



## Review

Biological water oxidation: Lessons from Nature<sup>☆</sup>

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## ARTICLE INFO

## Article history:

Received 31 January 2012

Received in revised form 2 April 2012

Accepted 4 April 2012

Available online 10 April 2012

## Keywords:

Artificial photosynthesis

Water oxidation

Water oxidizing complex

Water splitting

Natural photosynthesis

Manganese–calcium cluster

## ABSTRACT

Hydrogen production by water splitting may be an appealing solution for future energy needs. To evolve hydrogen efficiently in a sustainable manner, it is necessary first to synthesize what we may call a 'super catalyst' for water oxidation, which is the more challenging half reaction of water splitting. An efficient system for water oxidation exists in the water oxidizing complex in cyanobacteria, algae and plants; further, recently published data on the Manganese–calcium cluster have provided details on the mechanism and structure of the water oxidizing complex. Here, we have briefly reviewed the characteristics of the natural system from the standpoint of what we could learn from it to produce an efficient artificial system. In short, to design an efficient water oxidizing complex for artificial photosynthesis, we must learn and use wisely the knowledge about water oxidation and the water oxidizing complex in the natural system. This article is part of a Special Issue entitled: Photosynthesis Research for Sustainability: from Natural to Artificial.

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## 1. Introduction

Photosynthesis has a great potential in the field of Bioenergy [1–8]. Hydrogen production from water splitting has been considered as an ideal fuel for the future [9–18]. Water is the source of both oxygen and hydrogen, but energy is needed for hydrogen production by water splitting. Using sunlight, splitting of water into hydrogen and oxygen is one of the most important goals of some of the research on 'artificial photosynthesis', and this could be one of the solutions for future energy needs [9–17]. The development of a catalyst for water oxidation to evolve oxygen is an important key goal for a technology-based water splitting since the reaction involves a multi-electron transfer and is much more difficult due to thermodynamic and kinetic limitations [10]. Other strategies involve attempts to employ not only energy obtained directly from the Sun, but also from the wind, ocean currents, tides or waves for water splitting, some of which may turn out to be impractical or uneconomical [1].

<sup>☆</sup> This article is part of a Special Issue entitled: Photosynthesis Research for Sustainability: from Natural to Artificial.

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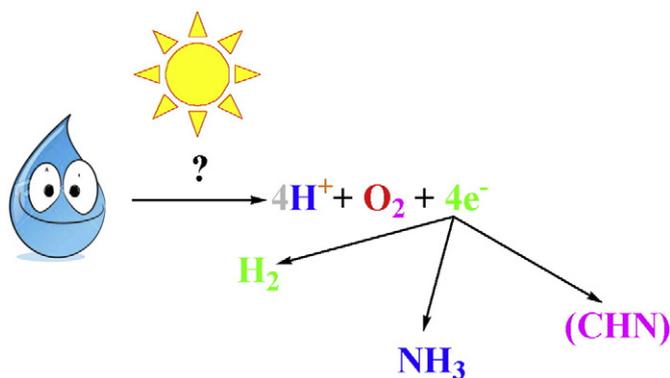
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An efficient system for water oxidation has already evolved in cyanobacteria, algae and plants [19–35]. The biological water oxidation in the natural system is catalyzed by a  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster housed in a protein environment in Photosystem II (PSII) that controls reaction coordinates, proton movement and water access. The cluster is the only biological catalyst that could oxidize water to molecular oxygen, and it appears that it has remained basically unchanged during 2 billion years of evolution [19–37].

In this review, we focus on the art of *Nature* to oxidize water for the production of hydrogen. To evolve hydrogen in a sustainable manner, it is necessary to first synthesize a stable, low cost, and efficient, environmentally friendly and easy to use catalyst for water oxidation [10]. The water oxidation half reaction in water splitting is both overwhelmingly rate limiting and environmentally unacceptable for large-scale  $\text{H}_2$  production as at this high voltage, other chemicals will be oxidized [9,10]. Thus, a significant challenge in the sustainable hydrogen economy is to design a 'super anode' for water oxidation [10]. The role of such a super anode is not only for sustainable hydrogen economy, but also for providing electrons for other reduction-reactions which are equally important in artificial photosynthesis (Scheme 1) [9].

Photosynthesis has a long history [25,38]. Joseph Priestley (1733–1804) described the ability of plants to generate power to restore the air which had been injured by the burning of candles. Carle Wilhelm Scheele (1742–1786) and Antoine Laurent Lavoisier (1743–1794) identified this gas as oxygen. Jan Ingenhousz



**Scheme 1.** During water oxidation that leads to oxygen evolution, electrons and protons are also produced that could be used in synthesizing fuel and useful compounds. In the natural system, protons are released in the lumen, and electrons are transferred to the reaction center  $P_{680}$  that had been oxidized during a light reaction.

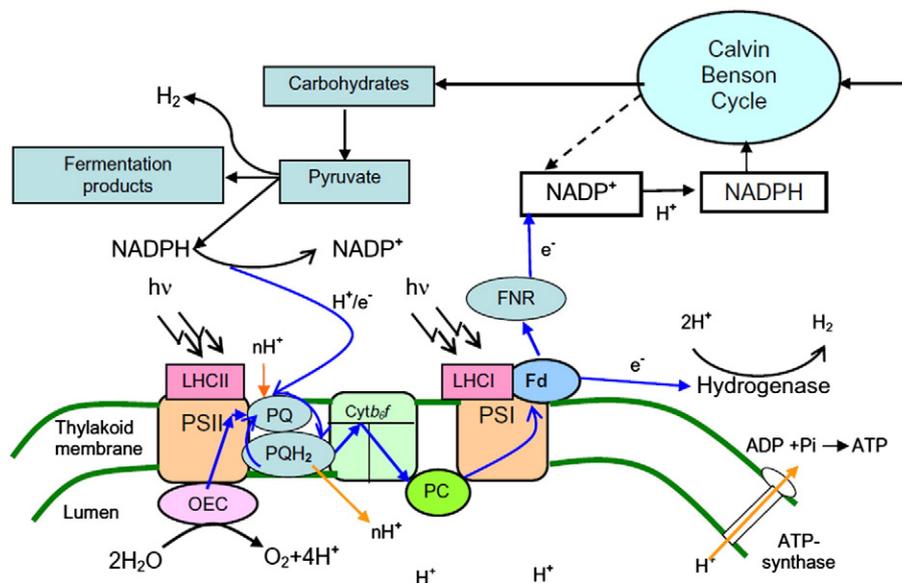
(1730–1799) discovered the role of light and of the importance of the green color of plants, and Jean Senebier (1742–1809) discovered the role of  $\text{CO}_2$  in photosynthesis. Nicholas Theodore de Saussure (1767–1845) established the role of water, and finally Julius Robert Mayer (1814–1878) provided the most important concept that in photosynthesis light energy is converted into chemical energy (for a time line of discoveries in photosynthesis, see [39]). Ludvig Boltzmann (1844–1906) looked upon photosynthesis from a thermodynamic perspective. He suggested that plants in their struggle for survival exploit the difference between the energy of sunlight, with low entropy, and the radiation emitted by the Earth, with high entropy [38]. Robert Hill (1899–1991) discovered that when ‘chloroplasts’ were exposed to light in the presence of an artificial electron acceptor, oxygen evolution was observed; the ‘Hill reaction’ shows that carbon assimilation and oxygen evolution are not obligatorily linked and two distinct systems may exist [40–44]. Thus, there are two parts to photosynthesis (Fig. 1)

[40–42]: the first, the reactions that depend directly on light take place in specific pigment–protein complexes in the thylakoid membranes; they are called ‘Light Reactions’. In these reactions light energy is converted into chemical energy. The end product of this set of reactions, that includes many dark reactions as well, is the production of oxygen, the reducing power (NADPH) and ATP. We now know that there are two pigment systems and two light reactions (see [30] for the historical development of the scheme, called the Z-scheme).

