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Multielectron transfer water oxidation catalysts as models for photosynthetic oxygen evolving centre

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Oxygen evolution is one of the most important processes in photosynthesis. Several proposals have been made to elucidate the role of manganese ions and the mechanism involved in photosynthetic oxygen evolution. Metal oxides such as RuO_2, PtO_2, etc have been initially reported as oxygen-evolving catalysts. However, redox chemistries and mechanisms associated with such catalysts were difficult to evaluate and they are non-specific. Although several manganese complexes are reported as models, the manganese model complexes show that they are active for water oxidation only in the heterogeneous state since each metal centre in such systems acts as one-electron oxidant only and the four-electron water oxidation is efficiently coupled in the heterogeneous system. In recent times, by choosing proper chemical model systems, the mechanism of oxygen evolution as a model for water oxidation centre in photosystem II has been studied. The report of dimer $[(bpy)_2(H_2O)Ru–O–Ru(H_2O)(bpy)_2]^{4+}$ with aquo ligands has shown the way to look for molecular catalysts which are well characterized. In a further understanding, poly-nuclear metal complexes like Ru-red and Ru-brown are found to be efficient catalysts for water oxidation. Although monomeric $[Ru(bpy)_2(H_2O)_2]^{2+}$ could not oxidize water, it was found that other monomeric ruthenium complexes are active for water oxidation as two-electron oxidant in both homogeneous as well as in heterogeneous systems. The visible light splitting of water with such catalysts has been achieved by a system mimicking photosystem II. In this review we present artificial model systems for photosynthetic oxygen evolution.

SOLAR energy conversion is becoming increasingly important and urgent as an alternative new energy resource since the global environmental problems such as CO_2 increase have come to be serious. Photosynthesis is an excellent photochemical model for achieving artificial solar energy conversion systems, for which water oxidation is the most important primary step to provide electrons to the whole system to produce energy-rich reduction compounds[1–4]. Water oxidation in photosystem II of the green plant photosynthesis is the essential reaction to pump electrons from water molecules to biological systems (eq. (1)).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

$$\Delta G = 575 \text{ kJ/mol } O_2.$$

To achieve photosynthesis, a minimum of 475 kJ energy per mol of evolved oxygen (or per consumed carbon dioxide) must be introduced in the system. The ability of green plants to produce molecular oxygen from water using sunlight energy is a mystery which remains to be

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explained at the molecular level. In artificial photosynthesis, the goal is to mimic the ability of green plants or other photosynthetic organisms in their use of sunlight to produce high energy chemicals[5]. It is a chemically difficult problem to account for the complexity of natural photosynthetic reactions. In the field of artificial photosynthesis, attempts are currently being made to design molecular units that mimic the function of the oxygen-evolving centre (OEC), a key constituent of the plant photosystem II.

Water oxidation in photosynthesis

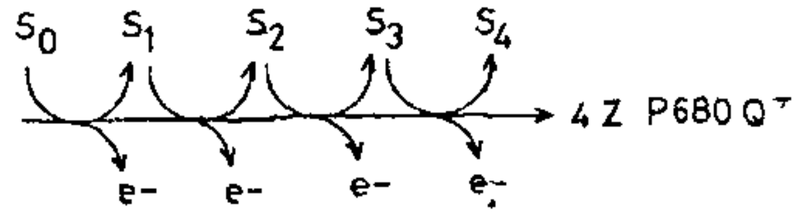
Joseph Priestley demonstrated in 1771 that green plants could 'purify' air made 'foul' by animals. Since the early experiments, there have been considerable efforts to understand how green plants can efficiently bring about photo-oxidation of water[1–4]. This study has been highlighted by major advances in our understanding of molecular components essential for the photosynthetic process. These advances led to a more rational design and synthesis of a variety of complex molecular systems aimed at increasing the efficiency of charge transfer and charge separation in the molecular level[5]. The other major development culminated in the recent crystallization and direct structure determination of the *in vivo* bacterial photosynthetic centres[6].

Photosynthetic oxygen evolution is associated with photosystem II as shown in Figure 1. To form one molecule of oxygen it is necessary to remove four electrons from two water molecules. The potential of the four holes must be higher than + 0.82 V vs NHE at pH 7. Therefore, in green plants, either four reaction centres cooperate together to bring about the evolution of one oxygen molecule, or charge storage occurs within a single reaction centre to carry out water oxidation.

In the photosynthetic oxygen-evolving centre, the oxidation state is represented by the so-called *S*-state model (*S* = the redox state of the oxygen-evolving system and also to express the charge accumulation process) (scheme 1). In this scheme, P680 is chlorophyll *a* molecule; *Z* is the electron donor and *Q* the electron acceptor in PS-II. It is envisaged that holes are accumulated as S_4 state after successive four-electron oxidation of S_0 by photoinduced charge separation occurring successively at the photoreaction centre.

$$4\ Z\ P680\ Q \xrightarrow{4\,h\nu} 4\ Z\ P680^{*}\ Q^{-} \longrightarrow$$

$$4\ Z^{+}\ P680\ Q^{-} \longrightarrow$$



Scheme 1.

Involvement of Mn ions in the photosynthetic oxygen evolution

Evidence has been accumulated linking the oxygen evolution process with the presence of manganese ions in chloroplasts[1–4]. There is considerable support for the binding of at least four Mn ions to the oxygen evolution centre in a variety of photosynthetic organisms. The most highly resolved submembrane that exhibits high oxygen evolution activity contains a tightly associated reaction centre in which Mn ions are present as a protein complex.

Despite considerable variability in oxygen evolution rate there remains good agreement that four Mn ions are present in PS-II membrane having optimal activity[1–4,7,8]. One report of two Mn ions in spinach PS-II[9] has now been shown to be an underestimate, and a revised value of about four Mn in PS-II is now reported[10,11]. The requirement of four Mn/PS-II for optimal activity would not necessarily imply that all four Mn ions are involved in water oxidation.

