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# Polypeptide and Mn–Ca oxide: Toward a biomimetic catalyst for water-splitting systems

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## ABSTRACT

Water oxidation is the bottleneck for hydrogen production by water-splitting systems using sunlight or other sustainable energies. Herein we report nano-sized Mn–Ca oxide in an engineered polypeptide (Glu-Glu-Glu-Glu-Glu-Glu-Glu-His-Val-Val-Val-Val-Val-Val-Val-Val) as a structural model for biological water-oxidizing site in plants, algae, and cyanobacteria. The compound was synthesized by a simple procedure and characterized by transmission electron microscopy, atomic absorption spectroscopy, scanning electron microscopy, energy-dispersive spectroscopy, X-ray diffraction spectrometry, UV–Visible spectroscopy, dynamic light scattering, and some electrochemical methods. Using hydrogen to store sustainable energies is a promising strategy in near future and such nano-sized Mn–Ca oxide/polypeptide is a promising strategy in water-splitting systems to provide cheap electrons from water toward hydrogen production.

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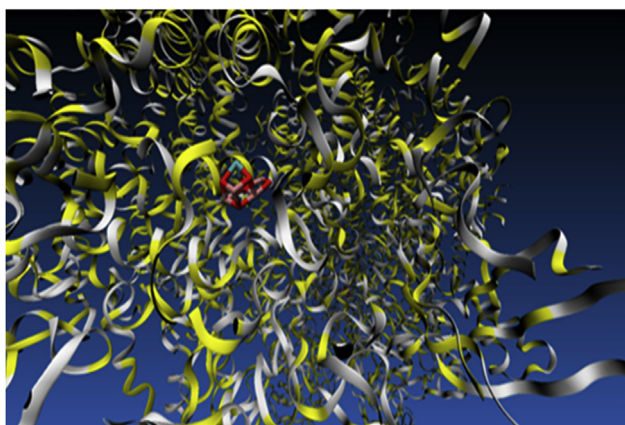
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## Introduction

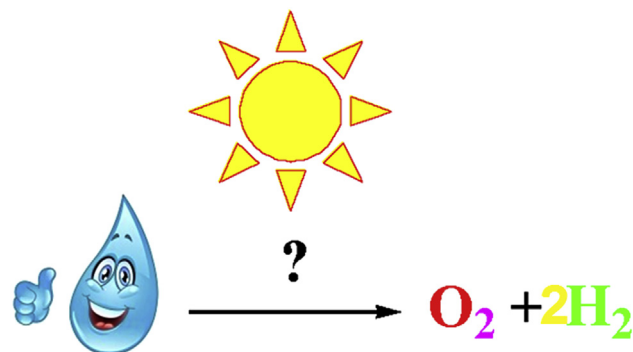
The nucleation and assembly of inorganic materials in biological systems are controlled by organic molecules [1]. In this context, an enzyme may be considered as a nano-sized inorganic core in a protein matrix [2–5]. Thus, the cofactor formation particular in enzymes may be known as a biomineralization in the presence of the protein [3,4]. The water-oxidizing complex (WOC) or oxygen-evolving complex (OEC) of Photosystem II (PSII) in plants, algae and cyanobacteria is a  $\text{Mn}_4\text{CaO}_5$  cluster catalyzing light-induced water oxidation [6,7]. PSII consists of hundreds of amino acids, but there is only a small fraction of the residues that comes in contact directly with the Mn–Ca cluster. Other residues are involved in stability of the structure of this cluster, proton, water or oxygen transfer [6,7]. A careful analysis shows that after hydrophilic groups, carboxylate and imidazole groups, the second sphere around Mn cluster are hydrophobic residues (Fig. 1). The hydrophobic residues are important to oxygen transfer and most probably to provide a hydrophobic and insoluble matrix for Mn–Ca cluster.

In view of the increasing energy consumption and the serious environmental problems, finding sustainable and clean energy sources is a kind of urgent demand in the entire world. However, many sustainable and clean energies are intermittent and, to be practical at a large scale, a good energy storage is necessary for them. Among different compounds, hydrogen has been vigorously considered an energy storing material [8]. A promising way to produce hydrogen is through water splitting by electrochemical or photochemical reactions. Water splitting (Scheme 1) composed of both hydrogen evolution reaction at cathode and oxygen evolution reaction at anode [8].

However, water oxidation in anode needs high activation energy barrier for O–O bond formation and thus hydrogen production is severely restricted by the anodic reaction [8]. Thus, great efforts should be made to find an efficient and stable catalyst for water oxidation [5,8].



