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ARTICLE TYPE

Nano-sized layered manganese oxide in a poly-L-glutamic acid matrix: A biomimetic homogenized heterogeneous structural model for water-oxidizing complex in Photosystem II†

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We, for the first time, report a nano-sized layered Mn-Ca oxide in poly-L-glutamic acid as a structural model for biological water-oxidizing site in plants, algae and cyanobacteria. The compound was synthesized by a simple method and characterized by transmission electron microscopy, atomic absorption spectroscopy, scanning electron microscopy, UV-Visible spectroscopy, dynamic light scattering, Fourier transform infrared spectroscopy and electrochemistry. The results show the important effect of PGA on electrochemistry of Mn-Ca oxide.

Introduction

Energy crisis, as one of the most important challenges, has led researchers to look for a good solution. One known way for H₂ production as an efficient renewable energy is water splitting, but water-oxidation reaction is a bottleneck for water splitting.¹ So, design and synthesis of an inexpensive and high efficient catalyst for this reaction is a major subject proposed for researchers.¹ To this end, the water-oxidizing complex (WOC) of Photosystem II (PSII) in plants, algae and cyanobacteria is taken into consideration as a good practical model (Fig. 1). The WOC is a Mn-Ca cluster catalyzing light-induced water oxidation,^{2,3} which is housed in a large molecule with low active site densities of PSII. The site can be considered as a nano-sized Mn-Ca oxide in a protein environment.⁴ Among different residues around the Mn-Ca cluster in biological site, the content of carboxylate residues is higher than others (Fig. 1).^{2,3}

At least six proteins are required for water oxidation by the WOC but only a small fraction of the residues, 3-4 residues on the average are directly coordinated to the Mn ions.

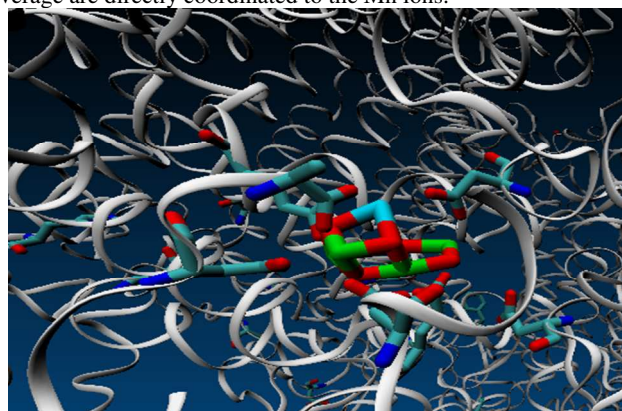
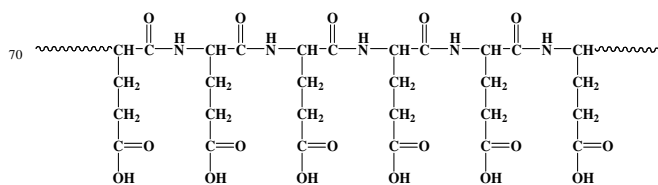


Fig. 1 The CaMn₄O₅ cluster (O: red; Mn: green; Ca: blue) and its

surrounding carboxylate residues in PSII (a). The CaMn₄O₅ cluster in PSII has dimensions of about ~ 0.5 × 0.25 × 0.25 nm³. Six carboxylate groups are directly coordinated to Mn and Ca ions.

The proposed roles for residues that coordinate directly to the metal ions in the cluster include regulation of charges, and electrochemistry of the Mn-Ca cluster, help in coordinating water molecules at appropriate metal sites and stability of this cluster.^{2,3} So far, many reports have been provided concerning synthesis of various Mn complexes, but an efficient water-oxidation catalyst could not be found among them.⁵ However, Mn oxides are promising compounds for water oxidation.⁶ A few research groups reported that treatment of Mn oxide with organic compounds produces an efficient catalyst for water oxidation.^{7,8} Ryuhei Nakamura and Kazuhito Hashimoto groups at the University of Tokyo introduced amine-Mn oxide as efficient catalysts for water oxidation and proposed that for such systems the N-Mn bond formation stabilizes the Mn(III) species, resulting in oxygen production at an onset potential close to the thermodynamic reversible potential of the four-electron oxidation of H₂O.⁷ However, these Mn oxides lack the extensive surrounding protein matrix of the WOC in PSII. In this study, we placed poly-L-glutamic acid (PGA) around Mn-Ca oxide (Scheme 1).



