Review article

A nano-sized manganese oxide in a protein matrix as a natural water-oxidizing site

Mohammad Mahdi Najafpour^{a,b*}, Mohadeseh Zarei Ghobadi^a, Behzad Haghighi^{a,b},

Tatsuya Tomo^{c,d}, Robert Carpentier^e, Jian-Ren Shen^f, Suleyman I. Allakhverdiev^{g,h*}

^aDepartment of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

^bCenter of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

^cDepartment of Biology, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan

^dPRESTO, Japan Science and Technology Agency (JST), Saitama 332-0012, Japan

^eDépartement de Chimie Biochimie et Physique, Université du Québec à Trois Rivières, C.P. 500, Québec, G9A 5H7, Canada

^fGraduate School of Natural Science and Technology/Faculty of Science, Okayama University, Okayama 700-8530, Japan

^gInstitute of Plant Physiology, Russian Academy of Sciences, Botanicheskaya Street 35, Moscow 127276, Russia

^hInstitute of Basic Biological Problems, Russian Academy of Sciences, Pushchino, Moscow Region 142290, Russia

***Corresponding Authors:**

E-mail: mmnajafpour@iasbs.ac.ir (MMN); Phone: (+98) 241 415 3201; Fax: (+98) 241 415 3232;

E-mail: suleyman.allakhverdiev@gmail.com (SIA); Phone: (+7) 496 7731 837; Fax: (+7) 496 7330 532;

Abstract

The purpose of this review is to present recent advances in the structural and functional studies of water-oxidizing center of Photosystem II and its surrounding protein matrix in order to synthesize artificial catalysts for production of clean and efficient hydrogen fuel.

Keywords: H₂ production, Photosystem II, Nano-sized Mn-Ca cluster, Water-oxidizing center, Oxygen evolution, Artificial photosynthesis , Nano-layered Mn oxide

1. Introduction

Nowadays, one of the significant threats facing mankind is the climate change caused by the increased CO₂ production associated with the consumption of fossil fuels. The aftermath of this global warming problem is the reduction of food sources because of unfavorable conditions for plants growth. Hence, active research for the production of clean and affordable energy is needed [1]. To this end, nature has been an inspiration wellspring.

Photosynthesis is a process used by green plant, algae, and cyanobacteria to convert carbon dioxide and into organic molecules and oxygen in the presence of light. Despite numerous proposals for the origin of photosynthesis on Earth, there is no detailed information to support any of them [2]. Most researchers agree that nonoxygenic photosynthesis performed approximately 3.2 to 3.5 billion years ago. Also, the evidence from rock fossils indicates that the great oxidation event (GOE) occurred from 2.48 billion years ago, coinciding with the evolution of cyanobacteria [3, 4]. Probably, the first experiment exploring the nature of photosynthesis was performed by van Helmont in 1648 [5]. Now, we have extensive information about the details of this phenomenon. Photosynthesis is a two-step process: light reactions in the grana and CO₂ fixation in the stroma of the chloroplast. The light dependent part is fulfilled by two sequential photosystems (photosystem II (PSII) and photosystem I (PSI)).

The first step in the PSII (membrane-protein complex) is the light-induced excitation of chlorophyll a (P₆₈₀) and loss one electron. P₆₈₀⁺ compensates its electron deficient state by the donation of an electron from the amino acid tyrosine (Y_z) and subsequently, Y_z⁺ is rereduced by an electron obtained from water cleavage into O₂, electrons and H⁺ owing to the catalytic action of the water-oxidizing center known as the WOC (or oxygen-evolving center (OEC)) [6-8]. The

electron lost by P_{680} passes through a series of electron carriers, then is trapped by another chlorophyll a (P_{700}) in the PSI. P_{700} also loses an electron following light-induced excitation that will be used to produce NADPH. This series of electron transfers will also lead to ATP synthesis. The second step of photosynthesis known as the Calvin Cycle can take place in the absence of light. In this process, the atmospheric carbon dioxide is captured and converted to carbohydrate by the use of the energy from the NADPH and ATP produced in the first stage [9]. The scrutiny of the photosynthesis process can help the researchers to find a compound with high efficiency and stability in artificial systems for water splitting (Eq. 3), water oxidation (Eq. 1) and reduction (Eq. 2), that can also be used to store renewable energies [10-13]. However, in water splitting, water oxidation is a bottleneck.

Such reactions (Eq. 1-3) can occur in both artificial and natural systems. In this review, we will highlight the importance and the structure of the WOC in PSII. Furthermore, we will discuss various proposed mechanisms for the WOC in the nature and synthetic compounds.

2. Water-Oxidizing Center: Position, Significance, and Structure

One of the most important reactions in nature is the photosynthetic water oxidation. As a result, oxygen is evolved with a turnover of up to 100-400 released O_2 molecules per second [14], which is the main source of the atmosphere's oxygen. Also, this process is a major inspiration source for scientists to synthesize new compounds in view of the production of clean hydrogen fuel. The main focus is the reaction center of the WOC that includes a $\text{Mn}_4\text{O}_5\text{Ca}$ cluster which is

surrounded by a protein environment managing reaction coordinates, proton motion, and water availability. The four-electron oxidation mechanism of water oxidation with an undermost activation energy is as follows [15].

From the thermodynamic point of view, four-electron water oxidation is most likely to occur because other possible reactions such as four-sequential one-electron oxidation or two-sequential two-electron oxidation are more energy-consuming. Each oxidation state of the WOC is known as an “S-state”, in which the oxidation level gradually increases from S_0 to S_4 (Fig. 1) [16, 17]. The WOC couple the sequential one-electron reduction of P_{680} to the four electrons oxidation of water. All the S-state transitions, except the $S_4 \rightarrow S_0$, are induced by the photochemical oxidation of chlorophyll (P_{680}^+), which oxidizes the WOC via a redox-active tyrosine. Oxygen evolution occurs in the light independent transition of $S_4 \rightarrow S_0$ [6].

In this section, we briefly go over the history of the structural investigation of the Mn cluster. The first idea about Mn involvement in photosynthesis was introduced in 1937 by A. Pirson [18]. About 40 years later, Jaklevic et al. recorded the X-ray absorption spectrum of the Mn in a leaf [19]. They estimated a Mn concentration of 10-50 ppm in the chloroplast of green plants. Continuous studies conducted by M. P. Klein et al. revealed that: i) the presence of di- μ -oxo bridged pairs of Mn atoms in the WOC by EXAFS analysis [20]; ii) the attendance of Mn with oxidation state higher than +2 via analysis of the X-ray absorption edges [21]. By observing the variations in X-ray absorption edge of Mn in PSII, Yachandra group concluded that Mn partaked in the light-driven electron-transfer and was oxidized as the WOC advances from the S_1 to S_2 state [22]. V. K. Yachandra et al. in 1986 surveyed the K-edge spectra and EXAFS of Mn complex. It was deduced that the oxidation state of Mn increased in the transition from S_0 to S_1 and S_1 to S_2 but no change occurred from S_2 to S_3 . In addition, by observation of similarity

between the structural analysis results of the complexes from spinach and *Synechococcus*, they suggested the basic structure of the Mn center was conserved over the two billion years [23]. Therefore, the bridged Mn complex was proposed as an essential feature of the O₂ evolving complex. The attendances of two inequivalent di- μ -oxo bridged binuclear structures in the S₃ state were suggested by Guiles in 1990 [24].