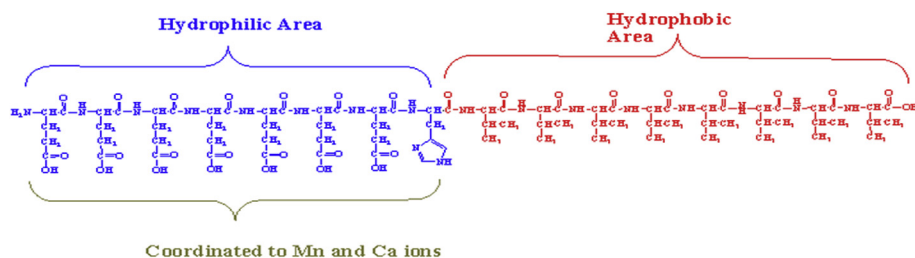
**Fig. 1 – Hydrophilic (white) and hydrophobic (yellow) residues around Mn–Ca cluster from data and PDB (3ARC) from Ref. [7]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)**



**Scheme 1 – Hydrogen production using sunlight and water.**

The design and synthesis of efficient, low-cost, and environmentally friendly water-oxidizing manganese-based compounds are highly desirable because they are not only as a model for the WOC, but also as a key component of artificial photosynthesis for water splitting into  $\text{H}_2$ , fuel, and  $\text{O}_2$  [5]. PSII is a large molecule with low active site densities and can be considered as a small nano-sized Mn–Ca oxide ( $\sim 0.5 \times 0.25 \times 0.25 \text{ nm}^3$ ) in a huge protein environment ( $\sim 10.5 \times 20.5 \times 11.0 \text{ nm}^3$  for cyanobacterial PSII dimers) [6,7]. However, industrial processes and artificial photosynthetic systems need high active site densities.

Among Mn compounds [8–12], Mn oxides were reported as good biomimetic models for the WOC in PSII [13–29]. Russian scientists introduced Mn oxides as catalysts toward water oxidation in the presence of chemical oxidants [13,15]. Electrochemical water oxidation by  $\text{MnO}_2$  was reported by Morita in 1977 [14]. Harriman's group in 1988 extensively studied many metal oxides as water-oxidizing catalysts in the presence of chemical oxidants [16]. Among these metal oxides, cobalt, iridium, manganese(III) and ruthenium oxides were reported as efficient catalysts [16]. The calcination temperature, surface effects and also different supports were considered by this group [16]. Efficient water oxidation by nanostructured Mn oxide clusters supported by mesoporous silica in the presence of  $\text{Ru}(\text{bpy})_3^{3+}$  was reported by Frei and Jiao [17]. They proposed important roles for the silica support: providing high surface area for Mn oxides, protecting the Mn ions from deactivation by surface restructuring and helping in proton transfer [17]. Water oxidation by Mn oxide minerals [18], Mn oxide with organic groups [19,20], protein [21] and Mn oxide/photosensitizer [22] were also reported. Among different Mn oxides, layered A-Mn oxides (A: inert-redox ions) were reported as efficient catalysts for water oxidation [23–28]. The effects of biogenic synthesis [29], the manganese precursors [30], calcination temperature [31] and partial oxidation of nanostructured MnO particles [32] on water oxidation were reported by different research groups. Dismukes group synthesized very pure  $\beta\text{-MnO}_2$ ,  $\text{R-MnO}_2$ ,  $\alpha\text{-MnO}_2$ ,  $\delta\text{-MnO}_2$ ,  $\lambda\text{-MnO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{Mn}_3\text{O}_4$  compounds [33]. They found that  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  are among the most active Mn oxides for water oxidation. The Mn(III)–O bonds in edge sharing octahedra at the surface are proposed as active sites for water oxidation [33].

