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Chemical, electrochemical and photochemical molecular water oxidation catalysts

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ABSTRACT

Hydrogen release from the splitting of water by simply using sunlight as the only energy source is an old human dream that could finally become a reality. This process involves both the reduction and oxidation of water into hydrogen and oxygen, respectively. While the first process has been fairly overcome, the conversion of water into oxygen has been traditionally the bottleneck process hampering the development of a sustainable hydrogen production based on water splitting. Fortunately, a revolution in this field has occurred during the past decade, since many research groups have been conducting an intense research in this area.

Thus, while molecular, well-characterized catalysts able to oxidize water were scarce just five years ago, now a wide range of transition metal based compounds has been reported as active catalysts for this transformation. This review reports the most prominent key advances in the field, covering either examples where the catalysis is triggered chemically, electrochemically or photochemically.

1. Introduction

Nature has always been a source of inspiration for human kind. The astonishing complexity and perfection of the biochemical processes occurring every second within our natural environment still amaze us every day. Sunlight, a free and inexhaustible energy source, is efficiently used every day by green plants, algae and cyanobacteria in order to produce energetically rich biomolecules. The emulation of this process in the sense of storing the energy of sun into the bonds of a chemical fuel would be a solution for our global energy demand. Moreover, if the combustion of this fuel was carbon free, the whole process would constitute a clean approach for fighting against climate change. From this point of view, the use of sunlight in order to split water into oxygen and hydrogen has become one of the most brilliant feasible ideas during the last three decades, since hydrogen combustion only produces energy and water, thus closing the whole cycle in a perfectly sustainable manner.

The molecular machinery involved in photosynthesis consists in two families of electronically coupled protein complexes, named Photosystem I (PSI) and Photosystem II (PSII), embebed within the thylakoid membrane of green plant and algae chloroplasts and cyanobacteria. During photosynthesis, 4 protons and 4 electrons are detached in PSII from 2 H_2O molecules after the absorption of 4 sunlight photons by chlorophyll P_{680}, generating O_2 and a gradient of electrons and protons that are used by PSI to generate 2 NADPH and 3 ATP molecules. These constitute the necessary reducing equivalents and energy needed during the Calvin–Benson cycle for generating carbohydrates from CO_2 outside of the thylakoid membrane at later stages of the photosynthetic process [1,2].

From a chemical point of view, the most important process takes place at the Oxygen Evolving Centre (OEC) of PSII, where the oxidation of H_2O happens in the absence of light in a Mn_4CaO_5 cluster shown in Fig. 1. In this cluster, five acidic amino acids, one His and one Ala coordinate the Mn and Ca atoms. In addition, four H_2O molecules are also present in the cluster, two of which binding to the Ca ion [3]. Although the exact mechanism of water oxidation is still a mater of intense debate, it is accepted that during the so-called S-cycle or Kok-cycle four electrons are released from the Mn_4CaO_5 cluster, provoking the oxidation of the Mn ions and the formation of an O–O bond from two water molecules [4–8].

Following the oxidation of H_2O within the OEC-PSII, the released electrons are then transferred to the $Tyr_ZO\cdot$radical (Tyr161) formed after oxidative quenching of the excited P^*_{680}, which at the same time is stabilized by the presence of a proximal His190 [9,10]. Afterward, the electrons flow from Tyr_Z through an electronic transport channel that consecutively involves P_{680}, pheophytin and plastoquinones A and B, until finally reaching PSI [11].

It has been hypothesized that the oxo ligands in OEC are needed for the neutralization of the positive charges of the Mn ions [12].

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Furthermore, it has been suggested that the Ca ion may play a significant role as a Lewis acid during water oxidation by modifying the nucleophilicity of its bounded H_2O molecules [13]. Indeed, Stranger et al. have recently shown that in the Sr(II) analogue of PSII, the region containing the alkaline earth metal and its associated H bonding network is closely related to the substrate water binding and O–O bond formation [14]. Furthermore, very recently, with the use of femtosecond X-ray laser spectroscopy, a series of snap shots of PSII at 5 Å resolution during the dark state (S_1) and the putative excited state (S_3) have shown that the Mn_4CaO_5 cluster elongates, accompanied by changes in the protein environment, allowing for binding of a second substrate water molecule between Mn4 (see Fig. 1) and the rest of the cluster [15].

Inspired, but not constrained, by nature, chemists have designed artificial molecular systems in order to capture light with the aim of using this energy to oxidize water and at the same time employ the released electrons to form hydrogen from water protons, since water cannot be directly excited by the electromagnetic radiation of the sun. Therefore, three different chemical components are needed for this purpose: a light harvesting device (or photosensitizer, P), a water oxidation catalyst (WOC) and a hydrogen evolving catalyst (HEC). These three components can be assembled in a photo-electrochemical cell (PEC), such as the one drawn in Fig. 2 [16–18]. This cell needs to be robust, and contains a proton-exchange membrane (PEM) that allows diffusion of protons to the cathode and, at the same time, physically separates the anodic and the cathodic compartments, thus avoiding the potential hazardous recombination of H_2 and O_2 to form back water. Besides, the cell should work harmonically and should also be economically viable.