Sauer and his colleague offered the dimer of dimers model which assumed the Mn complexes composed of two Mn “dimers”. Several structural models including 3 + 1 arrangement of Mn atoms in the cluster were also investigated based on the EXAFS data by V. J. DeRose et al. [25]. This structure was confirmed by magnetic resonance experiments [26], and theoretical studies [27]. The first detailed structure study of PSII was reported by Witt and Saenger [28]. They isolated dimeric PSII from the thermophilic cyanobacterium and depicted the three-dimensional structure of WOC at 3.8 Å resolution (Fig. 2). The identified cluster structure was introduced as follows: three Mn ions located in the corners of an isosceles triangle accompany with a fourth Mn ion near the center of the triangle. Nobuo Kamiya and Jian-Ren Shen in 2003 analyzed the PSII which was extracted from *Thermosynechococcus vulcanus* [29]. They confirmed the previous provided structure with a difference that all four Mn atoms were placed approximately in the same plane. J. Barber and S. Iwata in 2004 suggested a cubane-like Mn₃CaO₄ cluster with a mono- μ -oxo bridge to a fourth Mn ion and accordingly a mechanism for water oxidation was proposed [30]. Their study was the first reported structure that included a Ca ion. One year later, B. Loll et al. offered a different structure for the Mn₄Ca cluster, thus the distances between Mn-Mn in the pyramid (three Mn and Ca) were not equal and Mn₄ adjoin asymmetrically to the pyramid [31]. J. Yano et al. considered an extended set of hypothetical models of the Mn₄Ca cluster so that the calculated EXAFS spectra matched the polarized EXAFS data which were

acquired for PSII crystals [32]. In 2010, the X-ray Emission Spectroscopy was utilized for the detection of oxo-bridges in the Mn_4Ca cluster by analysis of its spectrum [33]. The most considerable information was gained by Shen and Kamiya research groups via the record the PSII crystal structure at 1.9 Å resolution (Fig. 3) [34, 35]. The electron densities illustrated that the WOC cluster is composed of 4 Mn atoms, 1 Ca atom, and 5 oxygen atoms. They showed that 3 Mn and Ca atoms formed four corners and 4 oxygen atoms occupied the other four corners of a cubane-like structure. The fourth Mn was placed outside of the cubane structure, and was linked to two Mn atoms within the cubane by O5. Moreover, four water molecules were bound to the Mn_4CaO_5 -cluster ($\text{Mn}_4\text{O}_5\text{Ca}(\text{H}_2\text{O})_4$), with two molecules are coordinated to Ca and two other to Mn4. Probably, some of these molecules are involved in water oxidation. At least 1300 water molecules were found in a PSII monomer. The formation of hydrogen bonding by some of these molecules may act as protons, water or oxygen molecule channels. The structural details of the ligands around each of Mn and Ca in the cluster are mentioned as follows. Mn1: three $\mu_3\text{-O}$, two carboxylates (D1-Glu189 and D1-Asp342) and one imidazole group (D1-H332) stabilize the oxidation state of III or IV. Mn2: three $\mu_3\text{-O}$ and three bridging COO^- (D1-Glu342, CP43-Glu 354 and D1-Ala344) could be stabilizer factors of the oxidation number of III or IV. Mn3: three $\mu_3\text{-O}$, one $\mu_2\text{-O}$ and two bridging COO^- (CP43-Glu 354 and D1-Glu333) groups are present. Four hard $\mu\text{-O}$ ligands could stabilize Mn (IV). Mn4: one $\mu_4\text{-O}$, one $\mu_2\text{-O}$, two bridging COO^- (D1-Asp170 and D1-Glu333) groups and two H_2O molecules are present. These ligands could stabilize the oxidation state of (III), although deprotonation of water molecules could lead to the stabilization of the oxidation state of (IV). Ca: three $\mu_3\text{-O}$ bridges, two bridging COO^- (D1-Ala 344 and D1-Asp170) groups and two H_2O molecules are involved.

Recently, crystallographic studies have determined the position and bonding distances of Ca in the WOC showed a key role of Ca in oxygen evolution [29, 30, 36-39]. The importance of the presence of a Ca ion in the WOC was revealed in 1984 [40]. A. Boussac and A. W. Rutherford showed that Ca removal from the cluster hampered the splitting of water due to blocking the S_2 to S_3 transition [41]. T. A. Ono and Y. Inoue in 1989 investigated the role of Ca in O_2 evolution and found three tasks for it: (i) adjustment of oxidation potential (ii) structural regulation of the cluster; (iii) conformational adjustment of the whole water oxidation structure [42]. Using XANES, T. A. Ono et al. in 1993 considered flash-induced changes the WOC (depleted of Ca). The results indicated that the Mn-cluster and/or its direct ligand could be oxidized up to two electrons but further events are blocked [43]. T. A. Ono and T. Noguchi has considered important issues such as the role of cofactors, structural changes for the WOC and so on in PSII by Fourier transform infrared difference spectroscopy [44-48]. In the same year, A. Boussac et al. could deplete the PSII enriched membrane from Ca and found O_2 evolution did not occur unless Ca ion was added. So, the absence of Ca leads to a disordered Mn cluster [49]. Various studies have been conducted to find a replacement for Ca and only Sr could reconstitute the function of water-splitting in Mn_4O_xSr as Mn_4O_xCa [40, 41, 50]. This is perhaps due to the similar Lewis acidity of Sr and Ca [51, 52]. C.-I. Lee et al. demonstrated a structural role for Ca in the beginning of S state transitions and also showed that it could be carried out by the cations with the same ionic radius [36]. Finally, T. Lohmiller et al. have shown in 2012 that Ca removal does not affect the electronic properties of the Mn cluster and is not required for structural preservation of the WOC [53]. Instead, they proposed that Ca is necessary to preserve the hydrogen bonding between the amino acid tyrosine (Y_z) and the Mn cluster.

In addition to direct binding ligands to the WOC, indirect ligands include D1-Asp61, D1-His337, and CP43-Arg357 amino acids that were detected in the second coordination domain, in which two guanidinium η -nitrogen of CP43-Arg357 and the imidazole of D1-His337 are bound to different oxygen groups in the cluster. More information about the interaction of His337 with the cluster were revealed by Petrie et al. [54]. They found that His337 residue interacts with WOC through μ_3 -oxo bridge connecting Mn(1), Mn(2) and Mn(3) which may lead to prolongation of Mn-Mn distances monitored in the PSII crystal structure at 1.9 Å resolution. Furthermore, density functional theory displayed that hydrogen bonding of the cluster with His337 residue caused the extension of some of the Mn-Mn distances, specially the distance of 2.7 Å.

The last known cofactor of the WOC is Cl^- . D. I. Arnon and F. R. Whatley in 1949 showed the isolated photosynthetic membranes need to Cl^- , Br^- , NO_3^- or I^- to produce O_2 [55, 56]. Subsequent studies identified Cl^- is needed for the electron donor reactions in the WOC [56-58]. P. O. Sandusky and C. F. Yocum proposed that the chloride ion could act as bridge between Mn atoms [59]. H. J. Van Gorkom et al. found that superseded ions eg. iodide or bromide decreased the stability of the advanced S-states [60]. Further experiments revealed Cl^- was needed to the $\text{S}_2 \rightarrow \text{S}_3$ and $\text{S}_3 \rightarrow \text{S}_4 \rightarrow \text{S}_0$ transitions of the WOC [61]. A role in the regulation of the redox properties of WOC was also proposed [62]. Radioisotope labeling studies indicated that only one Cl^- ion would be bound per each WOC unit [6, 63]. K. Olesen and L. -E. Andreasson, using EPR spectroscopy, suggested that Cl^- like Ca could be involved in the proton transfer away from the WOC [64]. The detailed structural data of the WOC obtained by X-ray crystallography at 1.9 Å which was described above, have shown that two chloride ions are present in the cluster [34]. The recent mutagenesis studies of D2-K317 by G. W. Brudvig [65] and T. Noguchi [66] have

clearly suggested the possibility that Cl-1 is involved in the proton pathway. I. Rivalta et al. found by structural analysis of the WOC that chloride removal impel the salt-bridge formation between D2-K317 and D1-D61 that may cause the proton transfer repression to the lumen [67].

3.Mn stabilizing protein auxiliary

The heart of PSII reaction center is consisted of polypeptides D1 (PsbA) and D2 (PsbD) which are essentially preserved in the oxygenic photosynthesis species (higher plants, algae, and cyanobacteria). These proteins are liable for binding of all the redox cofactors involved in electron transfer. Also, PSII includes antenna proteins CP47 (PsbB) and CP43 (PsbC) as well as the two subunits (PsbE and PsbF) of cytochrome b559 [68]. In addition, there are several subunits with low molecular mass (10 KDa) which are necessary for stabilizing the assembled PSII dimer. In contrast to the conservation of the PSII reaction center and the WOC during the evolution, the subunits stabilizing of the WOC differ between various organisms. The extrinsic proteins of plants and green algae are PsbO, PsbP and PsbQ. However, cyanobacteria and diatoms contain PsbO, PsbV and PsbU but red algae includes PsbQ in addition to PsbO, PsbV and PsbU [68-70]. Here, we only describe the PsbA, PsbD, and PsbO proteins of higher plant (for more details of other proteins, see ref [68]).

