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Nano-sized Mn oxide: A true catalyst in the water-oxidation reaction

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ABSTRACT

The short perspective highlights new results by water-oxidizing Mn-based catalysts in artificial photosynthetic systems.

How the catalytic centres of metalloenzymes came about is a key question of evolution. In this context, one intriguing metalloenzyme is Photosystem II (PSII) (Fig. 1) [1,2], an enzyme which catalyses the most fundamental large scale reaction of our planet, namely the light-driven spitting of water into oxygen and "hydrogen" (in the form of reducing equivalents). The reducing equivalents are further energised by a second light reaction provided by Photosystem I, and are then used to power the conversion of carbon dioxide to the organic molecules of life [3].

In so doing, the biosphere, our food supply, the oxygen we breathe and the ozone layer are maintained. Oxygen is the optimal electron acceptor for respiration as it yields more energy per electron transfer than any other element that is also sufficiently stable to build up to appreciable concentrations in our planet's atmosphere [4]. It has also been hypothesized that many biological patterns, such as body size, are depended on the high concentration of oxygen [5]. Moreover, it is photosynthesis that has given us fossil fuels.

The water-splitting reaction of PSII has served humankind, but with the looming problem of generating non-fossil energy on an enormous scale, there is a mood to develop artificial photosynthetic systems that use solar energy to "extract" hydrogen from water and to then either use it directly as an energy source or employ it to reduce CO_2 to carbon based fuels, like methanol or methane, and also fine chemicals [6–9].

In photosynthetic water spitting, the mechanistically complex and energetically demanding water-oxidation reaction occurs at a catalytic centre composed of four Mn ions and a Ca ion, the structure of which is now known at high resolution [2]. The fact that it is preserved in all photosynthetic organisms coupled with its ability to efficiently catalyse water oxidation at low overpotential, this centre has been considered a blueprint for catalyst development [6–9]. In the catalytic site, three Mn ions and the Ca ion are arranged as a distorted cubane with bridging oxygen atoms, and the fourth Mn linked to the cubane via oxo-bridges [2]. When first proposed, this arrangement seemed unique to PSII, but since then it has been found that very similar geometry for Mn and Ca can readily form under a number of synthetic models such as Mn oxides containing Ca, and a structural model of the $CaMn_3$ sub site of the water-oxidizing complex (WOC) containing a high-oxidation-state heterometallic $Mn_3^{IV}CaO_4$ moiety [10,11]. The Mn_4O_5Ca cluster in the PSII has dimensions of about $\sim 0.5 \times 0.25 \times 0.25$ nm and it may be considered a nano-sized Mn–Ca oxide in a protein environment (Fig. 1) [1,2]. Therefore, the assembly of the Mn–Ca cluster in PSII essentially involves the formation of an inorganic core.

Ca ion has high affinity for Mn oxido-cluster and such interaction enables protocyanobacteria to form an oxido-cluster as the early water-oxidizing site of PSII [10–12]. When an organism has such structure, it no longer needed to large amounts of Mn as oxidizing agents, and a few Mn ions were enough to oxidize a large amounts of water to provide cheap electrons. In all of the proposed mechanisms for the origin of PSII, biomineralization and Mn oxido cluster formation are important components.

In recent years, many metal compounds have been reported as water-oxidizing catalysts in the presence of different chemical or electrochemical oxidants [12–21]. A variety of metal complexes and metal oxides, such as iridium, ruthenium, platinum, cobalt, manganese, nickel and iron as redox active centers have been shown to be effective homogeneous or heterogeneous catalysts for water oxidation. However, recent experiments show that many of these complexes are really the precursors to the active catalysts rather than being the actual water-oxidation catalysts [14–21] (Fig. 2). Nano-sized metal oxides meet criteria with being stable,

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of low cost, efficient, easy to use, synthesize and manufacture, at least when compared to elaborate metal complexes [12–21].

Mn is an attractive metal for developing water oxidation catalysts as its oxides are stable, low cost, efficient, environmentally friendly catalysts, easy to use, synthesize and manufacture as well as being related to the only '*true water-oxidizing Mn based catalyst*' [14–18].

These compounds also have *high active-site densities,* high amounts of sites, comparing with enzymes. Recently, there have been reports that synthetic Mn oxides, which are not derived from special or pre-organized Mn precursors and are made in purely aqueous solution, show structural similarities to the thermodynamically favored and photo-assembling WOC [11,12]. These oxides are efficient catalysts for water oxidation in the presence of (electro) chemical oxidants. Such structures could be modified or tuned for water oxidation by applying the environmental groups (amino acids) supporting the WOC cluster in PSII. The similarities between the mechanism of the WOC in PSII and Mn oxides in the presence of (electro) chemical oxidants are also being proposed [22].

The catalysts for multielectron reactions are prone to structural rearrangement, and instability, during turnover [23]. Thus, the design of catalysts that repair themselves is very important for large-scale applications. Self-healing mechanisms are also observed in these Mn oxides. For example, a birnessite-like Mn oxide, generated in Nafion films, was found to sustain water oxidation by cycling between a Mn(II) state and birnessite during photon-assisted electro-catalysis [14]. Catalyst repair was conveniently achieved through electro-oxidation [14]. Other self-healing mechanisms are also proposed for Mn oxides in the presence of chemical oxidant [24–26]. In such self-healing reactions, decomposed products from Mn oxide in the water-oxidation reaction can react or combine to remake Mn oxide [14,24–26].

