# The Photodissociation of Water

## PLATINUM METAL CATALYSTS PROMOTE THE PRODUCTION OF HYDROGEN AND OXYGEN

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*The development of artificial photosynthesis units capable of converting solar energy into useful chemical products is still at a very preliminary stage, although some progress has been made during the last few years. Most work concerns the photodissociation of water, and this paper considers the two basic strategies that are being followed. Both of these require the use of a catalyst and, to date, platinum metal catalysts have proved to be the most efficient. With many laboratories actively investigating photodissociation, rapid progress should ensue.*

Over the past twenty years there has been a steady growth in research effort directed towards the construction of a practical device capable of the collection and storage of solar energy. Considerable progress has been made during this time and, already, solar energy is used in many countries to heat water for domestic purposes. Similarly, the space programme has resulted in the development of photovoltaic cells that are able to convert solar energy into electrical energy with efficiencies around 15 per cent. Only cost limits the widescale use of such cells. Solar energy can also be converted into chemical potential although, here, development is still at a preliminary stage and no practical system exists at present. The scope of this field is enormous but, on practical grounds, it seems necessary that the final chemical product is a gas. This is because sunlight is a dilute form of energy and large collection areas are required so that the concentration of the product will always be quite low. Filtration and distillation are too expensive to be off-set by the price of the product. Collection of a gas, provided it is evolved at a specific site and not throughout the entire collection area, should be straightforward. In terms of cost and availability, the gas must be derived from a cheap, inorganic

source; water, carbon dioxide or nitrogen. Of these materials, the large scale consumption of carbon dioxide involves problems with conservation of the atmosphere but both the photodissociation of water into hydrogen and oxygen and the photoreduction of nitrogen to ammonia appear to be promising systems for the conversion of solar energy into useful chemical products. So far, most work has been concerned with the photodissociation of water and the photoreduction of nitrogen has been virtually ignored.

Two basic strategies are being followed in the design of systems for the photodissociation of water into hydrogen and oxygen. The first approach involves systems that are homogeneous, or nearly so, in which a photosensitiser is used to promote electron transfer between suitable electron mediators. The oxidised and reduced forms of these mediators can be used to liberate oxygen and hydrogen, respectively, from water, provided suitable catalysts are present. The second approach is based upon the irradiation of inorganic semiconductors, either macroelectrodes or colloidal particles, with light of energy higher than the band gap. The electron/hole pair which is formed upon such illumination can migrate separately to the
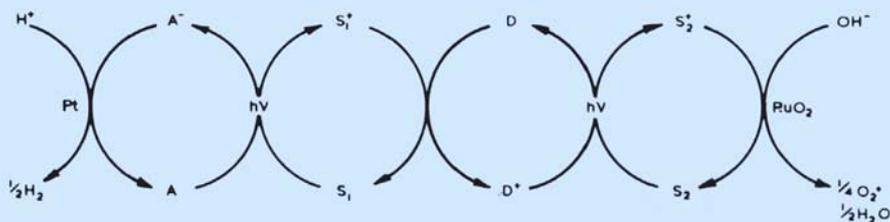
Fig. 1 During the photodissociation of water using coupled photosystems, photosystem 1 forms oxidised sensitiser ($S_1^+$) and reduced acceptor ($A^-$). A donor (D) recycles $S_1^+$ while platinum catalyses hydrogen formation via $A^-$. Photosystem 2 reduces the oxidised donor ($D^+$), forming oxidised sensitiser ($S_2^+$) which generates oxygen via a ruthenium dioxide catalyst

surface of the semiconductor where water reduction and oxidation can occur. Again, catalysts are required to promote gas evolution and, in all cases, the most efficient catalysts involve the platinum group metals.

## Homogeneous Systems

Here, a photosensitiser ($S_1$), such as a water-soluble metalloporphyrin, is used to reduce an electron acceptor (A), such as methyl viologen, in aqueous solution. The oxidised form of the sensitiser is reduced by an electron donor (D) so that the sensitiser is recycled and the reduced form of the electron acceptor is used to liberate hydrogen from water in the presence of a platinum catalyst, see Figure 1. In a separate photosystem, the oxidised form of the donor ($D^+$) is used to oxidise a photosensitiser ($S_2$), such as tris(2,2'-bipyridyl)ruthenium (II), which is able to oxidise water to oxygen in the presence of a suitable catalyst, for example $RuO_2$ or $IrO_2$.