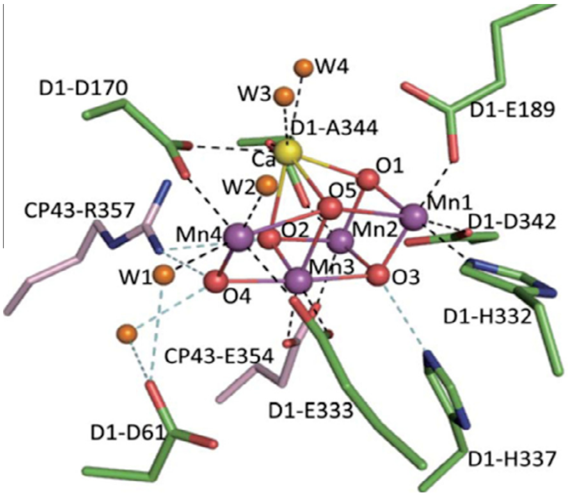

Fig. 1. X-ray structure of the OEC–PSII at 1.9 Å resolution. Reprinted with permission from Macmillan Publishers Ltd.: Nature, Y. Umena, K. Kawakami, J.R. Shen, N. Kamiya, N. Nature 473 (2011) 55–60, copyright (2011).

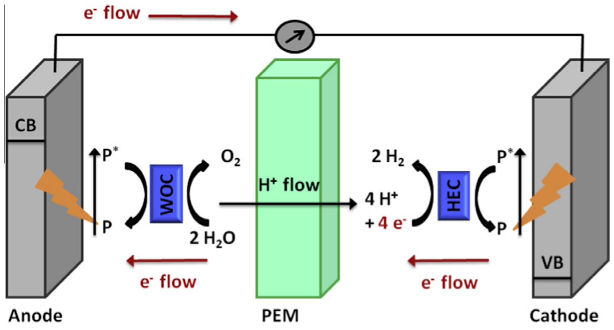

Fig. 2. Schematic representation of a photo-electrochemical cell (PEC) designed for water splitting using sunlight. P: photosensitizer, WOC: water oxidation catalyst, HEC: hydrogen evolving catalyst, PEM: proton-exchange membrane, CB: conduction band, and VB: valence band.

Excellent works have demonstrated the viability of hydrogen production from protons by using molecular catalysts [19–24]. However, the development of efficient WOCs has been, up till the last decade, continuously hampered by the complex mechanistic and thermodynamic unfavorable nature of this reaction that involves the removal of 4 H^+ and 4 e^- from two H_2O molecules together with the formation of an O–O bond. In spite of the inherent difficulties, the field is nowadays effervescent, with numerous research groups involved and an awesome amount of papers describing new and improved WOCs appearing every year.

This review highlights the main achievements obtained in chemically, electrochemically and photochemically-driven molecular WOCs. Additionally, the inclusion of the latter on real PECs will also be described, and the future goals in the field will be briefly discussed.

2. Chemically and electrochemically-driven water oxidation catalysis

As stated before, the detailed knowledge of the structure of the Mn_4CaO_5 cluster of PSII has clearly become a source of inspiration for the generation of artificial catalysts based on transition metal ions that oxidize water to oxygen. In order to chemically activate a transition-metal catalyst for successfully oxidize water, the use of a sacrificial chemical oxidant is compulsory. A salt of Ce(IV) has been by far the most employed one. It should be noticed that although the generation of light-driven systems is the final goal in the field, the use of these chemical oxidants allows a simple and fast way of assessing the catalyst performance. However, the applicability of chemically-driven molecular WOCs in real and sustainable PECs for the photo-production of H_2 (Fig. 2) is impractical because the sacrificial chemical oxidant is irreversibly consumed, has a non-innocent character (since it is an indiscriminate oxidant) and is energetically inefficient (usually presenting high overpotentials).

Within this context, the use of electrochemically-driven WOCs addresses some of the above-mentioned issues, allowing the control of the applied overpotential. Therefore, in the way from chemical to light-driven WOCs potentially applicable in the modular construction of real PECs, electrochemically-driven systems have been developed as a step forward in this field. However, the direct application with a potentiostat of a redox potential through an electrode to an homogeneous catalyst usually ends up with a diffusion/electron-transfer (catalyst-electrode) controlled catalytic system [25]. In order to overcome this hurdle, the WOCs can be anchored onto the electrode surface, thus providing the necessary catalyst-support electric connection for the efficient electron removal and collection taking place during the oxidation process. The anchoring approach constitutes a step further towards the final incorporation of WOCs into feasible PECs. However, these hybrid systems must be stable against the oxidative and acidic conditions employed, and there must also exist a fast catalyst-electrode electron transfer when pursuing long-term reliable PECs.

The following subsections will point the most relevant examples reported until now of chemically and electrochemically-driven molecular WOCs.

2.1. Manganese and other first-row transition metal complexes

Since manganese is the transition metal selected by nature in the OEC to carry out the oxidation of H_2O, it has been the focus