3.1. D1(PsbA)

This protein has a molecular mass of **approximate** 38 KDa and contains **about** 344 amino acids depending on species. PsbA is composed of five transmembrane α -helices and two surface α -helices (A–E), DE stromal and CD luminal surface α -helices [68, 71]. PsbA with PsbD form the heterodimer which is bound to the cofactors involved in PSII-mediated electron transport including: Mn cluster (Asp170, Glu189, His332, Glu333, Asp342, and the C-terminus of

Ala344), Y_Z (Tyr161), two pheophytins *a* (H-bounded by Tyr126 and Glu130), Q_A, non-heme Fe and Q_B (interacting via His215 and Ser264) as well as six chlorophyll *a* molecules. P_{D1} is responsible for the charge separation and connect to PsbA through His198. Also, excluding the four mentioned chlorophylls, the PsbA/PsbD heterodimer binds two chlorophyll *a* molecules named Chl_{ZD1} and Chl_{ZD2}. Moreover, PsbA binds two chloride ion via D1-Glu333 and D1-Asn338. A significant property of the D1 protein is its high susceptibility to photodamage that leads to decreasing of photosynthetic efficiency.

3.2. D2 (PsbD)

PsbD protein has about 350 amino acids and a molecular mass of approximate 39.5 kDa, regarding to the species. It has 5 transmembrane α -helices (A-E) and two surface α -helices which are localized between C-D (luminal) and between D and E (stromal). The D2 protein binds P_{D2} (by His197), Chl_{D2} (by a water molecule), the lateral chlorophyll *a* molecule Chl_{ZD2}, Q_A (His214, Phe261, probably Trp253 and Leu267), and non-haem Fe (interacting via His214 and His268). One β -carotene molecule that is possibly relevant to PsbD involve in transfer of excitation energy from Chl_{ZD2} to P₆₈₀. In higher plants, the reversible acetylation and phosphorylation of N-terminal Thr residue can occur for PsbD [68].

3.3. PsbO

PsbO known as the “Mn-stabilizing” protein is present in all oxygen evolving photosynthetic organisms [72, 73]. It includes 240–257 residues depending on species. It has a molecular mass of about 33 kDa. Two major domains of PsbO are (i) a filled cylindrical b-barrel structure which has a key role in stabilizing the Mn cluster [30] (ii) a head domain that operates as a docking site. In contrast to cyanobacteria, PsbO removal from green algae and higher plant affected the water

oxidation efficiency and modulate the Ca and Cl⁻ requirements for oxygen evolution [68, 70]. The detailed structural survey of cyanobacterial and plant PSII indicate one and two PsbO per PSII monomer, respectively. Popelkova et al. showed that plant PsbO had two sequence motifs at its N-terminus in contrast to cyanobacterial PsbO which had only one sequence motif [74-76].

4. Proposed mechanisms for water oxidation in PSII

One of the most important unresolved ambiguity in PSII is the water oxidation mechanism. Several research groups have attempted to define an acceptable mechanism by considering the structural evidence.

The first major studies that led to understand the mechanism of water oxidation were done by P. Joliot et al. in 1969 [77]. They demonstrated that a four step flash illumination of PSII generates a fluctuating pattern of oxygen evolution, in which utmost yield arises from fourth flash. This result was significant since the oxidation of two water molecules for the production of one oxygen molecule requires the removal of four electrons.

Based on this finding, B. Kok et al. in 1970 proposed that in each of the four stages, a single electron is removed from the WOC (Fig. 1). The accumulated four oxidizing equivalents caused the two water molecules oxidation [78]. Following to the Kok cycle, numerous groups represented the proton transfer pattern from the WOC into the lumen in the different S-state as: 1:0:1:2 [16, 79, 80]. In 1997, J. Babcock et al. proposed that tyrosine 161 may abstract hydrogen atoms from substrate water bound as ending ligands to two different Mn ions. In the final stage (hydrogen atom transfer), an O-O bond would be formed between the two terminally coordinated oxides or oxyl radicals (Fig. 4) [81].

M. Kusunoki in 2007 measured the ^{18}O exchange rates of two substrate water molecules for S_0 - S_3 states [82]. The formation of $^{34}\text{O}_2$ and $^{36}\text{O}_2$ identified the substrate binding sites depending on S-state. He proposed that two substrate water molecules are bound to asymmetric *cis*-positions on the terminal Mn ion being triply bridged (μ -oxo, μ -carboxylato, and a hydrogen bond) to the Mn cluster (Fig. 5). Also, it was suggested that chloride ion bound to CP43-Arg357 close to Ca ion and D1-His337 may be involved in trapping the released proton from the S_2 -state. Pecoraro et al. suggested the nucleophilic attack of Ca coordinated by hydroxide to a terminal Mn(V)=O leads to formation of Mn-bound hydroperoxide [83].

On the other hand, G. W. Brudvig's group proposed that the O-O formation is a result of nucleophilic attack of a Ca-bound water on the electrophilic oxygen atom of a Mn(V)=O species [84]. V. S. Batista et al. using comparison of the DFT QM/MM models with high-resolution extended X-ray absorption found that S_3 , S_4 , and S_0 states include an additional μ -oxo bridge between Mn(3) and Mn(4) (Fig. 6) [85]. The catalytic reaction is done via an oxyl radical formation by deprotonation of the substrate water molecule coordinated to Mn(4). It leads to accumulation of the fourth oxidizing equivalent in the oxidized substrate water. At last, a nucleophilic attack of substrate water molecule ligand of Ca to the oxyl radical causes the formation of dioxygen. The reaction continues by the replacement of the water molecules bound to Ca by a water molecule in the second coordination sphere of Ca, deprotonation of the displaced water, releasing a proton to the lumen via CP43-R357, and transferring the other proton to the basic μ -oxo bridge linking Mn(4) and Mn(3).

H. Dau and his colleagues in 2001 discussed the hypotheses of the oxidizing transitions as based on EXAFS and XAS data. They proposed that during the S_2 - S_3 transition, the mono- μ -oxo bridge was transformed to di- μ -oxo bridge along with deprotonation of hydroxide or water ligand by aid

of transition from five-coordinated Mn(III) to six-coordinated Mn(IV) (Fig. 7a) [86]. Also, EXAFS results revealed that the $S_0 \rightarrow S_1$ transition included deprotonation of a μ -oxo- μ -hydroxo bridge leading to shortening of Mn-Mn distance from 2.8 to 2.7 Å. Moreover, the changes in electrochromic absorption showed the charge was not accumulated by the WOC during the $S_0 \rightarrow S_1$ transition. The observation of positive charge accumulation at the WOC could be a result of charge decompensation by the ligand deprotonation. Recently, P. Glatzel et al. using resonant inelastic X-ray scattering spectroscopy showed that in the multinuclear clusters like the Mn_4CaO_5 cluster, electrons are strongly delocalized in the cluster, and probably including ligands involved in the redox chemistry [87].

Per E. M. Siegbahn at Stockholm University used the high-resolution (1.9 Å) structure by Shen et al. [34] in his calculations. The amino acids included in the model are:

- 1) The first shell of directly binding amino acids, Asp170, Glu189, His332, Glu333, Asp342, Ala344 and Glu354.
- 2) The second shell residues Asp61, His337 and Arg357 and the chloride. Lys317 and three water molecules, forming a hydrogen bonding network were also considered in this calculation.

In the proposed mechanism, the $S_2 \rightarrow S_3$ and the $S_3 \rightarrow S_4$ transitions start with an electron transfer from Y_Z to P_{680}^+ followed by an exergonic release of a proton of the WOC. Next step in the $S_2 \rightarrow S_3$ transition is the oxidation of Mn1.

In this state, the substrate water becomes more strongly bound to Mn1 and the Jahn–Teller axis on that center disappears. In the $S_3 \rightarrow S_4$ transition, there is a proton transfer, which unlike the previous S-state transition precedes the oxidation step (Fig. 7b). After an oxyl radical formation, there is another proton transfer before the S_4 -state is reached at which O-O bond formation

occurs. In this mechanism, the O-O bond is formed between an oxyl radical in the center of the cluster and a Mn-bridging μ -oxo ligand (Fig. 7b) [80].

5. Artificial photosynthesis based on synthetic catalysts

As mentioned before, the researchers have been exploiting the obtained structural details of PSII to reach an efficient catalyst compound for water oxidation and as a result hydrogen production, an appropriate alternative to fossil fuels. To this end, the main focus is on the WOC [10, 11, 88]. There are some reports for PSII extraction and its immobilization on the surface of electrodes [89-93]. These PSII coated electrodes act as an heterogenous catalyst for water oxidation (Fig. 8) [94]. Under illumination, they have the ability for water splitting at oxidation potentials as low as ~ 0 V vs. NHE [90]. However, the low operational stability of PSII under light exposure limits their use. Therefore, this is the main reason to synthesize new catalysts instead of the direct use of PSII.

There are some aspects that should be considered for synthesis of new catalysts: i) facilitation of electron transfer between the catalyst and an oxidizing equivalent that could be done by decreasing the oxidation potentials of the catalyst. ii) balancing between reducing the redox potential of the catalyst and the sustainability of oxidizing power for water oxidation. iii) non-toxicity and cheapness. Among the introduced catalysts, the preferred ones contain Fe, Ni, Ru, Co, or Mn transition metals [95-98].