The two separate photosystems have been well developed, a wide variety of systems are available, and quantum efficiencies for formation of hydrogen and oxygen of 60 per cent and 20 per cent, respectively, have been obtained (1,2). Tables I and II give summaries of the best developed systems. In all cases listed there, the reversible redox couple $D^+/D$ has been replaced with a sacrificial (or irreversible) couple which undergoes destruction upon oxidation or reduction. So far, it has not been possible to link together two such photosystems so that the

complete, cyclic dissociation of water still eludes us. In part, this failure is due to the poor performance of the catalysts employed and greatly improved catalysts must be developed before we can progress much further.

Because of its low overpotential ($\eta$), platinum is the most commonly used electrode material for the liberation of hydrogen from water and it has enjoyed considerable success as a catalyst in model hydrogen producing photosystems. With a macroelectrode in acidic solution, the Butler-Volmer equation can be used to relate the overpotential to the net current density (i, measured in A/cm²).

$$i = i_{AN} - i_{CAT}$$

$$= i_0 \left\{ \exp \frac{(1 - \alpha)zF\eta}{RT} - \exp \frac{-\alpha zF\eta}{RT} \right\} \quad (i)$$

where $\alpha$ is the cathodic transfer coefficient ($\alpha = 0.5$ for hydrogen evolution) and z is the charge transfer valence ($z = 1$). The exchange current density ($i_0$) is a known function of the concentrations of $H^+$ and $H_2$. In acidic solution, the reoxidation of evolved hydrogen is not too important and the rate-determining step is discharge of an electron to an adsorbed proton. Therefore, the above equation can be simplified to

$$i = i_0 \exp \frac{-0.5F\eta}{RT} \quad (ii)$$

$$\text{or} \quad i = F k_0 C_{H^+} \exp \frac{-0.5F\eta}{RT} \quad (iii)$$

where $C_{H^+}$ refers to the concentration of protons in the bulk electrolyte. This simplified equation

## Table I
### Hydrogen-Evolving Photosystems

| Sensitiser | Electron acceptor | Electron donor | Catalyst | Quantum efficiency $\phi \tfrac{1}{2}H_2$ per cent |
|---|---|---|---|---|
| $bipy_3Ru^{2+}$ | methyl viologen | EDTA | platinum colloid | 26 |
| " | " | cysteine | $PtO_2$ | — |
| proflavine | " | EDTA | platinum/asbestos | — |
| acridine yellow | " | " | platinum colloid | 32 |
| $ZnTMPyP^{4+}$ | " | " | platinum colloid | 60 |
| " | none | " | platinum colloid | 7 |
| $ZnTSPP^{4-}$ | methyl viologen | " | platinum colloid | 2 |

## Table II
### Oxygen-Evolving Photosystems

| Sensitiser | Electron acceptor | Catalyst | Quantum efficiency $\phi \tfrac{1}{4}O_2$ per cent |
|---|---|---|---|
| $bipy_3Ru^{2+}$ | $Co(NH_3)_5Cl^{2+}$ | $RuO_2$ powder | 1.2 |
| " | " | $RuO_2$ colloid | 20 |
| " | " | $CoSO_4$ | 8 |
| " | " | $RuO_2$/zeolite | 5 |
| " | " | $RuO_2$/$TiO_2$ | 12 |
| " | " | $MnO_2$ | — |
| $bipy_3Ru^{2+}$ | $S_2O_8^{2-}$ | $RuO_2$/$TiO_2$ | 24 |
| " | " | $IrO_2$ | 14 |
| $bipy_3Ru^{2+}$ | $Ti^{3+}$ | $RuO_2$ colloid | <1 |

$ZnTMPyP^{4+}$ = zinc tetra(N-methyl-4-pyridyl)porphine    $ZnTSPP^{4-}$    zinc tetra(4-sulphophenyl)porphine

relates the net current density to the applied, or available, overpotential, the pH of the bulk solution and the heterogeneous rate constant for the electron transfer process ($k_0$). At high overpotential, the current/voltage curve flattens out due to rate determining diffusion of the electroactive species to the electrode surface. Here, the limiting current density ($i_1$) is given by

$$i_L = \frac{zFDC}{\delta} \qquad (iv)$$

where D is the diffusion coefficient of the species in the medium, C is its concentration and $\delta$ is the thickness of the diffusion layer.

