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Invited review

Comparison of nano-sized Mn oxides with the Mn cluster of photosystem II as catalysts for water oxidation

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ABSTRACT

"Back to Nature" is a promising way to solve the problems that we face today, such as air pollution and shortage of energy supply based on conventional fossil fuels. A Mn cluster inside photosystem II catalyzes light-induced water-splitting leading to the generation of protons, electrons and oxygen in photosynthetic organisms, and has been considered as a good model for the synthesis of new artificial water-oxidizing catalysts. Herein, we surveyed the structural and functional details of this cluster and its surrounding environment. Then, we review the mechanistic findings concerning the cluster and compare this biological catalyst with nano-sized Mn oxides, which are among the best artificial Mn-based water-oxidizing catalysts.

1. Introduction

The water-splitting reaction is widely considered as a way to store sustainable energy from sunlight and to overcome the problem of environmental pollution caused by the excessive and indiscriminate consumption of fossil fuels [1–11]. This reaction refers to the chemical reaction in which water is split into oxygen and hydrogen. Efficient and economical production of hydrogen as a clean, renewable energy source is considered to be an important way to replace fossil fuels. However, the oxidation reaction to split water is faced with thermodynamic and kinetic restrictions [1–11]. Therefore, many researchers have tried to find a proper catalyst for this oxidation reaction. Among the catalysts introduced, nanostructured IrO_2, RuO_2, Mn- and Co-based compounds [1–11] may serve as efficient water oxidation catalysts; the first two of which show high turnover frequencies (TOF) under mild conditions. However, the use of Ru and Ir oxides is limited by their high cost and rareness in the nature.

The Mn-Ca cluster known as the water-oxidizing complex (WOC), which is surrounded by a protein matrix in photosystem II (PSII), is the only catalyst used for light-induced water oxidation in Nature [12–14]. Therefore, it is considered as a good blueprint from which to design effective synthetic catalysts. The recent high-resolution (1.9 Å) X-ray crystallographic structure reported by Shen and his colleagues revealed the detailed structure of the cluster for the first time [14], which showed that the cluster is consisted of four Mn, five oxygen, and one Ca atoms, as well as four water molecules. It appears that biological systems use interesting strategies and arts to oxidize water, such as the utilization of abundant and environmentally friendly ions in the form of a heterogenized catalyst (a tetra nuclear nanoscale Mn structure) for the WOC, selection of a neutral, physiological pH at which to conduct the water-oxidation reaction [15,16], and the utilization of channels within the protein matrix for proton-coupled electron transfer. To regulate oxidizing power in each charge accumulation step in the WOC, biological systems exploit amino acid side chains for different applications, such as the regulation of charges and hydrogen bonding. On the other hand, there are important factors that should

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be taken into account when designing the synthesis of new artificial catalysts: a) decreasing the oxidation potentials of the catalyst for the simplification of electron transfer between the catalyst and an oxidizing equivalent; b) adjusting the balance between reducing the redox potential of the catalyst and preserving its oxidizing power for water oxidation; c) lack of toxicity and low cost; d) heterometallic nature of the cluster and the role of Ca(II); e) photoactivation/photoassembly - repair cycle to cope with the possible photodamage/photoinhibition; f) substrate access/delivery; g) proton coupled electron transfer, concomitant oxidation and proton transfer steps, redox leveling; h) coupling of the reaction center photochemistry with water splitting catalysis [for more details see 16, 17].

The acquired information, combined with the advantages of Mn, has been used in the development of artificial water-oxidizing catalysts [8, 18–20]. Considering the nanoscale-size of the Mn-Ca cluster and the presence of a high percent of active sites at the surface, nano-sized Mn oxides are promising catalysts for water oxidation [9,10,19,21–23]. Nature uses a heterogenized catalyst, and heterogeneous catalysts were also found to have a greater ability to catalyze water oxidation in the presence of non-oxo transfer oxidants than do homogeneous catalysts [10]. In this review, we compare the structural and functional details of synthetic water oxidation catalysts inspired by nature. To this end, we investigate the roles of different elements and matrices in the operation of artificial catalysts, and then compare them with catalysts found in nature.

2. Mn compounds as water-oxidizing catalysts

One way to design an efficient catalyst is to focus on the water-oxidizing enzyme. Pirson, in 1937, recognized that plants and algae are unable to release O_2 in the absence of Mn in their growth medium [24]. Jaklevic et al., in 1977, confirmed this observation by recording the X-ray absorption spectrum of Mn in a leaf [25]. In 1981, X-ray absorption studies carried out by Klein et al. revealed the presence of di-μ-oxo bridged pairs of Mn atoms with oxidation states higher than +2 in the WOC [26,27]. Mn has special properties, which may be the reason why Nature chose Mn as the main element in the water-splitting complexes of the photosynthetic organisms. Mn is the third most abundant transition metal on the earth. The attainable oxidation states of Mn in biological systems are II, III, and IV. In Nature, the oxidation of water is achieved via the four-electron oxidation mechanism with a low activation energy. Each oxidation state of the WOC is known as an “S-state”, in which the oxidation level progressively increases from S_0 to S_4 [28]. All the S-state transitions, except the $S_4 \rightarrow S_0$, are induced by the photo-oxidization of the reaction center's chlorophyll species of photosystem II.

There are two usual methods for driving the synthetic water-oxidizing catalysts: i) electrochemical/photochemical methods, which can be used to probe the behavior of WOCs, determine TOFs, and screen the potential; and ii) the use of sacrificial oxidants [29]. The most important feature required for the sacrificial oxidants is a suitable reduction potential to be able to oxidize the catalyst. Applying oxidants has been found to have some advantages over electrochemical methods, including the ability to study the catalyst in bulk solution, which results in the generation of large amounts of oxygen, the ease of measurement for TOF and turnover number (TON), the ability to make rapid measurements, and the ability to vary reaction conditions and to screen various compounds rapidly.

The commonly used oxidants are: cerium (IV) ammonium nitrate (Ce(IV)), ruthenium (III) tris (bipyridine), sodium peroxodisulfate, potassium peroxymonosulfate, sodium periodate, sodium hypochlorite, and peroxides.

Generally, the main Mn compounds synthesized as water-oxidizing catalysts can be divided into two groups: Mn complexes and Mn oxides. In the next sections, we compare what has become known about the WOC (natural photosynthesis) with the characteristics of synthetic Mn-based catalysts.

2.1. Mn complexes

Sauer and his colleague suggested that the Mn complex in the WOC is composed of two Mn “dimers” [30]. As shown in Fig. 1, several early structural models, including the 3 + 1 arrangement of Mn atoms in the cluster, were constructed based on the EXAFS data obtained by Derose et al. [31].

In 2001, Witt and Saenger determined the three-dimensional structure of the WOC at 3.8 Å resolution [12]. The structure of the cluster was proposed as three Mn ions located in the corners of an isosceles triangle, accompanied with a fourth Mn ion near the center of the triangle (Fig. 2).

In 2003, Kamiya and Shen confirmed the proposed structure with only a slight difference. Their crystallographic studies showed that all four Mn atoms are located roughly in the same plane [32]. Barber and Iwata subsequently suggested a cubane-like Mn_3CaO_4 cluster with a mono-μ-oxo bridge to a fourth Mn ion and, accordingly, a mechanism for water oxidation. Their proposed structure is shown in Fig. 3 [13].

Despite the synthesis of many Mn compounds that mimic the WOC of PSII, few Mn complexes have been shown to act as a proper catalyst for the oxidation of water. However, Mn oxides, as heterogeneous catalysts, show efficient activity toward water oxidation in the presence of non-oxo transfer oxidants. Among the reported Mn complexes, the cases presented below are noteworthy (Fig. 4).

In 1974, at the time of the first oil crisis, Calvin proposed $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ as a model for the WOC and as a catalyst for water splitting and artificial photosynthetic solar energy conversion [33]. This model was important for the development of new artificial models.