Based on recent high resolution crystallography of PSII, it is interesting that despite the existence of hundreds amino acids around the Mn cluster, only 3-4 residue are directly coordinated to the cluster. The possible roles of these residues are regulation of charges and stabilizing the cluster. Besides, the activity of the WOC is decreased in the absence of specific amino acids [99]. Thus,

the synthetic *super anode* compounds should use strategic groups for facilitation of proton transfer, regulation of charges, and help in coordination of water molecule at appropriate sites [8].

In catalyst optimization, measurements are usually done by driving the WOC with a sacrificial oxidant. The oxidants like cerium(IV), ruthenium(III) tris(bipyridine) cation, sodium peroxodisulfate, potassium peroxymonosulfate, and sodium periodate allow the production of abundant oxygen in bulk solution.

Recently, G. W. Brudvig et al. published a tutorial review and extensively surveyed the advantages and disadvantages of different oxidants [100]. Also, electrochemical methods are useful to activate the catalyst by applying potential and probe the water oxidation [100-103]. Other method for production of H₂ is light-driven water oxidation at PSII which can be connected to H₂ production by hydrogenase (an enzyme in the many green algae and cyanobacteria that can convert the released protons into dihydrogen). A general plan for H₂ production using water and solar energy is shown in Fig. 9 [104], in which two dyes are a representative of the two photosystems in oxygenic photosynthesis. At first, a dye molecule (A) that mimics PSII absorbs the visible wavelength of light and then the photoexcited dye (A^{*}) reduces a redox mediator (R). The hole produced in A is transferred to the adjacent water-oxidation catalyst (Cat_{ox}).

In the PSI mimic, a photoexcited dye (D^{*}) reduces the proton-reducing catalyst. The reduced redox mediator provides electrons to the oxidized dye like plastocyanin in the natural PSI. In this way, light-driven water oxidation is coupled with light-driven hydrogen production [104, 105]. Some groups have reported different Mn oxides as catalysts toward water oxidation[97, 106-108]. In 2010, a new Mn-Ca oxide catalyst by oxidation of Mn(II) ions in the presence of

KMnO₄ was synthesized which was inspired by the Mn-Ca cluster structure in PSII [109]. The next results showed that nanolayered Mn oxides (Fig. 10) are efficient catalysts for water oxidation [110-115]. However, these model systems contain no groups analogous to amino acids, as exist in PSII. There are a few reports of the synthesis of new Mn oxides-based catalysts inside an organic compound matrix as a proper alternative for the amino acids [116-122].

Recently, Najafpour et al. introduced a novel efficient nanolayered Mn oxide/poly(4-vinylpyridine) catalyst with only 50 mV overpotential needed for water oxidation [119]. The reasons of using poly(4-vinylpyridine) (PVP) were: i) providing a suitable buffered medium for Mn oxide. ii) the operation of pyridine groups in the polymer as proton acceptor, Mn (III) stabilizer, and also overpotential reducer for water. iii) the polymer stability against strong oxidants. iv) the conductivity and polyelectrolyte properties of the polymer. Various compounds with different Mn oxide and a certain PVP values (l-MnO_x-PVP, m-MnO_x-PVP, h-MnO_x-PVP) were synthesized. TEM images illustrated the layered structure of Mn oxides which is the optimal structure for artificial photosystem (Fig. 11). As illustrated in Fig. 12, similar to natural PSII, the one with low MnO_x and high PVP contents show lower overpotential toward water oxidation on the platinum electrode surface at near natural pH. Moreover, oxygen evolution occurred at 700 mV (Fig. 13). Also, they found that the mentioned catalyst could apply successfully for the Persian Gulf water oxidation with a turnover frequency of 0.07 s⁻¹. This is a great outcome because in the presence of catalyst, the harmful chlorine gas was not formed on the anode. So, such catalysts open the way for H₂ fuel production from the great source of water oceans in the future.

Artificial solar fuel apply the basic principles of photosynthesis, such as light harvesting, charge separation between donor and acceptor molecules, electron transfer, and the multi-electron

catalytic processes to design systems for cheap and environmentally friendly fuel production by renewable energy sources. Among of different reactions, water splitting is very promising [123-125]

6. Conclusion

Synthesis of new catalysts for the oxidation of water using environmentally friendly materials is a big challenge in order to achieve clean fuel. Artificial solar fuel applying the basic principles of photosynthesis to design systems for fuel production by renewable energy sources. The art of water oxidation by PSII can be considered in artificial photosynthesis. This purpose is accomplished by a precise look at the Mn cluster structure found in PSII. Mn oxides are promising compounds for water oxidation with high efficiency.

Acknowledgments

Authors (MMN, MZG, BH) are grateful to Institute for Advanced Studies in Basic Sciences and the National Elite Foundation for financial support. This work was also supported by grants from the Russian Foundation for Basic Research (Nos: 13-04-91372; 14-04-01549; 14-04-92102; 14-04-92690), and by Molecular and Cell Biology Programs of the Russian Academy of Sciences, and by BMBF (no. 8125) Bilateral Cooperation between Germany and Russia to SIA. This work was also supported by Grant-in-Aids for Scientific Research from the Ministry of Education of Japan (21570038 and 22370017), and grant from JST PRESTO to TT.

References

- [1] J. Barber, P. Tran, From natural to artificial photosynthesis, Journal of the Royal Society, Interface/the Royal Society, 10 (2012) 20120984-20120984.
- [2] J.M. Olson, R.E. Blankenship, Thinking about the evolution of photosynthesis, Photosynthesis Research, 80 (2004) 373-386.
- [3] K.O. Konhauser, S.V. Lalonde, N.J. Planavsky, E. Pecoits, T.W. Lyons, S.J. Mojzsis, O.J. Rouxel, M.E. Barley, C. Rosiere, P.W. Fralick, Aerobic bacterial pyrite oxidation and acid rock drainage during the Great Oxidation Event, Nature, 478 (2011) 369-373.
- [4] S. Govindjee, D. Adventures with cyanobacteria: a personal perspective, Frontiers in plant science, 2 (2011) 28.
- [5] L.P. Williams, The Historical Background of Chemistry, The Yale Journal of Biology and Medicine, 29 (1957) 556.
- [6] J.P. McEvoy, G.W. Brudvig, Water-splitting chemistry of photosystem II, Chemical reviews, 106 (2006) 4455-4483.

- [7] M.M. Najafpour, Current molecular mechanisms of photosynthetic oxygen evolution, *Plant Biosystems*, 140 (2006) 163-170.
- [8] M.M. Najafpour, A.N. Moghaddam, S.I. Allakhverdiev, Biological water oxidation: Lessons from Nature, *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, 1817 (2012) 1110-1121.
- [9] J.H. Golbeck, *Photosystem I: the light-driven plastocyanin: ferredoxin oxidoreductase*, Springer, 2006.
- [10] M.M. Najafpour, A soluble form of nano-sized colloidal manganese (IV) oxide as an efficient catalyst for water oxidation, *Dalton Transactions*, 40 (2011) 3805-3807.
- [11] M.M. Najafpour, S. Nayeri, B. Pashaei, Nano-size amorphous calcium–manganese oxide as an efficient and biomimetic water oxidizing catalyst for artificial photosynthesis: back to manganese, *Dalton Transactions*, 40 (2011) 9374-9378.
- [12] F. Jiao, H. Frei, Nanostructured cobalt and manganese oxide clusters as efficient water oxidation catalysts, *Energy & Environmental Science*, 3 (2010) 1018-1027.
- [13] Y. Xu, T.r. Åkermärk, V. Gyollai, D. Zou, L. Eriksson, L. Duan, R. Zhang, B.r. Åkermärk, L. Sun, A new dinuclear ruthenium complex as an efficient water oxidation catalyst, *Inorganic chemistry*, 48 (2009) 2717-2719.
- [14] G.C. Dismukes, R. Brimblecombe, G.A. Felton, R.S. Pryadun, J.E. Sheats, L. Spiccia, G.F. Swiegers, Development of bioinspired Mn_4O_4 - cubane water oxidation catalysts: Lessons from photosynthesis, *Accounts of chemical research*, 42 (2009) 1935-1943.
- [15] M. Wiechen, H.-M. Berends, P. Kurz, Water oxidation catalysed by manganese compounds: from complexes to ‘biomimetic rocks’, *Dalton Transactions*, 41 (2012) 21-31.
- [16] H. Dau, M. Haumann, The manganese complex of photosystem II in its reaction cycle—basic framework and possible realization at the atomic level, *Coordination Chemistry Reviews*, 252 (2008) 273-295.
- [17] J. Barber, Photosystem II: a multisubunit membrane protein that oxidises water, *Current opinion in structural biology*, 12 (2002) 523-530.
- [18] A. Pirson, A study of the nutrition and metabolism of *Fontinalis* and *Chlorella*, *Z Bot*, 31 (1937) 193-267.
- [19] J. Jaklevic, J. Kirby, M. Klein, A. Robertson, G. Brown, P. Eisenberger, Fluorescence detection of EXAFS: Sensitivity enhancement for dilute species and thin films, *Solid State Communications*, 23 (1977) 679-682.
- [20] J. Kirby, A. Robertson, J. Smith, A. Thompson, S. Cooper, M. Klein, State of manganese in the photosynthetic apparatus. 1. Extended x-ray absorption fine structure studies on chloroplasts and di- μ -oxo-bridged dimanganese model compounds, *Journal of the American Chemical Society*, 103 (1981) 5529-5537.
- [21] J. Kirby, D. Goodin, T. Wydrzynski, A. Robertson, M. Klein, State of manganese in the photosynthetic apparatus. 2. X-ray absorption edge studies on manganese in photosynthetic membrane, *Journal of the American Chemical Society*, 103 (1981) 5537-5542.
- [22] D.B. Goodin, V.K. Yachandra, R.D. Britt, K. Sauer, M.P. Klein, The state of manganese in the photosynthetic apparatus. 3. Light-induced changes in X-ray absorption (K-edge) energies of manganese in photosynthetic membranes, *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, 767 (1984) 209-216.
- [23] V. Yachandra, R. Guiles, A. McDermott, R. Britt, J. Cole, S. Dexheimer, K. Sauer, M. Klein, The state of manganese in the photosynthetic apparatus determined by X-ray absorption spectroscopy, *Le Journal de Physique Colloques*, 47 (1986) 1121-1128.