A speculative scheme (Figure 2) has been suggested[12] for the involvement of four Mn ions in water oxidation, and this scheme considers the fact that protons are released at other stages in the cycle and not just at the $S_4 \rightarrow S_0$ transition. It seems likely that the four coordinated Mn ions in the proposed complex could be sufficiently close (only few Å) to facilitate the O–O bond formation without the involvement of free radicals. It would be expected that spatial distances must be very short between the redox centres to allow the formation of an O–O bond for oxygen evolution.

The photosynthetic oxygen evolution proposed[13] based on the early experimental data is shown in Figure 3. It visualizes a structural conversion of a Mn_4O_6 'adamantane'-like complex to a Mn_4O_4 'cubane'-like complex as the mechanism of photosynthetic oxygen evolution. As each manganese ion is proposed to be anchored on the

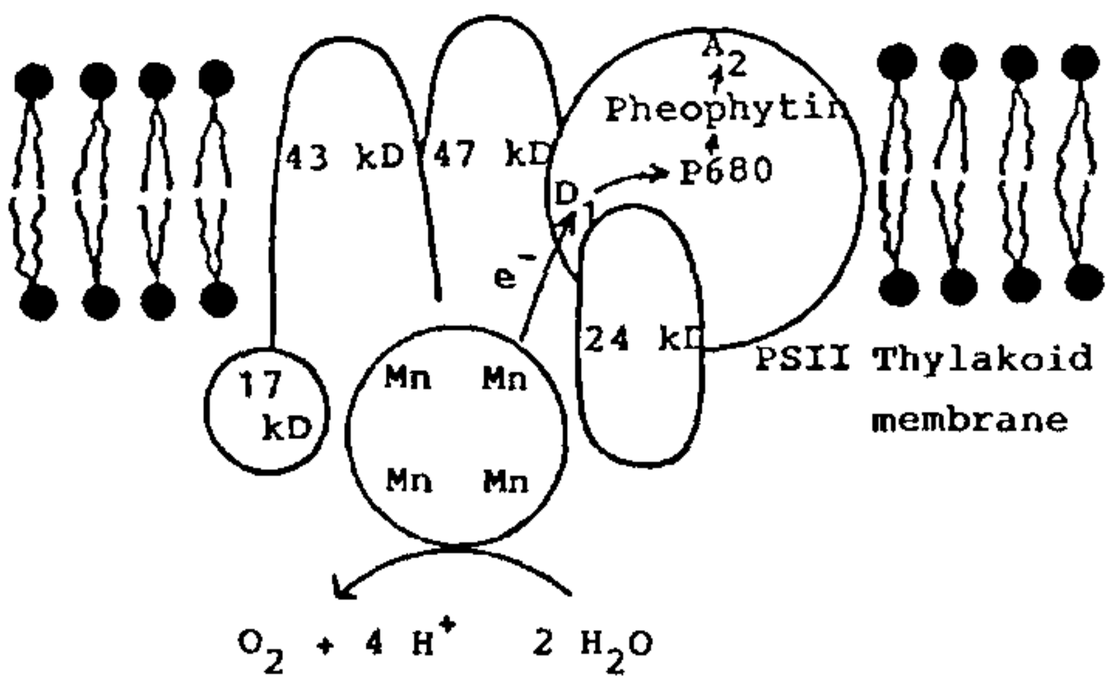


Figure 1. Water oxidation centre in photosynthesis (photosystem II)

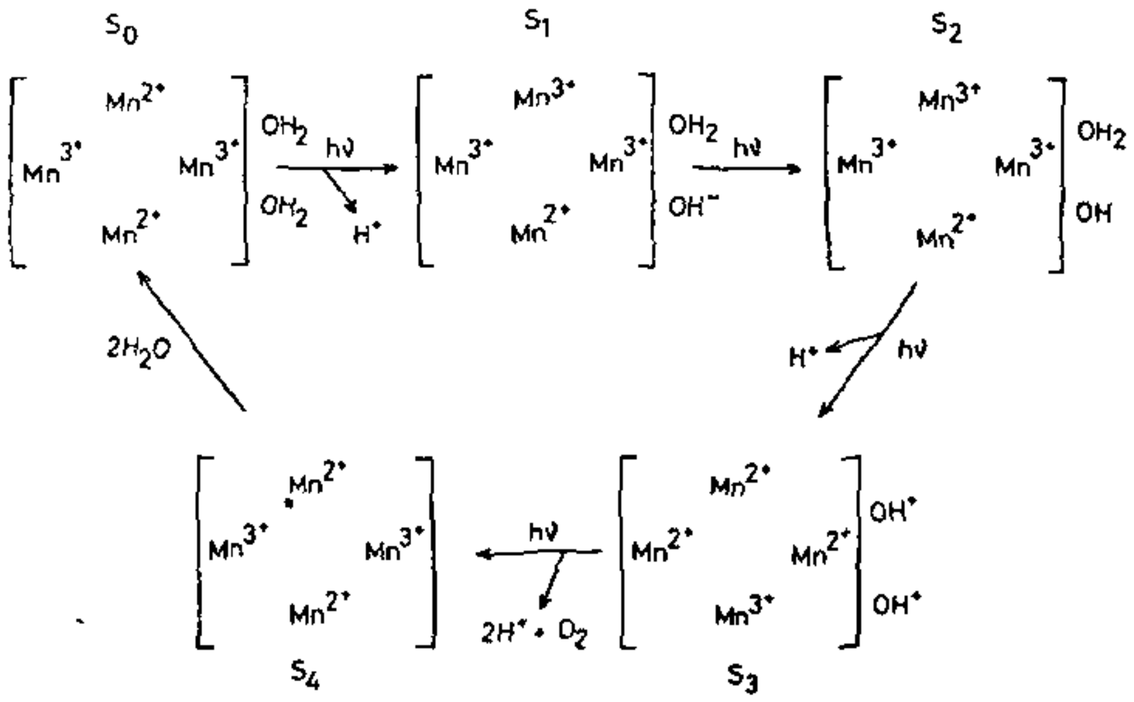


Figure 2. A model for the mechanism of photosynthetic water oxidation centre shown as *S*-state.