McAuliffe and his colleague introduced $[Mn(saltm)(H_2O)]_2(ClO_4)_2$ [saltm = *N*,*N*′-propylenebis(salicylideneaminato)] and a number of Mn(III) complexes of the type $[\{MnL(H_2O)\}]^{2+}$ (L = dianion of O,N, tetradentate Schiff base), which are susceptible to the release of O_2 [34,35]. They stated that their synthetic complexes contain high-valent Mn capable of forming di-μ-hydroxo- or di-μ-oxo-species transiently, so that these complexes may be similar to the active site of PSII. Although, Bouche and Coe demonstrated the catalytic ability of the dimeric Mn Schiff base complex with a μ-dioxo bridge [36], Shono and his colleague introduced the trans-$Mn(IV)L_2Cl_2$ (L: N-alkyl-3-Nitrosalicylimide) complex and demonstrated its capability to react with water to liberate molecular oxygen [37]. Kaneko et al., reported the synthesis of the complexes $[(bpy)_2Mn(\mu\text{-}O)_2Mn(bpy)_2]^{3+}$ and $[(phen)_2Mn(\mu\text{-}O)_2Mn(phen)_2]^{3+}$ (bpy: 2,20-bipyridyl; phen: 1,10-phenanthroline) and demonstrated that these di-μ-oxo-bridged, binuclear Mn complexes can oxidize water when suspended in water as a heterogeneous catalyst, in the presence of an oxidant, such as Ce(IV) ion [38].

Brudvig et al., in 1997, examined the reaction between potassium peroxymonosulfate and $[Mn(dpa)_2]^-$ (dpa: dipicolinate) to form a Mn(III/IV) dimer [39]. The complex could then react to evolve O_2, leading to the stoichiometric formation of MnO_4^-. In 1999, Brudvig and Crabtree's groups introduced $[(OH_2)(terpy)Mn(\mu\text{-}O)_2Mn(terpy)(OH_2)]^{3+}$ [40], a complex that evolves O_2 in the presence of potassium peroxymonosulfate or ClO^-. Subsequently, Yagi's group reported that $[(OH_2)(terpy)Mn(\mu\text{-}O)_2Mn(terpy)(OH_2)]^{3+}$ adsorbed on clay is an efficient water-oxidizing catalyst [41].

Shimazaki et al., in 2004, assessed the di-Mn(III) tetra arylporphyrin dimer complex as a water oxidation catalyst and observed O_2 release [42]. They proposed that the oxidation of the di-Mn (III) tetra aryl porphyrin dimer could result in a high-valent [Mn(V)] = O complex, which may be the active intermediate in water oxidation. They reported the oxidation of the di-Mn porphyrin dimer using meta-chloroperoxybenzoic acid as an oxidant.

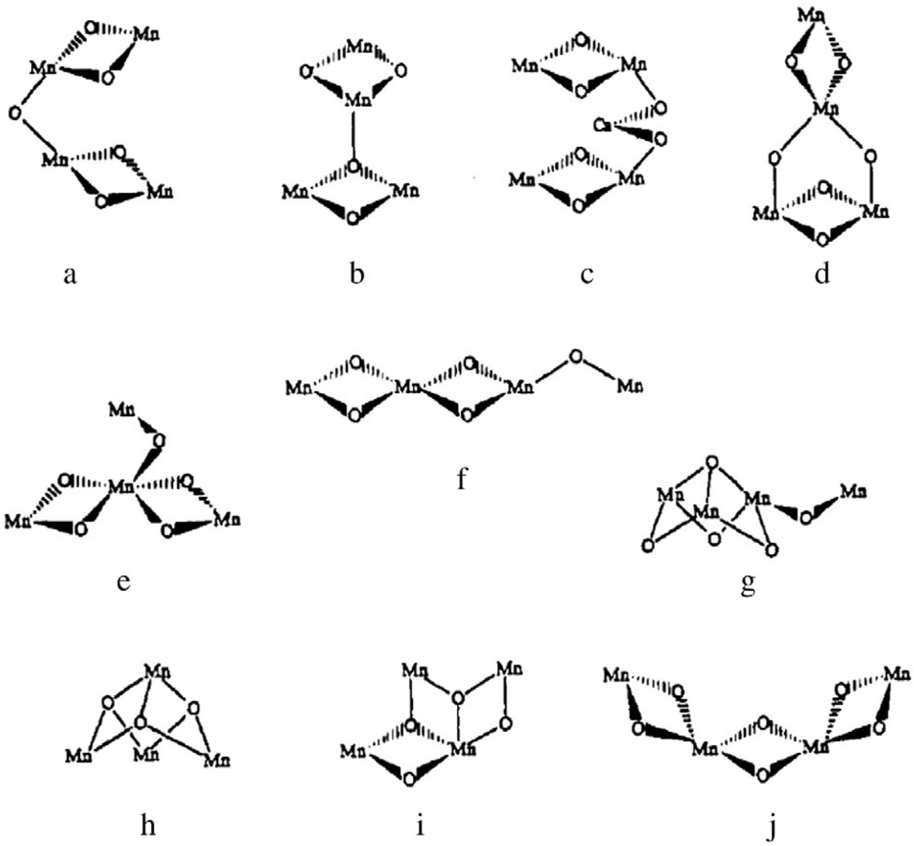

Fig. 1. Arrangement of four Mn and associated bridging atoms giving Mn-Mn distances of 2.7 and >3 Å. The predicted coordination numbers for the neighboring Mn and bridging O atoms in these compounds are compared with those determined from EXAFS studies of the WOC [31]. Reproduced with permission from ref [31]. Copyright (2001) by American Chemical Society.

Dismukes et al. reported the complex [$Mn_4O_4L_6$], where L is a diarylphosphinate ligand, which contains a $Mn_4O_4^-$ cubane core [43]. They proposed that the cubane core is a structural model for the highest oxidation state of the WOC. Their proposal is based on the finding that the complex produced O_2 after elimination of one of the Ph_2PO_2 ligands via a photochemical reaction that is highly selective for the $Mn_4O_4^-$ cubane topology.

However, Mn oxides, which are the products of the complex's decomposition, are the most likely candidates for the true catalyst of the water-oxidation reactions which occurs in the presence of many Mn complexes.

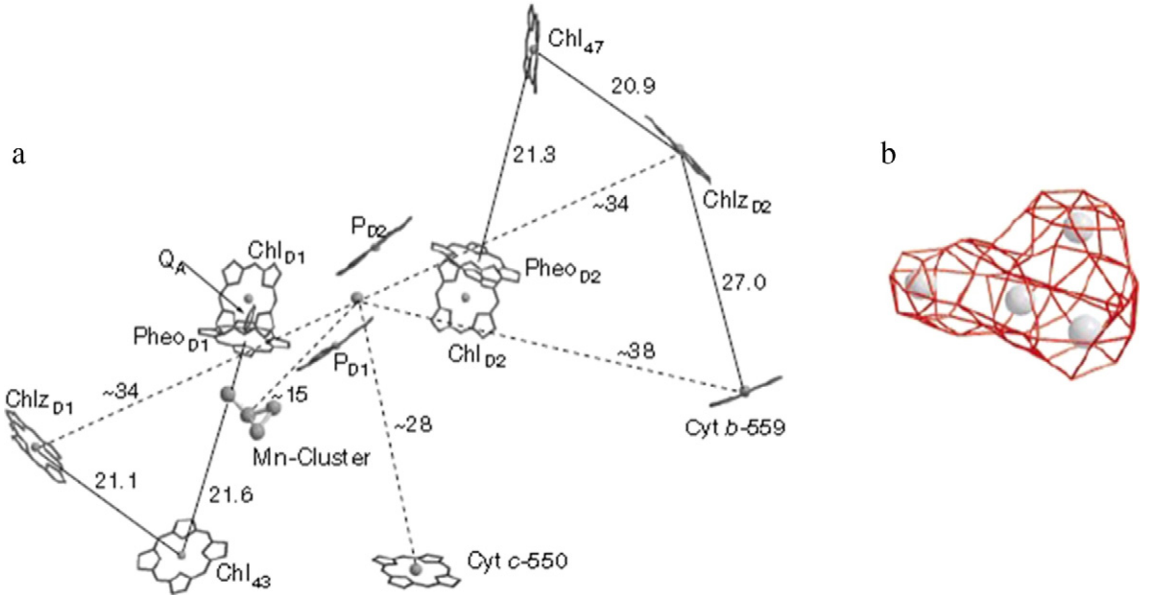

Fig 2. Arrangement of cofactors of the electron transfer chain located in subunits D1 and D2(a) Enlarged view of the electron density of the Mn cluster (b) [12]. Reproduced with permission from ref [12]. Copyright (2001) by Mcmillan.

