Light-induced Hydrogen Evolution in Oxidising Media promoted by Catalytic Sites encapsulated by Phospholipid Membranes

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Encapsulation of the well known photochemical system consisting of electron donor [ethylenediaminetetra-acetic acid (EDTA)], photosensitizer [Ru(bpy)$_3$$^{2+}$ (bpy = 2,2′-bipyridine)], electron acceptor [Rh(bpy)$_3$$^{3+}$], and catalytic sites (Pt particles, produced by reduction of K_2PtCl_4) in a DPPC (dipalmitoyl-D,L-α-phosphatidylcholine) membrane allows light-induced H_2 evolution in the presence of an oxidant [$K_3Fe(CN)_6$] in the bulk solution.

Separation of the electron transfer reactions in chloroplasts and the redox potential of a bulk solution is an essential property of the *in vivo* system providing the energy-trapping reactions of photosynthesis. This property of the photosynthetic components can be simulated *in vitro* by encapsulating a catalytic site of the photosystem inside a lipid vesicle.

We now describe light-induced H_2 evolution in the presence of an oxidant in the bulk solution promoted by catalytic sites encapsulated in a DPPC (dipalmitoyl-D,L-α-phosphatidylcholine) membrane. The well known photochemical system[1] of ethylenediaminetetra-acetic acid (EDTA), Ru(bpy)$_3$$^{2+}$ (bpy = 2,2′-bipyridine), Rh(bpy)$_3$$^{3+}$, Pt catalyst, and Fe(CN)$_6$$^{3-}$ oxidant, which mimics photosystem I of green plant photosynthesis,[2] has been used.

Pt-deficient vesicles were prepared by sonication (30 min) of DPCC (1.25×10^{-5} mol) in 0.04 M acetate buffer solution

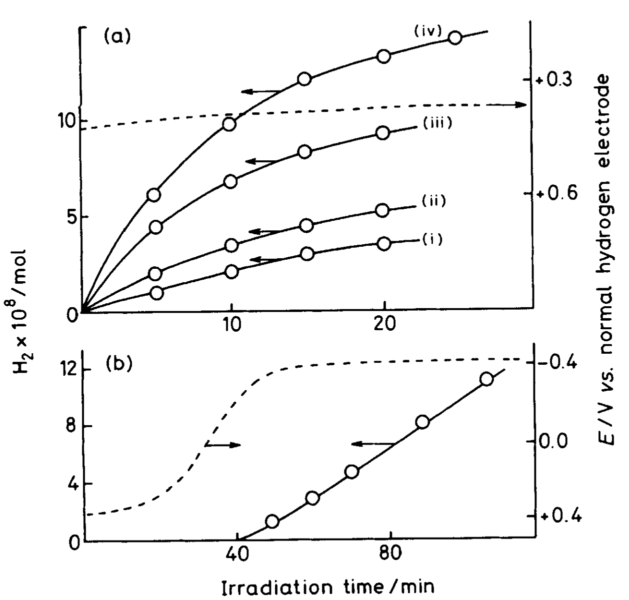

Figure 1. H_2 evolution and redox potential, E, of the bulk solution in (a) vesicular and (b) homogeneous systems in the presence of oxidant [10^{-4} M $Fe(CN)_6^{3-}$] as a function of irradiation (λ 436 nm, I_0 1.8×10^{-7} Einstein s^{-1}) time. Solution volume 5 ml. (a) [DPPC] = 2.5×10^{-3} M; 0.04 M acetate buffer (pH 5); localised concentrations of encapsulated reactants: $[EDTA]_l$ = 0.1 M; $[Ru(bpy)_3^{2+}]_l$ = 0.01 M; $[Rh(bpy)_3^{3+}]_l$ = 0.02 M. [K_2PtCl_4] in the initial solution used for sonication: (i) 0; (ii) 1×10^{-3}; (iii) 2×10^{-3}; (iv) 5×10^{-3} M. (b) [$Ru(bpy)_3^{2+}$] = 1×10^{-5} M; [MV^{2+}] = 1.10^{-4} M; [EDTA] = 0.01 M; [Pt] = 1×10^{-5} M; [PVA] = 0.5 g/l; 0.04 M phosphate buffer (pH 6).

