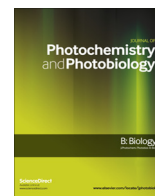




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The mechanism of water oxidation catalyzed by nanolayered manganese oxides: New insights



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ABSTRACT

Herein we consider the mechanism of water oxidation by nanolayered manganese oxide in the presence of cerium(IV) ammonium nitrate. Based on membrane-inlet mass spectrometry results, the rate of H₂¹⁸O exchange of μ-O groups on the surface of the nanolayered Mn–K oxide, and studies on water oxidation in the presence of different ratios of acetonitrile/water we propose a mechanism for water oxidation by nanolayered Mn oxides in the presence of cerium(IV) ammonium nitrate.

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1. Introduction

Water oxidation is a very important reaction in both natural [1] and artificial photosynthesis [2]. In natural photosynthesis, as a result of water oxidation, oxygen gas is produced, which is necessary to sustain living organisms. On the other hand, many biological events depend on the concentration of oxygen. For example, body size depends on the concentration of oxygen in the Earth's atmosphere [3].

In the artificial photosynthesis water-splitting to hydrogen and oxygen is suggested as a way to store sustainable energy from sunlight and overcome the problem of environmental pollution caused by the excessive and indiscriminate consumption of fossil fuels. However, the water-oxidation reaction, which is one of the half-reactions in water splitting to oxygen and hydrogen, is difficult to perform due to thermodynamic and kinetic limitations [2]. Water oxidation is not only important in water splitting, but also it can provide 'cheap electrons' for many other reduction reactions, such as CO₂ and N₂ reduction in artificial photosynthesis [4–8]. Unfortunately, many efficient catalysts available so far for water oxidation are expensive and (or) toxic. Nature in the oxygenic photosynthesis phenomenon uses a Mn₄CaO₅ cluster (known as the water-oxidizing complex, WOC, or the oxygen-evolving complex, OEC) (Fig. 1) to perform water oxidation [1]. Mn compounds are

attractive for water oxidation because Mn ions are not only used by Nature to oxidize water [1], but also are environmentally friendly and low-cost [6–12].

In the biological water oxidation process, it has been proposed that a terminal Mn(V)=O moiety undergoes a nucleophilic attack by a Ca(II)-bound hydroxide or water ligand to form an Mn-bound hydroperoxide [13].

Among different Mn compounds, Mn oxides were reported as efficient water-oxidizing catalysts for artificial photosynthetic systems [6–12] and are the true catalysts for water oxidation in the water oxidation process catalyzed by Mn complexes [14–16]. Finding how Mn oxides oxidize water in detail is important for the design of new and robust catalysts but the molecular mechanism of water oxidation by these compounds remains still unknown. Herein we discuss the mechanism of water oxidation catalyzed by nanolayered manganese oxide in the presence of cerium(IV) ammonium nitrate (Ce(IV)) using results by membrane-inlet mass spectrometry studies [17], the rate of H₂¹⁸O exchange for μ-O groups on the surface of nanolayered Mn–K oxide studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) [18], and the new experiments on water oxidation in the presence of different amounts of acetonitrile. According to these data, we propose a mechanism for water oxidation process under the reported conditions.

2. Experimental

2.1. Material

All reagents and solvents were purchased from commercial sources and were used without further purification.

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2.2. Synthesis of the layered K-Mn oxide

Synthesis and characterizations for the oxide were previously reported and are not discussed here (see Ref. [18] and Supplementary material).

2.3. Characterizations of the layered K-Mn oxide

TEM and SEM were carried out with Philips CM120 and LEO 1430VP devices, respectively. Mn atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (1.0–10.0 mg) was added to a solution containing 10 mL of concentrated nitric acid (5 M), and H₂O₂ (0.5 mL, 30%). The mixture was left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted to 25.0 mL and analyzed by AAS. Cyclic voltammetry and amperometric studies were performed using an Autolab potentiostat–galvanostat model PGSTAT30 (Utrecht, The Netherlands). In this case a conventional three electrode set-up was used in which a Pt electrode or Pt electrode modified with Mn oxide, a Ag|AgCl|KCl_{sat} electrode and a platinum rod served as the working, reference and auxiliary electrodes, respectively. The working potential was applied in the standard way using the potentiostat and the output signal was acquired with Autolab Nova software.

2.4. Water oxidation in the presence of Ce(IV)

Oxygen evolution from aqueous solutions in the presence of Ce(IV) was measured using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor with digital readout. The reactor was maintained at 25.0 °C in a water bath. In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continually with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, the water in the reactor was replaced with a Ce(IV) solution. Without catalyst, Ce(IV) was stable under these conditions and oxygen evolution was not observed. After deaeration of the Ce(IV) solution with argon, Mn oxides as several small particles were added, and oxygen evolution was recorded with the oxygen-meter under stirring (Fig. S1, ESI[†]). The formation of oxygen was followed,

and oxygen formation rates per Mn site were obtained from linear fits of the data. Only the dissolved oxygen can be measured by the oxygen-meter.