- [24] R. Guiles, J. Zimmermann, A.E. McDermott, V.K. Yachandra, J.L. Cole, S. Dexheimer, R. Britt, K. Wieghardt, U. Bossek, The S3 state of photosystem II: differences between the structure of the manganese complex in the S2 and S3 states determined by X-ray absorption spectroscopy, *Biochemistry*, 29 (1990) 471-485.
- [25] V.J. DeRose, I. Mukerji, M.J. Latimer, V.K. Yachandra, K. Sauer, M.P. Klein, Comparison of the manganese oxygen-evolving complex in photosystem II of spinach and *Synechococcus* sp. with multinuclear manganese model compounds by X-ray absorption spectroscopy, *Journal of the American Chemical Society*, 116 (1994) 5239-5249.
- [26] J.M. Peloquin, K.A. Campbell, D.W. Randall, M.A. Evanchik, V.L. Pecoraro, W.H. Armstrong, R.D. Britt, 55Mn ENDOR of the S2-state multiline EPR signal of photosystem II: implications on the structure of the tetranuclear Mn cluster, *Journal of the American Chemical Society*, 122 (2000) 10926-10942.
- [27] P.E. Siegbahn, Theoretical models for the oxygen radical mechanism of water oxidation and of the water oxidizing complex of photosystem II, *Inorganic chemistry*, 39 (2000) 2923-2935.
- [28] A. Zouni, H.-T. Witt, J. Kern, P. Fromme, N. Krauss, W. Saenger, P. Orth, Crystal structure of photosystem II from *Synechococcus elongatus* at 3.8 Å resolution, *Nature*, 409 (2001) 739-743.
- [29] N. Kamiya, J.-R. Shen, Crystal structure of oxygen-evolving photosystem II from *Thermosynechococcus vulcanus* at 3.7-Å resolution, *Proceedings of the National Academy of Sciences*, 100 (2003) 98-103.
- [30] K.N. Ferreira, T.M. Iverson, K. Maghlaoui, J. Barber, S. Iwata, Architecture of the photosynthetic oxygen-evolving center, *Science*, 303 (2004) 1831-1838.
- [31] B. Loll, J. Kern, W. Saenger, A. Zouni, J. Biesiadka, Towards complete cofactor arrangement in the 3.0 Å resolution structure of photosystem II, *Nature*, 438 (2005) 1040-1044.
- [32] J. Yano, J. Kern, K. Sauer, M.J. Latimer, Y. Pushkar, J. Biesiadka, B. Loll, W. Saenger, J. Messinger, A. Zouni, Where water is oxidized to dioxygen: structure of the photosynthetic Mn4Ca cluster, *Science*, 314 (2006) 821-825.
- [33] Y. Pushkar, X. Long, P. Glatzel, G.W. Brudvig, G.C. Dismukes, T.J. Collins, V.K. Yachandra, J. Yano, U. Bergmann, Direct Detection of Oxygen Ligation to the Mn4Ca Cluster of Photosystem II by X-ray Emission Spectroscopy, *Angewandte Chemie International Edition*, 49 (2010) 800-803.
- [34] Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å, *Nature*, 473 (2011) 55-60.
- [35] K. Kawakami, Y. Umena, N. Kamiya, J.-R. Shen, Structure of the catalytic, inorganic core of oxygen-evolving photosystem II at 1.9 Å resolution, *Journal of Photochemistry and Photobiology B: Biology*, 104 (2011) 9-18.
- [36] C.-I. Lee, K. Lakshmi, G.W. Brudvig, Probing the functional role of Ca²⁺ in the oxygen-evolving complex of photosystem II by metal ion inhibition, *Biochemistry*, 46 (2007) 3211-3223.
- [37] M.J. Latimer, V.J. DeRose, I. Mukerji, V.K. Yachandra, K. Sauer, M.P. Klein, Evidence for the proximity of calcium to the manganese cluster of photosystem II: determination by X-ray absorption spectroscopy, *Biochemistry*, 34 (1995) 10898-10909.
- [38] R.M. Cinco, J.H. Robblee, A. Rompel, C. Fernandez, V.K. Yachandra, K. Sauer, M.P. Klein, Strontium EXAFS reveals the proximity of calcium to the manganese cluster of oxygen-evolving photosystem II, *The Journal of Physical Chemistry B*, 102 (1998) 8248-8256.

- [39] M.J. Latimer, V.J. DeRose, V.K. Yachandra, K. Sauer, M.P. Klein, Structural effects of calcium depletion on the manganese cluster of photosystem II: determination by X-ray absorption spectroscopy, *The Journal of Physical Chemistry B*, 102 (1998) 8257-8265.
- [40] D.F. Ghanotakis, G.T. Babcock, C.F. Yocum, Calcium reconstitutes high rates of oxygen evolution in polypeptide depleted photosystem II preparations, *FEBS letters*, 167 (1984) 127-130.
- [41] A. Boussac, A.W. Rutherford, Nature of the inhibition of the oxygen-evolving enzyme of photosystem II induced by sodium chloride washing and reversed by the addition of calcium(2+) or strontium(2+), *Biochemistry*, 27 (1988) 3476-3483.
- [42] T.-A. Ono, Y. Inoue, Roles of Ca²⁺ in O₂ evolution in higher plant photosystem II: Effects of replacement of Ca²⁺ site by other cations, *Archives of biochemistry and biophysics*, 275 (1989) 440-448.
- [43] T.-a. Ono, T. Noguchi, Y. Inoue, M. Kusunoki, H. Yamaguchi, H. Oyanagi, Flash induced XANES spectroscopy for the Ca-depleted Mn-cluster in the photosynthetic O₂-evolving enzyme, *FEBS Letters*, 330 (1993) 28-30.
- [44] T. Noguchi, T. Ono, Y. Inoue, Detection of structural changes upon S₁-to-S₂ transition in the oxygen-evolving manganese cluster in photosystem II by light-induced Fourier transform infrared difference spectroscopy, *Biochemistry*, 31 (1992) 5953-5956.
- [45] T. Noguchi, Y. Inoue, K. Satoh, FT-IR studies on the triplet state of P680 in the photosystem II reaction center: triplet equilibrium within a chlorophyll dimer, *Biochemistry*, 32 (1993) 7186-7195.
- [46] T. Noguchi, Y. Inoue, X.-S. Tang, Structural coupling between the oxygen-evolving Mn cluster and a tyrosine residue in photosystem II as revealed by Fourier transform infrared spectroscopy, *Biochemistry*, 36 (1997) 14705-14711.
- [47] T. Noguchi, Y. Inoue, X.-S. Tang, Structure of a histidine ligand in the photosynthetic oxygen-evolving complex as studied by light-induced Fourier transform infrared difference spectroscopy, *Biochemistry*, 38 (1999) 10187-10195.
- [48] T. Noguchi, M. Sugiura, Flash-induced Fourier transform infrared detection of the structural changes during the S-state cycle of the oxygen-evolving complex in photosystem II, *Biochemistry*, 40 (2001) 1497-1502.
- [49] A. Boussac, J.L. Zimmermann, A.W. Rutherford, EPR signals from modified charge accumulation states of the oxygen-evolving enzyme in calcium-deficient photosystem II, *Biochemistry*, 28 (1989) 8984-8989.
- [50] A. Boussac, F. Rappaport, P. Carrier, J.-M. Verbavatz, R. Gobin, D. Kirilovsky, A.W. Rutherford, M. Sugiura, Biosynthetic Ca²⁺/Sr²⁺ exchange in the photosystem II oxygen-evolving enzyme of *Thermosynechococcus elongatus*, *Journal of Biological Chemistry*, 279 (2004) 22809-22819.
- [51] J.S. Vrettos, D.A. Stone, G.W. Brudvig, Quantifying the ion selectivity of the Ca²⁺ site in photosystem II: Evidence for direct involvement of Ca²⁺ in O₂ formation, *Biochemistry*, 40 (2001) 7937-7945.
- [52] C.-I. Lee, G.W. Brudvig, Investigation of the functional role of Ca²⁺ in the oxygen-evolving complex of photosystem II: A pH-dependence study of the substitution of Ca²⁺ by Sr²⁺, *J. chin. chem. Soc*, 51 (2004) 1221-1228.
- [53] T. Lohmiller, N. Cox, J.-H. Su, J. Messinger, W. Lubitz, The basic properties of the electronic structure of the oxygen-evolving complex of photosystem II are not perturbed by Ca²⁺ removal, *Journal of Biological Chemistry*, 287 (2012) 24721-24733.