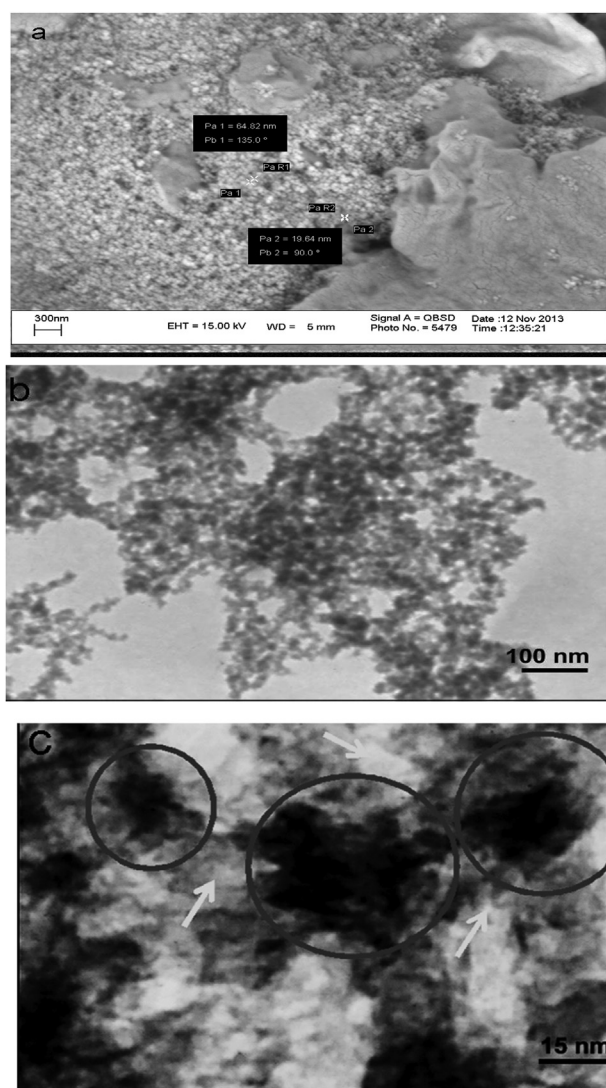


**Scheme 2 – Schematic structure of the engineered polypeptide used in the catalyst (1).**

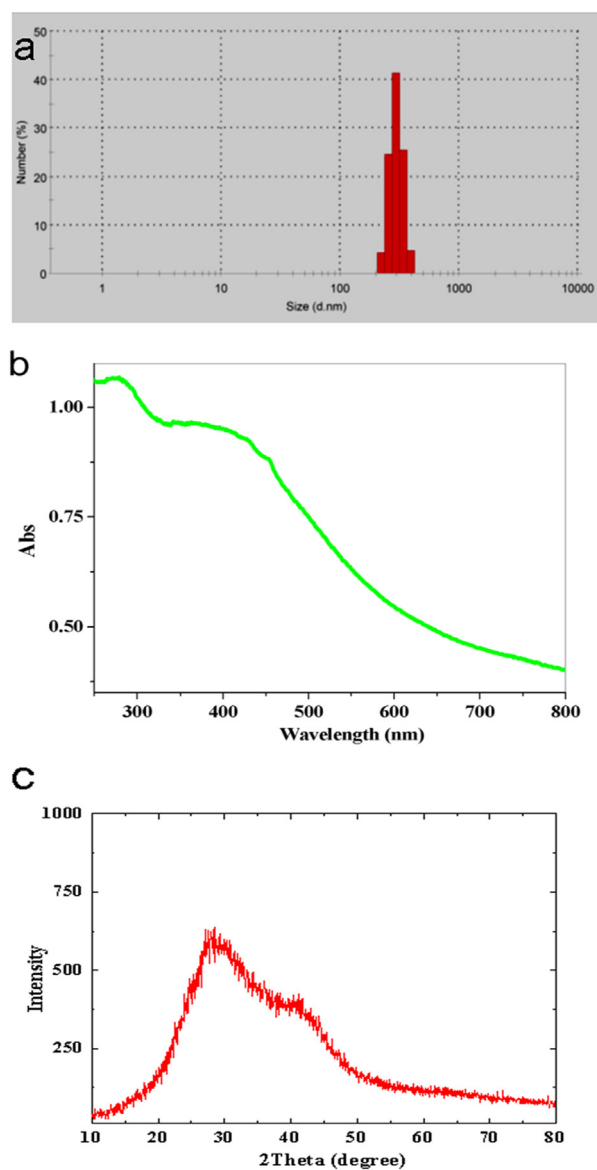
The roles of inert-redox ions in the structure are not known, but considerable thermodynamic stability, high surface area, smaller oxidation enthalpy, low surface enthalpy, and also relatively loose binding of H<sub>2</sub>O on the nanoparticle surfaces are proposed as the efficiency of water oxidation by these oxides [34].

Some groups reported that gold particles on these layered Mn oxides improve their activity towards water oxidation both chemically and electrochemically [35,36].

It was shown that many phases from Mn oxide in the presence of Ce(IV) or in electrochemical water oxidation convert to a layered Mn oxide [37,38]. Self-healing for Mn