Scheme 1 Structure of poly-L-glutamic acid (PGA).

Experimental Section

Materials

All reagents were purchased from commercial sources and were used without further purification. PGA (wt: 50,000-100,000) was purchased from Aldrich.

Synthesis

CaMnO_x-PGA: The compound was synthesized by a very simple method. In brief, to PGA (25 mg) in water (10 mL), Mn(OAc)₂·4H₂O (10 mg) and Ca(NO₃)₂ (5 mg) were added and stirred for 1 h. Then, a solution of KMnO₄ (3.0 mg) in water (2 mL) containing Ca(OH)₂ (pH = 9) was added at 4 °C and stirred for 30 minutes.

Characterization

MIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400-4000 cm⁻¹. TEM, EDX and SEM images were obtained with Philips CM120, VEGA\TESCAN-XMU and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-Kα radiation). Mn atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectra AA 110. Prior to analysis, the oxide (2.0 mg) was added to concentrated nitric acid and H₂O₂, left at room temperature to ensure that the oxides were completely dissolved. The solutions were then diluted to 50.0 or 100.0 mL and analysed by AAS.

Cyclic voltammetry 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 MnO_x-PGA, 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 by Autolab Nova software.

Fabrication of modified electrode

The Pt electrode was mechanically polished with 1, 0.3 and 0.05 μm alumina and washed ultrasonically with ethanol and distilled water. Then, 30 μL of the suspension was dripped on the Pt electrode surface and dried at room temperature. Eventually, 10 μL of 0.5 wt % Nafion solution was deposited onto the center of the modified electrode. A three-electrode system was applied for investigation of electrochemical properties of modified electrodes by cyclic voltammetry in a 0.1 M pH 6.3 lithium perchlorate solution.

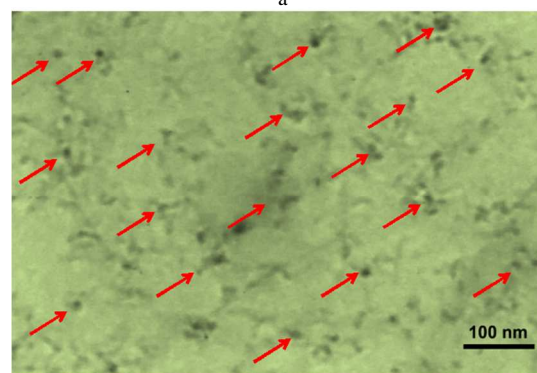
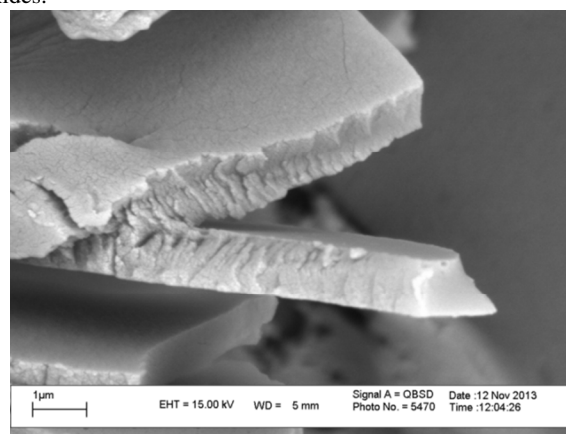
Results and discussion

We synthesized MnCaO_x-PGA in water by a simple method as a soluble brown solution. The main purpose of choosing PGA was simulation of the WOC for developing new efficient catalyst. Carboxylate groups in the protein can act as proton acceptor, inhibit acidic condition and provide a buffer-like environment for Mn-Ca oxide (buffer-like effect). The pK_a of PGA in solution is

close to 4.2.⁹

The residues participate in proton transfer and management (proton management effect).¹⁰ The carboxylate groups, similar to N-donor ligands,¹⁷ stabilize Mn(III) or Mn(IV) and can reduce over potential for water oxidation (electrochemical effect). Similar to ferritin,¹¹ glutamic acid residues are involved in Mn-Ca oxide core nucleation. The primary amino acid sequence of the proteins involved in biomineralization often includes high amounts of aspartic acid and glutamic acid residues,¹² which have a high affinity for Ca, Mn, Fe and other hard ions. The Mn cluster formation in PSII may be also considered as biomineralization.⁴ Similar to PSII, these groups may inhibit leaking Mn ions from the surface of oxide to solution (chelating effect).¹³ The peptide bonds can transfer electron to electrode.¹⁴ PGA around Mn-Ca oxides is important to obtain a soluble Mn-Ca oxide (a homogenized heterogeneous catalyst) (dispersing effect). It is found that the protein inhibits aggregation of nanoparticles. Such proteins in the structure of compounds can be also used as linkers or erector sets to join complex synthetic systems such as photosensitizers.¹⁵