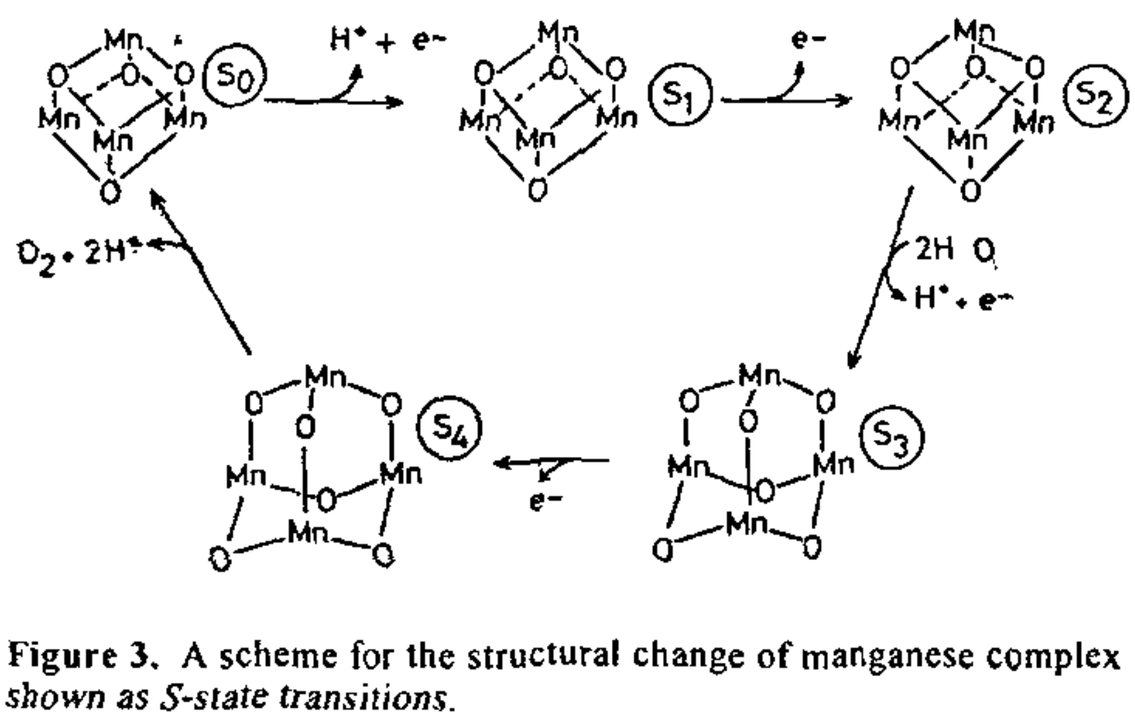


Figure 3. A scheme for the structural change of manganese complex *shown as S-state transitions.*

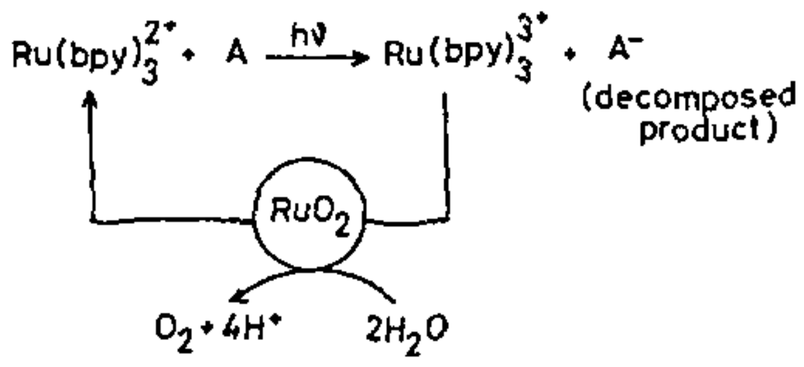
protein matrix via three N or O ligands, one would expect that the positions of the four manganese ions would remain essentially fixed in this model. In the proposed structural conversion between an Mn_4O_4 structure and an Mn_4O_6 structure, the positions of the four manganese ions need only very little change, if at all, to accommodate the change in O ligand environment for O_2 liberation from S_4 (Figure 3).

Model systems for photosynthetic oxygen evolution

Catalyst for water oxidation

It is reasonable to choose manganese compounds as possible catalysts for water oxidation by taking the photosynthetic oxygen evolution as a model. Previous attempts to realize such water oxidation included oxo-bridged dinuclear manganese complexes and manganese porphyrins[14,15]. Although a number of manganese complexes have been proposed as model complexes for water oxidation, the evolution of oxygen has hitherto never been observed[16].

It was reported that oxygen was evolved with a strong one-electron oxidant $Ru(bpy)_3^{3+}$ at pH 8 without any catalyst[17], but later no oxygen evolution was observed with $Ru(bpy)_3^{3+}$ in the absence of a catalyst[18,19]. It is now known that $Ru(bpy)_3^{3+}$ is able to bring about four-electron oxidation of water to oxygen if it is coupled with a solid catalyst such as RuO_2 and PtO_2[18–25] (scheme 2). Even though oxygen evolution is realized using model systems, the mechanism of oxygen evolution and the catalytic activity of this solid catalyst systems are still unclear. These solid catalysts are heterogeneous in nature and their redox chemistries are difficult to study. They are non-specific and active for hydrogen evolution as well. It is necessary to design and study a chemical model of the photosynthetic oxygen evolution, to understand the mechanism of oxygen formation from two water molecules in a homogeneous solution as well as in a heterogeneous state[26].



