



Electrochemistry  
 Nano-sized manganese oxide  
 Water-oxidizing enzyme  
 Hydrogen production

Mn(III)/Mn(IV) oxidation on Mn–Ca oxide and it is decreased in the presence of the polypeptide. We also found that the peptide has an important role on morphologies of Mn–Ca oxide.

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## Introduction

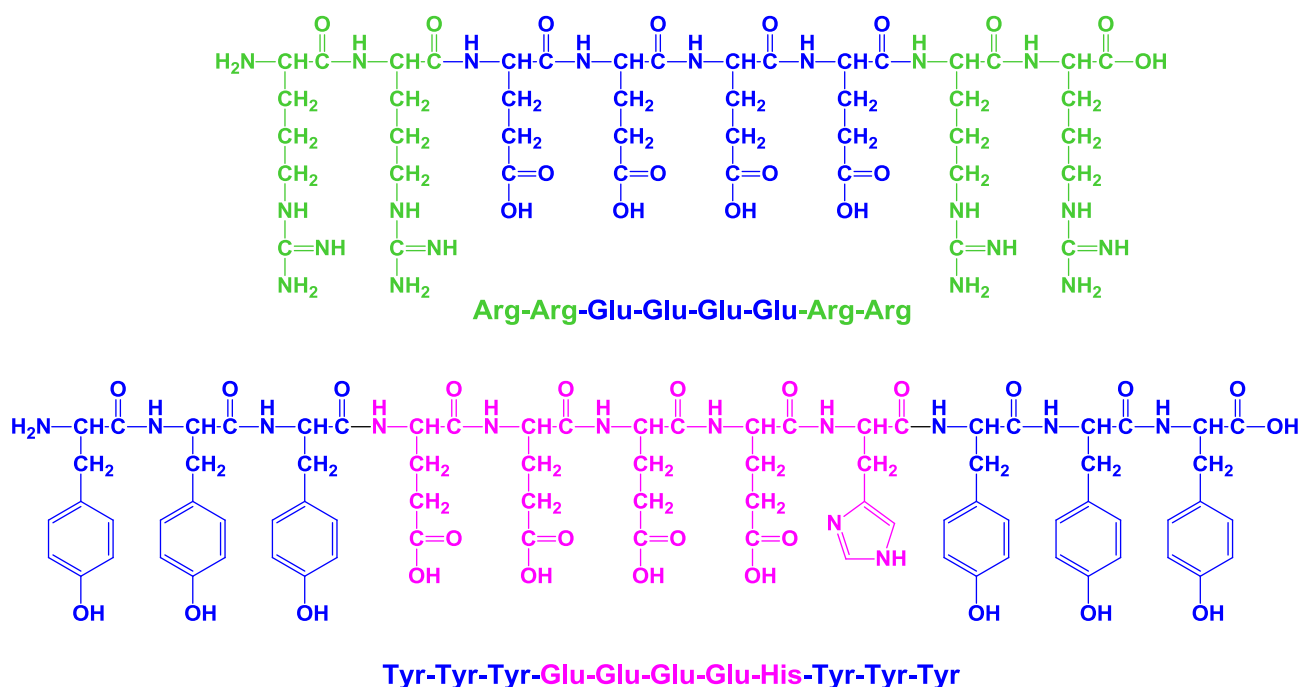
The water oxidation, which occurs in oxygenic photosynthesis, is the main source of the atmospheric oxygen and the  $\text{Mn}_4\text{CaO}_5$  cluster in Photosystem II (PSII) which is the only known water-oxidizing enzyme in Nature [1–3]. Recently, Shen's group reported the crystal structure of the Mn–Ca cluster at 1.9 Å resolution [1–3]. The  $\text{Mn}_4\text{CaO}_5$  cluster is surrounded by a protein environment. Seven amino acid-side chains are coordinated to the  $\text{Mn}_4\text{CaO}_5$  cluster, of which six are carboxylate residues and one is an imidazole residue [1–3]. These amino acids and terminal water ligands are coordinated to Mn(III) or (IV) and  $\text{Ca}^{2+}$  ions, constitute an environment for the Mn–Ca cluster [1–3]. In addition to it, other amino acid residues are H-bonded to oxo-bridged oxygen atoms of Mn–Ca cluster [1–3]. Hydrogen bonds to the oxo-bridges involving two positively charged residues (Arg357 and His337) provide an important role for stability, proton transfer and the flexibility of the Mn–Ca cluster to undergo structural changes during the catalytic cycle (S-state transition). The distorted chair form of the cluster with high

flexibility can be important for the water-oxidizing activity [1–3].

Inspired by Nature, designed efficient catalysts for water oxidation have been reported by different groups [4–10]. Among many metal oxides, Mn oxides are promising as catalysts for water oxidation because they are low-cost, non-toxic, stable, and environmentally friendly [5–28]. Glikman and Shcheglova first reported on water-oxidizing activity of  $\text{MnO}_2$  in the presence of ceric perchlorate [20]. The Morita's group investigated electrochemical water oxidation of  $\text{MnO}_2$  [21]. Harriman's experiments showed that Mn(III) oxide is an efficient catalyst for water oxidation in the presence of Ce(IV) or  $\text{Ru}(\text{bpy})_3^{3+}$  as chemical oxidant [22].

Najafpour and Kurz, inspired by the Mn–Ca cluster structure in PSII, synthesized a new Mn–Ca oxide catalyst by oxidation of  $\text{Mn}^{2+}$  ions in the presence of  $\text{KMnO}_4$  [14].

The  $\text{Mn}_4\text{CaO}_5$  cluster in PSII is surrounded by specific protein environment. Such organic matrix is believed to improve buffering and stabilize environmental conditions for the water-oxidizing activity of the  $\text{Mn}_4\text{CaO}_5$  cluster [1–3]. Among these amino acid residues, tyrosine 161 ( $\text{Y}_2$ ) functions as a mediator of the electron transfer between the  $\text{Mn}_4\text{CaO}_5$



Scheme 1 – Schematic structure of the engineered polypeptides used to obtain the title catalysts.

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