3. Results and discussion

To answer the question how O₂ is formed on addition of layered Mn oxide in the presence of Ce(IV), we considered all important cases involving eight different proposed mechanisms (Fig. 2).

We could eliminate the cases involving vi or viii mechanisms because we observed no O₂ evolution in the absence of nanolayered Mn oxide. To find out if other mechanisms are possible, we should consider the results of studies with membrane-inlet mass spectrometry (MIMS) [17,18]. MIMS was used to detect the produced O₂ in the reactions of Mn oxides in the presence of cerium(IV) ammonium nitrate (Ce(IV)) or [Ru^{III}(bpy)₃]³⁺ in H₂¹⁸O and to calculate the signals for the O₂ isotopologues ¹⁶O₂ (*m/z* = 32), ¹⁶O¹⁸O (*m/z* = 34) and ¹⁸O₂ (*m/z* = 36) [18]. In this study $^{18}\alpha = ([^{18}\text{O}_2] + 0.5 [^{16}\text{O}^{18}\text{O}]) / [\text{O}_2]_{\text{total}}$, which is the total fraction of ¹⁸O atoms in the produced O₂ and the development of ¹⁸α over time could then be plotted for the course of the catalytic O₂ formation [18].

The role of nitrate counter ion from the Ce(IV) solution in O₂ evolution (the mechanisms vii and viii in Fig. 2) was confirmed to be insignificant in MIMS experiments [18]. From the results we concluded that [18]:

- The bridging oxido (μ-O) groups on the oxide surface are themselves not involved in the O–O bond formation (thus, only i or (and) ii in Fig. 2 are the proposed mechanism(s)).
- μ-O groups on the surface are oxidized to form O₂ (the mechanisms iii and iv in Fig. 2 are possible). Under these conditions the μ-O groups on the surface should exchange with the bulk solution very rapidly because if the exchange is slow, more ¹⁶O₂ and ¹⁶O¹⁸O will be formed.

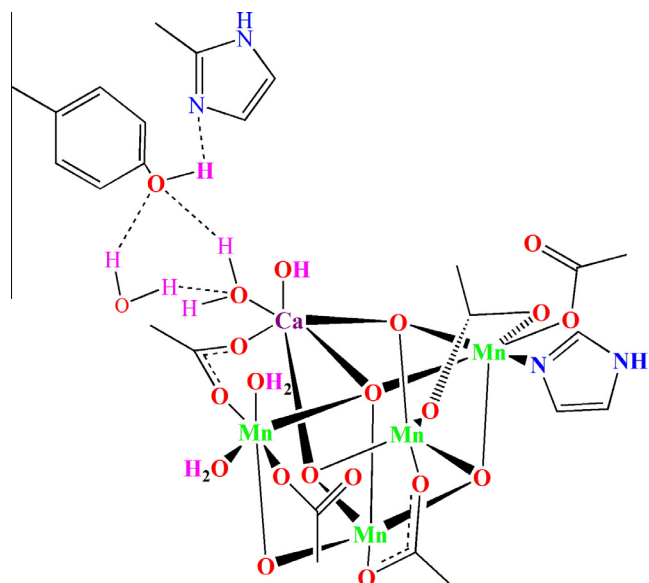


Fig. 1. Water-oxidizing complex in photosystem II contains four Mn ions and one calcium ion [1].

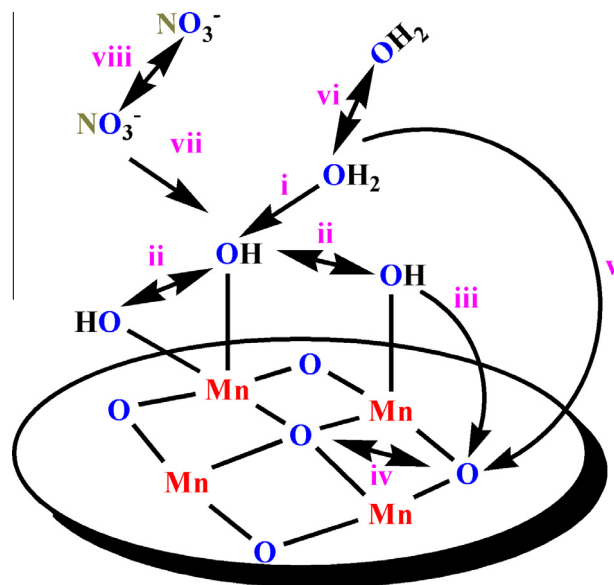


Fig. 2. Proposed mechanisms for water oxidation catalyzed by the layered Mn oxide: nucleophilic attack of water molecule on a terminal hydroxide group (i); coupling of the terminal hydroxide ligands (ii), the attack of terminal hydroxide group on a bridging oxido ligand (iii), coupling of the bridging oxido ligands (iv), the attack of water molecule on a bridging oxido ligand (v), and the reaction between two water molecules (vi). The oxygen evolution by the reaction of nitrate ions is also possible (vii, viii).

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