Scheme 2.

Model manganese complexes

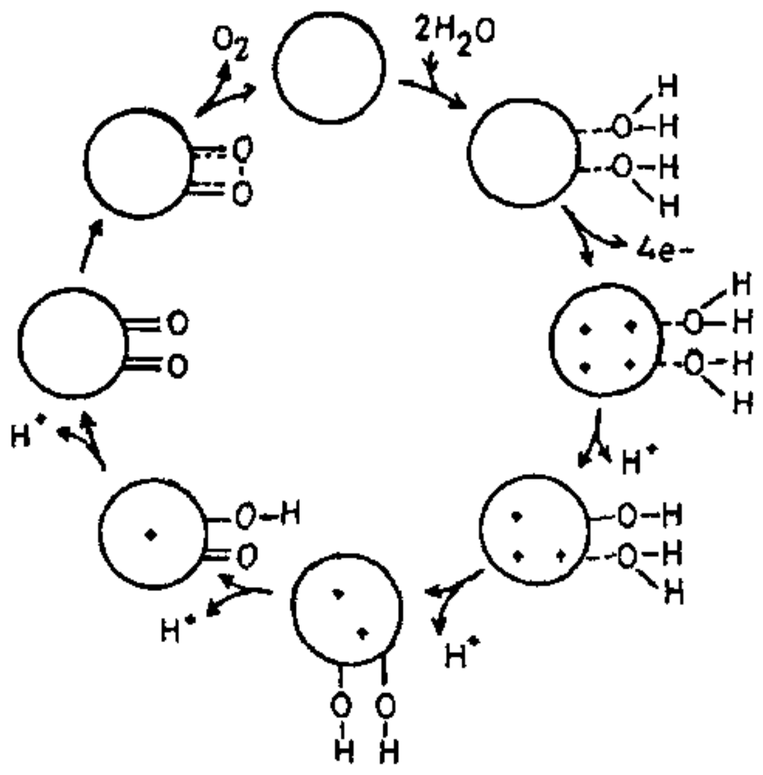
In chloroplasts of green plants there is a loosely bound pool of Mn ions that act as a multielectron transfer catalyst for the oxidation of water to oxygen[1–4]. Many models for the participation of manganese ions have been proposed based on available data and on thermodynamic considerations of the properties of manganese and water[16]. It was reported[14] that the dioxo-bridged dinuclear manganese complex was able to decompose water photolytically, but the initial claims of success on photolytic dioxygen evolution had to be withdrawn[27]. Later, it was found that dinuclear manganese complexes oxidize water during formation of visible oxygen bubbles when suspended in water as a heterogeneous catalyst in the presence of an oxidant such as Ce(IV) ion. However, the same complex cannot oxidize water when used in a homogeneous solution[28,29]. The monomeric Schiff base manganese complexes were reported as model complexes for photosynthetic oxygen evolution[16,30]. Oxygen electrode was mainly used to detect dissolved oxygen in solution, but this oxygen electrode is sensitive to temperature changes caused by photolysis[27]. It has now been found that these Schiff base complexes of manganese become insoluble upon addition of Ce(IV) ions, and the solid complex oxidizes water by the Ce(IV) oxidant with the formation of visible oxygen gas bubbles[31]. The redox potentials of

these manganese complexes show that they can be used only as one-electron transfer agents for water oxidation. Since four electrons are required to form one oxygen molecule, water oxidation can be achieved only when the one-electron processes can be efficiently coupled (eq. (2)). This is obviously not the case in a homogeneous phase, but is so in a heterogeneous phase.

$$4Mn^{III} - Mn^{IV} \rightarrow 4Mn^{IV} - Mn^{IV} \xrightarrow{2H_2O}$$

$$4Mn^{III} - Mn^{IV} + O_2 + 4H^+. \qquad (2)$$

The heterogeneous water oxidation system described here is of special interest with regard to oxygen evolution in photosynthesis. The probable role of heterogeneity is to bring oxygen atoms of two water molecules into close proximity to form an O–O bond at the manganese complex where the bound peroxide is binuclearly complexed[32]. It was earlier suggested[1–4,12,32] that the microheterogeneous environment around manganese and the close proximity of manganese atoms to one another are responsible for water oxidation in photosynthesis. It is conceivable that four molecules of manganese complex may be oxidized by four Ce(IV) ions to produce a four-electron depletion centre in the aggregated Mn complex. The oxidizing centre would realize four-electron oxidation of two molecules of weakly bound water with subsequent evolution of oxygen (scheme 3).



Scheme 3.

Model ruthenium complexes

It has been suggested that the oxo-bridged ruthenium complex, $[(bpy)_2(H_2O)Ru–O–Ru(H_2O)(bpy)_2]^{4+}$, leads to oxidation of water upon oxidation by four equivalents of Ce(IV)[33,34] and this provided a basis for the catalytic oxidation of water. Unlike RuO_2 and PtO_2,[25] the dinuclear ruthenium complex is well characterized[34]. The interesting aspects of this oxo-bridged dimer complex are the presence of two ruthenium centres with two aquo ligands and multiple redox states with suitable redox potential to catalyse water oxidation. Oxygen evolution by water oxidation with dimer ruthenium complex in the presence of strong oxidant such as Ce(IV) was studied by mass spectrum and gas chromatography[35,36]. It was also reported[37,38] that the substituted 2,2'-bipyridine complexes of dimer ruthenium complexes acts as water oxidation catalysts in combination with $Ru(bpy)_3^{2+}$ complex photolytically (eq. (3)). However, during