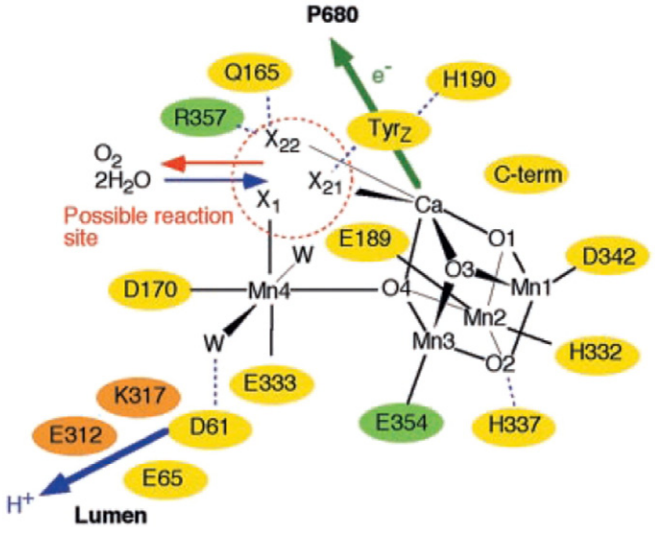

Fig. 3. Schematic view of the WOC. Residues in the D1, D2, and CP43 subunits are shown in yellow, orange, and green, respectively. X11, X21, and X22 are the possible positions for substrate water binding to Mn4 (X11) and to Ca2 (X21 and X22), identified from the positions of non-protein ligands and the coordination patterns of Mn and Ca ions. Possible water molecules, which are not visible at the current resolution, are indicated as W. Possible hydrogen bonds are shown as light-blue dotted lines [13]. Reproduced with permission from ref [13]. Copyright (2004) by American Association for the Advancement of Science.

The Shen and Kamiya research groups, in 2011, determined the most complete crystal structure of PSII, at 1.9 Å resolution [14]. The electron density they obtained revealed that the WOC cluster is composed of 3 Mn and Ca atoms in four corners and 4 oxygen atoms in the other four corners of a cubane-like structure. The fourth Mn is placed outside the cubane and is linked to two Mn atoms within the cubane by O_5. Moreover, four water molecules are bound to the Mn_4CaO_5-cluster ($Mn_4O_5Ca(H_2O)_4$), among which, two are coordinated to Ca and the other two to Mn4 (Fig. 5). The structure shows that the cluster is surrounded by carboxylate and imidazole ligands, which stabilize Mn oxidation states III and IV.

The enzyme is very important as a model for the design of new catalysts. For example, Karlsson et al., in 2011, synthesized a new complex containing imidazole and carboxylate ligands, like the WOC [44]. The complex, which included four proximal Mn atoms that were bridged by oxygen atoms reminiscent of the Mn_4Ca cluster in the WOC, could oxidize water to oxygen in the presence of the single-electron oxidant $[Ru(bpy)_3]^{3+}$.

Model complexes that mimic the structure of the WOC are also very interesting. Mechanistic studies of the roles of the μ_3-oxido moieties were performed through the synthesis of structurally related cuboidal Mn_3MO_n complexes (M = Mn, Ca, Sc; n = 3,4) [45]. The outcomes showed that $Mn(IV)_3CaO_4$ lacks reactivity in the presence of tri-methyl phosphine (PMe_3), but that $Mn(III)_2Mn(IV)_2O_4$ cubane reacts with tri-methyl phosphine within minutes to produce a novel $Mn(III)_4O_3$ partial cubane and tri-methyl phosphine oxide. Also, theoretical calculations revealed that the favored mechanism for oxygen transfer from $Mn(III)_2Mn(IV)_2O_4$ and $Mn(IV)_3CaO_4$ involves CH_3COO^- ligand dissociation in the presence of Mn(III) and coordination with PMe_3. Isotope experiments demonstrated that ligand liability is important in the transfer of oxygen atoms from Mn_3MO_4 cubanes.

2.2. Mn oxides

The idea of using Mn oxides as catalysts for water oxidation has been presented by Glikman and Shcheglova [46], Morita [21], Shilov [23], and Harriman [47]. In contrast to Mn complexes, Mn oxides have no easily oxidizable ligands; thus, they are stable under different conditions. They can also be easily synthesized and used in bulk, supported, and colloidal forms.

Although, the importance of the presence of Ca in the WOC was revealed in 1984 [48], the position of Ca ion in the cluster was confirmed for the first time by Barber and Iwata in 2004 [13]. Also, the crystallographic studies of the Shen and Kamiya groups at the atomic resolution approved and refined their report [14]. So, Mn(III)-Ca oxide ($CaMn_2O_4.xH_2O$) was synthesized to simulate the Mn_4O_5Ca cluster in PSII which was the most similar structural and functional analog of the WOC in PSII [8]. The concatenation of Ca ions to Mn oxides leads to an improvement in the water-oxidation activity of Mn oxides.

In 2003, X-ray absorption near-edge structure (XANES) studies of the WOC by the Dau group showed the oxidation of Mn^{III} to Mn^{IV} ions during the S_1/S_2 and probably also during the S_3/S_4 transition [49].

Amorphous synthetic layered Mn(III)-Ca oxide was also investigated at the atomic level [11]. Based on the XANES studies, the formula of $CaMn^{IV}{}_{1.6}Mn^{III}{}_{0.4}O_{4.5}(OH)_{0.5}$ and $CaMn^{IV}{}_{1.6}Mn^{III}{}_{0.4}O_{4.5}(OH)_{0.5} \cdot 3H_2O$ are proposed for calcinated oxides at 60 and 400 °C, respectively. These catalysts can be compared with the Mn_4Ca complex of PSII in its S_2-state, which is a mixed-valent $Mn_2^{III}Mn_2^{IV}Ca$, whereas oxides such as α-Mn_2O_3 or marokite, which have an α-Mn oxidation state of +3.0, or β-MnO_2, which has a Mn oxidation state of +4.0, are inactive in water oxidation. Thus, an intermediate $Mn^{III/IV}$ oxidation state was suggested as an essential feature of an active water-oxidizing catalyst in its resting state, both for synthetic Mn oxides and the Mn_4Ca complex of PSII. Therefore, O-O formation is certainly preceded by “oxidative charging” of the catalysts through Mn^{III}/Mn^{IV} oxidation. Overall, taking into account this body of literature, it can be concluded that the effect of oxidation state on water oxidation decreases in the order of Mn(III,IV) > Mn(III) > Mn(IV), Mn(II) and Mn(II,III).

Furthermore, the structures proposed for the Mn_4Ca complex of PSII and the catalytic oxides are proper for the coordination of a terminal H_2O in proximity of the $\mu_{2/3}$-oxido-bridges. The μ-oxido ligands could also play a key role in O-O bond formation by accepting protons from “substrate water”.

3. The substructures of the WOC and the synthetic structure

The substructures of the WOC and the synthetic $[CaMn_4]$ structure are also comparable. Yano and Yachandra showed that the Ca atom in the WOC is at an apex 3.4 Å from each of the three Mn ions and that the distal Mn lies in the same plane as the other three, 3.3 Å from its nearest neighbor [50]. Similarly, the substructure of synthetic $CaMn_2O_4$ was shown to be a $[CaMn_4]$-structure consisting of a trigonal pyramid with Ca at the apex, 3.4, 3.1, and 3.5 Å from each of the three Mn ions. The distal Mn lies in the same plane as the other three and 3.1 Å from the closest adjacent Mn. The precipitation of Ca and Mn ions together under changing pH conditions in the archean ocean was also suggested to produce Mn-Ca hydroxides; this can explain the origin of the WOC [51,52].

4. Mechanism of water oxidation

So far, numerous mechanisms have been proposed for the oxidation of water in nature. Babcock and coworkers suggested O-O formation between the two terminally coordinated oxides or oxyl radicals resulting from the deprotonation of two different waters coordinated to Mn ions (Fig. 6a) [53]. Another proposal was that O-O bond formation (Fig. 6b) occurs between the oxygen's of two water molecules coordinated to one Mn ion [54].