(2.5 ml; pH 5) containing 0.1 M EDTA, 0.01 M $Ru(bpy)_3^{2+}$, and 0.02 M $Rh(bpy)_3^{3+}$ at 58—62 °C and separated by chromatography on a Sephadex G-150 column. Visible light irradiation (λ 436 nm, I_0 1.8×10^{-7} Einstein s^{-1}) of a deoxygenated solution containing Pt-deficient vesicles resulted in the reduction of $Rh(bpy)_3^{3+}$ to $Rh(bpy)_2^{+}$ (decay of $\lambda_{max.}$ 306 and 320 nm),[1b] as shown in equations (1)—(5). The addition of $K_3Fe(CN)_6$ to the bulk solution did not affect the accumulation of $Rh(bpy)_2^{+}$ inside the vesicle, *i.e.* the DPPC vesicle wall is of sufficient thickness to suppress electron transfer from $Rh(bpy)_2^{+}$ to $Fe(CN)_6^{3-}$.†

$$^{*}Ru(bpy)_3^{2+} + Rh(bpy)_3^{3+} \rightarrow Ru(bpy)_3^{3+} + Rh(bpy)_3^{2+} \quad (1)$$

$$Ru(bpy)_3^{3+} + EDTA \rightarrow Ru(bpy)_3^{2+} + EDTA_{ox} \quad (2)$$

$$Ru(bpy)_3^{3+} + Rh(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + Rh(bpy)_3^{3+} \quad (3)$$

$$Rh(bpy)_3^{2+} \rightarrow Rh(bpy)_2^{2+} + bpy \quad (4)$$

$$Rh(bpy)_3^{2+} + Rh(bpy)_2^{2+} \rightarrow Rh(bpy)_3^{3+} + Rh(bpy)_2^{+} \quad (5)$$

A small amount of hydrogen [quantum yield, $\Phi(H_2)$ 2.8×10^{-3}] was produced during irradiation of Pt-deficient vesicles in both pure buffer and $Fe(CN)_6^{3-}$ solution owing to further reduction of the $Rh(bpy)_2^{+}$ complex by $Rh(bpy)_3^{2+}$ to Rh hydride[1b] (Figure 1a).

H_2 production can be increased by encapsulating the catalytic Pt site inside a vesicle. It has been shown recently that encapsulated catalytic sites can be prepared by treatment of K_2PtCl_4[3] and by photochemical reduction of $Pt(NH_3)_4Cl_2$[4] or $RhCl_3$.[5] In the present work it has been found that a very active caged catalyst is formed by sonication of DPPC in 0.04 M acetate buffer solution (pH 5.0) containing 10^{-3}—5×10^{-3} M K_2PtCl_4‡ and the other necessary components [0.1 M EDTA, 0.01 M $Ru(bpy)_3^{2+}$, and 0.02 M $Rh(bpy)_3^{3+}$].§ The Pt concentration in the vesicle solution after gel filtration is 1—2×10^{-5} M as measured by atomic absorption spectrometry.

