQ are incorporated into an anionic micelle (figure 4). Light is used to excite Chla and to promote electron transfer to DQ. A radical ion pair is thereby produced within the aggregate. In an anionic micelle DQ^{-} is clearly destabilized with respect to the aqueous bulk solution and will therefore be ejected into the water. Conversely, $Chla^{+}$ is electrostatically stabilized by the micelle and remains associated with it. Once $Chla^{+}$ and DQ^{-} are separated, their diffu-

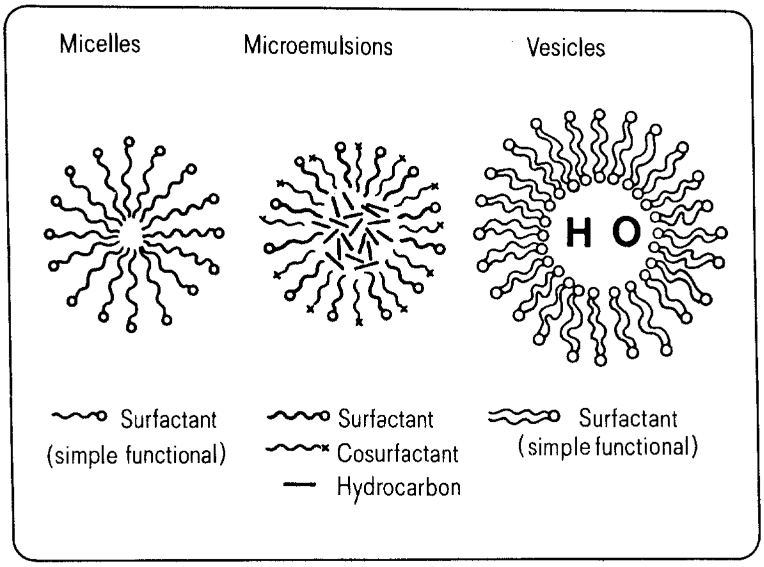

Figure 3. Structural features of colloidal assemblies employed in light-induced charge separation.

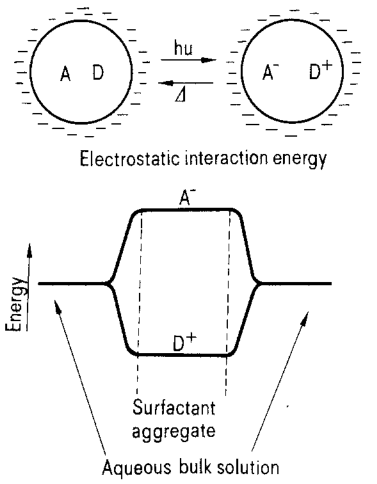

Figure 4. Schematic illustration of a light-induced charge transfer reaction in an anionic surfactant aggregate.

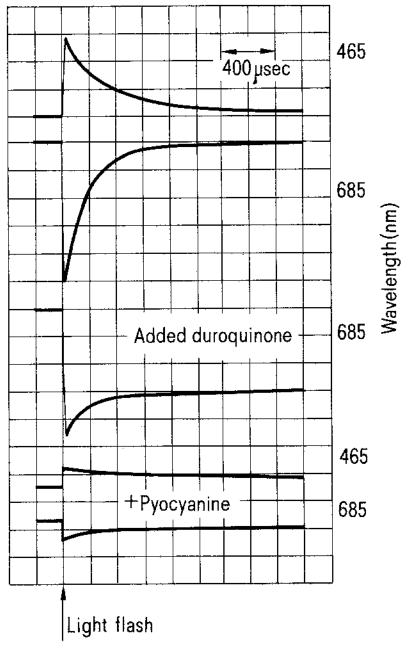

Figure 5. Oscilloscope traces obtained in the 694 nm laser photolysis of chlorophyll a (3×10^{-5} M) in sodium lauryl sulfate (0.1 M) micelles. From the top: decays of chlorophyll a triplet (trace 1) and bleaching of absorption (trace 2) in the absence of additives; traces 3 and 4: same decays in presence of 3×10^{-3} M duroquinone; trace 5: added 3×10^{-3} M duroquinone and 8×10^{-5} M pyocyanine.

sional re-encounter will be obstructed by the ultrathin barrier of the micellar double layer. The efficiency of the charge separation process will crucially depend on the relative rates of DQ^- ejection and intramicellar back transfer of electrons from DQ^- to $Chla^+$. Flash photolysis data obtained from this system are presented in figure 5. The upper 2 traces reflect the behaviour of Chla-triplet states in the absence of DQ. The time course of both the 685 and 465 nm absorption is drastically affected when DQ is added to the micelles. The long term bleaching can be attributed to the formation of $Chla^+$ cation radicals which through the field gradient in the micelle/water interface are prevented from recombining with DQ^-. If pyocyanine (PC^+) is added to the solution the charge separation is annihilated as PC^+ reoxidizes DQ^-. The neutral PC radical produced can enter the micelle and reduce in turn $Chla^+$.