- [54] S. Petrie, P. Gatt, R. Stranger, R.J. Pace, The interaction of His337 with the Mn₄Ca cluster of photosystem II, *Physical Chemistry Chemical Physics*, 14 (2012) 4651-4657.
- [55] D.I. Arnon, F.R. Whatley, Is Chloride a Coenzyme of Photosynthesis?, *Science*, 110 (1949) 554-556.
- [56] C.F. Yocum, The calcium and chloride requirements of the O₂ evolving complex, *Coordination Chemistry Reviews*, 252 (2008) 296-305.
- [57] J. Bove, C. Bove, F. Whatley, D. Arnon, Chloride requirement for oxygen evolution in photosynthesis, *Z Naturforsch*, 18 (1963) 683-688.
- [58] S. Izawa, R. Heath, G. Hind, The role of chloride ion in photosynthesis III. The effect of artificial electron donors upon electron transport, *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, 180 (1969) 388-398.
- [59] P.O. Sandusky, C.F. Yocum, The chloride requirement for photosynthetic oxygen evolution. Analysis of the effects of chloride and other anions on amine inhibition of the oxygen-evolving complex, *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, 766 (1984) 603-611.
- [60] H. Wincencjusz, C.F. Yocum, H.J. van Gorkom, S-State Dependence of Chloride Binding Affinities and Exchange Dynamics in the Intact and Polypeptide-Depleted O₂ Evolving Complex of Photosystem II[†], *Biochemistry*, 37 (1998) 8595-8604.
- [61] H. Wincencjusz, C.F. Yocum, H.J. van Gorkom, Activating Anions That Replace Cl⁻ in the O₂-Evolving Complex of Photosystem II Slow the Kinetics of the Terminal Step in Water Oxidation and Destabilize the S₂ and S₃ States[†], *Biochemistry*, 38 (1999) 3719-3725.
- [62] A.W. Rutherford, Photosystem II, the water-splitting enzyme, *Trends in Biochemical Sciences*, 14 (1989) 227-232.
- [63] K. Lindberg, L.-E. Andréasson, A one-site, two-state model for the binding of anions in photosystem II, *Biochemistry*, 35 (1996) 14259-14267.
- [64] K. Olesen, L.-E. Andréasson, The function of the chloride ion in photosynthetic oxygen evolution, *Biochemistry*, 42 (2003) 2025-2035.
- [65] R. Pokhrel, R.J. Service, R.J. Debus, G.W. Brudvig, Mutation of Lysine 317 in the D2 Subunit of Photosystem II Alters Chloride Binding and Proton Transport, *Biochemistry*, 52 (2013) 4758-4773.
- [66] H. Suzuki, J. Yu, T. Kobayashi, H. Nakanishi, P.J. Nixon, T. Noguchi, Functional Roles of D2-Lys317 and the Interacting Chloride Ion in the Water Oxidation Reaction of Photosystem II As Revealed by Fourier Transform Infrared Analysis, *Biochemistry*, 52 (2013) 4748-4757.
- [67] I. Rivalta, M. Amin, S. Lubner, S. Vassiliev, R. Pokhrel, Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, D. Bruce, Structural-functional role of chloride in photosystem II, *Biochemistry*, 50 (2011) 6312-6315.
- [68] C. Pagliano, G. Saracco, J. Barber, Structural, functional and auxiliary proteins of photosystem II, *Photosynthesis Research*, (2013) 1-22.
- [69] I. Enami, A. Okumura, R. Nagao, T. Suzuki, M. Iwai, J.-R. Shen, Structures and functions of the extrinsic proteins of photosystem II from different species, *Photosynthesis research*, 98 (2008) 349-363.
- [70] T.M. Bricker, J.L. Roose, R.D. Fagerlund, L.K. Frankel, J.J. Eaton-Rye, The extrinsic proteins of Photosystem II, *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, 1817 (2012) 121-142.
- [71] R. Luciński, G. Jackowski, The structure, functions and degradation of pigment-binding proteins of photosystem II, *Acta Biochim Pol*, 53 (2006) 693-708.

- [72] M. Miyao, N. Murata, Role of the 33-kDa polypeptide in preserving Mn in the photosynthetic oxygen-evolution system and its replacement by chloride ions, *FEBS letters*, 170 (1984) 350-354.
- [73] M.M. Najafpour, A.N. Moghaddam, Y.N. Yang, E.-M. Aro, R. Carpentier, J.J. Eaton-Rye, C.-H. Lee, S.I. Allakhverdiev, Biological water-oxidizing complex: a nano-sized manganese–calcium oxide in a protein environment, *Photosynthesis research*, 114 (2012) 1-13.
- [74] H. Popelkova, M.M. Im, J. D'Auria, S.D. Betts, N. Lydakis-Simantiris, C.F. Yocum, N-terminus of the photosystem II manganese stabilizing protein: effects of sequence elongation and truncation, *Biochemistry*, 41 (2002) 2702-2711.
- [75] J.L. Roose, K.M. Wegener, H.B. Pakrasi, The extrinsic proteins of photosystem II, *Photosynthesis Research*, 92 (2007) 369-387.
- [76] J. Nield, M. Balsera, J. De Las Rivas, J. Barber, Three-dimensional electron cryo-microscopy study of the extrinsic domains of the oxygen-evolving complex of spinach Assignment of the PsbO protein, *Journal of Biological Chemistry*, 277 (2002) 15006-15012.
- [77] P. Joliot, G. Barbieri, R. Chabaud, UN NOUVEAU MODELE DES CENTRES PHOTOCHIMIQUES DU SYSTEME II*, *Photochemistry and Photobiology*, 10 (1969) 309-329.
- [78] B. FORBUSH, B. KOK, M.P. McGLOIN, COOPERATION OF CHARGES IN PHOTOSYNTHETIC O₂ EVOLUTION-II. DAMPING OF FLASH YIELD OSCILLATION, DEACTIVATION*, *Photochemistry and Photobiology*, 14 (1971) 307-321.
- [79] Y. Pushkar, J. Yano, K. Sauer, A. Boussac, V.K. Yachandra, Structural changes in the Mn₄Ca cluster and the mechanism of photosynthetic water splitting, *Proceedings of the National Academy of Sciences*, 105 (2008) 1879-1884.
- [80] H. Suzuki, M. Sugiura, T. Noguchi, Monitoring proton release during photosynthetic water oxidation in photosystem II by means of isotope-edited infrared spectroscopy, *Journal of the American Chemical Society*, 131 (2009) 7849-7857.
- [81] C.W. Hoganson, G.T. Babcock, A metalloradical mechanism for the generation of oxygen from water in photosynthesis, *Science*, 277 (1997) 1953-1956.
- [82] M. Kusunoki, Mono-manganese mechanism of the photosystem II water splitting reaction by a unique Mn₄Ca cluster, *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, 1767 (2007) 484-492.
- [83] V.L. Pecoraro, M.J. Baldwin, M.T. Caudle, W.-Y. Hsieh, N.A. Law, A proposal for water oxidation in photosystem II, *Pure and applied chemistry*, 70 (1998) 925-930.
- [84] G. Brudvig, Water oxidation chemistry of photosystem II, *Philosophical transactions of the Royal Society of London. Series B, Biological sciences*, 363 (2008) 1211-1218.
- [85] E.M. Sproviero, J.A. Gascón, J.P. McEvoy, G.W. Brudvig, V.S. Batista, Quantum mechanics/molecular mechanics study of the catalytic cycle of water splitting in photosystem II, *Journal of the American Chemical Society*, 130 (2008) 3428-3442.
- [86] H. Dau, L. Iuzzolino, J. Dittmer, The tetra-manganese complex of photosystem II during its redox cycle—X-ray absorption results and mechanistic implications, *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, 1503 (2001) 24-39.
- [87] P. Glatzel, H. Schroeder, Y. Pushkar, T. Boron, S. Mukherjee, G. Christou, V.L. Pecoraro, J. Messinger, V.K. Yachandra, U. Bergmann, J. Yano, Electronic Structural Changes of Mn in the Oxygen-Evolving Complex of Photosystem II during the Catalytic Cycle, *Inorganic Chemistry*, 52 (2013) 5642-5644.