Photosystem II oxidizes water to oxygen and reduces plastoquinone to plastoquinol [8], whereas Photosystem I oxidizes plastocyanin and reduces  $\text{NADP}^+$ ; in addition, plastoquinol reduces oxidized plastocyanin via a cytochrome  $b_6/f$  complex. The second, ‘Dark Reactions’ that do not depend directly on light take place in the stroma region; in these reactions  $\text{CO}_2$  is converted to sugar. The dark reactions involve a cycle called the Calvin–Benson cycle in which  $\text{CO}_2$  and energy from NADPH and ATP are used to form sugars (Fig. 1). In the *Light Reaction of PSII*, there is a manganese–calcium cluster that performs one of the most important reactions in Nature: *water oxidation* [44–48]. Water oxidation is an important reaction on Earth since it is the source of nearly all the atmosphere’s oxygen resulting in the development of modern organisms using respiration on our planet.

## 2. Structure of the water oxidizing complex

The structure of the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster is important for the understanding of the mechanism of water oxidation in the natural system, and it is the first step in synthesizing the *super anode* for water oxidation in artificial photosynthesis. Studies on the structure of the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster was pioneered by the research group of Horst Witt and W. Saenger in Berlin [22,28] followed by the research group of Shen and Kamiya [49]. In 2004, the research groups of James Barber and So Iwata published a detailed paper that provided a rather complete structure of PSII, from the cyanobacterium *Thermosynechococcus elongatus* [29]. They assigned the positioning of most



**Fig. 1.** Carbon fixation and oxygen evolution take place in two distinct spaces in oxygenic photosynthesis. The diagram shows a schematic view of light-powered hydrogen production during oxygenic photosynthesis, as well as carbohydrate synthesis that can also be followed by hydrogen production. The photosynthetic processes are driven by the light energy captured by the light-harvesting complexes (LHCII and LHCI) of Photosystem II and Photosystem I. Electrons are derived from  $\text{H}_2\text{O}$  by water oxidation at the WOC, also known as oxygen evolving complex (OEC), of PSII; these electrons are passed along the photosynthetic electron-transport chain via plastoquinone (PQ), the cytochrome  $b_6/f$  complex (Cyt  $b_6/f$ ), plastocyanin (PC), Photosystem I (PSI), and to ferredoxin (Fd). Then, ferredoxin– $\text{NADP}^+$  oxidoreductase (FNR) transfers the electrons to  $\text{NADP}^+$  with the final production of NADPH. Protons ( $\text{H}^+$  ions) are released into the thylakoid lumen by the WOC as water is oxidized, as well as when PQH<sub>2</sub> delivers electrons to Cyt  $b_6/f$  complex. The proton gradient across the thylakoid membrane is used by ATP synthase to produce ATP. The ATP and NADPH generated during the primary photosynthetic processes are consumed for  $\text{CO}_2$  fixation in the Calvin–Benson cycle, which produces sugars and ultimately starch. Under anaerobic conditions, hydrogenase can accept electrons from the reduced Fd molecules and use them to reduce protons to molecular hydrogen. Anaerobic conditions also allow us to use starch as a source of protons and electrons for  $\text{H}_2$  production (via NADPH, PQ, Cyt  $b_6/f$ , PC and PSI) using a hydrogenase enzyme. Thylakoid membrane is denoted with green color. Source of the figure and caption: [19].

of the subunits [29]. Importantly, they provided, for the first time, information on calcium in the structure. In other words, they introduced the water oxidizing complex (WOC) as a  $\text{Mn}_3\text{Ca}$ -cubane with a Mn attached a bit far away [29]. However, the investigations did not provide enough details for the structure of the cluster, the location of the substrate water molecules, or the precise arrangement of the amino-acid side chains and cofactors that may have significant mechanistic consequences in water oxidation.

In 2011, the research groups of Jian-Ren Shen and Nobuo Kamiya dramatically improved the resolution of the PSII crystals from the thermophilic cyanobacterium *Thermosynechococcus vulcanus* (*T. vulcanus*) to 1.9 Å and analyzed their structure in details [32,33]. Their investigation has provided many more details of the structure of the WOC containing a number of bridged oxygen, the location of substrate water molecules and the precise arrangement of the amino-acid side chains [32,33]. In the structure of the WOC, they found four manganese ions, one calcium ion, and five oxygen atoms that serve as oxo bridges linking the five metal ions (four manganese and one calcium ions) (Fig. 2) [32,33].

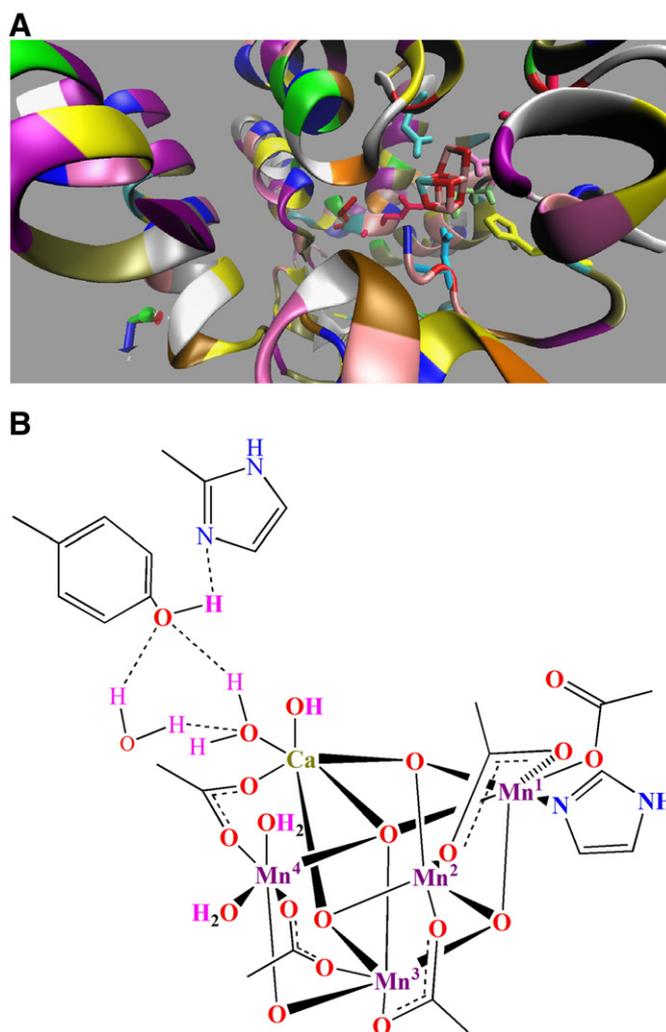
These results showed that the manganese–calcium cluster could be written as  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$ . Of these five metals and five oxygen atoms, the calcium and three manganese ions occupy four corners and four oxygen atoms form the other four corners of the cubane-like structure. Regarding the Ca–O and Mn–O bond lengths, the cubane-like structure is not an ideal and symmetric one. Another manganese ion is located outside the cubane and is linked to two manganese ions within the cubane by one oxygen of the cubane and the fifth oxygen by a di- $\mu$ -oxo bridge [32,33]. The location of substrate water molecules is very important for the understanding of the mechanism of water oxidation by the WOC.

Four water molecules have been detected in the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster of the water oxidizing complex [32,33]. Two water molecules are coordinated to a manganese ion located outside the cubane and two water molecules are coordinated to the calcium ions [32,33]. A few amino acids with carboxylate and imidazole groups are coordinated to the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster [32,33]. Generally, the carboxylate ion may coordinate to a metal in different modes (Scheme 2). In the WOC, only one monodentate mode of carboxylate is observed and other carboxylate groups serve as bidentate modes [32,33]. Each of the four manganese ions has six ligands whereas the calcium has seven ligands.

