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Covalent bonds immobilization of cofacial Mn porphyrin dimers on an ITO electrode for efficient water oxidation in aqueous solutions

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ABSTRACT

We previously reported several manganese porphyrin dimers as the first manganese-containing molecular catalysts for water oxidation, however, in non-aqueous CH_3CN solution containing 5% H_2O. Here, we successfully fabricated these dimers with mono- and hexaphosphonic acid groups, $Mn_2DP\text{-}PO_3H_2$ and $Mn_2DP\text{-}(PO_3H_2)_6$, to covalently assemble them on the surface of ITO electrode (ITO = indium-doped tin oxide) and use the $Mn_2DP\text{-}PO_3H_2$ and $Mn_2DP\text{-}(PO_3H_2)_6|ITO$ assemblies as heterogeneous catalysts for electrochemical water oxidation in aqueous buffer solutions. The mono-phosphonic acid fabricated assemblies showed unprecedent high turnover frequencies (TOFs) (up to 44.9 s^{-1}) at a low overpotential (η = 0.47 V) in a neutral buffer solution. In acidic buffered solutions (pH = 1.5), they showed higher TOFs (up to 47.4 s^{-1}) at a very low overpotential (η = 0.26 V). The robustness of the mono-phosphonic acid fabricated catalysts, $Mn_2DP\text{-}PO_3H_2|ITO$, was tested at a high overpotential (η = 0.80 V). Although they showed an oxygen evolution with 178.3 s^{-1} TOF, the oxygen evolution completely stopped after 11 h electrolysis. UV–vis spectra monitored during the electrolysis clearly indicated the gradual detachment of the catalysts from the ITO surface is likely the main reason of stopping the oxygen evolution. The hexa-phosphonic acid catalyst assembly, $Mn_2DP\text{-}(PO_3H_2)_6|ITO$, however, showed a continuous oxygen evolution without stopping even after 23 h of electrolysis with 199.3 s^{-1} TOF. Tafel plots in different pHs give insights on the mechanism of H_2O oxidation.

1. Introduction

Hydrogen is currently emerging as a clean and eco-friendly fuel to substitute for the current fossil fuels [1–5]. For its sustainable and large-scale production, H_2O via its thermal, chemical, electrochemical, or photochemical splitting is the ideal source [6–10]. H_2O splitting, however, is a challenging process due to its high thermodynamic oxidation potential (E^0 = 1.229 V) and its high kinetic oxidation barrier that leads to the requirement of an extra input energy over 1.229 V known as overpotential, η. Indeed, η is one of the main obstacles toward a successful H_2O splitting at low energy [11,12]. To reduce η, H_2O oxidation catalysts (WOCs) are required. The WOCs should satisfy many other requirements, the most important are as follows: they should be based on earth abundant eco-friendly elements, robust (i.e. show high turnover number, TON) and highly active (i.e. show high turnover frequency, TOF) under benign conditions (pH 7, 1 atm., and room temperature) [11,12].

In the last four decades, extensive efforts have been made to design or discover a robust water oxidation earth-abundant metal-based catalyst with high TON and TOF at a low η. The Nocera group developed efficient water oxidation catalysts based on the earth abundant Co and Ni metals [13–19]. The Co-based catalyst oxidized water with ~15 TON and 0.008 s^{-1} TOF at a relatively low η (0.47 V) in neutral water under ambient conditions. The catalyst forms *in situ* upon the oxidative polarization of an ITO electrode in phosphate- or borate-buffered solutions containing Co^{II} ions. The Ni-based catalyst that electrodeposited on ITO electrode from a Ni^{II}-containing borate solution (pH 9.2) oxidized water at moderate η, 0.61 V. Recently, efficient earth abundant Cu- [20,21] and Fe- [22–24] based water oxidation catalysts have been reported.

Mn is one of the most abundant elements (10th most abundant one in the earth crust [25,26]), the lowest toxic, and the element that has been selected by nature to achieve the highest water oxidation activity in photosynthetic organisms (in photosynthetic organisms, the water oxidation catalyst is a

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μ-oxido-Mn_4Ca-cluster that embedded in a protein ensemble called photosystem II [27–29]). Consequently, a plenty of Mn-based water oxidation molecular [20–39] and/or hetereogeneous [40–47] catalysts have been reported.