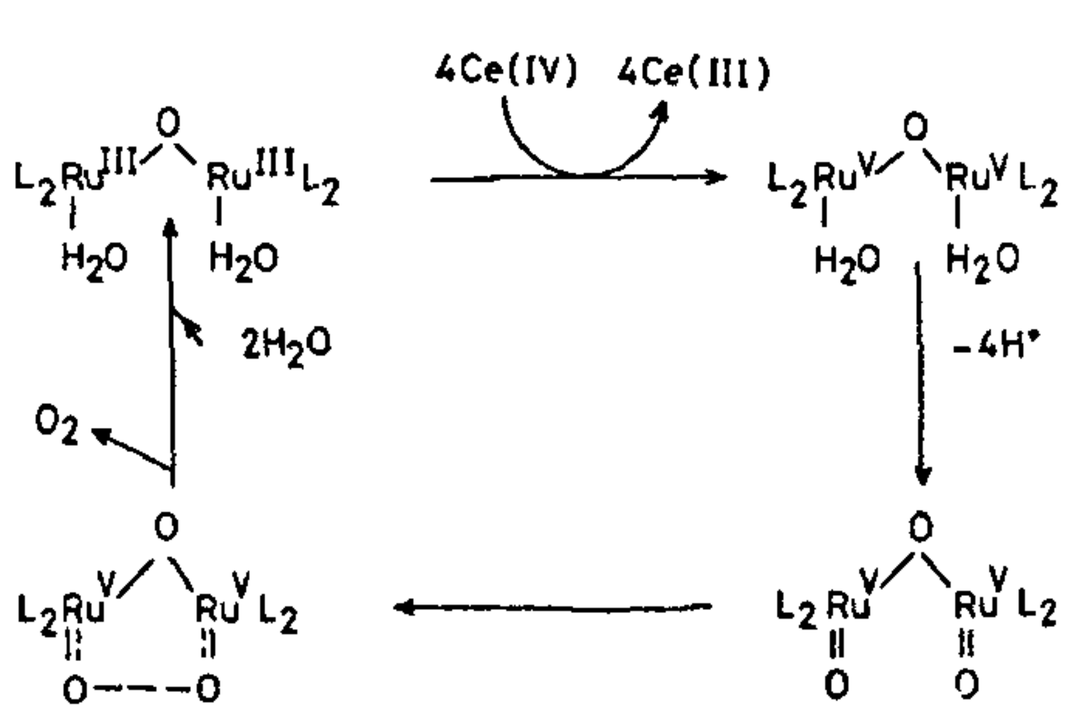
$$4Ru(bpy)_3^{2+} + 2S_2O_8^{2-} \xrightarrow{h\nu} 4Ru(bpy)_3^{3+} + 4SO_4^{2-}$$

$$+2H_2O \;\Big|\; \text{Catalyst } (Ru^{IV} - Ru^{III})$$

$$O_2 + 4H^+ + 4Ru(bpy)_3^{2+} \qquad (3)$$

photolysis, $Ru(bpy)_3^{2+}$ undergoes decomposition to produce a dimer complex which catalyses water oxidation in the subsequent reaction. Dimer plays the role of a catalyst in the oxidation of water by $Ru(bpy)_3^{3+}$ albeit with a very small yield[39].

The electrochemical properties of dimer ruthenium complexes show that these complexes can be used as multielectron transfer catalysts[33–38]. The dimer complexes are stable in the Ru^{III}–Ru^{III} oxidation state and easily form Ru^{V}–Ru^{V} upon electrochemical or chemical oxidation. Recently, the existence of higher oxidation state Ru^{V}–Ru^{V} has been characterized by resonance Raman spectroscopy[40]. The higher oxidation state of one molecule of the ruthenium complex (Ru^{V}–Ru^{V}) realizes four-electron water oxidation to evolve oxygen in a homogeneous solution with the formation of Ru^{III}–Ru^{III}. A picture of the water oxidation redox cycle using the dimer is shown in scheme 4. This scheme supports the discussion that the loosely bound water molecule in the protein bound manganese would lead to



Scheme 4.

water oxidation as discussed in the case of dimer manganese complex.