### 2.1. The water oxidizing complex: further details

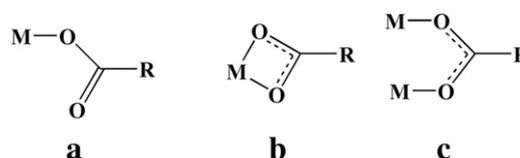
In the 2011 structure, Mn(1) has six ligands: three  $\mu_3$ -O, one monodentate carboxylate, one bridging carboxylate and one imidazole ligand [32,33]. The ligands around Mn(1) are similar to what is found in manganese ions in manganese catalase enzymes. As usual, the coordination number, i.e., the number of nearest neighbors, for Mn(III) or (IV) is 6, and no other ligand could coordinate to it. Three  $\mu_3$ -O as hard ligands and two carboxylate and one imidazole groups as a borderline ligand could stabilize the oxidation state of (III) or (IV) for the manganese ion.

The six ligands around Mn(2) are: three  $\mu_3$ -O and three bridging  $\text{COO}^-$ . These ligands could stabilize the oxidation state of (III) or (IV) for the ion. The ion is coordinated to calcium and two manganese ions with a bridging carboxylate and three oxo groups. The six ligands around Mn(3) ion are three  $\mu_3$ -O, one  $\mu_2$ -O and two bridging  $\text{COO}^-$ . Four  $\mu$ -O as a hard group could stabilize manganese (IV) [50]. The ligands around Mn(4) are one  $\mu_4$ -O, one  $\mu_2$ -O, two bridging  $\text{COO}^-$  and two water molecules ( $\text{H}_2\text{O}$ ). These two water molecules are very important and it is suggested that one of them may serve as one of the substrates for water oxidation. Regarding these ligands, the oxidation state of (III) or (IV) could be stabilized for Mn(4), but deprotonation of water molecules could be the stabilized oxidation state of (IV) and an even higher oxidation state.



**Fig. 2.** Top (A):  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster and the surrounding amino acids. Many amino acids in PSII are involved in proton, water and oxygen transfer. Roles for the residues that come in contact directly with the manganese–calcium cluster include regulation of charges and electrochemistry of the Mn–Ca cluster, and help in coordinating water molecules at appropriate metal sites and stability of this cluster. (Data from [32].) Bottom (B): the entire structure of the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster that resembles a distorted cubane, with the asymmetric cubane,  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$ . (See a cartoon of a distorted chair in [15]; original data is from [32]; PDB ID: 3ARC.) Image A was made with VMD, owned by the Theoretical and Computational Biophysics Group, NIH Resource for Macromolecular Modeling and Bioinformatics, at the Beckman Institute, University of Illinois at Urbana-Champaign.

Calcium has also been identified as an essential cofactor in water oxidation and the calcium-binding sites in PSII have been previously studied by several methods. Strontium (II) is the only cation that can functionally substitute for Ca in the water oxidizing complex. In the 1.9 Ångstrom structure of the WOC, Ca has seven ligands, three  $\mu_3$ -O, two bridging  $\text{COO}^-$  and two  $\text{H}_2\text{O}$  molecules [32,33]. Similar to  $\text{H}_2\text{O}$  molecules coordinated to Mn(4), these two  $\text{H}_2\text{O}$  molecules are



**Scheme 2.** This scheme shows unidentate (A), bidentate (B) and bridging carboxylate modes (C).

very important and it is also suggested that one of them may serve as the substrate for water oxidation [32,33]. The coordination number of Ca ions varies from 6 to 10 in different compounds. Thus, a ligand may coordinate or decoordinate to this ion in different states of water oxidation. The location of the substrate water binding sites on the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  inorganic core has been an important question in the study of the mechanism of water oxidation. Hillier and Wydrzynski [48] used  $^{18}\text{O}$  exchange kinetics of the substrate water molecules in PSII to examine the interactions of Ca and Sr with substrate water and to probe a number of point mutations surrounding the catalytic site. The most direct approach to follow water ligand exchange is by using mass spectrometry. This involves the addition of  $^{18}\text{O}$  water and then time dependent sampling of the product. In this technique, two kinetic phases at  $m/e = 34$ , representing separate  $^{18}\text{O}$  exchange rates for the two substrate water molecules, were detected [48]: the slow and fast phases that show the exchange of the two non-equivalent substrate sites. The high resolution, i.e., the 1.9 Ångstrom, resolution structure of PSII revealed that there are four water molecules coordinated to the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster, and two of them may serve as the substrate for water oxidation. Other suggested substrates for water oxidation are  $\mu\text{-O}$  groups [32,33]. Another water molecule, also found around the WOC, is hydrogen-bonded to one of the  $\mu\text{-O}$  and one carboxylate group in this structure. This water molecule could also serve as a substrate for water oxidation.

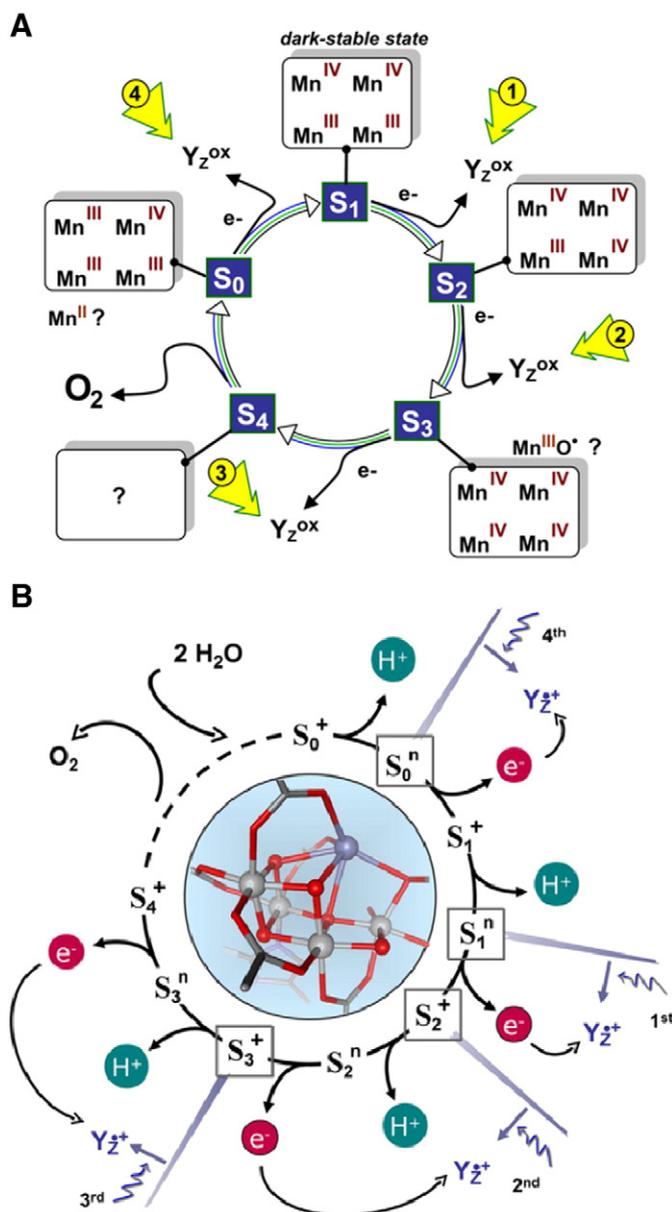
Other groups in the WOC are amino acids. The imidazole nitrogen of Histidine 337 is hydrogen-bonded to one of the  $\mu\text{-O}$ . The role of this hydrogen bond may be as a stabilizer for the WOC. There is an arginine in the second coordination sphere of WOC, and this may have an important role in maintaining the structure of the metal cluster, in stabilizing the cubane structure and (or) in providing partial positive charges to compensate for the negative charges induced by the oxo bridges and carboxylate ligands of the WOC. One of the guanidinium nitrogen atoms of CP43-Arg 357 is hydrogen-bonded to both  $\mu\text{-O}$  in the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster, whereas the other is hydrogen-bonded to the carboxylate oxygen of D1-Asp 170 and to that of D1-Ala 344. The structure shows that the distances between the nitrogen atoms of the arginine side chain and Ca are 4.2 and 4.4 Å. Also, the distances between the nitrogen atoms of the arginine side chain and Mn (4) are 4.7 Å and 6.0 Å. The side chain of arginine may stabilize the structure of the WOC as there are hydrogen bonds between this amino acid and two  $\mu\text{-O}$  bridges and one carboxylate bridged between Ca and a Mn (2). Umena et al. [32,33] have identified two chloride ions in the structure of the WOC. Both  $\text{Cl}^-$  ions are surrounded by water molecules and amino acids. Umena et al. [32,33] have further suggested that the two chloride anions may function to maintain the coordination environment of the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  and allow the water oxidation reaction to proceed properly.

