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Invited Review

Molecular complexes in water oxidation: Pre-catalysts or real catalysts

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ABSTRACT

Artificial photosynthesis is considered a promising method to produce clean and renewable energy by sunlight. To accomplish this aim, development of efficient and robust catalysts for water oxidation and hydrogen production is extremely important. Owing to the advantages of easily modified structures and traceable catalytic processes, molecular water oxidation catalysts (WOCs) attract much attention during the past decade. However, the transformation of molecular WOCs to metal oxides/hydroxides or metal ions may occur under the harsh catalytic conditions, making the identification of true active species difficult. In this article, recent progress on molecular complexes acting as real catalysts or precursors toward water oxidation was briefly reviewed. We summarized the commonly used physical techniques and chemical methods that enable to distinguish homogeneous catalysts from heterogeneous catalysts. The factors that affect the nature of WOCs, such as reaction conditions, transition metal centers, and supporting ligands were discussed as well.

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Biaobiao Zhang received his B.S. in the Department of Chemistry and Chemical Engineering from Qufu Normal University in 2009 and PhD in Applied Chemistry from Dalian University of Technology (DUT) in 2015 under the guidance of Prof. Licheng Sun. His current work focuses on molecular catalysts for water oxidation and PEC cells for advanced solar fuel production.

Prof. Licheng Sun received his PhD in 1990 from Dalian University of Technology (DUT). He went to Germany as a postdoc at Max-Planck-Institut für Strahlenchemie (now changed the name to Max-Planck-Institut für Schemische Energie konversion) with Dr. Helmut Görner (1992–1993), and then as an Alexander von Humboldt fellow at Freie Universität Berlin (1993–1995) with Prof. Dr Harry Kurreck. He moved to KTH Royal Institute of Technology, Stockholm in 1995 and became assistant professor in 1997, associate professor in 1999 (at Stockholm University) and full professor in 2004 (KTH). He is presently also a distinguished professor in DUT. His research interests cover artificial photosynthesis, molecular catalysts for water oxidation and hydrogen generation, functional devices for total water splitting, dye sensitized, quantum dot/rod sensitized solar cells, perovskite solar cells. He has published more than 400 peer reviewed papers in the fields of solar cells and solar fuels with total citations of >16,000, and H-index of 66.

1. Introduction

Photosynthesis converts solar energy into chemical energy by plants and other organisms, which plays a crucial role in nature. This chemical energy exists in various forms, such as carbohydrates (food), oxygen (O_2), and fuels, supporting all life forms on the earth. Photosystem II (PS II) is one of the essential enzymes of photosynthesis, which produces O_2 and four protons ($4H^+$) via successive proton coupled electron transfer (PCET) processes by a Mn_4CaO_5 cluster of oxygen-evolving complex (OEC, Fig. 1) in water oxidation [1–4].

To produce clean and renewable energy by sunlight, artificial photosynthesis serves as one of the most promising methods. In an artificial photosynthetic cell, solar energy is collected and used to split water into O_2 and H_2 (Eqs. (1)–(3)). As one of the half reactions in water splitting, water oxidation releases O_2 with the production of four protons and four electrons, which is considered as the bottleneck of overall water splitting [5–7].

$$2H_2O \rightarrow O_2 + 2H_2O \quad (1)$$

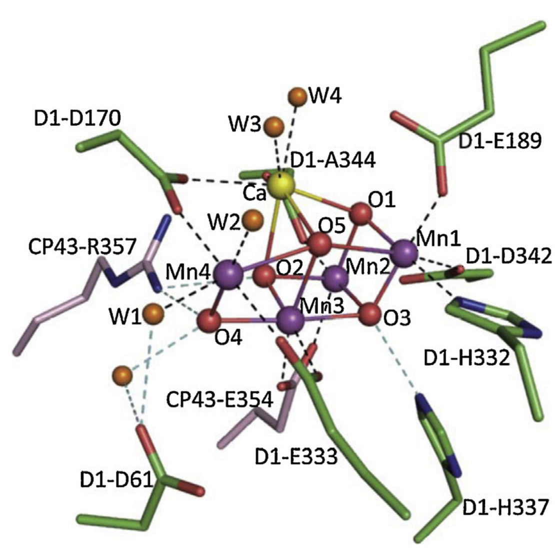

Fig. 1. Stereo view of the Mn_4CaO_5 cluster and its ligand environment. Reprinted with permission from Ref. [2]. Copyright 2011 Macmillan Publishers Ltd.