As shown in Fig. 6c, two bridging oxygen atoms can be considered to be the source of O-O bond formation, although the μ-O pairs are too inert for bond formation in the WOC [55]. Nucleophilic attack by water or hydroxide has also been considered as a mechanism for water oxidation (Fig. 6d–f) [56,57]. Dau and coworkers suggested that

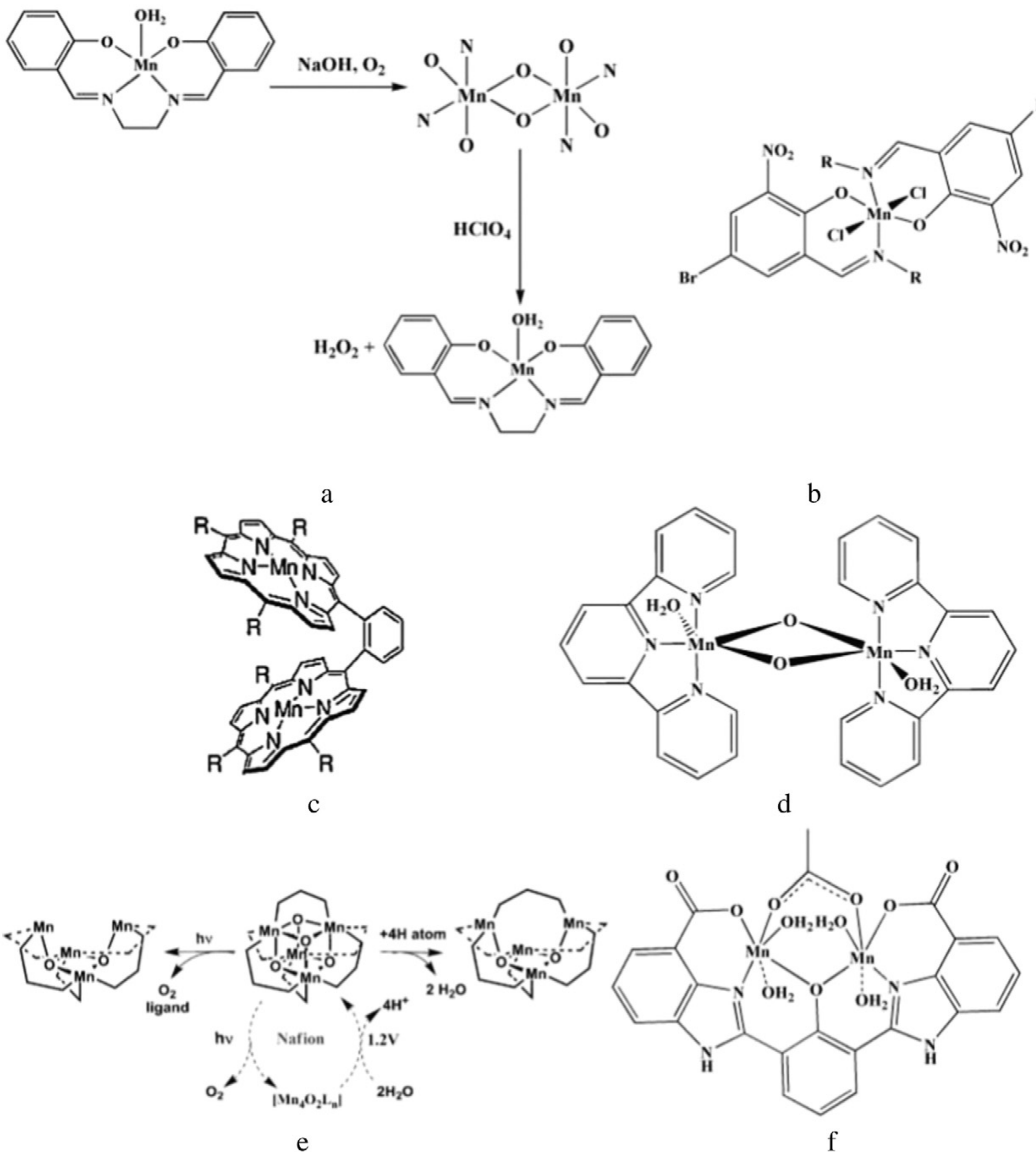

Fig. 4. Important functional models for the WOC in PSII. Complex reported by Coe [36] (a), Shono [37] (b), Shimazaki [42] (c), Brudvig [40] (d), Dismukes [43] (e), and Åkermark groups [44] (f).

O-O formation occurs by nucleophilic attack of an outer-sphere water molecule on a Mn = O with the help of proton transfer from an outer-sphere substrate water molecule to a bridging oxygen molecule (Fig. 6f) [58]. Siegbahn proposed the formation of an O-O bond between a μ-oxo-bridged oxygen and a possibly newly inserted water/oxygen, based on DFT calculations (Fig. 6g) [59].

Recently, X- and Q-band EPR and ^{55}Mn electron nuclear double resonance (ENDOR) data showed the invariability of the electronic structure upon removal of the calcium. The Ca in the WOC may play two roles: it may be involved in efficient proton-coupled electron transfer by maintaining a hydrogen-bonding network, and it may serve as an initial binding site for substrate water [60]. A similar situation can be proposed for the mechanism of water oxidation by Mn oxides. The water-oxidation reaction can take place via two mechanisms: a concerted four-electron reaction or multiple reaction steps with intermediates such as $^{\bullet}OH$, H_2O_2, or $O_2^{\bullet-}$. Based on the standard reduction potentials shown in Table 1, the fact that the redox potential of Ce(IV)/Ce(III) is lower than that of $H_2O/^{\bullet}OH$, H_2O/H_2O_2,or $H_2O/O_2^{\bullet-}$ means that Ce(IV)/Ce(III) cannot oxidize water to $^{\bullet}OH$, H_2O_2 or $O_2^{\bullet-}$. In the Mn oxides, multiple Mn sites are likely involved in charge delocalization and accumulation, allowing a single four-electron water oxidation step.

As shown in Fig. 7, four charge-accumulation steps result from the step-by-step oxidation of four Mn ions by four Ce(IV) ions, and O_2 is released from water in one final step [61].

The O-O bond may be formed by the attack of an outer-sphere water molecule on an OH molecule attached to a high-valent Mn ion in the oxide structure (pathway 1 in Fig. 7) or by a reaction between two OH groups coordinated to high-valent Mn ions (pathway 2 in Fig. 7). Two areas in the redox potential for water oxidation by Mn oxides have been seen: an area near the peak related to Mn(III)/Mn(IV) and another