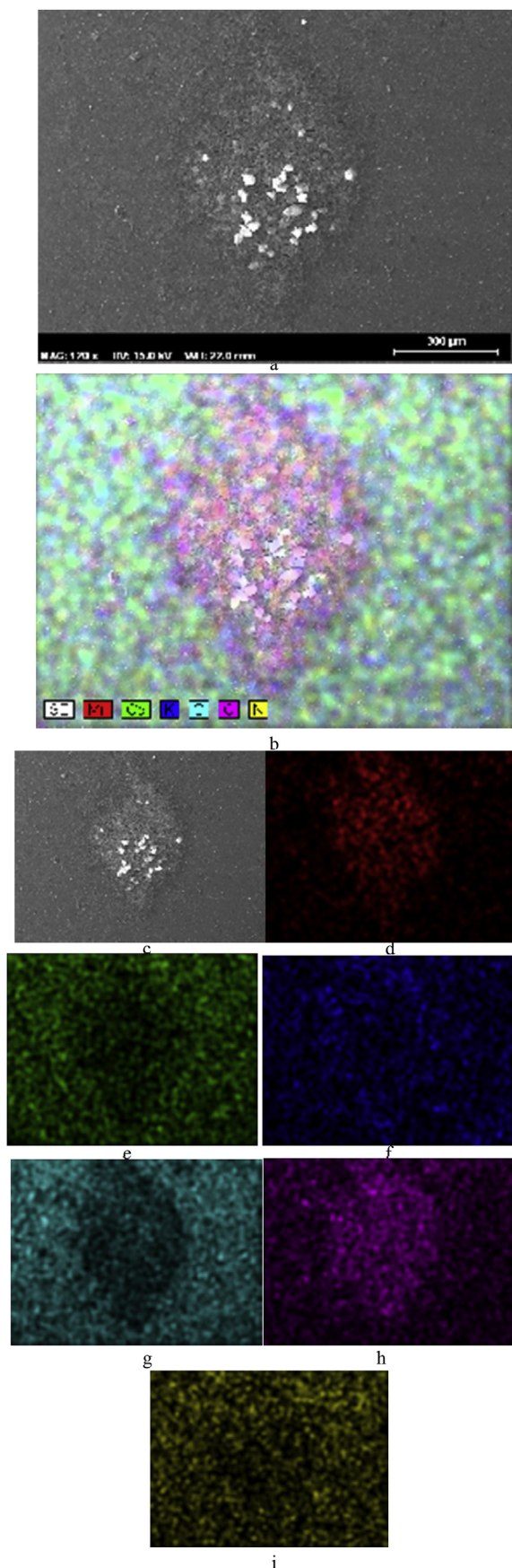


**Fig. 2 – SEM (a) and TEM (b, c) images of 1. The Mn–Ca oxide particles are located in black circle. The polypeptide is around Mn–Ca oxide nanoparticles (shown by white arrows).**



**Fig. 3 – DLS (a), UV–Vis spectrum (b) and XRD (c) for 1.**





oxides were also reported by some groups in water-oxidation condition [39–43]. In the self-healing reaction, decomposition products from Mn oxide in the water-oxidation reaction can react or combine to remake Mn oxide [39–43]. Dutta and Suib's groups reported amorphous, birnessite, and cryptomelane type tunnel Mn oxides as water-oxidizing catalyst. Among them, amorphous Mn oxide was reported as an efficient catalyst toward water oxidation [44].

On the other hand, a few groups reported that treatment of Mn oxide with organic compounds produce an efficient catalyst for water oxidation with a low overpotential [45–48].

Herein, based on the efficiency of Mn–Ca oxido cluster in the presence of organic matrix in natural [6,7] and artificial systems [45–48], we report a nano-sized Mn–Ca oxide with an engineered polypeptide-matrix as a promising bio-mimetic model for water-oxidizing catalyst in water-splitting systems.

## Material and methods

All reagents were purchased from commercial sources and were used without further purification. The engineered polypeptide (purity ~ 90%) was ordered Peptidebiotech co., ltd.

### Synthesis

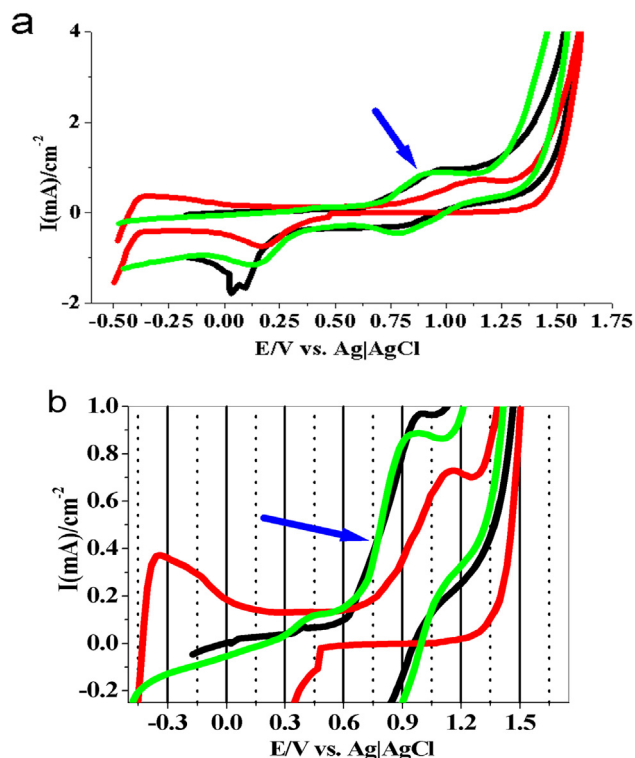
1: The compound was synthesized by a very simple method. In brief, to the engineered polypeptide (25 mg) (Scheme 2, Figs. S1 and S2, ESI†) in water (10 mL),  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (6 mg) and  $\text{Ca}(\text{NO}_3)_2$  (3 mg) was added and stirred for 1 h. Then, a solution of  $\text{KMnO}_4$  in water (1.8 mg in 2 mL) containing  $\text{Ca}(\text{OH})_2$  (pH = 9) was added at 4 °C and the mixture was stirred for 30 min.