Another group near the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster is Tyrosine 161. In PSII, after photons are absorbed by antenna molecules and the excitation energy is transferred to the reaction centers, primary charge separation occurs: formation of  $\text{P}^+_{680} \text{P}^-_{\text{heo}}$  [8]. This is followed by reduction of  $\text{P}^+_{680}$  by electron transfer from a specific tyrosine (tyrosine 161) residue ( $\text{Y}_2$ ), located on the D1 protein of PSII, and the formation of a tyrosine radical ( $\text{Y}_2^*$ ). When  $\text{Y}_2$  is oxidized by  $\text{P}^+_{680}$ , the phenolic group becomes very acidic and deprotonates to form a neutral radical phenolic group. The proton acceptor is a histidine residue, histidine 190, which is hydrogen bonded to the phenolic proton [8]. Electrons for the reduction of  $\text{Y}_2^*$  are extracted from the WOC leading, finally, to the oxidation of water to molecular oxygen.

### 3. Mechanism of oxygen evolution by water oxidizing complex

An unsolved mystery in bioinorganic chemistry is the mechanism of water oxidation by the WOC of PSII. In 1969, Pierre Joliot's experiments showed a flash number dependent oscillating pattern in  $\text{O}_2$  evolution; a maximum of oxygen evolution occurred on every fourth

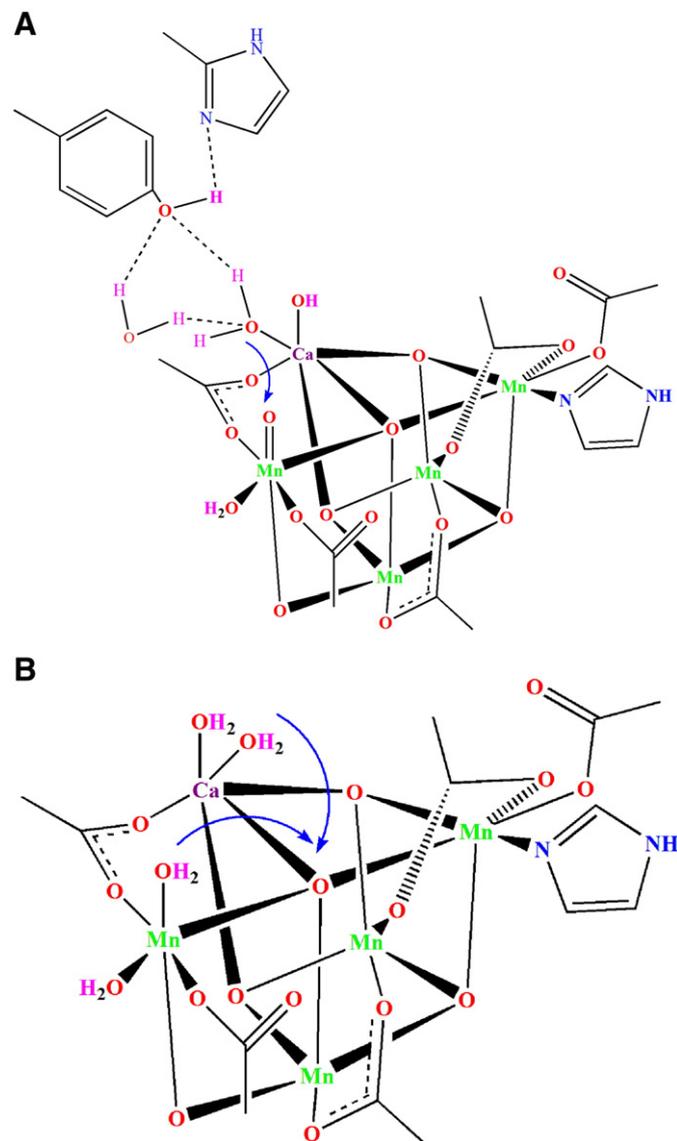
flash, with the first maximum on the 3rd flash [51–57]. In 1970, Kok et al. [52] proposed an explanation for the observed oscillation of the oxygen evolution pattern. Kok's hypothesis was that in a cycle of water oxidation, succession of oxidizing equivalents is stored on each separate and independent WOC, and when four oxidizing equivalents have accumulated, an oxygen is spontaneously evolved [51–57]. Each oxidation state of the WOC was termed a 'S-state', with  $\text{S}_0$  being the most reduced state and  $\text{S}_4$  the most oxidized state in the catalytic cycle (Fig. 3) under normal turnover conditions, but 'super-reduced states'  $\text{S}_{-i}$  can also be populated ( $i = 1, 2, 3, 4$  or  $5$ ) [51–57]. It is essential to recognize that in order to explain the fact that the first maximum of oxygen evolution was after the 3rd flash,



**Fig. 3.** Classical S-state cycle of photosynthetic water oxidation. A dark-adapted system, that usually starts with 75%  $\text{S}_1$  and 25%  $\text{S}_0$  [47]. Absorption of a photon causes charge separation at the reaction center  $\text{P}_{680}$  of PSII; the oxidized  $\text{P}_{680}$  ( $\text{P}^+_{680}$ ) oxidizes  $\text{Y}_2$  to form  $\text{Y}_2^+$  (oxidized tyrosine-160 on the D1-protein) within less than 1  $\mu\text{s}$  (for a review on PSII, see [8]). Reduction of  $\text{Y}_2^+$  by electron transfer (ET) from the manganese complex results in  $\text{S}_i \rightarrow \text{S}_{i+1}$  transition; typical time constants of the ET step are indicated in the diagram. There are several similar S-state cycle schemes. Here we show plausible oxidation-states of the four Mn ions in the different S-states; figure from [8] (A, top). The extended S-state cycle (B, bottom) includes not only four oxidation but also four deprotonation steps (figure from [58]).

and then after the 7th, and 11th flashes, the  $S_1$  state must be dark-stable. Thus, the system starts mostly in  $S_1$  in dark-adapted samples. Further,  $S_4 \rightarrow S_0$  transition is light independent and in this state oxygen is evolved. Other S-state transitions are induced by the photochemical oxidation of oxidized chlorophyll ( $P_{680}^+$ ) [51–57].

There are many proposals, based on artificial systems, for the detailed mechanism of water oxidation by the WOC in PSII. Three of them are shown in Fig. 4. They are not discussed here and the reader is referred to several excellent reviews on this topic [58,59]; instead, we discuss below the strategies used by *Nature* to oxidize water.



**Fig. 4.** Three proposed mechanisms of water oxidation by  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster in PSII. Pecoraro and co-workers [60] have proposed (A) that a terminal  $\text{Mn(V)=O}$  undergoes a nucleophilic attack by a Ca bound hydroxide ligand to form a Mn-bound hydroperoxide. Brudvig and co-workers [61] have proposed (B) a mechanism in which a Ca ion plays a role as a weak Lewis acid. In this mechanism, a water molecule bound to calcium reacts with a  $\text{Mn(V)=O}$  species to form the  $\text{O=O}$  bond through a nucleophilic attack. Lee and Brudvig [61] provided direct support for the proposal that Ca plays a structural role in the early S-state transitions which can be also fulfilled by other cations with similar ionic radius. Umena et al. [32] have suggested that one oxygen that bridges between Ca, Mn(4), Mn(3) and Mn(1) may exist as a hydroxide ion in the  $S_1$  state and it may provide one of the substrates for dioxygen evolution. One of the water molecules coordinated to calcium or manganese (4) may provide another substrate for oxygen evolution.