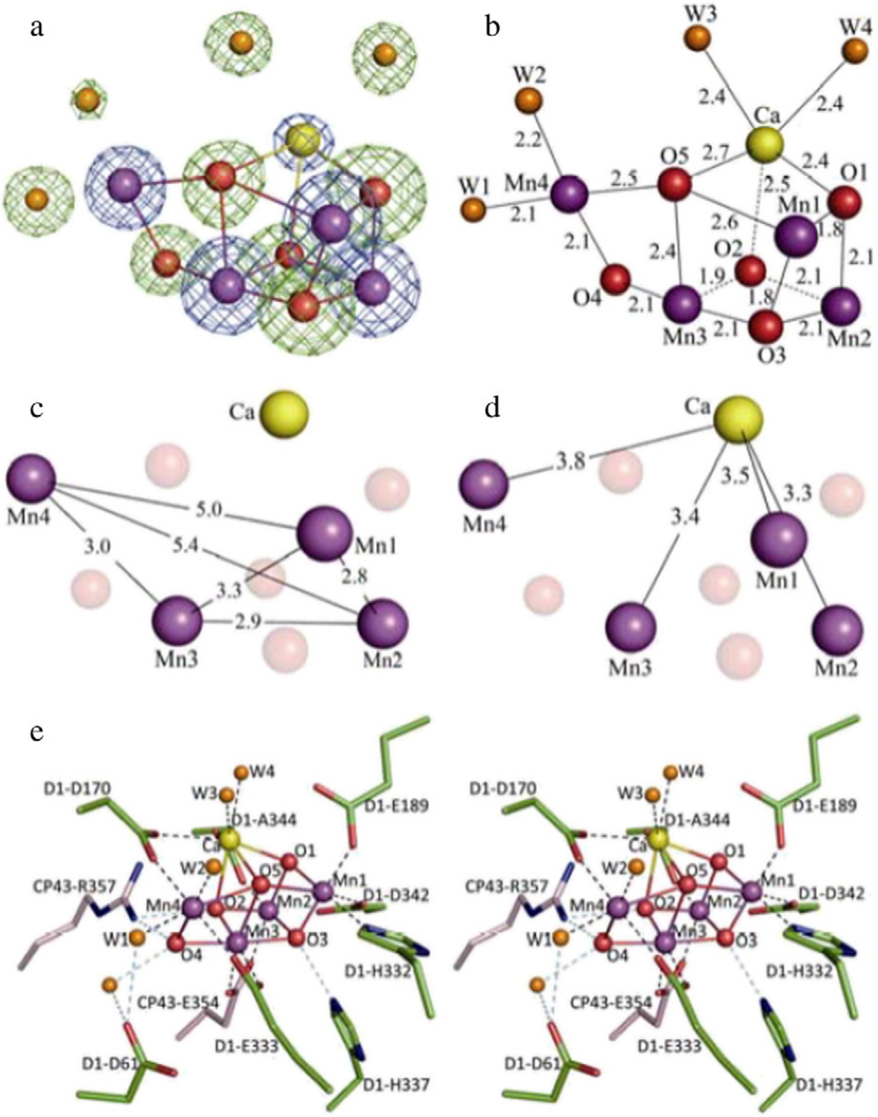

Fig. 5. Structure of the Mn_4CaO_5 cluster. (a) Determination of individual atoms associated with the Mn_4CaO_5cluster. Structure of the cluster was superimposed on the 2Fo-Fc map (blue), contoured at 5 σ, for the Mn and Ca atoms, and the omit map (green), contoured at 7 σ, for the oxygen atoms and water molecules. (b) Distances between metal atoms and oxo-bridges or water molecules (Å). (c) Distances between each pair of Mn atoms. (d) Distances between Mn atoms and the Ca atom. (e) Stereo view of the Mn_4CaO_5cluster and its ligand environment. Color codes: Mn, magenta; Ca, yellow; oxygen, red; D1, green; CP43, pink [14]. Reproduced with permission from ref [14]. Copyright (2011) by Mcmillan.

area 0.5 V higher than the first area. These points have been attributed to pathways 2 and 1 in Fig. 7, respectively [61].

Recently, Frei's group detected two water oxidation intermediates on the surface of Co_3O_4 using rapid scan FTIR spectroscopy [62]. The ^{18}O isotopic composition and the final O_2 gas product provided evidence for the kinetic competency of this three-electron oxidation intermediate. A second observed intermediate was related to oxo Co(IV) = O (Fig. 8) [62]. Although similar results have not been reported for Mn oxides, similar mechanisms have been proposed for water oxidation by Mn oxides [61]. On the other hand, Åkermark's group showed that oxygen can be produced from Mn(V) = O species and hydroxide ions based on their studies on model Mn complexes [63].

5. Nano scale Mn oxides

The Mn_4O_5Ca cluster in PSII has been shown to have the dimensions of approximately 0.5 × 0.25 × 0.25 nm [63]. Maier et al. stated in 2002 that there are two types of size effects: increasing the surface-to-volume ratio and true-size effects, which also involve changes in local material properties [64]. Therefore, nanoscale particles may have completely different redox potentials and different water oxidation activity compared with bulk Mn oxides [65].

Harriman and his colleague used gamma radiolysis for the production of finely dispersed colloids of MnO [66]. In the presence of a strong oxidant, such as Ce(IV), the Mn oxide did not function as efficient O_2-evolving catalyst.

In 2010, Jiao and Frei introduced nanometer-sized Mn oxide clusters supported on a mesoporous silica scaffold as efficient water oxidation catalysts in aqueous solution at room temperature and pH 5 [67]. They stated that the high-surface-area silica support may be critical for the integrity of the catalytic system by offering a perfect, stable dispersion of the nanostructured Mn oxide clusters. In addition, the silica environment may protect the active Mn centers of the catalyst from deactivation by surface restructuring. One year later, Jiao and Boppan reported α-MnO_2 nanotubes, α-MnO_2 nanowires, and β-MnO_2 nanowires as highly efficient and robust water oxidation catalysts driven by visible light [68]. All compounds displayed high TOFs and strong stability under strongly acidic conditions.

In the same year, nano-sized amorphous Mn-Ca oxides were synthesized with the aim to produce better functional models for the $CaMn_4$

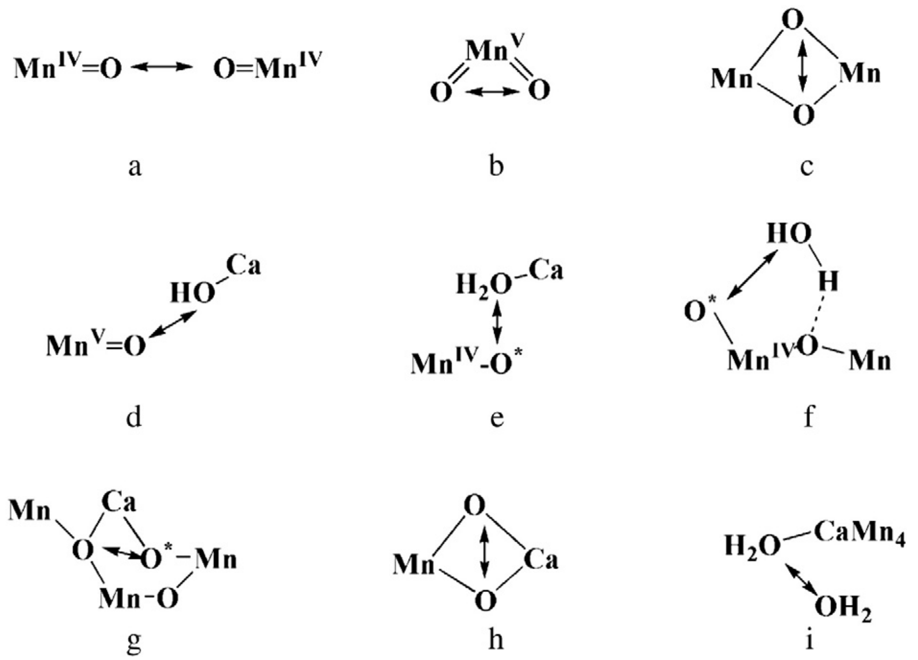

Fig. 6. Proposed mechanisms for the water-oxidation reaction by the WOC. For details see text.

cluster in PSII [9,10,69]. The results demonstrated that the novel compound was one of the best Mn-based water oxidation catalysts. Navrotsky's group reported that nanophase transition metal oxides show large thermodynamically driven shifts in oxidation–reduction equilibria [65]. Two types of size effects may be important in such shifts in oxidation–reduction equilibria at the nanoscale compared with bulk [10]. The first, one relies on increased surface-to-volume ratio. The unsaturated sites increase the energy of the system, and activates it for many reactions. For example, many metal ions in solid state compounds materials prefer to be bound to six neighbors, whereas those atoms on the surface are five-coordinated, or four coordinated in the edges, or even three-coordinated in the corners. Such sites are active for many reactions. The point, linear, planar, or volumetric defects which, are also important for many reactions, are much more abundant at surfaces than in bulk. The second, true-size effects also involve changes of local properties. Such effects are related to changes in the electronic properties such as HOMO (highest occupied molecular orbital) or LUMO (lowest unoccupied molecular orbital) of nano compounds compared to the bulk compounds (lowest unoccupied molecular orbital).

Table 1
Standard reduction potentials measured in aqueous solution (pH = 0) for water oxidation regarding different mechanisms (E_0 vs. SHE). Data are from [102].

Reaction	Standard E_0
Four-electron reactions	
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	1.229
$OH^- + H_2O \rightarrow O_2 + 3H^+ + 4e^-$	1.022
$2OH^- \rightarrow O_2\ 2H^+ + 4e^-$	0.815
$4OH^- \rightarrow O_2 + 2H^+ + 4e^-$	0.401
Two-electron reactions	
$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$	1.776
$2OH^- \rightarrow H_2O_2 + 2e^-$	0.948
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	0.682
$H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^-$	−0.146
One-electron reactions	
$H_2O \rightarrow OH + H^+ + e^-$	2.848
$OH^- \rightarrow OH + e^-$	2.020
$H_2O_2 \rightarrow HO_2 + H^+ + e^-$	1.495
$H_2O_2 + OH^- \rightarrow HO_2 + H_2O + e^-$	0.667
$HO_2 \rightarrow O_2 + H^+\ e^-$	−0.130
$HO_2 + OH^- \rightarrow O_2 + H_2O + e^-$	−0.958

These effects could change the redox potential as well as the water-oxidizing activity of the nano-sized Mn oxides, when compared with those of bulk Mn oxides. Recently, the importance of Mn oxide size was revealed by the synthesis of angstrom-scale particles of Mn oxide within HY zeolite. The catalytic activities of different Mn oxides toward water oxidation were shown to follow the order of nano-sized > bulk > angstrom-scale, most probably resulting from the fragile structure of the angstrom-scale catalyst [70].