Further progress in the development of molecular assemblies converting light into chemical energy was made by designing and synthesizing surfactants with suitable functionality. These are distinguished from simple surfactants by the fact that the micelle itself participates in the redox events. Noteworthy examples include:

a) micelles with acceptor relays as counterions (transition metal ion micelles[27,28]),

b) crownether surfactants[29],

c) amphiphilic redox relays[30,31] and redox chromophores[32].

The advantage of these aggregates is that electron donor and acceptor are held in close proximity. Thus, although the analytical amounts of these species in solution may be small, the formation of aggregates provides high local concentration which, in turn, insure that the photoredox reaction proceeds at a high rate. Very often these types of molecular assemblies display also cooperative effects assisting light-induced charge separation.

As an example, consider the detergent cupric lauryl sulfate ($Cu(LS)_2$) which is obtained from the commercially available sodium lauryl sulfate via ion exchange[27,28]. The counter ion atmosphere of these micelles is constituted by cupric ions. It has been shown that the reduction of cupric to cuprous ion by a sensitizer incorporated into these aggregates can occur at extremely high rates. The electron is transferred from the excited state of the sensitizer to the Cu^{2+} ions in less than 1 nsec. Thus, as is the case in photosynthesis, even singlet excited states can be used for this reaction. The Cu^{+} ion escapes into the aqueous phase before back reaction can occur and charge separation can be achieved.

Apart from micelles, molecular assemblies such as microemulsions[33,34] and vesicles[35] deserve particular attention in the context of photoredox reactions in biomimetic aggregates. Calvin and co-workers have for the first time illustrated light-included electron transfer across the bilayer of liposomes[35]. $Ru(bipy)_3^{2+}$ was incorporated together with a sacrificial electron donor into the inner water core of a vesicle while a viologen was the ultimate electron acceptor in the bulk aqueous phase. The formation of the viologen radical was detected under illumination and from the kinetic analysis rate parameters obtained for the transmembrane electron transfer. This process requires a time of several µseconds and follows probably an electron exchange mechanism involving $Ru(bipy)_3^{2+}$ and $Ru(bipy)_3^{3+}$ on opposite sides of the membrane.

The same group has also performed elegant studies of electron transfer reaction in the water core of inverted micelles[34].

Artificial systems

Totally artificial systems are presently under intense investigation that show no apparent similarity with their natural counterpart. Figure 6 summarizes the principle of light harvesting and energy conversion of 3 systems typically employed here. A sensitizer/relay pair is used in the first device. Light induced electron transfer produces the radical ions S^{+} and R^{-} which are subsequently employed to oxidize and reduce water respectively. The success of this system is mainly dependant on the use of active redox catalysts that can intervene extremely rapidly and, moreover, specifically in the hydrogen and oxygen formation from water. Several formidable problems have to be overcome here.

a) the catalysts have to intercept the thermal back reaction which occurs in the micro-to-millisecond time domain.

b) The water reduction catalyst 2 must compete with oxygen reduction by R^{-} which is expected to occur at a diffusion controlled rate. This sets the rate limit required for H_2 generation at several µseconds.

c) The intervention of the catalysts has to be specific in order to avoid short circuitry of the back reaction.

d) In order to achieve H_2/O_2 separation an oxygen carrier has to be present in solution that adsorbs the oxygen produced during photolysis.

A few years ago it would have seemed impossible to overcome all of these difficulties. At that time there was even no O_2 producing catalyst available. This was discovered in 1978 in our laboratory[36,37] in the form of noble metal oxides such as PtO_2, IrO_2 and RuO_2. The latter has been most widely investigated since then[38–40]. Platinum has been known for a long time to mediate water reduction by agents such as V^{2+}, Cr^{2+} and also reduce viologens. However, it required several years of research to develop a Pt catalyst that would

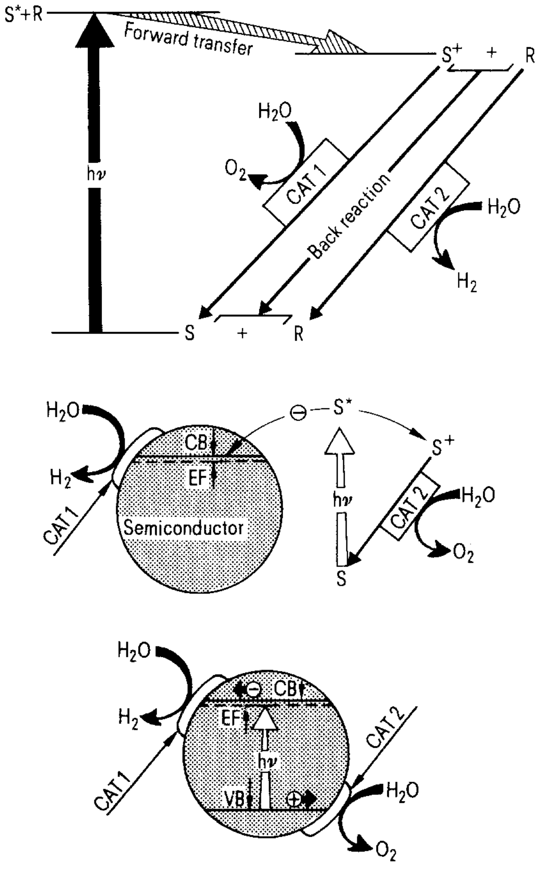

Figure 6. Light harvesting and catalytic units for light-induced water decomposition.