### Characterization

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-K $\alpha$  radiation). Atomic Absorption Spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectra AA 110 to detect Ca and Mn ions. Prior to analysis, the compound (2.0 mg) were added to concentrated nitric acid and  $\text{H}_2\text{O}_2$ , then 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 analyzed by AAS to detect calcium and manganese ions.

Electrochemical experiments were performed using an EmStat<sup>3+</sup> from PalmSens Company (Netherlands). In this case, a conventional three electrodes set-up were used in which a Pt electrode or Pt electrode modified with 1-Pt, an Ag|AgCl|KCl<sub>sat</sub> electrode and a Pt rod served as the working, reference and auxiliary electrodes, respectively.

**Fig. 4** – EDX-Mapping for a film of 1 (a, b). SEM image (c) and EDXMapping for Mn (d), Ca (e), K (f), O (g), C (h) and N (i) in a film of 1.



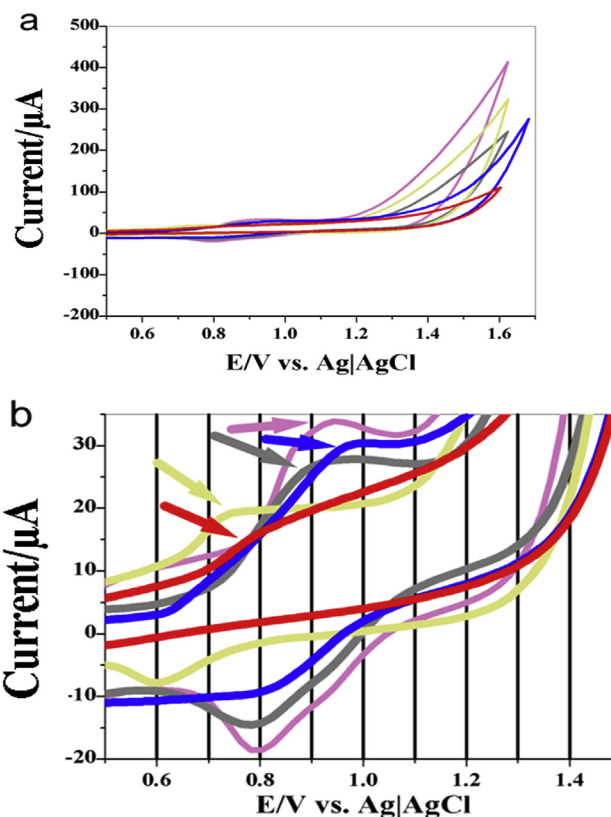
**Fig. 5** – CVs of a peptide-Pt electrode (red), 1-Pt (green), and  $\text{MnCaO}_x$ -Pt (black) in  $\text{LiClO}_4$  solution (0.1 M,  $\text{pH} = 6.3$ ) vs.  $\text{Ag|AgCl|KCl}_{\text{sat}}$ , at a scan rate of  $100 \text{ mV s}^{-1}$ . The blue arrow shows the  $\text{Mn(III)/Mn(IV)}$  oxidation peak. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

#### Fabrication of modified electrode

The Pt electrode was mechanically polished with 1, 0.3 and  $0.05 \mu\text{m}$  alumina and ultrasonicated in distilled water and ethanol to remove the adsorbed alumina particles. Then,  $30 \mu\text{L}$  of compound (1) suspension was dripped on the Pt electrode surface and dried at room temperature. Eventually,  $10 \mu\text{L}$  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, linear sweep voltammetry, differential pulse voltammetry and differential pulse voltammetry and Square wave voltammetry.

## Results and discussion

We used engineered polypeptide (Glu-Glu-Glu-Glu-Glu-Glu-Glu-His-Val-Val-Val-Val-Val-Val-Val-Val-Val, Scheme 2, for characterizations see: Figs. S1 and S2, ESI†) around nano-sized Mn–Ca oxide to obtain 1 inspired by the WOC in PSII. We selected this sequence because carboxylate and imidazole groups in the polypeptide can act as Mn–Ca oxide core nucleation agent, proton acceptors, proton transfer, and inhibitor for acidic condition [49,50]. They can also provide a buffering environment for Mn–Ca oxide (buffering effect).