We previously reported the use of several cofacial porphyrin dimers linked by a 1,2-phenylene bridge as suitable ligands for holding two Mn or two Fe ions to promote water oxidation to oxygen [48,49] or CO_2 to CO reduction [50,51], respectively. The homogeneous solution of Mn porphyrin dimers, Mn_2DP, in an aqueous acetonitrile solution (5% v/v H_2O in CH_3CN) upon electrolysis at a potential $\geq$1.2 V *vs.* Ag/Ag$^+$ afforded the evolution of oxygen with up to 9.2 TON (based on all dimer concentrations) [48,49]. The decomposition of the Mn porphyrin catalyst during electrolysis, possibly due to the formation of the Mn^{IV} species by incomplete oxidation, might be the reason of its low TON. With use of chemical oxidation, a dinuclear Mn^V-oxo porphyrin species, $HO{-}Mn^V{=}O$ (HO- and =O are axial ligands for a Mn tetraarylporphyrin unit) was successfully prepared as a stable species at rt in the presence of water and was characterized by a vibrational spectroscopy. Upon acidification of the corresponding solution, $HO{-}Mn^V{=}O$ turns to an active species, $[(H_2O){-}Mn^V{=}O]^+$ that quickly oxidizes H_2O to evolve O_2 [48,49]. In order to realize the efficient water oxidation/O_2 evolution system, the complete formation of the active species for water oxidation, $(H_2O){-}Mn^V{=}O$, is essential. In this context, the rapid oxidation of the Mn species to the corresponding Mn^V state is a key for the catalytic system design, so that it does not keep the unstable Mn^{IV} state. To attain this purpose, the direct modification of the Mn catalysts on a conducting electrode through chemical bonds is one of promising ways. Herein, we successfully fabricated these dimers with mono- and hexaphosphonic acid anchor groups, $Mn_2DP\text{-}PO_3H_2$ and $Mn_2DP\text{-}(PO_3H_2)_6$ to strongly fix them on a surface of ITO electrode and use the $Mn_2DP\text{-}PO_3H_2$ or $Mn_2DP\text{-}(PO_3H_2)_6$|ITO assemblies as heterogeneous H_2O oxidation system in pure buffered aqueous solutions. We realized the assemblies catalyze water oxidation to oxygen at low η in acidic, neutral, and basic solutions with unprecedented high TONs and TOFs. Moreover, the monophosphonic acid fabricated assemblies, $Mn_2DP\text{-}PO_3H_2$|ITO, showed an oxygen evolution at TOF = 178.3 s^{-1}, though the oxygen evolution stopped after 11 h of catalysis at η = 0.80 V in 25 mM $Na_2B_4O_7$/0.1 M $NaClO_4$ buffer solution (pH 4.0). UV–vis spectroelectrochemical spectra monitored during the electrolysis clearly indicated the detachment of the catalysts from the ITO surface is likely the main reason of stopping the oxygen evolution. The hexaphosphonic acid dimer assembly, $Mn_2DP\text{-}(PO_3H_2)_6$|ITO that has a stronger binding to the ITO surface than the monophosphonic derivative showed continuous oxygen evolution without stopping even after 23 h of electrolysis with 199.3 s^{-1} TOF under the same conditions applied for the monophosphonic acid dimer assembly.

2. Results and discussion

2.1. Synthesis

The porphyrin dimer ligands bearing mono- and hexaphosphonic acid anchor groups were synthesized by a stepwise method outlined in Schemes S1–S3 (supporting information, SI). Two Mn ions were then inserted into the ligands cavities using reported procedures [48,49]. The mono- and hexaphosphonic acid fabricated Mn porphyrin dimer WOCs, $Mn_2DP\text{-}PO_3H_2$ (**1a-1c**, Fig. 1) and $Mn_2DP\text{-}(PO_3H_2)_6$ (**1d**, Fig. 1) were purified by a flash column chromatography and characterized by traditional spectroscopic techniques including UV–vis and Matrix Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) mass spectra (Fig. S1).

