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From manganese complexes to nano-sized manganese oxides as water-oxidizing catalysts for artificial photosynthetic systems: Insights from the Zanjan team

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ABSTRACT

On the occasion of the international year of light and light-based technologies, I provide a short overview of our recent findings and personal view on the Mn-based water-oxidizing catalysts and the related sophisticated strategies toward water oxidation, which are promising in the artificial photosynthetic systems.

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1. Introduction

As an undergraduate student, I tried to synthesize some Ag(II) complexes with N-donor ligands. I found that the unstable Ag(II) complexes reduce to Ag(I) complexes in the presence of water. I suggested that either the wateroxidation or ligand-oxidation reaction is responsible for the reduction of Ag(II) complexes under these conditions. Although ligand oxidation in some cases may occur in the presence of water, I focused on the water-oxidation reaction hypothesis to synthesize stable Ag(II) complexes. Initially I did not think that water oxidation is an important reaction because the product of the reaction is O₂, which is present around us! However, on more deep search and the study of water oxidation, I found the importance of the reaction especially by reading the studies by Professor Stenbjörn Styring [1] and Professor Gary W. Brudvig [2]. On the other hand, I read about the role of an Mn compound in an

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unknown structure in biological water oxidation in a book, Advances in Photosynthesis and Respiration series, in Professor Govindjee series edited by D. R. Ort and C. F. Yocum [3]. After this time, water oxidation and artificial photosynthesis were, and are (!) very interesting for me because they are new, multidisciplinary fields which try to provide a clean environment on our planet.

Artificial photosynthesis is an umbrella term and refers to the processes that mimic natural photosynthesis (Scheme 1) [4–12]. One of the most important goals of the artificial photosynthesis is to use the cheap electrons generated by water oxidation to reduce CO_2 or H⁺ to fuel [4–12]. In contrast to the natural photosynthesis, artificial systems are usually a simplified way to produce clean and renewable fuels (Scheme 2).

In an artificial photosynthetic system, we usually need these features [4–12]:

- (1) absorption of a photon;
- (2) a charge-separated state;
- (3) a reducing catalyst:

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Scheme 1. A simple scheme of artificial photosystem to split water into H₂ and O₂. The following sections are required for both artificial photosynthetic systems: Photosenthisizer, composed of several molecules, electron transfer donor (Donor), electron transfer acceptor (Acceptor), catalyst for chemical H₂ reduction, catalyst for chemical water oxidation and light-harvesting molecular construction (Antenna).



Scheme 2. During water oxidation oxygen, cheap electron and proton are obtained that could be used for H₂ formation.

- (4) accumulation of electrons;
- (5) an oxidizing catalyst;
- (6) substrate(s) to be oxidized and reduced.

For six years, I synthesized and characterized many Mn complexes with different ligands [13–17]. I selected ammonium cerium(IV) nitrate (Ce(IV)), Oxone[®] (KHSO₄, K₂SO₄ and KHSO₅) and photochemically produced Ru(bpy)₃³⁺ to test oxygen evolution catalyzed by these complexes. However, no oxygen evolution was observed in many cases, but Oxone[®] was promising and a few complexes showed activity toward oxygen evolution [16]. However, the origin of oxygen may not be water under these conditions and the reaction is an oxygen-evolution reaction rather than the water-oxidation reaction [18].

In 2010, in Dr. Philipp Kurz's group, aimed at simulating the water-oxidizing complex (WOC) or oxygen-evolving complex (OEC) in Photosystem II (PSII) (Fig. 1a,b) [19], we showed that the incorporation of Ca ions into Mn oxides can improve the water-oxidation activity of Mn oxides toward water oxidation [20]. The WOC is the only compound to catalyze water oxidation in Nature [21,22] and, as we discussed, it may be considered as an Mn-Ca cluster housed in a protein environment in PSII that controls reaction coordinates, proton movement and water access [23,24]. Shen and his co-workers reported the crystal structure of the Mn-Ca cluster at an atomic resolution (Fig. 1a,b) [21,22]. In the WOC the metal ions, one Ca and four Mn ions, are bridged by five oxygen atoms. Two water molecules are also coordinated directly to both Mn and Ca ions in this structure (Fig. 1a,b) [21,22].

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