In order to apply the above equations to our proposed model photosystems, it is necessary to acknowledge two important points. First, the available overpotential for hydrogen production will be determined by the redox potential of the electron mediator used, usually methyl viologen for which $E^0 = -0.44$ V. Secondly, the limiting current density will be set by the rate of charging the catalyst rather than by the rate of discharge so that Equation (iv) will apply with D and C referring to the reduced electron acceptor. We can, therefore, express the efficiency of a photosystem in terms of the product of the rate of production of the reduced relay and the rate at which this species is reoxidised on the catalyst surface.

With methyl viologen as electron acceptor, the available overpotential for Equation (iii) can be expressed

$$\eta = (0.44 - 0.059 \text{ pH})$$

so that reaction is restricted to acidic solution.

In order to obtain the maximum rate of mass transfer to the electrode surface, it is seen from Equation (iv) that the thickness of the diffusion layer should be kept as small as possible whereas the total surface area of the catalyst should be as large as possible. For a given amount of platinum, high surface areas are obtained if the catalyst is in the form of colloidal particles (radius r nm) rather than as a planar sheet. For such particles, the bimolecular rate constant for interaction between a reduced acceptor and a platinum particle can be written

$$k = 4\pi NDr \qquad (v)$$

where N refers to Avogadro's number. If the concentration of particles exceeds the steady-state concentration of the reduced acceptor, then the pseudo-first order rate constant for interaction becomes
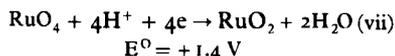
$$k^1 = \frac{0.027 \, D \, C_O}{r^2} \qquad (vi)$$

where $C_O$ is the molar concentration of platinum (3). Thus, smaller particles favour faster mass transfer to the catalyst surface and, therefore, allow higher current densities to be achieved. The importance of using colloidal platinum catalysts cannot be overstressed.
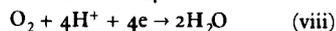
These colloidal platinum particles are made by the reduction of $H_2PtCl_6$ in aqueous solution, with hydrogen, citrate or pulse radiolysis and an inert support such as polyvinyl alcohol is added to stabilise the colloid against flocculation. According to Equation (vi), there are advantages in preparing very small platinum particles but the lower limit for hydrogen formation seems to be reached with $r \sim 1.0$ nm. Such particles do not scatter visible light and, when properly supported, they are stable over many months standing. However, they give rise to two major problems in that they cannot easily be recovered from the reaction solution and they facilitate hydrogen production throughout the entire volume of the photolysis cell. This latter point is extremely important because, in any practical system, the hydrogen should be evolved at a particular site where it can be collected. This can be achieved only with a macroelectrode and, therefore, although the

colloidal platinum particles work extremely well in model photosystems, they appear to have limited potential for practical applications.