The fragile ångström-scale Mn-Ca oxido cluster is shielded by amino acids. An interesting fact about the Mn cluster in PSII is the shielding of the WOC unit from the thylakoid lumenal solution by the Mn-stabilizing protein (PsbO) [71] and other hydrophilic protein components. Several groups have shown that the removal of PsbO from PSII leads to the decrease of water oxidation [72–74]. Miyao and Murata demonstrated the release of two Mn^{2+} ions from the WOC by the incubation of the PsbO-depleted PSII at low Cl^- concentrations [72]. However, this release was prevented by the presence of a high concentration of Cl^- ions. Thus, small-sized Mn oxide particles need stabilizing groups to catalyze the water-oxidation process.

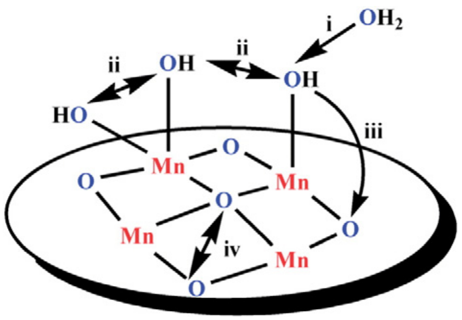

Fig. 7. Proposed mechanisms of oxygen evolution by Mn oxide (oxidized Mn ions are colored red [61]): nucleophilic attack of hydroxide on a terminal oxido (i); coupling of terminal oxido ligands (ii), attack of hydroxide on a bridging oxido ligand (iii), coupling of bridging oxido ligands (iv). Regarding data from membrane-inlet mass spectrometry [22] and diffuse reflectance infrared Fourier transform spectroscopy [61]. Reproduced from Ref. [61] with permission from The Royal Society of Chemistry. Copyright (2014).

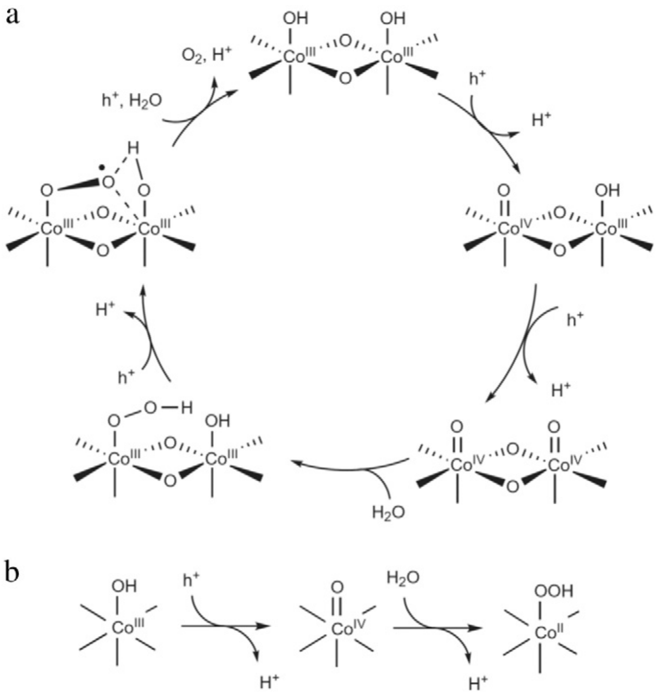

Fig. 8. Proposed mechanism for water oxidation at fast Co_3O_4 surface sites (a).Mechanism of water oxidation at slow Co_3O_4 surface sites. The O-O bond-forming step in the fast cycle features the cooperative effect of adjacent electronically coupled Co(IV) = O sites; this effect is absent in the H_2O addition reaction at the slow site (b) [62]. Reproduced with permission from ref [62]. Copyright (2014) by Mcmillan.

Several roles have been suggested for these residues: conserving the structure of the metal cluster; stabilizing the $CaMn_4$ structure by compensating for the negative charges brought about by the oxo bridges and carboxylate ligands of the WOC; regulating the electrochemistry of the Mn-Ca cluster; and helping water coordinate at the appropriate metal sites [75–77].

It has also been reported that positioning of groups similar to guanidiniumin synthetic model complexes for hydrolytic enzymes, can lead to more than 1000-fold increase in reactivity [78]. These facts prompted scientists to introduce layered structures of Mn oxide, including both guanidinium and imidazolium groups, as new biomimetic models for the WOC [20]. Although the WOC of PSII is a discrete structure, the model was the first step toward the synthesis of a self-assembled layered hybrid of amino acid residues and Mn oxide, which could serve as a good model for the WOC.

6. Mn oxide-organic compound conjugates

Also for the first time, a nano-sized Mn oxide–bovine serum albumin (BSA) conjugate was studied as a structural and functional model for the WOC in PSII [79]. The results demonstrated that BSA induces nucleation and restrains the further growth of Mn. Also, BSA improves the water oxidation activity of these compounds. It was stated that both BSA and the stabilizing protein in PSII proteins form hydrophilic and highly oxidation-stable environments for Mn oxides (Fig. 9a,b).

In a new step, a nano-sized layered Mn-Ca oxide in poly-L-glutamic acid has been reported to be a structural model for biological water-oxidizing site in plants, algae, and cyanobacteria [80] (Fig. 9c,d). Poly-L-glutamic acid is more stable than BSA under oxidative conditions. The glutamic acid residues can participate in proton transfer and

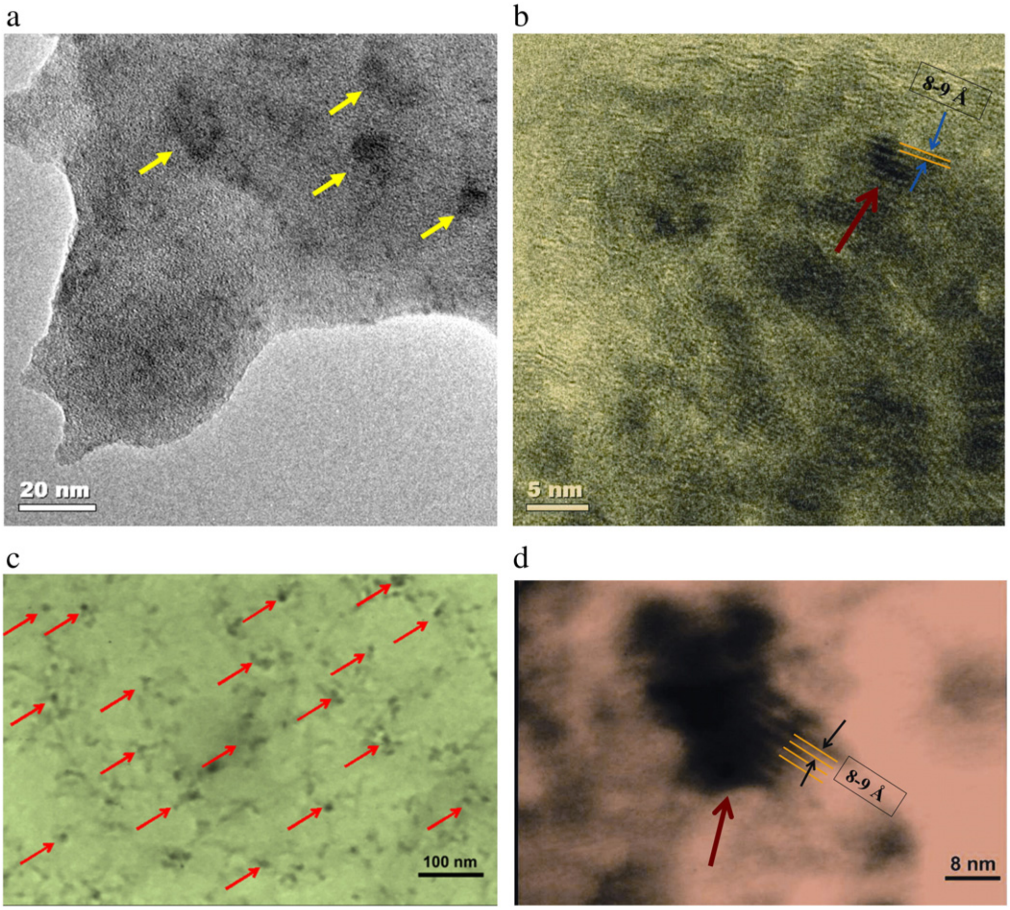

Fig. 9. TEM and HRTEM images of BSA (a,b) and $MnCaO_x$-poly-L-glutamic acid (c,d) in water [79,80]. Black particles show Mn oxides nanoparticles. In the case of crystalline particles, a layered Mn oxide with the distance of 8–9 Å between layers. Reproduced from Ref. [79] and [80] with permission from The Royal Society of Chemistry. Copyright (2012 and 2014).