The $Rh(bpy)_3^{2+}$ produced by irradiation of the Pt-containing vesicles [reaction (1)] reduces the Pt catalyst into an active form. The resulting Pt particles (10—30 Å) are well defined in electron micrographs and catalyse H_2 formation according to equation (6). The rate of H_2 evolution is not affected by addition of $K_3Fe(CN)_6$ to the bulk solution. Furthermore, the redox potential, E, of the solution remains practically the same on irradiation of the vesicular system (Figure 1a, broken line). H_2 evolution in the oxidising medium is the main advantage of the use of caged active sites. Indeed H_2 evolution in the classical homogeneous photochemical system[2] [EDTA, $Ru(bpy)_3^{2+}$, MV^{2+} (MV = methyl viologen), Pt–PVA (PVA = polyvinyl alcohol)] has a significant rate only when E is sufficiently negative (Figure 1b).

$$2Rh(bpy)_3^{2+} + 2H_2O \xrightarrow{Pt} 2Rh(bpy)_3^{3+} + 2OH^- + H_2 \quad (6)$$

The rate of H_2 evolution increases with increasing Pt concentration in the vesicles (Figure 1a). $\Phi(H_2)$ in the vesicular system prepared by sonication of the required components in 5×10^{-3} M K_3PtCl_4 has a value of 0.02; *i.e.* it is less than the cage escape yield, Φ(cage) = 0.15,[1b] of $Rh(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ in reaction (1). At localised concentrations, $[Rh(bpy)_3^{3+}]_l$ = 0.02 M, practically all the $^{*}Ru(bpy)_3^{2+}$ is quenched (k_q 6.2×10^{-8} $dm^3\ mol^{-1}\ s^{-1}$)[1b] so the difference between $\Phi(H_2)$ and Φ(cage) arises from the competition of $Rh(bpy)_3^{2+}$ decay in reaction (6) and reactions (3)—(5) at high local concentrations of $[Rh(bpy)_3^{2+}]_l$ (1 molecule in the vesicle inner volume corresponds to 10^{-3} M). The decrease in the rate of H_2 evolution during irradiation of Pt-vesicles (Figure 1a) is due to the formation of Rh^I which is inactive in Pt-catalysed H_2 production.[1b] The turnover number (per one electron) is about 7 for $Rh(bpy)_3^{3+}$ and 14 for $Ru(bpy)_3^{2+}$.

Significant improvement of the system described here may be expected on incorporation of a water-insoluble electron donor, D^1, in the vesicle wall, and an electron donor, D^2, in the bulk solution.¶ The sequence of redox potentials $E[Ru(bpy)_3^{3+/2+}] > E(D^{1+/0}) > E(D^{2+/0})$ could allow the unidirectional electron transfer from D^2 to $Ru(bpy)_3^{3+}$ produced in reaction (1) whereas the competition of D^1

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† Traditional electron acceptors such as viologens[2] cannot be used instead of $Rh(bpy)_3^{3+}$. The methyl viologen radical-cation, $MV^{+\cdot}$, diffuses rapidly across the vesicle wall. Radicals of viologens with charged groups (1,1′-ethylsulpho-4,4′-bipyridine, 1-β-ethylsulpho-1′-methyl-4,4′-bipyridine, 1,1′-γ-tetra-aminopropyl-4,4′-bipyridine, or 1-γ-tetra-aminopropyl-1′-methyl-4,4′-bipyridine) reduce $Fe(CN)_6^{3-}$ in the bulk solution at a remarkable rate though they all remain in the vesicles during irradiation. The mechanism of these reactions is being investigated.

‡ The activity of the catalyst prepared from $Pt(NH_3)_4^{2+}$ is rather low owing to incomplete reduction of the Pt complex.

§ The Pt encapsulation depends on [K_2PtCl_4], [EDTA], pH, and sonication temperature. The effects of these experimental conditions are being investigated.

¶ Generation of the strong oxidant in the vesicle system (model of photosystem II) with a water-insoluble electron acceptor, A^1, incorporated in the vesicle wall and an electron acceptor, A^2, in the bulk solution has recently been developed.[6]

oxidation by $Ru(bpy)_3^{3+}$ and back reaction (3) could allow reductant accumulation inside the vesicle with subsequent catalytic H_2 production. Such a construction of the photocatalytic system (model of photosystem I) may provide continuous H_2 production, which is independent of the donor content in the vesicle.

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