On the other hand, as layered nano-sized Mn oxide is an efficient and stable catalyst for water oxidation,¹⁶ we used a layered Mn-Ca oxide as active site for water oxidation and placed it in a PGA matrix. The compound was more characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and dynamic light scattering (DLS). SEM images show MnCaO_x-PGA consists of small nanoparticles (diameter: ~ 10 nm) that form films with thickness of ~ 880 nm. TEM images also showed that the compounds contain nano-sized layered Mn oxide (diameter < 10 nm) (Fig. 2). HRTEM images show that the distance between two layers is 0.8-0.9 nm related to layered Mn oxides.⁶



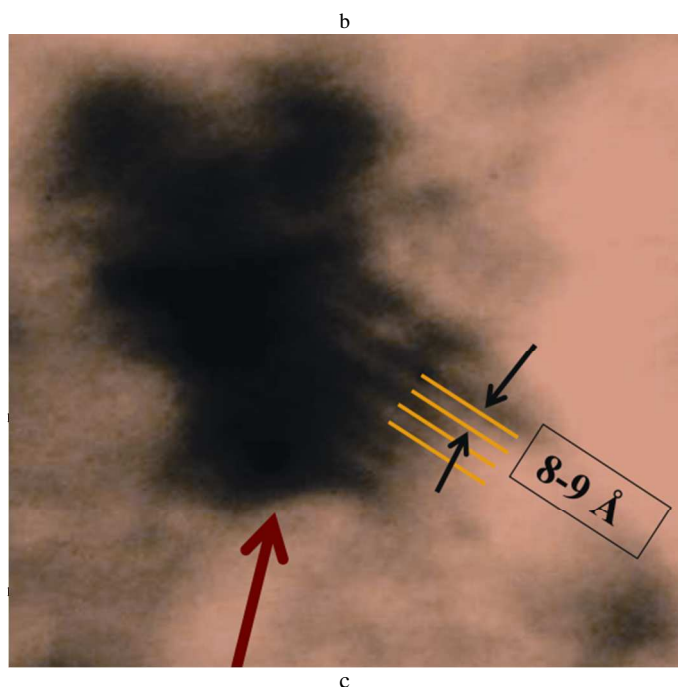


Fig. 2 SEM (a) TEM (b) and HRTEM (c) images of dispersed MnCaO_x-PGA in water. The red arrows show some nanolayered Mn-Ca oxide in PGA matrix. Yellow lines in c show layers. The distance between two layers is 0.8-0.9 nm related to layered Mn oxide.⁶

The compound shows a new peak in ~ 400 nm in UV-Vis related to Mn oxide formation in this compound (Fig. 3).¹⁸ The XRD patterns of MnCaO_x-PGA were of poor resolution and no pattern was detected. DLS indicated particles in the range of 20-70 nm. The FTIR spectrum of PGA-MnCaO_x shows a broad band at ~3200-3500 cm⁻¹ related to antisymmetric and symmetric O-H stretchings. At ~ 1630 cm⁻¹, H-O-H bending mode is observed. The absorption bands characteristic for a MnO₆ core in the region 488 and 657 cm⁻¹ assigned to stretching vibrations of Mn-O bonds in MnCaO_x was observed. Other peaks at 1599, 1413, 1093 and 1026, and 697 cm⁻¹ related to the modes of polypeptides were also observed. COOH modes for PGA is observed at 1640 cm⁻¹. In PGA-MnCaO_x, two modes are observed for the group at 1644 and 1559 cm⁻¹ that are related to coordination of COO⁻ to metal ions.¹⁹ Thus, from FTIR Spectra (Fig. S8 and S9 †ESI), we suggest coordination of carboxylate groups to Mn ions on the surface of Mn-Ca oxide.