## 4. Water oxidation in Nature

### 4.1. Abundant and non-toxic ions

The study of the WOC in PSII shows that a special arrangement of abundant and non-toxic ions like manganese and calcium forms a highly efficient catalyst for water oxidation [32,33]. Thus, it is also possible to use manganese and calcium as cheap and environmentally friendly ions as water oxidizing catalyst in artificial photosynthesis. Recently, there has been a tremendous surge in research on the synthesis of various model manganese complexes for the WOC [62–89]. Other metal-based catalysts also show promise for water oxidation. However, many of them are rare, expensive and (or) relatively toxic. As discussed by Ralph Dougherty's group the first-row transition metals have smaller d-orbitals compared to other metals and therefore have smaller crystal field activation energies for transitions between oxidation states during oxygen evolution reaction [90]. As for water oxidation, oxidation states of metal ions should change, and the first-row transition metals may have smaller activation energies for the reaction.

Recently, manganese oxides with open structures have been introduced as efficient catalysts for water oxidation [84–91]. These manganese oxides are very closely related to the water oxidizing cluster in PSII and since manganese is cheap and environmentally friendly, these compounds are expected to be good candidates for water oxidizing catalysts in artificial photosynthesis [91–97].

### 4.2. Heterogeneous catalyst

An important aspect related to the WOC of PSII is that it could act as a heterogeneous catalyst instead of a homogenous one. In other words, PSI and PSII, and also the WOC, are fixed in the thylakoid membrane; and this heterogeneity could increase the *robustness* of the catalyst. A review of manganese compounds as water oxidizing catalysts show that almost all efficient catalysts for water oxidation are heterogeneous [91–97]. The assembly of metal complexes into a crystalline, stable, and nanoporous array also shows promise for biomimetic catalysis. The interaction of two catalysts in the solid state is lower and it reduces decomposition, decoordination or disproportionation reaction.

### 4.3. Multinuclear manganese structure

Another strategy used by Nature has been in the selection of the special tetranuclear-manganese cluster to oxidize water. As discussed in the previous sections, the WOC in PSII is a tetranuclear manganese cluster that performs four-electron water oxidation [98,99]. Generally, multi-nuclear metal clusters, used in natural systems, favor the occurrence of multi-electron and multi-stage complex processes. There are many mono, di and tri nuclear manganese complexes as structural models for the WOC in PSII. However, we agree with the suggestion that tetra and even polynuclear compounds, similar to metal oxides, which favor the occurrence of four-electron water oxidation, would be better functional models for the WOC in PSII [15,87].

### 4.4. The pH value of the water oxidation reaction

The WOC of PSII occurs at  $\text{pH} \sim 5$  in the lumen of thylakoids [100–102]. This pH plays an important role in affecting and regulating the activity of PSII; also, it is one of the factors which can reduce the potential required for water oxidation considerably. Higher or lower pH values result in decomposition, disproportionation, and ligand decoordination of many manganese complexes [103]. At low pH, the formation of high valent Mn species is favored [104]. At pH values of 5–6, high valent manganese complexes form insoluble manganese oxide so that the compound could oxidize water [103]. On the other

hand, the influence of pH on efficiency and accumulation of manganese (III) would be important to design manganese compounds that can serve as efficient water oxidation catalysts.

#### 4.5. Proton and electron transfer in biological water oxidation

Any strategy, used in a natural system, to transfer electrons without any proton loss leads to an increase in positive charge on the WOC [105]. A high positive charge on the WOC can lead to a significant increase in its redox potential and unwanted reactions in a highly oxidized cluster. However, there is no charge accumulation in the WOC due to the coupled electron and proton transfer. To avoid the production of high-energy intermediates, the natural system uses proton-coupled electron transfer (PCET) mechanisms [105]. In PCET, either an electron transfer is followed by a proton transfer or a proton transfer is followed by an electron transfer. Both the electron and proton content between reactants and products is changed in PCET reactions [105]. PCET provides a molecular-level basis for energy transduction between proton transfer and electron transfer. In artificial photosynthesis, similar strategies should be used to avoid the production of high-energy intermediates that could decompose the catalyst.

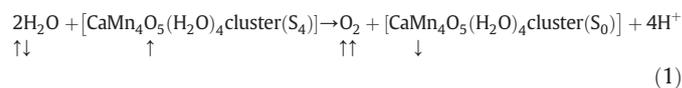
#### 4.6. Channels

Three types of channels exist that lead from the water-oxidizing complex to the luminal side of PSII for oxygen, water and protons [106,107]. Proposed functional assignments of these channels proceeded on electrostatic, structural and orientation grounds. Investigations of water movement in PSII introduced a novel perspective to the study of the supply of water to the WOC and showed that functional PSII is characterized by a branched water supply structure with multiple control points (Fig. 5). This strategy could avoid the interactions of unwanted chemicals with the WOC and increase the amount of the catalyst.

#### 4.7. Spin-flipping processes

Spin-flipping processes, during chemical reactions, often have a high activation energy as the spin balance theory predicts [108–110]. This

rule is known as the spin balance rule [108–110].



(The arrows in Eq. (1) show the spin of the electrons.)

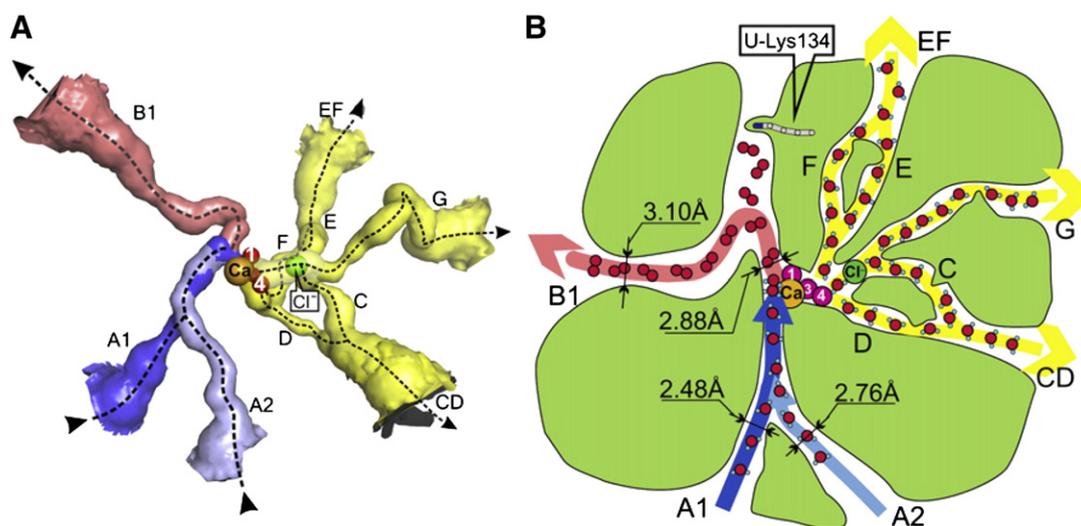
In the biological water oxidation, as shown in Eq. (1), H<sub>2</sub>O does not have an odd-electron state; however, the CaMn<sub>4</sub>O<sub>5</sub>(H<sub>2</sub>O)<sub>4</sub> cluster in S<sub>4</sub> may have an odd-electron; on the other hand, O<sub>2</sub> has two odd-electrons, and the CaMn<sub>4</sub>O<sub>5</sub>(H<sub>2</sub>O)<sub>4</sub> cluster in S<sub>0</sub> has one odd-electron [111]. Total spin states before and after biological water oxidation reaction, as shown in Eq. (1), involve no change. As suggested by some [108–110], the overvoltage of the oxygen evolution reaction may be the largest source of energy loss in water electrolysis, and the major source of this overvoltage is the spin inversion required to produce triplet oxygen [108–110].