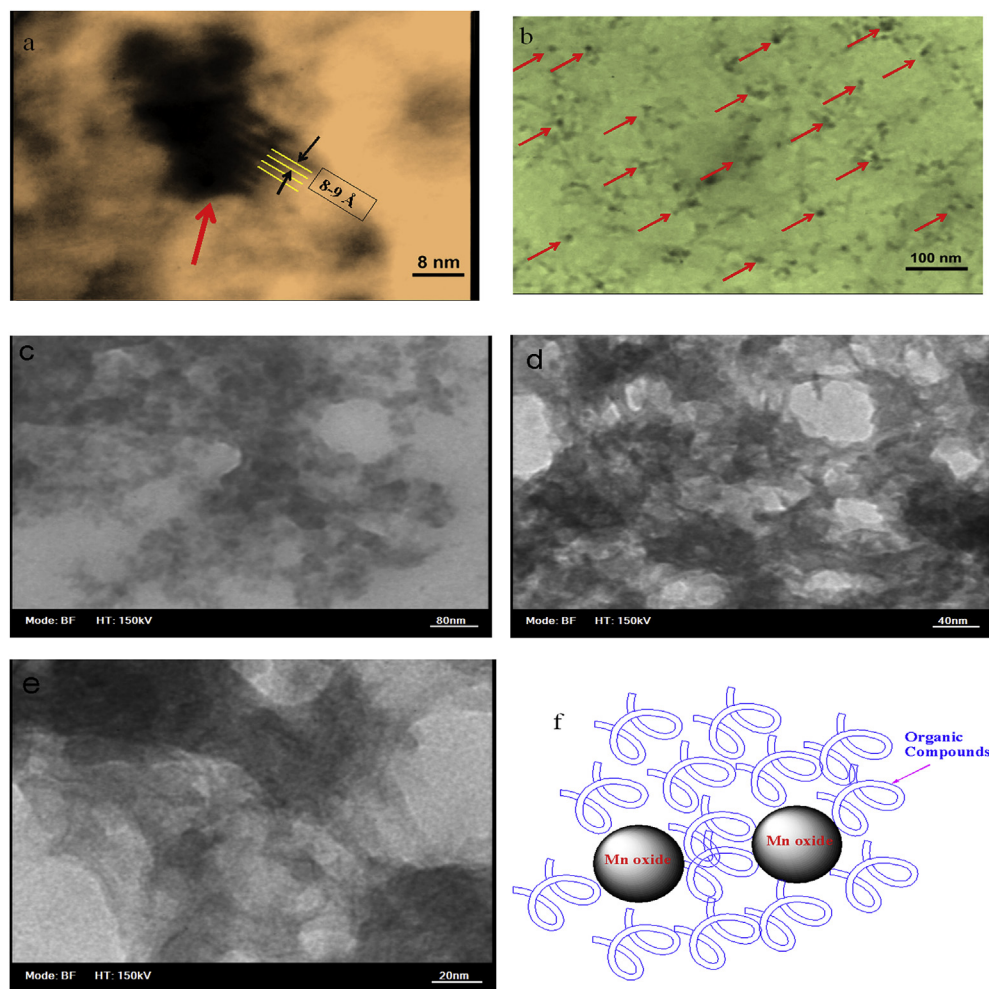


**Fig. 6** – CVs of a 1-Pt electrode (gray), poly(4-vinylpyridine)/ $\text{MnCaO}_x$ -Pt (red), Glu-Glu-Glu-Glu-Glu-Glu-Glu-His-Val-Val-Tyr-Val-Val-Tyr-Val-Val/MnCaO<sub>x</sub>-Pt (magenta), poly-L-glutamic acid/ $\text{MnCaO}_x$ -Pt (yellow), and  $\text{MnCaO}_x$ -Pt (blue) in  $\text{LiClO}_4$  solution (0.1 M,  $\text{pH} = 6.3$ ) vs.  $\text{Ag|AgCl|KCl}_{\text{sat}}$ , at a scan rate of  $100 \text{ mV s}^{-1}$ . The blue arrow shows the  $\text{Mn(III)/Mn(IV)}$  oxidation peak. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

These organic groups stabilize Mn(III) and reduce overpotential for water oxidation (electrochemical effect) [45–48]. Similar to PSII [6,7] the polypeptide is stable in the presence of oxidants and the peptide bonds can transfer electrons to an electrode (electron transfer effect) [51]. On the other hand, the hydrophobic and bulky groups from valine decrease the solubility in water that is necessary to use the compound as a heterogeneous catalyst.