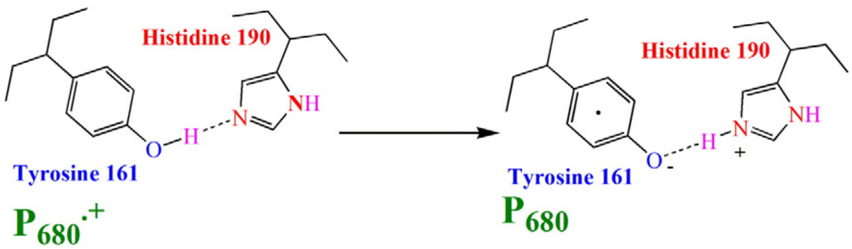

Fig. 10. Tyrosine 161 is oxidized by $P_{680}^{\cdot+}$. The dot within tyrosine shows that it is in its oxidized form. The hydrogen bond between Y_Z (tyrosine 161) and the ε-nitrogen of a histidine (D1-His 190) is important in proton-coupled electron transfer [101]. Reproduced from Ref. [83] with permission from The Royal Society of Chemistry. Copyright (2012).

management, stabilize Mn(III) or Mn(IV), and can reduce over potential for water oxidation. In Mn-Ca oxide core nucleation, similar to PSII, these groups may inhibit Mn ions from leaking from the surface of the oxide into the solution. The peptide bonds can also transfer electrons to an electrode. Poly-L-glutamic acid around Mn-Ca oxides is important to obtain a soluble Mn-Ca oxide and inhibit the aggregation of nanoparticles.

In PSII, a tyrosine residue, D1-Tyr161 (Y_z), serves as a redox mediator between the catalytic Mn cluster and the photochemically active chlorophyll moiety P_{680} [81]. After four steps with five intermediates (S_n, n = 0–4), water is oxidized by the WOC [82]. The oxidation of Y_z by P_{680}^{+} likely occurs with the transfer of the phenolic proton to a hydrogen-bonded histidine residue. When Y_z is oxidized by P_{680}^{+}, the phenolic group becomes very acidic and deprotonates to form a neutral radical phenolic group (Fig. 10). The proton acceptor is histidine 190 (His 190), which is hydrogen bonded to the phenolic proton [83,14].

The Aukauloo and Moore research groups used 2-(2-hydroxyphenyl)-1H-benzimidazole phenol (IP) as a model for Y_z/His 190 in PSII [84,85]. A new strategy to synthesize IP–Mn oxide as a model for Y_z and His 190 near the Mn cluster in PSII is IP (2-(2-hydroxyphenyl)-1H-benzimidazole) between Mn layers in Mn(III, IV) oxide with a birnessite structure (Fig. 11).

The function of tyrosine is highly dependent on the presence of His-190. The function of His-190 can be altered by a buffer [83] or high pH [86]. After accumulating four oxidizing equivalents in the WOC, two water molecules are oxidized, O_2 is released, and the $CaMn_4$ cluster returns to the reduced state. In 2013, poly-(4-vinylpyridine) (PVP) was considered as a model for Mn-stabilizing protein around Mn oxide [18]. The reasons for the selection of PVP were as follows: i) pyridine groups in the polymer could act as proton acceptors, stabilize Mn(III), and reduce overpotential for water oxidation; ii) the polymer was stable in the presence of powerful oxidants; and iii) the polymer, with its many pyridine groups, could inhibit acidic conditions and provide a buffered environment for the Mn oxide. As discussed above, very small particles may be efficient catalyst toward water oxidation but their structures are too fragile to be stabilized in harsh water-oxidation reaction. Polypeptides or polymers such as BSA, PGA and PVP can stabilize such particles.

7. A model for photoinhibition

Light from the solar radiation (400–700 nm) is a prerequisite for the production of organic compounds by oxygenic photosynthetic organisms. However, light has another contrasting role, as it can stop the photosynthesis through the photoinhibition phenomena, which is defined as the light-induced damage of PSII [87–91]. In the acceptor side photoinhibition hypotheses, strong illumination results in the accumulation of the anions of secondary electron acceptors (Q_A^-) and then induces the double reduction of Q_A, leading to the release of plastoquinone from the binding site [87,91]. In another hypotheses, UV or near-UV illumination is directly absorbed by the Mn-Ca cluster in PSII [92], leading to the disassembly of the Mn-Ca cluster. Hakala et al. and Ohnishi et al., proved that the release of Mn ions to the thylakoid lumen is the first detectable step of both UV- and visible-light-induced photoinhibition [93,94]. The oxidative damage occurs after the release of Mn from the WOC because the Mn-depleted WOC cannot reduce P_{680}^{+} normally. Yano and colleagues demonstrated that the WOC is sensitive to X-ray irradiation, during which Mn(II) ions are

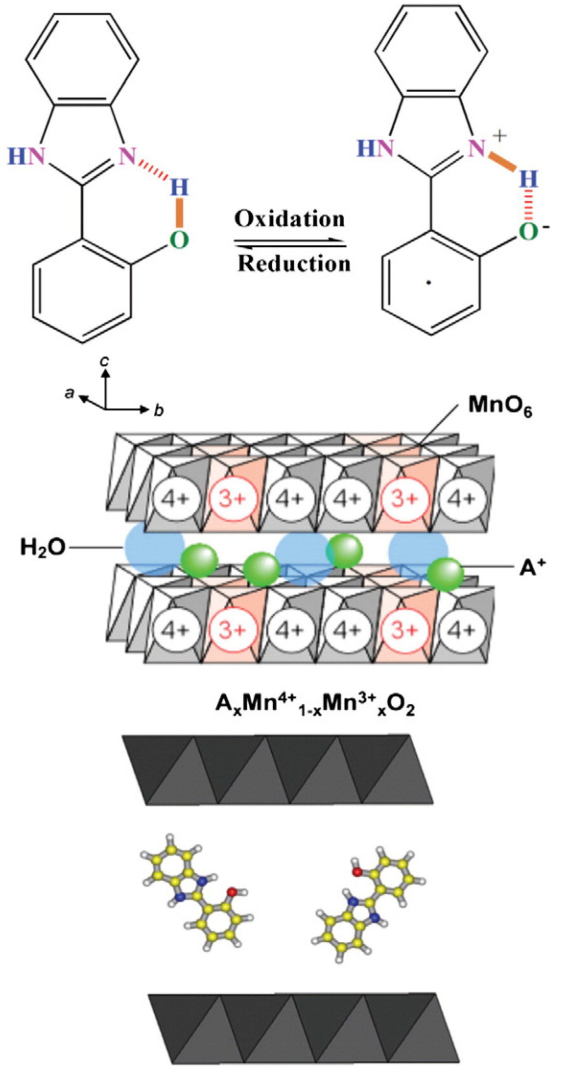

Fig. 11. 2-(2-Hydroxyphenyl)-1H-benzimidazole phenol (IP) is used as a model for Yz/His 190 in PSII. As shown in the scheme, oxidation of IP to oxidized IP could change the hydrogen bonding pattern, as observed in PSII. The dot shows an unpaired electron in IP (top). Schematic diagram of a birnessite-type layered manganese oxide incorporating inorganic or organic cations (A^+) (middle). Schematic representation of the structure of model compound 1. Hydrogen atoms are white; carbon atoms, yellow; oxygen atoms, red; nitrogen atoms, blue; and the blocks of MnO_6 are shown as triangles on the top and bottom of the IP molecules. (Bottom) [101]. Reproduced from Ref. [101] with permission from The Royal Society of Chemistry. Copyright (2012).