#### 4.8. Nanoscale cluster

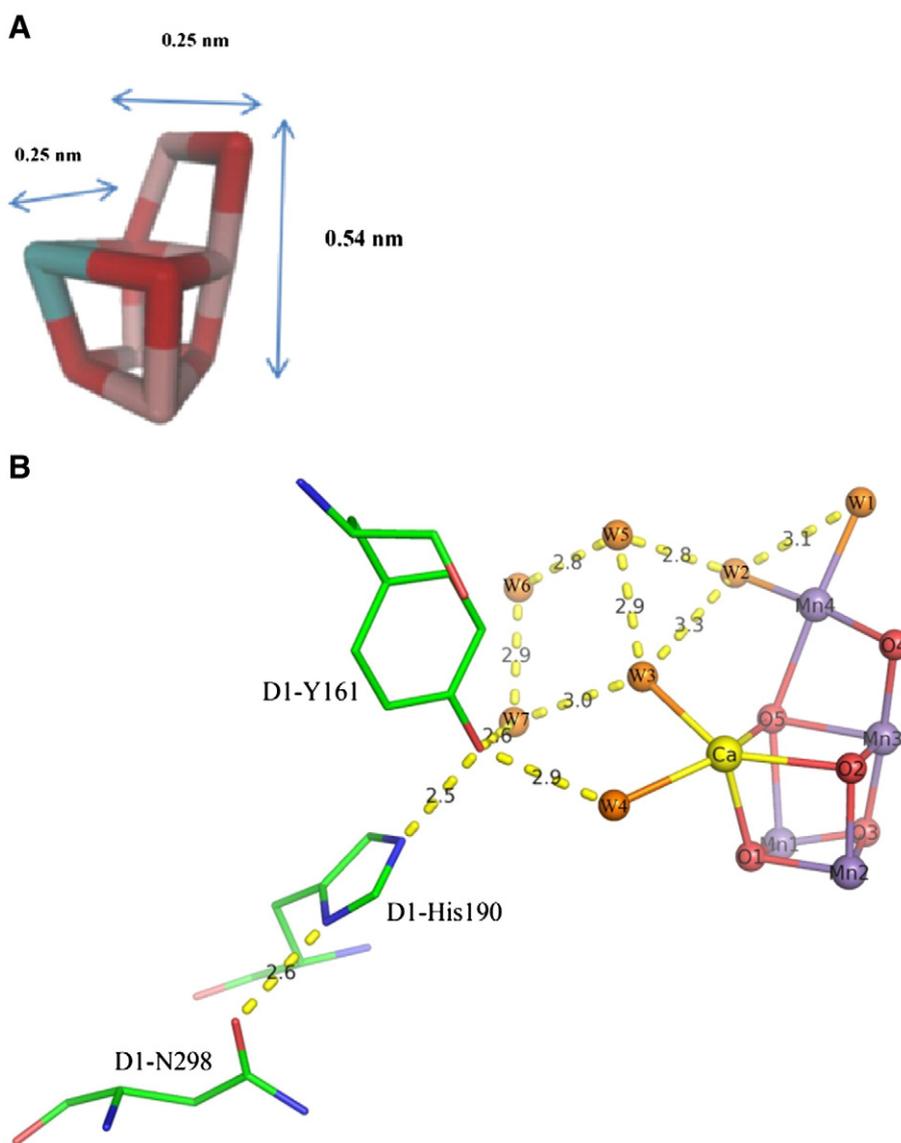
The molecular modeling of the CaMn<sub>4</sub>O<sub>5</sub>(H<sub>2</sub>O)<sub>4</sub> in PSII shows that it has a dimension of about ~0.5 nm (Fig. 6). Therefore, nano-scale (calcium) manganese oxides will be better functional models for the CaMn<sub>4</sub>O<sub>5</sub>(H<sub>2</sub>O)<sub>4</sub> in PSII. Alexandra Navrotsky's group reported that surface energy strongly influences their redox equilibria and phase stability of transition metal oxides [112]. This effect could change water oxidation or water reduction activity of nano-size metal oxides as compared to bulk metal oxides. In addition to this, the nanometer-size of the particles ensures that most of the active sites are at the surface where they can do their work as a water oxidizing catalyst. A nano-size amorphous manganese–calcium oxide has also been introduced as one of the best manganese compounds toward water oxidation [113].

#### 4.9. Oxidation states for manganese ions in the WOC

The high exchange energy for d<sup>5</sup> configuration means that only very strong-field ligands are able to cause spin pairing. Manganese (II) has high rapid ligand exchange, and is thus easily mobilized. Because of d<sup>4</sup> configuration of manganese (III), the ion is subject



**Fig. 5.** The CaMn<sub>4</sub>O<sub>5</sub>(H<sub>2</sub>O)<sub>4</sub> cluster of PSII and possible trajectories of substrate/product channels leading to lumen. (A) View from the stromal side onto the membrane plane showing the CaMn<sub>4</sub>O<sub>5</sub>(H<sub>2</sub>O)<sub>4</sub> cluster (only Ca [brown sphere], Mn(1) and Mn(4) [red spheres] are visible), the chloride ion (Cl<sup>-</sup>, green sphere), and putative channels connecting the cluster to the luminal side. Water/oxygen channels are in blue (A1), light blue (A2), and brown (B1); possible proton channels (C to G) are in yellow (Source: Gabdulkhakov et al. [107]). (B) A schematic of the view in panel A. It shows possible substrate and product channels in PSII. Minimum diameters of the water/oxygen channels (in Å) are indicated in the diagram. Thick colored arrows indicate the suggested paths for water supply (blue), oxygen (pink), and proton (yellow) removal. The diagram shows U-Lys134 from the subunit PsbU that closes a side-exit of channel B1 and could open it by a conformational change [107]. Source: Gabdulkhakov et al. [107].



**Fig. 6.** The  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster in PSII; it has a dimension of about  $\sim 0.5 \times 0.25 \times 0.25$  nm (A). The location of  $\text{Y}_z$  and the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster in PSII is shown (B). Source of the figure and caption: [33].

to Jahn–Teller distortion, which allows it to have fast rates of ligand exchange. Due to  $d^3$  configuration of manganese (IV), the ion shows much slower rates of ligand exchange than manganese (II) or (III).

Oxidation states of manganese ions in the WOC is III and IV that are important for the stability of the cluster. In other words, in model manganese complexes for the WOC, a facile ligand exchange in the labile manganese (II) could be an important factor in rapid catalyst deactivation [87,104].

#### 4.10. Oxidant

As discussed in the previous sections, the WOC is linked to the reaction center II chlorophyll ( $\text{P}_{680}$ ) via a redox-active tyrosine (tyrosine 161 as mentioned earlier) residue on the D1 subunit, labeled as  $\text{Y}_z$ . As shown in Fig. 6B,  $\text{Y}_z$  is close enough to the WOC to be intimately involved in the chemical catalysis of water oxidation, rather than simply acting as the immediate oxidant of the WOC. The redox potential of  $\text{Y}_z/\text{Y}_z^+$  is around 1.0–1.2 V [59]. Hammarstrom and Styring [114] have discussed the possible roles of  $\text{Y}_z$  in the WOC of PSII that are all important for the understanding of PSII and of design(s) of an

artificial photosynthetic system. Firstly,  $\text{Y}_z$  provides  $\text{P}_{680}^+$  with a rapid electron donor.  $\text{Y}_z$  reduces  $\text{P}_{680}^+$  quite rapidly which competes favorably with the recombination reaction at the reaction center [114]. Secondly, the presence of  $\text{Y}_z$  allows the WOC to be positioned at an appropriate distance from  $\text{P}_{680}$  [114]. Many of the oxidants used in water oxidation reactions (for example: ceric ammonium nitrate (1.4 V versus NHE) or oxone (1.7 V versus NHE (normal hydrogen electrode) are more powerful than PSII. These oxidants result in decomposition of catalysts in many reactions. Najafpour et al. [69] have found that Ce(IV) may act not only as a simple oxidant, but may simultaneously decoordinate manganese from other compounds.

#### 4.11. The role of outer bonds in the biological water oxidation

Similar to other biological systems, the secondary coordination sphere around the WOC is important and is strongly correlated with function [115,116]. The secondary coordination sphere could decrease the activation energy for water oxidation. Hydrogen bond is the most common type of secondary coordination sphere used by biomolecules. One factor that can considerably reduce the potential required for

water oxidation is binding of the released protons by hydrogen bonds [59].