Similar arguments can be applied to the oxygen-evolving photosystems. From electrochemical work, it is known that the most suitable anodes for oxygen liberation are constructed from $RuO_2$ and $IrO_2$ and both materials have been used in model photosystems. So far, most work has centred upon $RuO_2$ but it is known now that this is not a particularly good redox catalyst in photochemical systems. Although claims exist to the contrary, it is clear that $RuO_2$ is not a selective catalyst for oxygen production but it can be used for hydrogen generation; its overpotential in acidic solution is not much higher than that of platinum. This can lead to short-circuits in the photochemistry. More importantly, in acidic solution the overpotential that can be applied to an $RuO_2$ electrode is limited to low levels by a decomposition process:
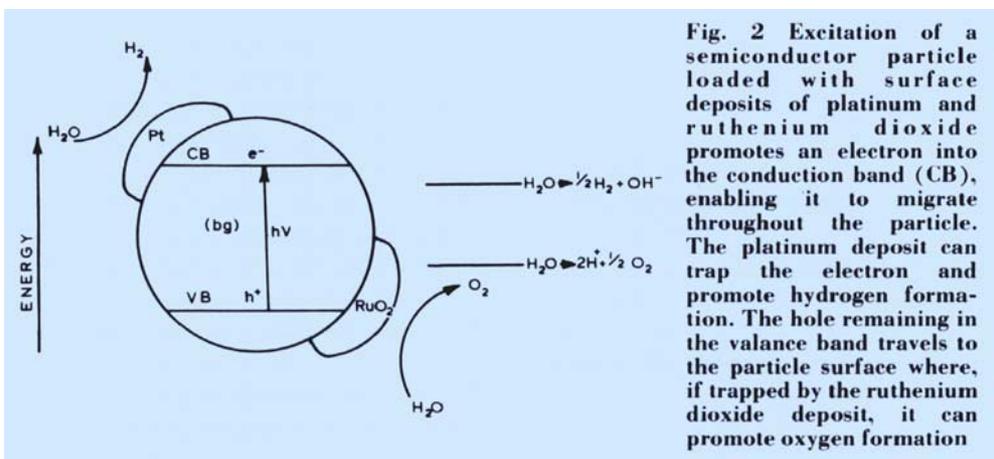
$$RuO_4 + 4H^+ + 4e \rightarrow RuO_2 + 2H_2O \quad (vii)$$
$$E^O = +1.4 \text{ V}$$
$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad (viii)$$
$$E^O = +1.23 \text{ V}$$

However, the dissolution of $RuO_2$, Equation (vii), can be inhibited almost completely by supporting the material on an inert oxide such as $TiO_2$. These mixed oxides function as effective oxygen-evolving catalysts and they can be obtained in particulate form. Using colloidal $TiO_2$ loaded with small (about 2 per cent w/w) deposits of $RuO_2$, Grätzel and his colleagues have reported that the oxidation of water to oxygen, via a powerful one electron oxidant (bipy$_3$Ru$^{3+}$), is a concerted process (4). This finding is based upon the observation that the reduction of bipy$_3$Ru$^{3+}$ and the formation of a proton, Equation (viii), occur simultaneously.

At the moment, the $TiO_2/RuO_2$ catalysts seem to be the most promising materials for use in oxygen-evolving photosystems but little work has centred upon the use of $IrO_2$. More studies are needed before we can be satisfied with these catalysts but the oxygen-evolving photosystem has a big advantage over the analogous hydrogen-photosystem. This concerns the use

Fig. 2 Excitation of a semiconductor particle loaded with surface deposits of platinum and ruthenium dioxide promotes an electron into the conduction band (CB), enabling it to migrate throughout the particle. The platinum deposit can trap the electron and promote hydrogen formation. The hole remaining in the valance band travels to the particle surface where, if trapped by the ruthenium dioxide deposit, it can promote oxygen formation

of colloidal catalysts. We have seen earlier that, because of their large surface area, colloidal catalysts offer important benefits for maximising the rate of gas evolution but they do not facilitate collection of the gas. For oxygen production, it may not be necessary to collect the gas and, provided it does not interfere too much with the photochemistry, it can be evolved throughout the entire volume of the photolysis cell. Thus, colloidal catalysts seem to have a future in oxygen-evolving photosystems.

Although it is important that more efficient oxygen-evolving catalysts are developed, the oxygen-photosystem is severely limited by the lack of suitable photosensitisers. As outlined in Table II, only tris(2,2'-bipyridyl)ruthenium (II) functions in this manner. Since this compound absorbs only a modest fraction of the solar spectrum and it is costly, it is therefore essential that new photosensitisers are identified soon.