1 was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and dynamic light scattering (DLS). Nano-sized Mn–Ca oxides (diameter: 20–70 nm) are observed in SEM images (Fig. 2a and Fig. S3, ESI†). TEM images also show amorphous nanoparticles from Mn–Ca oxides with diameter: 20–70 nm (Fig. 2b, c and Fig. S4, ESI†).

DLS results show bigger particles than they are observed in SEM images because of agglomeration of particles (Fig. 3a). In UV–visible spectrum of 1, a peak at  $\sim 400 \text{ nm}$  is observed which, is related to Mn–Ca oxide formation in this compound (Fig. 3b). This peak is also observed in layered Mn–Ca oxide without polypeptide (Fig. S5, ESI†).



**Fig. 7** – TEM images from poly-L-glutamic acid/MnCaO<sub>x</sub> (a, b), poly (4-vinylpyridine)/MnCaO<sub>x</sub> (c) and Glu-Glu-Glu-Glu-Glu-Glu-Glu-His-Val-Val-Tyr-Val-Val-Tyr-Val-Val/MnCaO<sub>x</sub>/MnCaO<sub>x</sub> (d, e). Schematic image of Mn oxide into organic matrix (f). c with modification is from Ref. [47]. d and e with modification are from Ref. [48].

The peak is related to the d–d transitions of Mn ions in the octahedral site. XRD patterns show that the structure of Mn–Ca oxide is amorphous (Fig. 3c).

Energy-dispersive spectroscopy (EDX)-Mapping images show different elements in the film (Fig. 4). EDX point analysis also shows that 1 is not a homogenous film and the islands of Mn–Ca oxide are detected (Fig. S6, ESI<sup>†</sup>).

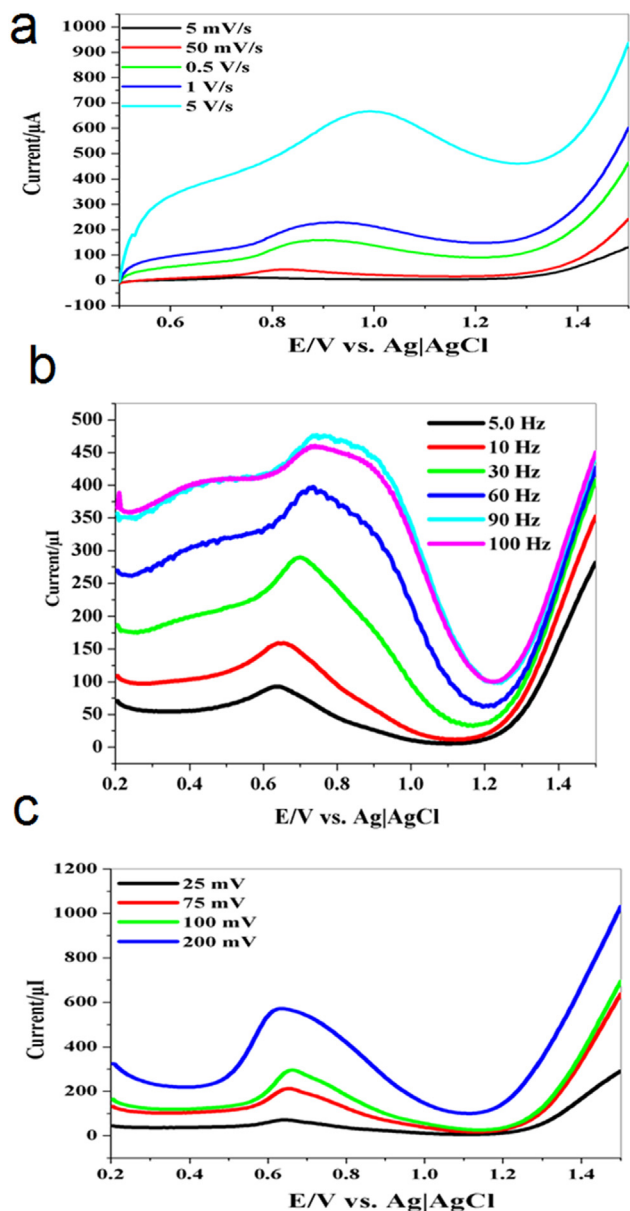
The presence of functional groups was analyzed by Fourier transform infrared spectra (FTIR). The FTIR spectrum of the homogeneous film with higher amounts of MnCaO<sub>x</sub> shows a broad band at ~3000–3600 cm<sup>-1</sup> related to asymmetric and symmetric O–H stretchings and at ~1635 cm<sup>-1</sup> related to H–O–H bending. The absorption bands characteristic for a MnO<sub>6</sub> core in the region 400–500 cm<sup>-1</sup> assigned to stretching vibrations of Mn–O bonds in Mn–Ca oxide were observed [52]. Other peaks for polypeptide at 1548, 1420, 1124, 1081, 1023, 883, 708 and 627 and for 1 at 1599, 1385, 1065 and 700 cm<sup>-1</sup> related to the modes of polypeptides were also observed (Figs. S8 and S9) [53]. After Mn–Ca oxide formation, the changes were observed at ~1400–1600 cm<sup>-1</sup> related to the binding mode of the COO<sup>-</sup> groups to Mn ions [53].