#### 4.12. Role of calcium and chloride

Calcium is as an essential cofactor in the WOC in PSII reaction, and Sr ion is the only cation that can functionally substitute for Ca in the WOC (see [59,117,118]). Also see Aedelroth et al. [119], who used  $^{45}\text{Ca}$  for obtaining information on the stoichiometry of Ca, in the WOC of the PSII. Recent data support an important role for calcium and several mechanisms have been proposed regarding the role of Ca in the oxygen evolution reaction. First Vincent Pecoraro's group has proposed that a terminal  $\text{Mn(V)=O}$  undergoes a nucleophilic attack by a Ca bound hydroxide ligand to form a Mn-bound hydroperoxide [60]. Brudvig and co-workers [61] have also proposed a mechanism in which a Ca ion plays a role as a weak Lewis acid. In this mechanism, a water bound to calcium reacts with a  $\text{Mn(V)=O}$  species to evolve oxygen through a nucleophilic attack. This idea has been further elaborated by Brudvig and co-workers [120,121] who have proposed a mechanism that accounts for the details of oxygen evolution by PSII. Recently, Agapie et al. [122] have reported a potential role for Ca in facilitating high oxidation states at a manganese–calcium multinuclear complex. A number of experiments also demonstrate a role for calcium in the assembly and stability of the WOC [122].

Chloride is also required for water oxidation [123]. Two  $\text{Cl}^-$  binding sites have been detected in the crystal structure of manganese–calcium cluster of PSII at an atomic resolution [32,33]. The results showed that there were no  $\text{Cl}^-$  ions in the first coordination sphere of the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster [32,33]. Kawakami et al. [33] have suggested that the two  $\text{Cl}^-$  ions may function in maintaining the proton exit pathways as these are located at the entrance of two possible proton exit paths. Understanding the roles of calcium and chloride in biological water oxidation are important in the design of a *super anode* for water oxidation in artificial photosynthesis.

#### 4.13. Four-electron water oxidation

In artificial water oxidizing catalysts, similar to the WOC in PSII, a four-electron water oxidation is certainly easier than four sequential, one-electron oxidation or two sequential two-electron oxidation because in these cases the first steps ( $\text{H}_2\text{O}$  to hydrogen peroxide and hydroxyl radical) are more endergonic than the four-electron water oxidation, that result in low over-voltage for practical operations [65].

#### 4.14. Redox accumulation in the WOC

The WOC could be considered as a redox accumulator to perform a four-electron reaction by collecting four electrons from four one-electron reactions (Fig. 3). Most probably, in biological water oxidation, oxidation of two or three manganese ions occurs and thus a four-electron reaction water oxidation could be performed (for reviews, see [65,66]). A similar strategy could be used to design an artificial water oxidizing catalyst. In other words, different manganese sites as charge accumulators and reaction centers could be considered in the design of multi-electron redox catalysis.

#### 4.15. Regulating oxidizing power

In a water oxidizing complex, oxidizing power in each charge accumulation step should be regulated carefully as is in the WOC in PSII. For example, if in the  $\text{S}_2 \rightarrow \text{S}_0$  (Fig. 3) two-electron couple ( $\sim 0.8\text{ V}$ ) has a higher potential than the  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  couple ( $\sim 1.5\text{ V}$ ), there could be a risk of oxidizing water too soon in the S-state cycle, producing  $\text{H}_2\text{O}_2$  [65].

#### 4.16. Amino acids

PSII consists of hundreds of amino acids; however, only a small fraction of the residues come in direct contact with the manganese–calcium cluster, and an even smaller fraction, 3 to 4 residues on the average, are directly involved in catalysis. Roles for the residues that come in contact directly with the manganese–calcium cluster could be regulation of charges and electrochemistry of the Mn–Ca cluster; they could help in coordinating water molecules at appropriate metal sites, and in the stability of this cluster [32,33]. The PSII manganese stabilizing protein (MSP) is a highly conserved extrinsic component of the WOC [124–129]. Its deletion from the PSII causes a dramatic lowering of the rate of oxygen evolution [124–129]. The PSII manganese stabilizing protein has also been suggested to be important in linking the active site of WOC with the lumen and to be involved in a proton transfer network. A simple inorganic manganese–calcium core without coordinated amino acids shows much less activity than the WOC in PSII [91–97]. Thus, the amino acids around the Mn cluster are very important indeed and the design of a *super anode* for water oxidation in artificial photosynthesis needs a detailed understanding of the roles of these amino acids in water oxidation [124–129].

#### 4.17. Suitable geometry for binding water molecules

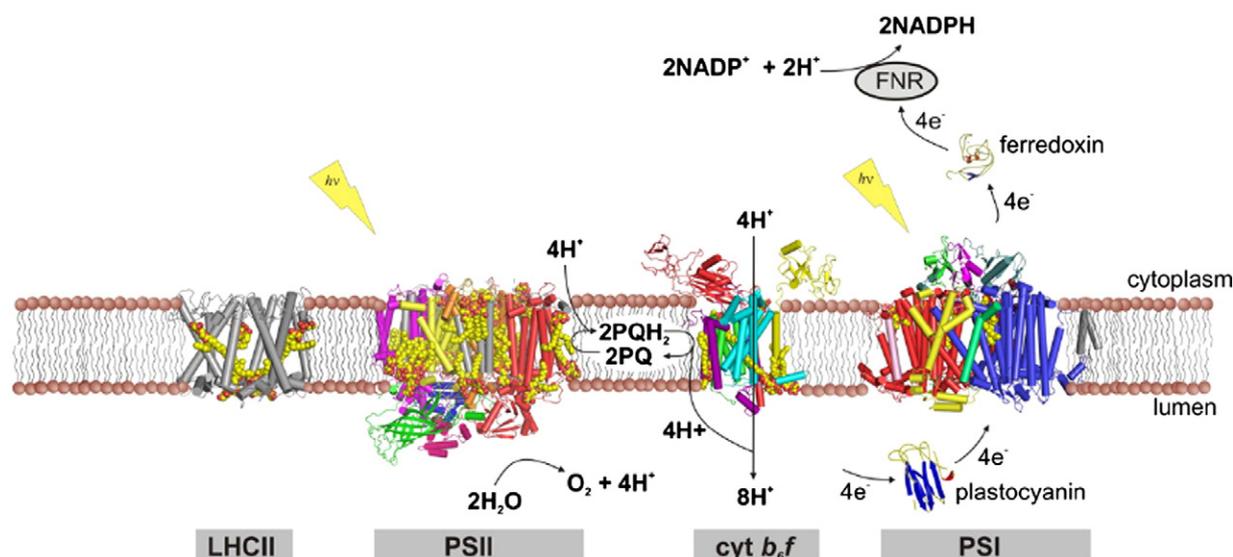
An important role of the WOC is binding of the substrate water molecules in a suitable geometry [43]. There are several water molecules near the WOC. Four water molecules are attached directly into manganese–calcium cluster. Two water molecules are coordinated to a manganese ion located outside the cubane and two water molecules are coordinated to the calcium ions that could be the substrate for oxygen evolution reaction. Five bridging oxygen atoms in the structure could be also considered as substrates for oxygen evolution.

#### 4.18. Photosystem II as a photoassembled complex

Water oxidizing complex is a photoassembled complex (Fig. 7) [130–132]. Thus, synthesis of efficient catalysts could be possible by self or photo-assembly. Amorphous manganese–calcium oxide involving no special pre-organized manganese or calcium precursors in purely aqueous solution, that has a similar structure to the WOC, has been reported in the literature [92]. This suggests to us that the understanding of the mechanism of assembly of the WOC could be very helpful in the design of an efficient catalyst for water oxidation [133,134].