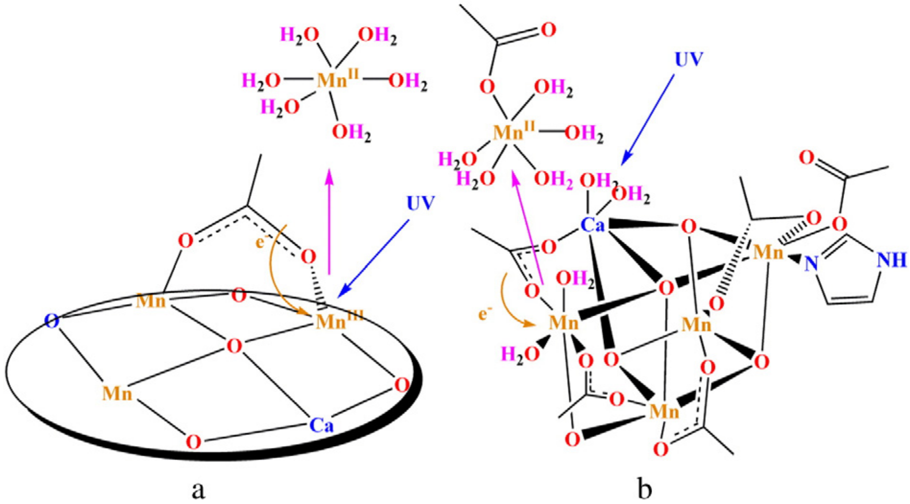

Fig. 12. The proposed mechanism for photoinhibition of Mn–Ca oxide (a) or the Mn–Ca cluster in PSII (b) by UV irradiation [96]. Reproduced from Ref. [96] with permission from The Royal Society of Chemistry. Copyright (2013).

released [95]. In 2012, Najafpour et al. studied the effects of UV radiation on Mn-Ca oxides in the presence of organic compounds [96]. In the absence of any organic compounds, UV radiation has no effect on the release of Mn(II) into solution. Carboxylate groups, which are hard and good ligands for Mn ions, accelerated the decomposition of the oxide, whereas phenoxy and imidazole, which are weaker ligands than carboxylate, had no effect on releasing Mn ions into solution. They stated that two characteristics of an organic compound are important for causing Mn ions to leak from Mn-Ca into solution: oxidizable groups in the organic compound to reduce Mn-Ca oxide and good ligands for Mn(II) in solution. Regarding the existence of many carboxylate groups in the structure of the WOC in PSII, it was suggested that these groups could be important in photodamage to the Mn-Ca cluster. Their proposed mechanism for the decomposition pathway is shown in Fig. 12.

Table 2
The rate of water oxidation catalyzed by various Mn based catalysts for water oxidation in the presence of non-oxygen transfer oxidant. Data are from [41].

Compound	Oxidant	TOF mmol O_2/mol Mn.s
Nanolayered Mn oxides supported on NiO	Ce(IV)	~5.0
Mn oxide supported on gold nanoparticle	Ce(IV)	~3.5
Nano-scale Mn oxide within NaY zeolite	Ce(IV)	2.6
Nanolayered Mn-Ca oxide	Ce(IV)	0.5–2.2
Nanolayered Mn-Al, Zn, K, Cd and Mg oxide	Ce(IV)	0.8–2.2
Gold deposited on layered Mn oxide	Ce(IV)	~2
Nanolayered Mn oxides supported on MgO, CuO, ZrO_2 and SiO_2	Ce(IV)	0.6>
Nanolayered Mn-Ni(II) oxide	Ce(IV)	0.4−0.6
$CaMn_2O_4 \cdot H_2O$	Ce(IV)	0.54
Amorphous Mn oxides	$Ru(bpy)_3^{3+}$	0.06
	Ce(IV)	0.52
$CaMn_2O_4 \cdot 4H_2O$	Ce(IV)	0.32
Mn oxide nanoclusters	$Ru(bpy)_3^{3+}$	0.28
Mn oxide-coated montmorillonite (low surface)	Ce(IV)	0.22
Nanolayered Mn-Cu(II) oxide	Ce(IV)	0.2−0.35
Octahedral molecular sieves	$Ru(bpy)_3^{3+}$	0.11
	Ce(IV)	0.05
MnO_2 (colloid)	Ce(IV)	0.09
α-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.059
$CaMn_3O_6$	Ce(IV)	0.046
$CaMn_4O_8$	Ce(IV)	0.035
α-MnO_2 nanotubes	$Ru(bpy)_3^{3+}$	0.035
Mn_2O_3	Ce(IV)	0.027
β-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.02
$Ca_2Mn_3O_8$	Ce(IV)	0.016
$CaMnO_3$	Ce(IV)	0.012
Nano-sized λ-MnO_2	$Ru(bpy)_3^{3+}$	0.03
Bulk α-MnO_2	$Ru(bpy)_3^{3+}$	0.01
Mn complexes	Ce(IV)	0.01−0.6
PSII	Sunlight	$100-400 \times 10^3$

Brudvig and Hou's groups studied the photochemical stability of $[Mn^{III}(O)_2Mn^{IV}(H_2O)_2(Terpy)_2](NO_3)_3$ (Terpy = terpyridine) (Fig. 4d) in aqueous solution by exposing to excess light irradiation at six different wavelengths in the range of 250–700 nm [97]. They concluded that ultraviolet light irradiation induced a new absorption peak at around 400–440 nm of the complex and decreases oxygen-evolving activity of this complex, but visible light did not have the same effect on the complex [97]. From these results we speculate that high valent manganese ions, or even many other metal ions, in the presence of ultraviolet light and organic compounds are not much stable.

8. Mn oxides with different ions between layers

Sr is the only proper alternative for Ca capable of supporting water oxidation with a reduced activity in WOC of PSII [98]. In 2013, Shen and his colleague compared the structure of Sr-PSII and Mn_4CaO_5 [98]. The general shape of the Sr-PSII cluster, a distorted chair form, is similar to that of the WOC cluster containing Ca^{2+}. Najafpour and his co-workers considered the same question concerning the special effect of Ca in the water oxidation activity of layered Mn oxides used as artificial water oxidizing catalysts [99]. They used Zn(II), Ni(II), Cd(II), Cu(II), La(II), Mg(II), and Al(III) instead of Ca(II) in the layered Mn oxides to assess the effect of replacing Ca(II) in the water oxidation reaction. In contrast to PSII, their results showed that replacing Ca by redox-inactive ions in layered Mn oxides did not alter the water oxidation activity of these compounds. Therefore, the suggested mechanism for water oxidation by Mn oxides was based on the participation of only Mn ions in water oxidation (Fig. 7), although, Kurz and Dau's group showed a specific effect of Ca in water oxidation by a more crystalline birnessite type Mn oxide [100]. Comparing the water oxidation of PSII with Mn oxides, we find that the Mn-Ca cluster of PSII is 10^5 (Table 2) more efficient than Mn oxides. Although some water-oxidizing catalysts with similar activities to PSII were reported by a few research groups [100–103], Nature used cheap and environmentally friendly ions to make such efficient catalyst, and also oxidizes water under ambient conditions. On the other hand, metal oxides are very stable in water-oxidation reaction even for years, but the water-oxidizing complex in Nature decomposed after 20 minutes. It is important to note that in artificial photosynthesis, and hydrogen production by water-splitting [104] it is not necessary to use a super catalyst, such as PSII, for industrial water oxidation toward hydrogen production, and moderate catalysts are enough in large-scale hydrogen production by water splitting.

The biological site is not only very efficient in terms of TOF but also uses a lower redox potential for water oxidation. Thus, P680$^+$ in PSII has a redox potential of ~1.3–1.4 V that is detuned to 1.0–1.1 V on Y$_Z$, before communicating directly with the WOC, which must operate at a level close to 0.9 V in moderate conditions. This yields a low over potenial of around 0.2 volt [105–107]. However, many artifiial water-oxidizing catalysts perform water oxidation in harsh conditon and using higher over potentials (0.6–1 volt) [108].

9. Conclusions

Nature has selected a complicated but highly efficient system for water oxidation in cyanobacteria, algae and plants. Crystallographic analysis at atomic resolution provided a structural basis for understanding the mechanim of biological water oxidation and for the design of an efficient and stable catalyst for water oxidation to develop artificial photosynthetic systems for harvesting and storing solar energy. Although Mn oxides have polynuclear structures, they have similarities between the WOC in PSII and Mn oxides. The similarities may include structures, water oxidation activity in the presence of oxidants, oxidation states, mechanism of water oxidation, decomposition pathways, etc. Thus, Mn oxides are promising compounds for many applications [109,110] because they are stable, low cost, environmentally friendly and easy to use, easy to synthesize and manufacture. From many experiments [for a recent paper see ref. 111], Mn oxides appear also very promising for water oxidation. It is important to note that the results show that, most probably, Mn oxides are true catalyst in water oxidation by many Mn compounds [69,110]. In other words, many Mn complexes in water-oxidation condition decompose to Mn oxides, and the Mn oxides are true catalysts for water oxidation [69,112–116].

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