2.2. Anchoring of 1a-1d to the ITO electrode

Soaking a pre-cleaned ITO electrode in a 1 mM ethanolic solution of **1a-1d** then careful washing the surface with EtOH resulted in a stable phosphonate anchoring of **1a-1d** on the ITO surface as indicated from the UV–vis absorption spectra measurements. In a control experiment, Mn porphyrin dimer lacking the phosphonic acid tether, $Mn_2DTPFPP$ did not show binding to the ITO surface indicating the importance of the phosphonic acid as an efficient linker for the catalysts to the ITO surface (Fig. S2, SI). Indeed, the phosphonic acid anchor group has been reported as a stable linker for immobilization of the Ru-based water oxidation dimer catalyst, $[(tpy\text{-}PO_3H_2)(H_2O)_2Ru^{III}]_2O^{4+}$ ($tpy\text{-}PO_3H_2$ = 4′-phosphonato 2,2′:6,2″-ter pyridine) to the surface of ITO electrode.[52] Moreover, the characteristic Soret bands of 1**a-1c**|ITO assemblies (Soret bands at 456 nm, 471 nm and 464 nm for **1a-1c**|ITO assemblies, respectively) were red shifted by ~5–8 nm relative to that of **1a-1c** catalysts in EtOH (Figs. S3a–S5a, SI). This feature is in agreement with that previously reported for other porphyrin and metalloporphyrin modified with an undecanoic acid linker on ITO surface and has been attributed to a side-by-side porphyrin π-aggregation (*J*-aggregate) [53]. The hexaphosphonic acid Mn porphyrin dimer (**1d**), however, exhibits a 2-nm blue shift of the Soret band (Fig. S6a, SI) indicative of a different arrangement of **1d** on ITO surface. The molecular structure of **1a-1d** necessitates the attachment of **1a-1c** through one phosphonate anchor and **1d** through, at least, two phosphonate anchors in a side or front attachment or four phosphonate anchors at the dihedral angles involving the four phosphonate anchors (Fig. S7, SI).

The extent of the surface loading of **1a-1d** on ITO surface increased with the soaking time of ITO in its solution to reach saturation coverage (Γ) in 5-days for **1a-1c** and in 1-day for **1d** at rt (Figs. S3b–S6b). We also found that Γ can be reached in a shorter time (1-day) by heating at 120 °C. The saturation coverage, Γ of **1a-1d** was evaluated from the absorption spectrum on the basis of the equation $\Gamma = 10^{-3}A/\varepsilon$ (*A* and ε are the absorbance of the monolayer and molar absorption coefficient, respectively) [52,54]. Using this equation, Γ of **1a-1d** on the ITO surface is estimated to be 6.9×10^{-12} mol·cm^{-2}, 7.8×10^{-12} mol·cm^{-2}, 5.2×10^{-12} mol·cm^{-2} and 4.3×10^{-12} mol·cm^{-2}, respectively. Also, Γ is estimated from the cyclic voltammetry measurements (see later) to be 6.8×10^{-12} mol·cm^{-2}, 7.6×10^{-12} mol·cm^{-2}, 5.2×10^{-12} mol·cm^{-2}, and 4.2×10^{-12} mol·cm^{-2} for **1a-1d**, respectively based on the i_p-ν relationship using the equation [55]: $i_p = n^2\Gamma F^2\nu/4RT$ where n, F, R, and T are the number of **e**$^-$ where n, F, R, and T are the number of **e**$^-$, Faraday constant, gas constant, and absolute temperature respectively. These values are consistent with those derived from UV–vis measurements.

2.3. Cyclic voltammetric behavior

The cyclic voltammetric (CV) behavior of **1a-1d**|ITO assemblies was studied in 25 mM $Na_2B_4O_7$/0.1 M $NaClO_4$ solution at different pH values. The CV of **1a**|ITO assembly (red line) and ITO blank (black line) at pH 7.0 are shown in Fig. 2a. In addition to the characteristic 2e$^-$ pH-dependent reversible couple of the two Mn centers ($2Mn^{III}/2Mn^{II}$) at −0.05 V *vs.* NHE that used to estimate the saturation surface coverage (Γ) of the catalyst on the ITO surface (Figs. 2a; Inset, S8, S9), a catalytic current peak was observed at ~1.1 V *vs.* NHE (η = 0.28 V) (hereafter, all potentials are indicated against NHE except as noted) that was assigned to the discharge wave of water oxidation to O_2. The catalytic current peak potential is a pH dependent. For example, η of the onset catalytic current potential is 0.15 V at pH = 1.0, 0.28 V at pH = 7.0, and 0.50 V at pH =10.0 (Fig. S10). Similar behaviors were observed with **1b**|ITO (Figs. S11, S12) and **1c**|ITO (Figs. S13, S14) assemblies. The CV