## Semiconductor Systems

The same type of considerations can be applied to the design of semiconductors for the photodissociation of water. Consider the case of a wide band-gap semiconductor, as shown in Figure 2. Irradiation, with light of energy greater than the band-gap, results in formation of an electron/hole pair ($e^-/h^+$) in which the electron resides in the conduction band and the positive hole remains in the valence band. Both the hole and the electron can migrate to the surface of the semiconductor, where recombination occurs. However, given appropriate thermodynamics, the electrons in the conduction band can be used to reduce water to hydrogen and the positive holes in the valence band can be used to oxidise water to oxygen. Catalysts are required for at least one of these processes, usually the reduction step, and the most commonly employed materials are platinum and/or $RuO_2$. There is now great activity in the design of suitable systems based upon colloidal semiconductors loaded with one or more of the above catalysts. The problems associated with finding a useful system can be summarised as: (a) the energetics must be carefully balanced so that visible light can be used to photodissociate water, and (b) many semiconductors undergo photocorrosion.

It is clear from Figure 2 that the positions of both CB and VB are critical if the photodissociation of water is to be realised. Very few known semiconductors have their energy levels located at appropriate positions while retaining a relatively small band-gap. The smallest band-gap that is consistent with efficient electron/hole separation and water dissociation is $(2.2 \pm 0.2)$ eV, which corresponds to a wavelength of about 500 nm. Unfortunately, semiconductors with band-gaps in this region are usually unstable with respect to photocorrosion. Only wide band-gap semiconductors, like $TiO_2$ (bg $= 3.0$ eV) or

SrTiO$_3$ (bg = 3.2 eV), are completely stable towards illumination, but these compounds absorb only a very small fraction of the solar spectrum. However, recent work has shown that it might be possible to stabilise semiconductors against photocorrosion by loading the surface with highly efficient catalysts (5). Thus, in the case of CdS (bg = 2.4 eV), which undergoes rapid anodic photodecomposition, loading with small amounts (about 1 per cent w/w) of RuO$_2$ results in a drastic improvement in stability. These systems are being investigated in many laboratories around the world and rapid progress should ensue.

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# Multi-Megawatt Fuel Cell Produces Electricity

## PLATINUM CATALYSTS PROMOTE EFFICIENT ENERGY CONVERSION

The Tokyo Electric Power Company (TEPCO) has recently commenced a year-long test of their 4.5MW demonstration fuel cell power plant, manufactured by United Technologies Corporation and incorporating platinum catalysts supplied by Johnson Matthey, at the Goi power station complex in Ichihara City.

In a special bulletin the Fuel Cell Users Group of the Electric Utility Industry, in the United States of America, reported that the Japanese plant first produced electricity on April 8th, 1983 and at the time of the announcement had accumulated over 55 hours of operating time at 2.4MW. Testing will continue to verify operating conditions and performance characteristics, and to provide data that will help to determine the potential of fuel cell technology for commercial power generation.

The plant, which is designed to have an average output of 4.8MW direct current — converted to 4.5MW alternating current for utility use — and a service life of twenty years, is a modified version of another United Technologies demonstration fuel cell power plant now in the final stages of preparation for operation by Consolidated Edison Company of New York, Inc. in Manhattan, New York City. The latter is an interim result of a research and development programme initiated in the early 1970s by a group of U.S. electric utilities and the U.S. Government to explore the feasibility of building and operating 27MW fuel cell generators, a size that would be suitable for the needs of 80 per cent of municipal and rural electricity producers in the United States. Although this demonstrator unit has not yet produced power, experience gained with it has already enabled improvements to be incorporated into the design of an 11MW commercial plant now being planned by U.T.C.

### Characteristics of Fuel Cells

The basic advantage of a fuel cell is its efficiency in converting chemical energy into electricity and heat, which is maintained over a wide range of operating loads, combined with an ability to respond quickly to load changes. Low levels of emissions, quiet operation and a minimal requirement for water are features that make installation of fuel cell power plants acceptable in environmentally sensitive areas close to the point of power requirement.

The TEPCO generator system was installed in less than two years, demonstrating an advantage of modular construction that will enable capacity to be increased incrementally and rapidly in response to growing demands. In addition TEPCO have postulated siting modules in multi-storey buildings, so saving space in areas with a high population density.

On the basis of accumulating experience with numerous kilowatt units and the two multi-megawatt demonstration plants, it seems most probable that phosphoric acid fuel cells incorporating electrodes catalysed with platinum group metals will make a significant contribution to the efficient commercial generation of both heat and electrical power over the next few decades.