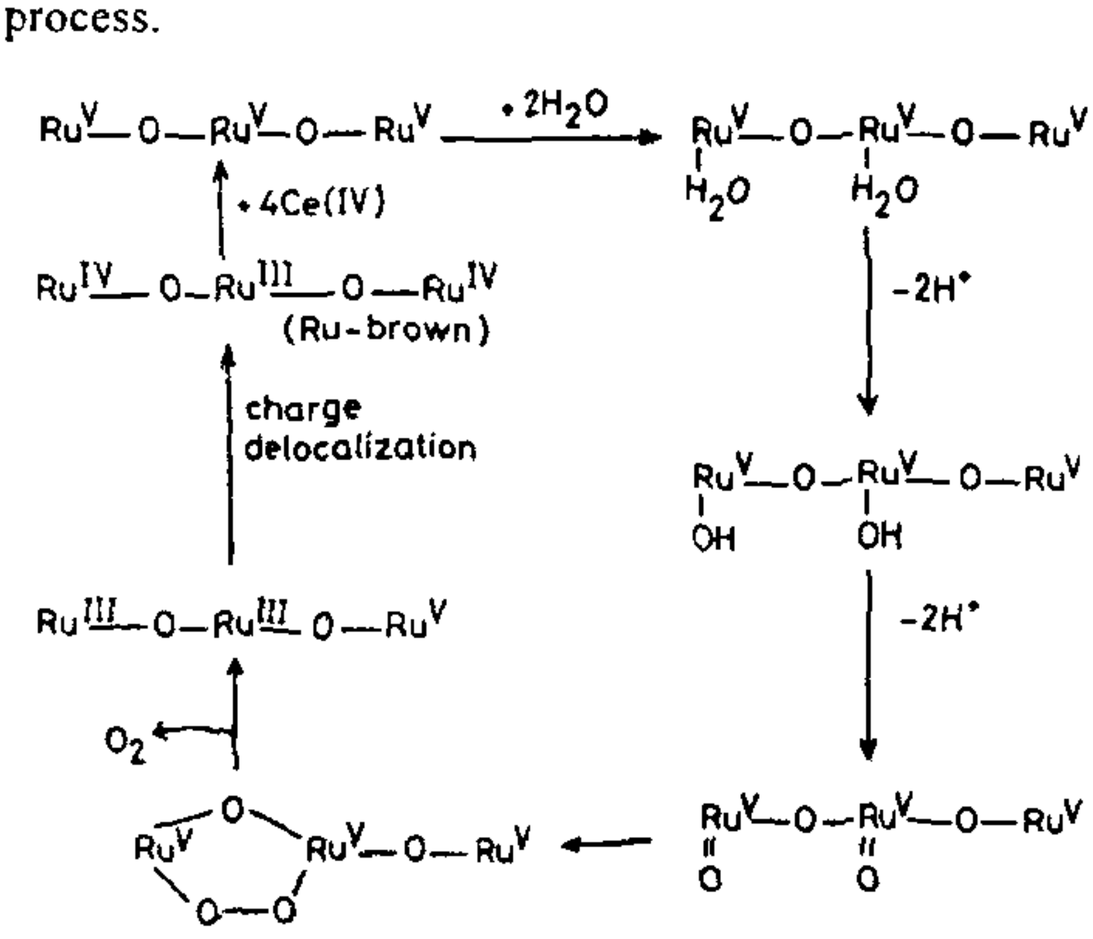
It is interesting that the linearly oxo-bridged trinuclear ruthenium complexes, $[(NH_3)_5–O–Ru(NH_3)_4–O–Ru(NH_3)_5]^{6+}$, (called Ru-red, $Ru^{III}–Ru^{IV}–Ru^{III}$, and Ru-brown, $Ru^{IV}–Ru^{III}–Ru^{IV}$) are better catalysts for water oxidation than dimer ruthenium complexes in homogeneous as well as in heterogeneous states[37,41]. It has been reported[42–44] that the difference in Mossbauer and electronic spectra of cations of Ru-red and Ru-brown are consistent with the charge distribution indicated in eq. (4).

$$Ru^{III}–Ru^{IV}–Ru^{III} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} Ru^{IV} – Ru^{III} – Ru^{IV} \qquad (4)$$

Ru-red in neutral and alkaline conditions

Ru-brown in acidic condition.

It has also been reported that reduction of Ru-brown ($Ru^{IV}–Ru^{III}–Ru^{IV}$) to Ru-red ($Ru^{III}–Ru^{IV}–Ru^{III}$) evolved oxygen[45]. However, the cyclic voltametric data show that Ru-red exhibits five reversible steps of electron transfer behaviour to produce $Ru^{V}–Ru^{V}–Ru^{V}$ and this higher oxidation state trimer catalysed water efficiently to evolve oxygen[37,41] (scheme 5). The Ru-brown formed in the first cycle is highly stable and catalyses water oxidation in the presence of excess Ce(IV) in the cyclic process.



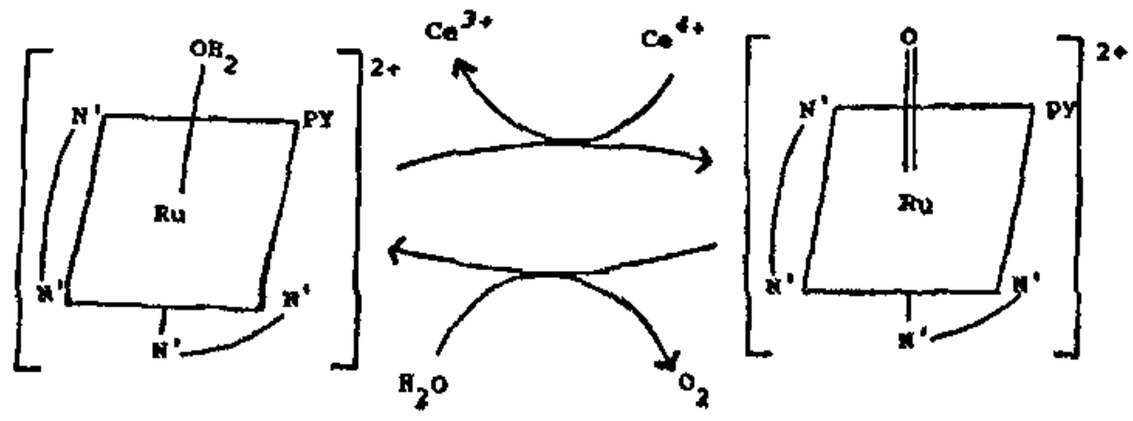
Scheme 5.

Earley and Fealey[44] studied the kinetics of the reduction of Ru-brown by hydroxide ion. They suggested that the attack of OH^- ion on the central ruthenium atom in Ru-brown would be the most probable step for which no symmetry restriction is to be anticipated, and that the reduction leads to the formation of Ru-red. According to Endicott and Taube[46] a spin-paired d^4 ion (Ru^{IV}) can accommodate seventh ligand in the coordination sphere; these authors assume that Ru^{III} also forms seven-coordinated species as kinetic intermediates. The first water molecule would attack the central Ru^{V} atom in the trimer and the second one coordinates at one of the terminal Ru^{V} atoms (scheme 5). This intermediate may lead to the formation of an O–O bond followed by release of oxygen and the reformation of the Ru-brown. The formation of an O–O bond in the linearly oxo-bridged trimer may cause a distortion of the Ru–O–Ru bond from 180°. Such a distortion of the Ru–O–Ru bond from linearity has been reported in the oxo-bridged dimer and in any ethylenediamine analogue of Ru-red trimer[34,35,42,47,48].

These results show that polynuclear ruthenium complex works as an efficient multielectron transfer catalyst in homogeneous and heterogeneous states to realize the four-electron oxidation of water to evolve oxygen. In a polynuclear metal complex, charge delocalization and stabilization as well as the close proximity of metal centres explain the mechanisms of oxygen formation through O–O bond formation from the loosely bound two-water molecules.