- [88] H.J.M. Hou, Structural and Mechanistic Aspects of Mn-oxo and Co-based Compounds in Water Oxidation Catalysis and Potential Applications in Solar Fuel Production, *Journal of Integrative Plant Biology*, 52 (2010) 704-711.
- [89] K. Ataka, F. Giess, W. Knoll, R. Naumann, S. Haber-Pohlmeier, B. Richter, J. Heberle, Oriented attachment and membrane reconstitution of His-tagged cytochrome c oxidase to a gold electrode: in situ monitoring by surface-enhanced infrared absorption spectroscopy, *Journal of the American Chemical Society*, 126 (2004) 16199-16206.
- [90] A. Badura, D. Guschin, B. Esper, T. Kothe, S. Neugebauer, W. Schuhmann, M. Rögner, Photo-Induced Electron Transfer Between Photosystem 2 via Cross-linked Redox Hydrogels, *Electroanalysis*, 20 (2008) 1043-1047.
- [91] A. Badura, B. Esper, K. Ataka, C. Grunwald, C. Wöll, J. Kuhlmann, J. Heberle, M. Rögner, Light-Driven Water Splitting for (Bio-) Hydrogen Production: Photosystem 2 as the Central Part of a Bioelectrochemical Device, *Photochemistry and photobiology*, 82 (2006) 1385-1390.
- [92] M. Kato, T. Cardona, A.W. Rutherford, E. Reisner, Photoelectrochemical water oxidation with photosystem II integrated in a mesoporous indium–tin oxide electrode, *Journal of the American Chemical Society*, 134 (2012) 8332-8335.
- [93] M. Kato, T. Cardona, A.W. Rutherford, E. Reisner, Covalent Immobilization of Oriented Photosystem II on a Nanostructured Electrode for Solar Water Oxidation, *Journal of the American Chemical Society*, 135 (2013) 10610-10613.
- [94] A. Badura, T. Kothe, W. Schuhmann, M. Rögner, Wiring photosynthetic enzymes to electrodes, *Energy & Environmental Science*, 4 (2011) 3263-3274.
- [95] P. Du, R. Eisenberg, Catalysts made of earth-abundant elements (Co, Ni, Fe) for water splitting: Recent progress and future challenges, *Energy & Environmental Science*, 5 (2012) 6012-6021.
- [96] J. Soriano-López, S. Goberna-Ferrón, L. Vigara, J.J. Carbó, J.M. Poblet, J.R. Galán-Mascarós, Cobalt Polyoxometalates as Heterogeneous Water Oxidation Catalysts, *Inorganic Chemistry*, 52 (2013) 4753-4755.
- [97] M.M. Najafpour, F. Rahimi, E.-M. Aro, C.-H. Lee, S.I. Allakhverdiev, Nano-sized manganese oxides as biomimetic catalysts for water oxidation in artificial photosynthesis: a review, *Journal of The Royal Society Interface*, 9 (2012) 2383-2395.
- [98] Y. Xu, L. Duan, T. Åkermarck, L. Tong, B.-L. Lee, R. Zhang, B. Åkermarck, L. Sun, Synthesis and Catalytic Water Oxidation Activities of Ruthenium Complexes Containing Neutral Ligands, *Chemistry – A European Journal*, 17 (2011) 9520-9528.
- [99] R.J. Debus, Protein ligation of the photosynthetic oxygen-evolving center, *Coordination chemistry reviews*, 252 (2008) 244-258.
- [100] A.R. Parent, R.H. Crabtree, G.W. Brudvig, Comparison of primary oxidants for water-oxidation catalysis, *Chemical Society Reviews*, 42 (2013) 2247-2252.
- [101] D.K. Bediako, Y. Surendranath, D.G. Nocera, Mechanistic Studies of the Oxygen Evolution Reaction Mediated by a Nickel–Borate Thin Film Electrocatalyst, *Journal of the American Chemical Society*, 135 (2013) 3662-3674.
- [102] A. Bergmann, I. Zaharieva, H. Dau, P. Strasser, Electrochemical water splitting by layered and 3D cross-linked manganese oxides: correlating structural motifs and catalytic activity, *Energy & Environmental Science*, 6 (2013) 2745-2755.
- [103] M. Dincă, Y. Surendranath, D.G. Nocera, Nickel-borate oxygen-evolving catalyst that functions under benign conditions, *Proceedings of the National Academy of Sciences*, 107 (2010) 10337-10341.

- [104] W. Lubitz, E.J. Reijerse, J. Messinger, Solar water-splitting into H₂ and O₂: design principles of photosystem II and hydrogenases, *Energy & Environmental Science*, 1 (2008) 15-31.
- [105] R. Pokhrel, G.W. Brudvig, 3.15 - Complex Systems: Photosynthesis, in: R. Editors-in-Chief: Jan, P. Kenneth (Eds.) *Comprehensive Inorganic Chemistry II* (Second Edition), Elsevier, Amsterdam, 2013, pp. 385-422.
- [106] V.Y. Shafirovich, A. Shilov, Catalytic oxidation of water with the participation of manganese compounds in neutral and slightly acid media, *Kinet. Catal.(USSR)(Engl. Transl.);(United States)*, 20 (1979).
- [107] M. Morita, C. Iwakura, H. Tamura, The anodic characteristics of manganese dioxide electrodes prepared by thermal decomposition of manganese nitrate, *Electrochimica Acta*, 22 (1977) 325-328.
- [108] A. Harriman, I.J. Pickering, J.M. Thomas, P.A. Christensen, Metal oxides as heterogeneous catalysts for oxygen evolution under photochemical conditions, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 84 (1988) 2795-2806.
- [109] M.M. Najafpour, T. Ehrenberg, M. Wiechen, P. Kurz, Calcium Manganese(III) Oxides (CaMn₂O₄·x H₂O) as Biomimetic Oxygen-Evolving Catalysts, *Angewandte Chemie International Edition*, 49 (2010) 2233-2237.
- [110] M.M. Najafpour, D.J. Sedigh, B. Pashaei, S. Nayeri, Water oxidation by nano-layered manganese oxides in the presence of cerium(IV) ammonium nitrate: important factors and a proposed self-repair mechanism, *New Journal of Chemistry*, 37 (2013) 2448-2459.
- [111] M.M. Najafpour, B. Pashaei, S. Nayeri, Nano-sized layered aluminium or zinc-manganese oxides as efficient water oxidizing catalysts, *Dalton Transactions*, 41 (2012) 7134-7140.
- [112] M.M. Najafpour, S.I. Allakhverdiev, Manganese compounds as water oxidizing catalysts for hydrogen production via water splitting: from manganese complexes to nano-sized manganese oxides, *International Journal of Hydrogen Energy*, 37 (2012) 8753-8764.
- [113] N. Birkner, S. Nayeri, B. Pashaei, M.M. Najafpour, W.H. Casey, A. Navrotsky, Energetic basis of catalytic activity of layered nanophase calcium manganese oxides for water oxidation, *Proceedings of the National Academy of Sciences*, 110 (2013) 8801-8806.
- [114] M.M. Najafpour, B. Haghighi, D. Jafarian Sedigh, M. Zarei, Conversions of Mn oxides to nanolayered Mn oxides in electrochemical water oxidation at near neutral pH, all to a better catalyst: catalyst evolution, *Dalton Transactions*, (2013).
- [115] M.M. Najafpour, D.J. Sedigh, Water oxidation by manganese oxides, a new step towards a complete picture: simplicity is the ultimate sophistication, *Dalton Transactions*, 42 (2013) 12173-12178.
- [116] M. Najafpour, M. Tabrizi, B. Haghighi, J. Eaton-Rye, R. Carpentier, S. Allakhverdiev, Imidazolium or guanidinium/layered manganese (III, IV) oxide hybrid as a promising structural model for the water-oxidizing complex of Photosystem II for artificial photosynthetic systems, *Photosynthesis Research*, (2013) 1-9.
- [117] M.M. Najafpour, M.A. Tabrizi, B. Haghighi, A manganese oxide with phenol groups as a promising structural model for water oxidizing complex in Photosystem II: a 'golden fish', *Dalton Transactions*, 41 (2012) 3906-3910.
- [118] M.M. Najafpour, M.A. Tabrizi, B. Haghighi, A 2-(2-hydroxyphenyl)-1H-benzimidazole-manganese oxide hybrid as a promising structural model for the tyrosine 161/histidine 190-manganese cluster in photosystem II, *Dalton Transactions*, 42 (2013) 879-884.