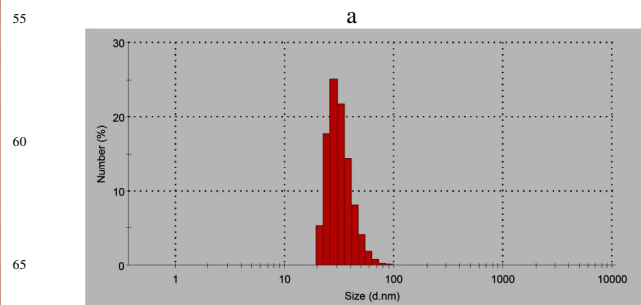
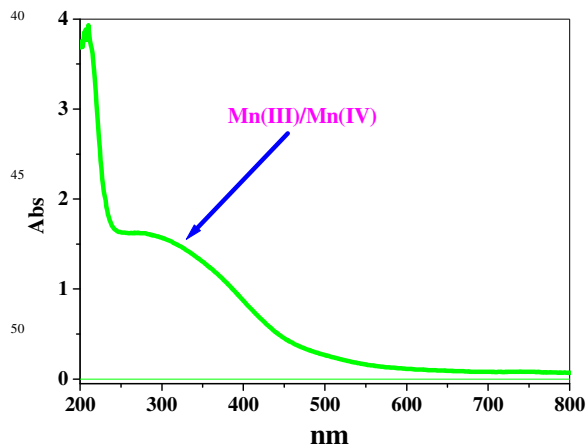


Fig. 3 UV-Vis spectrum of MnCaO_x-PGA. PGA shows no peak in the range of 400 nm (a). Results for DLS experiments without sonicated (error: 0.1 nm) (b).

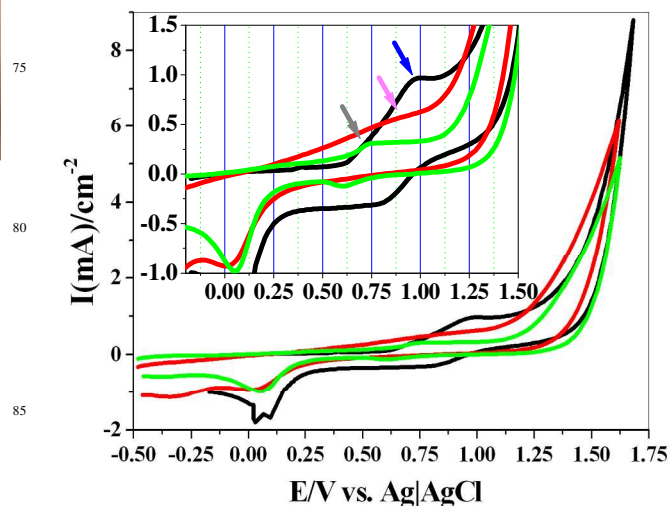


Fig. 4 Cyclic voltammograms (CVs) of a PGA-Pt electrode (red), MnCaO_x-PGA-Pt (green) and MnCaO_x-Pt (black) (LiClO₄ in water (0.1 M), pH = 6.3) at a scan rate of 100 mV s⁻¹. The grey and blue arrow indicates the potential at which Mn(III)/(IV) oxidation occurs for MnCaO_x-PGA and MnCaO_x, respectively. The magenta arrow shows the related peaks for PGA. Such peaks cannot be observed in Pt electrode (Fig. S11).

A peak is also observed around 0.72 (vs. Ag|AgCl|KCl) that shows some reversibility and is related to Mn(III)/(IV) oxidation. The related peak for Mn(III)/(IV) oxidation in Mn-Ca oxide, without PGA, is observed around 0.97 (vs. Ag|AgCl|KCl). It indicated that PGA stabilizes high valent Mn oxide (Fig. 4).

Recently, C. N. R. Rao suggested that the e_g orbital of the transition metal ions can form σ-bonds with anion adsorbates and influence the binding of intermediate species to the catalyst during oxygen evolution.²⁰ The localized single e_g electron in the antibonding σ*-state can be donated during the oxygen evolution cycle.¹⁸

Conclusion

In summary, we have depicted a novel structural model for the WOC in Photosystem II and a new viewpoint to the artificial photosynthesis field. MnCaO_x and PGA in the compound are similar to Mn cluster, and the protein environment in PSII, respectively. We also found PGA decrease Mn(III)/Mn(IV)

oxidation potential more than 0.2 V, and thus stabilizes high valen Mn ions. As in PSII, there are many carboxylate groups, we can relate the effects of such groups to stabilize Mn(IV) ions.

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Notes and references

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²⁰ † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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