A number of monomeric ruthenium complexes of sterically hindering diimine ligands have been prepared, and the catalytic activity of these monomer complexes towards water oxidation has been studied[49]. None of these complexes displayed catalytic activity for oxygen formation from water in the presence of Ce(IV). Based on their observations, they concluded that a multimetallic system is required to achieve water oxidation to oxygen. It has been quite rational that only the polynuclear complexes were considered as candidates for water oxidation because the reaction is a four-electron process.

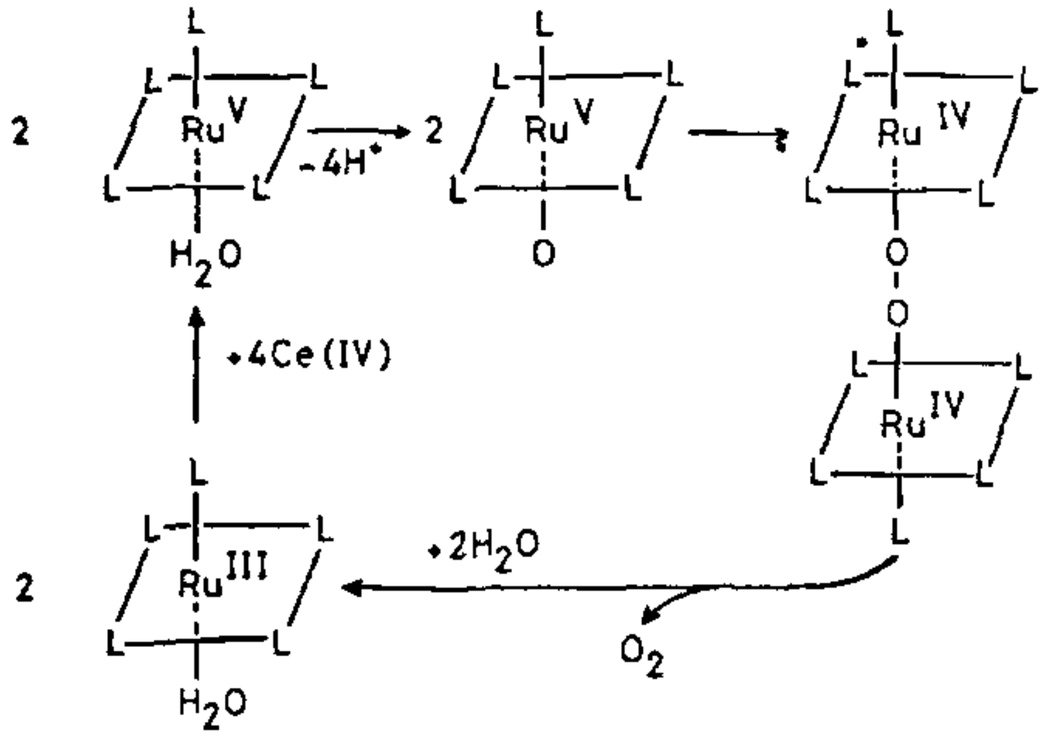
Water oxidation by the monomeric complex, $[Ru(H_2O)(py)L_2]^{2+}$ (py = pyridine, L = 2-(phenylazo) pyridine), was reported[50], and the mechanism was proposed (scheme 6); but oxygen was analysed only by



Scheme 6.

voltammetry. The present authors have found that mononuclear ruthenium-amine complexes such as $[Ru(NH_3)_5(H_2O)]^{3+}$ and $[Ru(NH_3)_6]^{3+}$ catalyse oxygen evolution by water oxidation even under homogeneous conditions[51–53]. The monomeric ruthenium-amine complexes easily form higher oxidation state complexes

(Ru^{V}) upon electrochemical or chemical oxidation, and the redox potentials of the ruthenium-amine complexes showed that they can be used as oxidant for water oxidation[51-53]. These monomeric complexes can act as two-electron oxidant, so that it might be able to bring about the four-electron oxidation of water to oxygen if two molecules of the complex can be coupled in the intermediate step. Considering the coordinated water molecule in the complex $[Ru(NH_3)_5(H_2O)]^{3+}$ or a seventh coordinated water molecule in the complex $[Ru(NH_3)_6]^{3+}$, water oxidation process was explained (scheme 7). Two molecules of the water-coordinated monomeric Ru^{V} complex would lead to the formation of a peroxo-bridged dinulcear ruthenium complex, Ru–O–O–Ru, and then the intermediate would release one molecule of oxygen. Such a peroxo-bridged ruthenium complex is not known; however, the oxo-bridged dinuclear ruthenium complex, $[(NH_3)_5Ru–O–Ru(NH_3)_5]^{4+}$, has been reported[54].



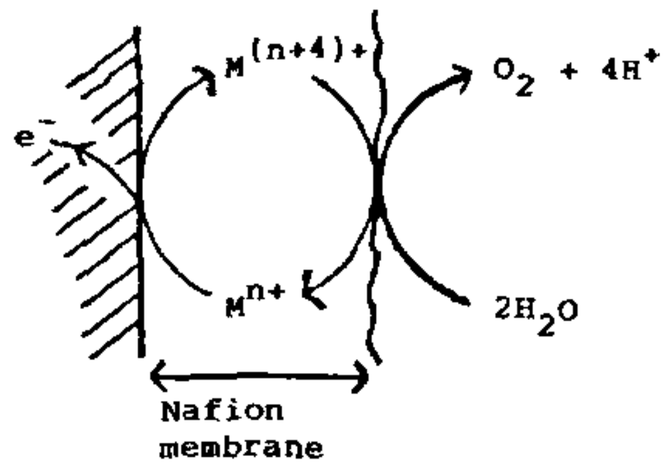
Scheme 7.