satisfy conditions (a)–(c) indicated above, i.e. produce H_2 in the microsecond time domain at reasonably low Pt concentrations. The water splitting catalyst which evolved finally[41,42] was colloidal TiO_2 loaded simultaneously with ultrafine deposits of Pt and RuO_2. Sustained water cleavage by visible light was observed in solutions containing $Ru(bipy)_3^{2+}$ as a sensitizer, methylviologen as an electron relay and this bifunctional catalyst, the quantum yield being around 6% (75 °C).

Figure 6b introduces a second light harvesting unit for light-induced water cleavage. It consists of a colloidal semiconductor loaded with a suitable catalyst that mediates hydrogen production from water. A dye S is adsorbed on the colloids which upon excitation injects an electron in the semiconductor particle. The electron is channelled to Pt sites where hydrogen evolution takes place. A 2nd catalyst converts S^+ back into S under simultaneous formation of oxygen from water. An experimental verification of this system was found in colloidal TiO_2 particles loaded with Pt and RuO_2 onto which a surfactant $Ru(bipy)_3^{2+}$ complex is adsorbed[43]. The maximum quantum efficiency of water splitting observed with such a system is ca. 7% so far.

The third device depicted in figure 6c requires neither sensitizer nor electron relay. A semiconductor particle is charged with both a catalyst for water oxidation and water reduction. Band gap excitation produces an electron/hole pair in the semiconductor particle. Both charge carriers diffuse to the aqueous interface where hydrogen and oxygen generation occurs. TiO_2 charged simultaneously with Pt and RuO_2 was the first material to be employed in such a system. In this case UV-irradiation is required to excite the semiconducting support. Hydrogen and oxygen are cogenerated rather efficiently, the quantum yield Ø (H_2) approaching 30%. The domain of photoactivity has recently been displaced into the visible by using n-CdS particles as carriers for Pt and RuO_2. Interestingly, the RuO_2 deposit prevents photocorrosion by valence band holes and instead allows water oxidation[44].

Finally, an analogy between colloidal semiconductors and photosynthetic bacteria should be pointed out. CdS particles when loaded with RuO_2 alone are capable of splitting hydrogen sulfide into sulfur and hydrogen when illuminated by visible light.

$$H_2S \xrightarrow{h\nu} H_2 + S \qquad (3)$$

The RuO_2 serves here as a hole transfer catalyst accelerating the rate of charge exchange between the valence band of CdS and the sulfide ions in solution. No Pt is required as water reduction by conduction band electrons occurs very rapidly. The quantum yield for H_2S splitting approaches 35%. A similar photoreaction can be performed by photosynthetic bacteria that also employ sulfides as an electron source.

The key advantage of colloidal semiconductors over other functional organizations is that light-induced charge separation and catalytic events leading to fuel production can be coupled without intervention of bulk diffusion. Thus a single particle can be treated with appropriate catalysts so that different regions function as anodes and cathodes. It appears that this wireless photoelectrolysis could be the simplest means of large scale solar energy harnessing and conversion.

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Concluding remarks

The articles published in this volume assess the current state of development of biological systems that are harnessing solar energy - and offer some outlooks for their use in the future. These systems may very well change our lives. Of course, it is not easy to make projections for the future when each projection must vary from country to country and with system to system. Certainly the options open to the Third World countries in answering their energy problems will be different from those in the industrial countries. Of great importance is how much a country's gross national product has to be spent for energy imports! Moreover, projections must account for economic and ecological alterations brought about by the implementation of such biological systems. The production of ethanol in Brasil, for example, has increased over the last years from $0.6 \cdot 10^6$ m^3 in 1975 to $3.7 \cdot 10^6$ m^3 in 1979; the forecast for 1987 is $14 \cdot 10^6$ m^3 (Trindade, 1980). Will such an increase in ethanol production not pose many new restrictions and limitations on food production or on the ecology of the land used for the sugar crop necessary to accomodate this high ethanol production?

Today, mankind does not seem to be optimistic enough about being able to solve the problems of energy supply without creating even more problems for future generations. However, when one looks back through history, one sees that man has always been engaged in a learning process that has demanded his adaptation to the changing conditions and pressures of the environment. Not always have the best long term solutions to his problems been selected, as we are well aware today. However, we should not lose confidence that appropriate solutions can be found to secure our future energy supply and that of our childrens' children.

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