In electrochemical studies, Cyclic voltammograms (CVs) of polypeptide shows a peak at 1.12 V vs. Ag|AgCl|KCl<sub>sat</sub> that related to oxidation of organic groups in the structure of the catalyst. A peak at about 1.0 V vs. Ag|AgCl|KCl<sub>sat</sub> in Fig. 5a, b is assigned to oxidation of Mn(III)/Mn(IV) in 1 [28,48].

Comparing the CV of 1 with Mn–Ca (without the polypeptide) displayed some similarities, but the peak potential for Mn(III)/Mn(IV) in 1 occur in lower potential. To confirm this statement, the CVs of Mn–Ca oxide in the presence of Poly (4-vinylpyridine) [47] poly-L-glutamic acid and a polypeptide contain tyrosine groups (Glu-Glu-Glu-Glu-Glu-Glu-Glu-His-Val-Val-Tyr-Val-Val-Tyr-Val-Val) [48] were studied and the results are displayed in Fig. 6.

The result implies that the potential of anodic peak for Mn(III)/Mn(IV) decreases in the presence of these polypeptide. For all of these compounds, very similar morphologies can be obtained, which contain a dispersed Mn–Ca oxide into an organic matrix (Fig. 7a–f). Comparing with Mn–Ca oxide formed in the absence of organic matrix, organic matrix dispersed Mn–Ca oxide significantly. The functional groups in





**Fig. 8** – LSV for 1 at different scan rates (a). SWV for 1 at different frequencies (b) and different pulse height (c). Experiments were performed in  $\text{LiClO}_4$  solution (0.1 M,  $\text{pH} = 6.3$ ) vs.  $\text{Ag|AgCl|KCl}_{\text{sat}}$ .

organic matrix cause a decrease in potential for Mn(III)/Mn(IV) oxidation peak.

The difference in the currents per pulse is measured and plotted the base potential peak-shaped voltammogram [54].

Linear sweep voltammetry is a very interesting method to obtain clearer peak [54]. In LSV a fixed potential range is employed much like potential step measurements, but the voltage is scanned from a lower limit to an upper limit. LSV plot for 1 at different scan rates is shown in Fig. 8a.

As can be seen, the oxidation peak for Mn(III)/Mn(IV) is clear and the current of peak increases with increasing scan rate. Square wave voltammetry (SWV) is a very promising and interesting method to study of low amount of Mn–Ca

oxide, which has excellent sensitivity and resolution for successive electroactive species in multi-component analyses. It can be used to perform an experiment much faster than normal and differential pulse voltammetry. The ability to measure the Faradaic current at a time when the double layer charging current is negligible, are primarily responsible for their success [55]. In this technique a symmetrical square wave is superimposed on an underlying staircase waveform and the current is sampled at two points for each square wave cycle, at the end of the forward pulse and at the end of the reverse pulse. Then the difference current is plotted as a function of the potential staircase [56]. Fig. 8b and c shows the SWV for 1 at different frequency and different scan rate, respectively. Using this technique for 1 displays clearly the related area for Mn(III)/Mn(IV) oxidation. In this method, the peak current is a function of the square root of the square wave frequency. Such biomimetic compound is promising to be used as a water-oxidizing catalyst in water splitting systems [57–63].

## Conclusions

Polypeptides and small proteins show great promise for the design and creation of new catalysts at the molecular or nanoscale levels for water oxidation. Using an engineered polypeptide, we could synthesize polypeptide/Mn–Ca oxide and used it as a structural model for the WOC in PSII. From the structural aspects, MnCaOx is similar to Mn cluster and polypeptide is similar to the protein environment in PSII. Using electrochemical data, we found that the potential for Mn(III)/Mn(IV) oxidation for Mn–Ca oxide is decreased in the presence of the polypeptide. Engineered polypeptides and small proteins around inorganic clusters can be a new class of water-oxidizing catalysts. The organic compounds may have important roles such as: buffering agent, proton management, electrochemical, bio-mineralization, chelating, dispersing, and electron transfer effects. The compound could be promising artificial enzyme with high active site densities. In the end, many Mn compounds with different strategies were synthesized to aim at the simulation of the WOC, we proposed a strategy to improve low-cost and environmentally friendly Mn–Ca oxides using polypeptides to modify the surface, morphology, redox and so on.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2016.01.131>.

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