Electrochemical water oxidation using metal complexes

The photosynthetic model metal complexes have been used in the electrochemically-catalysed oxygen evolution[55], since chemical oxidation of the catalysts often leads to its decomposition[35, 56]. Electrochemical water oxidation is usually carried out by using metal electrodes. When the water oxidation catalyst such as the dimer/trimer ruthenium complex or the dimer manganese complex was coated on a graphite electrode by using a polymer membrane, electrocatalytic oxygen evolution was observed (scheme 8).

Photochemical water cleavage by water oxidation catalyst mimicking photosystem II

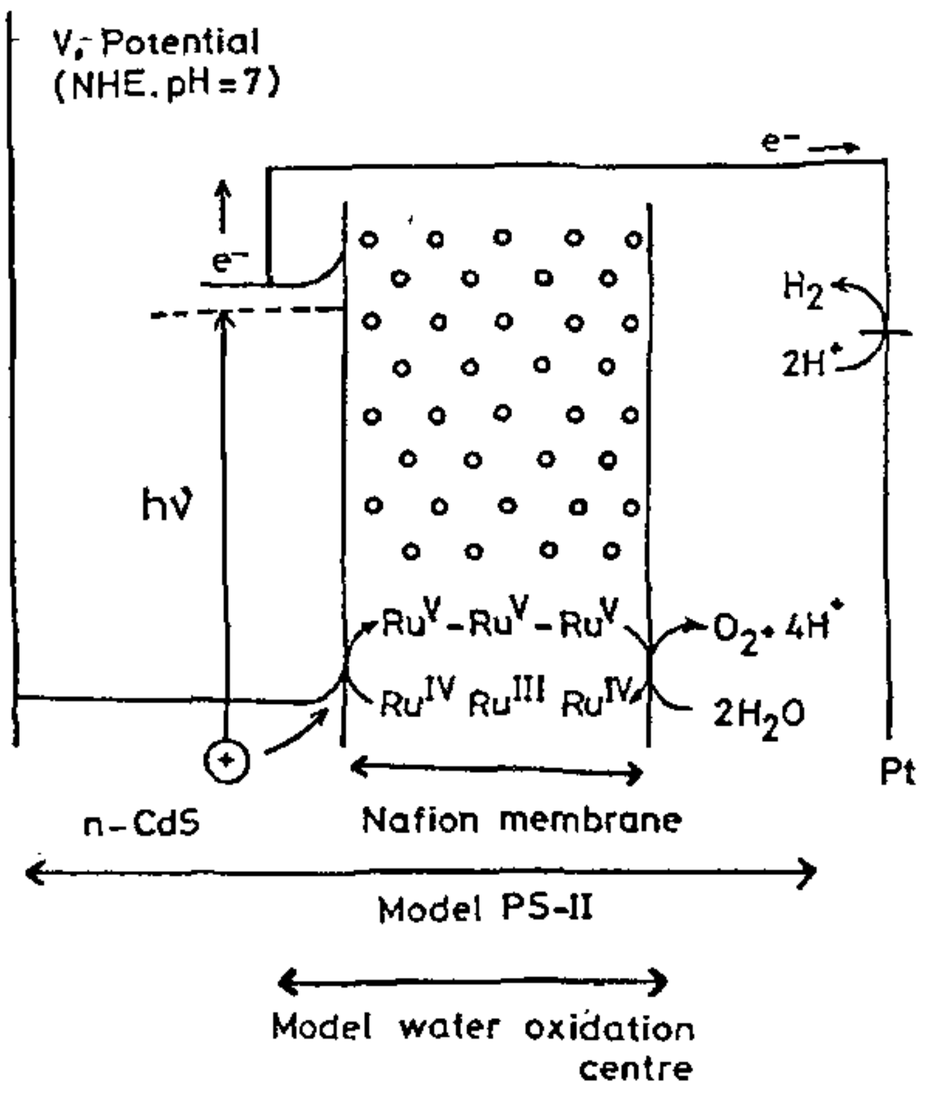
Water oxidation using semiconductor electrodes is an important subject not only relevant to conversion of



Scheme 8.

solar energy into chemical energy but also to the understanding of photosynthesis[25, 57, 58]. One of the most important studies on the artificial photosynthetic processes is concerned with photosystem II in which water is oxidized by visible light to evolve oxygen; however, very few studies have been carried out.

Efficient visible light cleavage of water with simultaneous evolution of hydrogen and oxygen has been achieved by a system mimicking photosystem II. This system was composed of a CdS photoanode modified with a Nafion membrane incorporating a highly active water oxidation catalyst like Ru-red, Ru-brown or dinuclear manganese complex[59]. A Nafion membrane was coated on the CdS surface and then the Nafion-coated CdS was dipped in a solution containing water oxidation catalyst to adsorb the complex into the membrane. Water photolysis was carried out using the CdS/Nafion/Ru-red complex electrode. Irradiation of the electrode induced gas evolution. The results showed that the ratio of the evolved H_2/O_2 was almost 2. The water oxidation process to evolve oxygen at the CdS/Nafion/Ru-brown is shown in scheme 9 in conjunction



Scheme 9.

with photosystem II oxygen-evolving centre. Thus, visible light water photolysis has been successfully carried out by a system mimicking photosystem II.

Concluding remarks

Water oxidation to evolve dioxygen is an important primary step in photosynthesis. In this review it has been shown that water is oxidized both in heterogeneous and homogeneous systems using metal complex as catalysts. The involvement of multimetal centre has been demonstrated to achieve the four-electron process of water oxidation. Water photolysis by semiconductor photoanode coupled with water oxidation catalyst was achieved mimicking photosystem II. In the photochemical solar energy conversion system, it is important to couple four-electron water oxidation catalyst with photoexcitation centre in a membrane to mimic the natural photosynthetic membrane processes.

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