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Review

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

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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.

1. Introduction

Nowadays, one of the significant threats facing mankind is the climate change caused by the increased CO_2 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 (Barber and Tran, 2012). 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 (Olson and Blankenship, 2004). Most researchers agree that nonoxygenic photosynthesis performed approximately 3.2–3.5 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 (Konhauser et al., 2011; Govindjee and Shevela, 2011). Probably, the first experiment exploring the nature of photosynthesis was performed by van Helmont in 1648 (see Williams, 1957). Now, we have extensive information about the details of this phenomenon. Photosynthesis is a two-step process: light reactions in the grana and CO_2 fixation in the stroma of the chloroplast. The light dependent part is fulfilled by two sequential photosystems (photosystem II (PSII) and photosystem I (PSI)).

☆ This article is dedicated to the memory of Dr. Warwick Hillier who died on January 10, 2014.

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The first step in the PSII (membrane–protein complex) is the light-induced excitation of chlorophyll a (P_{680}) and loss one electron. P_{680}^{+} 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 O_2, electrons and H^+ owing to the catalytic action of the water-oxidizing center known as the WOC (or oxygen-evolving center (OEC)) (McEvoy and Brudvig, 2006; Najafpour, 2006; Najafpour et al., 2012a). 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 (Golbeck, 2006). 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 (Xu et al., 2009; Jiao and Frei, 2010; Najafpour, 2011; Najafpour et al., 2011). However, in water splitting, water oxidation is a bottleneck.

$$4H_2O \rightarrow 4H^+ + O_2 + 4e \quad (1)$$

$$4H^+ + 4e \rightarrow 2H_2 \quad (2)$$

$$2H_2O \rightarrow 2H_2 + O_2 \quad (3)$$

Such reactions (Eqs. (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 (Dismukes et al., 2009), 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 Mn_4O_5Ca 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 (Wiechen et al., 2012).

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) (Dau and Haumann, 2008; Barber, 2002). 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 $S_4 \rightarrow S_0$ (McEvoy and Brudvig, 2006).

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 Pirson (1937). About 40 years later, Jaklevic et al. recorded the X-ray absorption

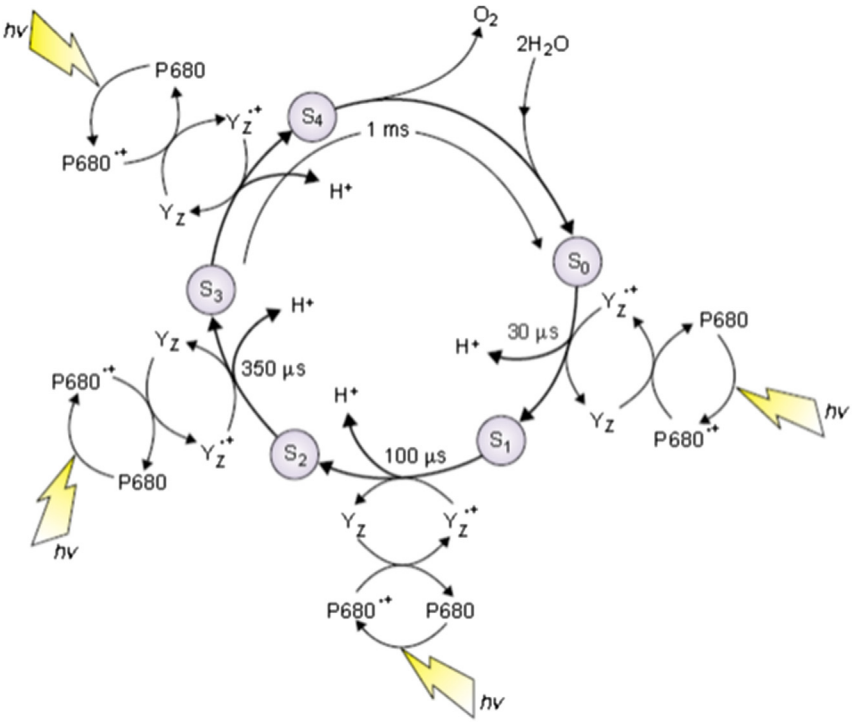

Fig. 1. The S-state cycle showing how the absorption of four photons of light (hν) by P_{680} drives the splitting of two water molecules and formation of O_2 through a consecutive series of five intermediates (S_0, S_1, S_2, S_3 and S_4). Protons (H^+) are released during this cycle except for the S_1 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 (Barber, 2002). Image was reprinted with permission from Barber (2002) Copyright (2008) by Elsevier.