#### 4.19. Electrochemistry of manganese

The natural system uses manganese ions for water oxidation. Manganese (II) or (III) ions are used as cofactors for a number of enzymes [136,137]. Manganese has a very rich redox chemistry compared with other elements. The most common oxidation states of manganese in biological systems are (II), (III) and (IV) but oxidation states of (V), (VI) and (VII) could be stabilized by special ligands in vitro. The usual oxidation state for manganese in many mononuclear manganese enzymes is (II) or (III). However, in water, manganese (III) ion is unstable and prone to be disproportionated to manganese (II) and manganese (IV). As shown in Fig. 2, there are four manganese ions in the WOC. Here, we will discuss details of coordination chemistry of metal ions and a few important groups near the manganese–calcium cluster. However, it is worth mentioning that in the manganese–calcium cluster, there is charge distribution, and the charge on each ion is lower than that suggested by its oxidation state. In other words, the  $\text{CaMn}_4\text{O}_5(\text{H}_2\text{O})_4$  cluster is a delocalized system and each ion should not be studied completely separately. Some experiments suggested a (III, III, III, IV), (III, III, IV, IV) and (III, IV, IV, IV) assignment for  $\text{S}_0$ ,  $\text{S}_1$  and  $\text{S}_2$ ,



**Fig. 7.** A schematic view of the thylakoid membrane with PSI, PSII, LHCII and Cyt  $b_6/f$  embedded in it. For simplicity only one monomer of each complex is shown, transmembrane helices are shown as cylinders, all cofactors except lipids are omitted. The lipids intrinsic to the structures are shown in space filling representation with yellow spheres for carbon and red spheres for oxygen. Proton as well as electron fluxes are indicated by arrows. PQ stands for plastoquinone, PQH<sub>2</sub> for plastoquinol, and FNR for Ferredoxin-NADP reductase [135]. Source of the figure and caption is ref. [135].

respectively. Probable oxidation states for the  $S_3$  and  $S_4$  states of the Kok cycle are currently being debated. It is known that the oxidation state changes in  $S_0 \rightarrow S_1$  and  $S_1 \rightarrow S_2$  for the WOC are manganese-based (for a review see [54]). The  $S_2 \rightarrow S_3$  and the  $S_3 \rightarrow S_4$  transitions are still controversial as to whether a metal-centered or a ligand-centered oxidation occurs (for a review see [59]). In the  $S_4 \rightarrow S_0$  transition (Fig. 4), rapid oxidation of two substrate water molecules occurs (for a review see [59]).

Recently, Takashima et al. [138] have reported that the control of disproportionation and comproportionation of manganese (III) is essential for the development of manganese catalysts that would lead to water oxidation with a small overpotential at neutral pH for manganese oxides [138]. It seems that the natural system uses appropriate and complex strategies for water oxidation by manganese ions [139].

#### 4.20. Applications of acid and base rules in water oxidizing complex

As stated in the previous sections, in water, manganese (III) ion is unstable because of its disproportionation to manganese (II) and manganese (IV). However, manganese (III) ion could be stabilized by increasing the pH or by providing good donor ligands. Manganese (IV) compounds are mainly found with bridging or terminal oxo-ligands because the water coordinated to high valent metal ions has a  $pK_a$  lower than free water [140]. We note that water molecule coordinated to various dipositive metal ions has  $pK_a$  values as low as 7.  $Mn(IV)-OH$ ,  $Mn(IV)=O$  or (and)  $Mn(V)=O$  is suggested to be an important intermediate in water oxidation [59,139].

#### 4.21. Contribution of water oxidation to the ATP synthesis

In water oxidation, in addition to oxygen release, electrons and protons are also produced. Electrons could be used to reduce a variety of molecules such as  $H_2O$ ,  $CO$ ,  $CO_2$  or  $N_2$  to produce useful compounds in artificial photosynthesis [87]. In Nature, these electrons are ultimately used to reduce  $CO_2$ . As is well known, proton motive force (from the proton gradient) produces ATP in photosynthesis.

ATP synthesis in photosynthesis depends not only on the pH difference ( $\Delta pH$ ) across the photosynthetic membrane, but membrane potential difference ( $\Delta\psi$ ), the two together, being the proton motive force (Fig. 8). In other words, protons flow back down its

electrochemical gradient through an enzyme ATP synthase, which catalyzes the synthesis of ATP from ADP and phosphate. This enzyme could serve the role of a turbine, permitting the proton gradient to drive the production of ATP (for a review see [8]). This process may or may not be used in artificial photosynthesis but the point is that Nature uses all strategies to increase efficiency and produce useful products in photosynthesis.

## 5. Nonbiomimetic water oxidation

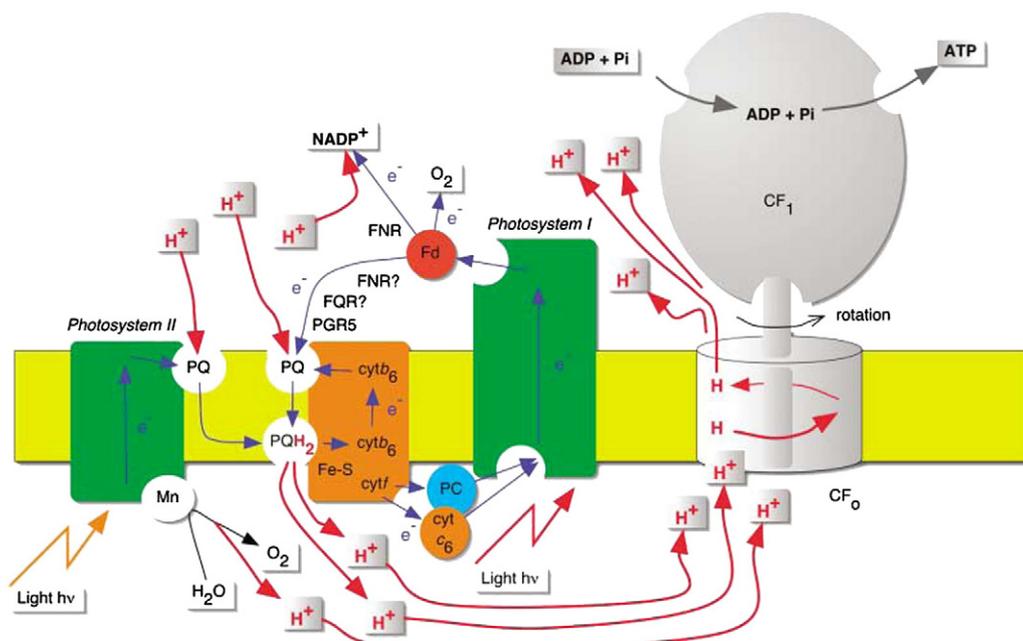
There have been many attempts to design catalysts for water oxidation with the use of chemicals and methods that may not have much to do with how photosynthesis does it [142–147]. All avenues must be encouraged, but we believe that learning from the natural systems [148,149] (cyanobacteria, algae and plants) makes sense since these have been doing it successfully for millions of years. However, for completeness, we draw the attention of the readers to selected papers to note the progress in this field of non-biomimetic systems: Liang et al. [142] used  $Co_3O_4$  nanocrystals on graphene [142]; Surendranath et al. [143] used cobalt phosphate catalyst; Li et al. [144] used titania anatase; Cummings et al. [145] used thin films at  $Fe_2O_3$  electrodes; Lyons and Brandon [146] used nonpassive oxide-covered transition metal electrodes; and Wang et al. [147] used a nickel hydroxide electrode.

## Acknowledgements

M. M. Najafpour and A. Nemati Moghaddam are grateful to the Institute for Advanced Studies in Basic Sciences for financial support.

This work was also supported by grants from the Russian Foundation for Basic Research (nos. 11-04-01389a, 11-04-92690a and 12-04-92101a), Russian Ministry of Science and Education (no. 16.740.11.0176), Molecular and Cell Biology Programs of the Russian Academy of Sciences, and by BMBF (no. 8125) Bilateral Cooperation between Germany and Russia.

Govindjee was supported, in 2011, by the Department of Plant Biology of the University of Illinois at Urbana-Champaign, and, in 2012, by the School of Life Sciences of Jawaharlal Nehru University, New Delhi, India, where this review was finalized.



**Fig. 8.** Proton translocation from the chloroplast stroma into the lumen of the thylakoid establishes a proton motive force that couples electron transport to ATP synthesis. The implied stoichiometry of  $3\text{H}^+/\text{e}^-$  is for noncyclic electron transport alone [141]. Source of the figure and caption: [141].

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