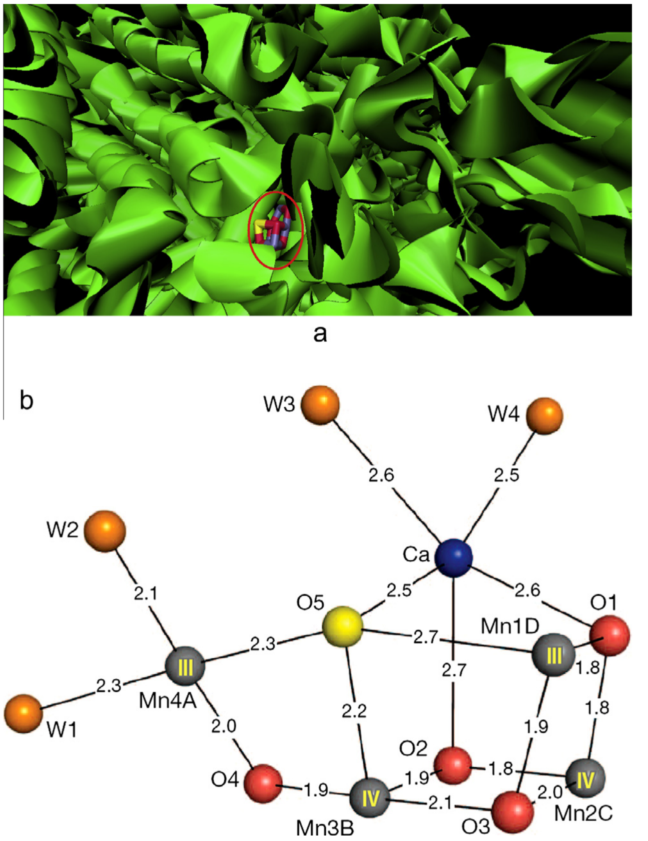

Fig. 1. The Mn–Ca cluster (circled in red) may be considered as a nano-sized manganese–Ca oxide in a protein environment (a). The Mn_4O_5Ca cluster in PSII Mn–O, Ca–O, Mn–water and Ca–water distances in Å (b). b: Reprinted with permission from Ref. [2]. Copyright (2014) by Nature publication group. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

After 3 billion years of evolutionary experiments, *Nature* found an efficient catalyst for water oxidation. The catalyst is a nano-sized Mn–Ca oxido cluster housed in amino acid residues that promotes the efficient transport of water and protons from the catalytic site [1,2]. In other words, it is important to note that, in addition to cofactors, enzymes are typically assemblies of many amino acids, but a few of them are directly coordinated to the metal ions [1,2]. The roles for the residues contacting the inorganic cores could include the regulation of charges and electrochemistry of the inorganic cores, aiding in coordinating water molecules at appropriate metal sites, and enhancing the stability of these inorganic cores. Other residues that are not in contact directly with the inorganic cores can have very important roles in enzymes and their deletion from enzymes causes dramatic decreases in the rate of reactions. Many of these amino acid residues are important in substrate or proton transfer processes. To design of a biomimetic *catalyst* a deep understanding of the roles of these amino acid residues in related enzymes is necessary. Introduction of the amino acid side chains could greatly improve the efficiency of catalytic reactions. The stabilization Mn(III) species on surface of Mn oxide relative to charge disproportionation is an effective strategy to lower the overpotential for water oxidation by MnO_2 [27]. The coordination of amine groups of poly(allylamine hydrochloride) to the surface Mn sites of MnO_2 electrodes effectively stabilized the Mn(III) species using N–Mn bond formation, resulting in $\sim$500 mV negative shift of the onset potential for the water oxidation at neutral pH. The number is as low as the overpotential used by the WOC of PSII [27,28]. It showed that additional organic groups, as are present in PSII, can increase catalytic activity of these clusters. In this context, it is worth noting that small, well-dispersed Mn oxide nanoparticles, confined within sulfonate group-laden channels of Nafion, achieve water oxidation at overpotential below 150 mV and with high turnover frequencies [29]. Recently, nanolayered Mn oxides on bovine serum albumin [30] or polyglutamic acid [31] was reported (Fig. 3). The rates of water oxidation by the compounds in the presence of cerium (IV) ammonium nitrate are low because of the decomposition reactions of organic matrix around Mn oxide. It means that cerium (IV) ammonium nitrate (Ce(IV)) is not only helps to water oxidation as an oxidant but also decomposes organic compounds around Mn oxides. Thus, in this condition we need a weaker oxidants than Ce(IV). As shown in Fig. 3, the structure of such compounds is the well-dispersed nano-sized Mn into an organic matrix.

Other interesting phenomenon can be observed in Mn oxides and most probably other metal oxides. As we know, a catalyst, unlike other reagents in the chemical reaction, is not consumed and the catalyzed reactions have a lower activation energy than the corresponding uncatalyzed reaction, resulting in a higher reaction rate at similar condition. Many of catalysts in long time change to an inactive compound. The "long time" may be a few hours or months. Using Mn oxides, an improving in water oxidation reaction was reported by time that most probably is related to the conversion of the Mn oxide to more amorphous one [32,33]. This conversion changes structures to a more open and active one. In other words, the catalyst improves its structure in the water oxidation reaction. Such phenomenon can be very important because in contrast to many catalysts, the used catalyst shows a better activity as compared with fresh catalyst [32,33]. In other words, in addition to water oxidation in the experimental condition, there is another reaction that helps to decrease crystallinity and changing structure of catalyst to a more active one [32,33]. Thus, after a few hours the activity will increase. In this