- [119] M.M. Najafpour, B. Haghighi, M.Z. Ghobadi, D.J. Sedigh, Nanolayered manganese oxide/poly(4-vinylpyridine) as a biomimetic and very efficient water oxidizing catalyst: toward an artificial enzyme in artificial photosynthesis, *Chemical Communications*, 49 (2013) 8824-8826.
- [120] A. Singh, R.K. Hocking, S.L.-Y. Chang, B.M. George, M. Fehr, K. Lips, A. Schnegg, L. Spiccia, Water Oxidation Catalysis by Nanoparticulate Manganese Oxide Thin Films: Probing the Effect of the Manganese Precursors, *Chemistry of Materials*, 25 (2013) 1098-1108.
- [121] T. Takashima, K. Hashimoto, R. Nakamura, Inhibition of charge disproportionation of MnO₂ electrocatalysts for efficient water oxidation under neutral conditions, *Journal of the American Chemical Society*, 134 (2012) 18153-18156.
- [122] M. MahdiáNajafpour, A. NematíáMoghaddam, Nano-sized manganese oxide: a proposed catalyst for water oxidation in the reaction of some manganese complexes and cerium (IV) ammonium nitrate, *Dalton Transactions*, 41 (2012) 10292-10297.
- [123] L. Alibabaei, M.K. Brennaman, M.R. Norris, B. Kalanyan, W. Song, M.D. Losego, J.J. Concepcion, R.A. Binstead, G.N. Parsons, T.J. Meyer, Solar water splitting in a molecular photoelectrochemical cell, *Proceedings of the National Academy of Sciences*, 110 (2013) 20008-20013.
- [124] J. Kern, R. Alonso-Mori, R. Tran, J. Hattne, R.J. Gildea, N. Echols, C. Glöckner, J. Hellmich, H. Laksmono, R.G. Sierra, Simultaneous femtosecond X-ray spectroscopy and diffraction of photosystem II at room temperature, *Science*, 340 (2013) 491-495.
- [125] D.G. Nocera, The artificial leaf, *Accounts of Chemical Research*, 45 (2012) 767-776.

Figure Legends:

Fig. 1. The S-state cycle showing how the absorption of four photons of light ($h\nu$) by P_{680} drives the splitting of two water molecules and formation of O_2 through a consecutive series of five intermediates (S_0 , S_1 , S_2 , S_3 and S_4). Protons (H^+) are released during this cycle except for the S_1 to S_2 transition. Electron donation from the Mn_4Ca cluster to P_{680}^{+} is aided by the redox active tyrosine Y_Z . Also shown are half-times for the various steps of the cycle [17]. Image was reprinted with permission from ref. 17 Copyright (2008) by Elsevier.

Fig. 2. Structure of PSII with assignment of protein subunits and cofactors. Arrangement of transmembrane α -helices and cofactors in PSII. One monomer of the dimer is shown completely, with part of the second monomer related by the local-C2 axis (filled ellipse on the dotted interface). Chl a head groups and haems are indicated by black wire drawings. The view direction is from the luminal side, perpendicular to the membrane plane. The α -helices of D1, D2 and Cyt b-559 are labelled. D1/D2 are highlighted by an ellipse and antennae, and CP43 and CP47 by circles. Seven unassigned α -helices are shown in grey. The four prominent landmarks (three irons and the Mn (Mn) cluster) are indicated by arrows [28]. Image was reprinted with permission from ref. 28 Copyright (2008) by Nature publications.

Fig. 3. Top the Mn–Ca cluster (circled in red) may be considered as a nanosized Mn–Ca oxide in a protein environment Bottom the Mn_4O_5Ca cluster in PSII that has dimensions of about $\sim 0.5 \times 0.25 \times 0.25$ nm. Adapted from ref [34,35].

Fig. 4. A model for the S state cycle of the Mn cluster of PSII. For clarity, Y_Z is shown only in the S_0 state. Ca and chloride ions are required for oxygen evolution activity, particularly for the formation of the S_2 state, and their specific functions within the context of the metalloradical mechanism are considered in detail elsewhere [73]. Image was reprinted with permission from ref. 73 Copyright (1997) by McMillan publications.

Fig. 5. Mono-metallic mechanism. In the mechanism, the O–O bond formation between the oxygens of the two water molecules coordinated to one Mn ion [74]. Image was reprinted with permission from ref. 74 Copyright (2007) by Elsevier.

Fig. 6. Catalytic cycle of water splitting suggested by DFT QM/MM models of the WOC of PSII. Dashed arrows indicate transformations leading to the following S state in the cycle. Changes caused by an S-state transition are highlighted in red. The blue circles highlight substrate water molecules. Coordination bonds elongated by the Jahn-Teller distortion are marked in green [77]. Image was reprinted with permission from ref. 77 Copyright (2008) by American Chemical Society.

Fig. 7. Hypothesis on the $S_2 \rightarrow S_3$ transition. In (A), the Mn complex in its S_3 -state contains three unprotonated di-W-oxo bridges; in (B), one of the three di-W-oxo bridges is protonated. In (A)

and (B), the oxidation of Mn(III) is linked to deprotonation of one water-derived ligand (marked by dotted circles) and formation of an additional bridge between Mn ions. In this scheme, an arrangement of the four Mn ions and six bridging ligands has been chosen for the Mn complex in its S_2 state; also other structural models for the Mn complex in its S_2 state models are in agreement with the EXAFS results (a). Hypothetical scheme on the mechanism of water oxidation and dioxygen formation upon the $S_3 \rightarrow S_0$ transition. Only three Mn ions are depicted because the proposed mechanism does not require that four Mn ions are actively involved [78]. Optimized transition state for O-O bond formation.

Fig. 8. Basic principle for the integration of PSII into bioelectrochemical devices [84].

Fig. 9. Light induced water splitting by PSII in photosynthesis and hydrogen production by an [FeFe] hydrogenase shown together with the structure of respective protein complexes and a possible scheme for mimicking the natural process. [94].

Fig. 10. TEM (a) and HRTEM (b) of nanolayered Mn-Ca oxide.

Fig. 11. TEM image of l-MnO_x-PVP [109] Image was reprinted with permission from ref. 109 Copyright (2013) by RSC publication.

Fig. 12. Cyclic voltammograms (CVs) of a PVP-Pt electrode (magenta), l-MnO_x-PVP-Pt (red), m-MnO_x-PVP-Pt (yellow), h-MnO_x-PVP-Pt (grey), and MnO_x on Pt (blue) (LiClO₄ in water (0.1 M), pH = 6.3) at a scan rate of 100 mV s⁻¹ in both 0.0–2.0 V and 1.0–1.4 V. The range of Mn(III) to Mn(IV) oxidation is 0.6–0.9 V. The broadening of these redox transitions is most probably due to electronic interactions of Mn sites in the material. The black arrow indicates the potential at which the oxygen measurements were performed [109]. Image was reprinted with permission from ref. 109 Copyright (2013) by RSC publication.

Fig. 13. Oxygen evolution by l-MnO_x-PVP-Pt at 700 mV (vs. Ag/AgCl) with only 50 mV overpotential. Oxygen evolution by l-MnO_x-PVP-Pt at potential of 700 mV using pure (red) and Persian Gulf (black). For water from Persian Gulf, no LiClO₄ was added.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7a

Figure 7b

Figure 8

Figure 9

Figure 10a

Figure 10b

Figure 11

Figure 12

Figure 13