Cooperative electrochemical water oxidation by Zr nodes and Ni-porphyrin linkers of a PCN-224 MOF thin film

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Experimental Methods

Materials: The following reagents and solvents were purchased from the indicated commercial suppliers: propionic acid (99% Acros); pyrrole (Aldrich); methyl 4-formylbenzoate (Aldrich); zirconium chloride (ZrCl₄, ≥99.5%, Sigma Aldrich); meso-Tetra(4-carboxyphenyl)porphine (TCPP, Frontier Scientific); N,N-dimethylformamide (DMF; spectrophotometric grade, Spectrum); formic acid (reagent grade, ≥99.5%, Sigma Aldrich); nickel(II) chloride hexahydrate (NiCl₂·6H₂O, 99.3% Alfa Aesar); fluorine-doped tin oxide (FTO, cleaned via sonication in Alconox/H₂O, isopropanol, acetone, then H₂O with rinsing with H₂O and drying in between, Hartford Glass); acetonitrile (distilled before use, HPLC grade, Spectrum); sodium perchlorate (NaClO₄; 99+%, Aldrich); tetrabutylammonium hexafluorophosphate (TBAPF₆; recrystallized × 4 from ethanol, electrochemical grade, Fluka Analytical).

Synthesis of Ni(II)TCPP: Free-base 5,10,15,20-(4-carboxymethoxyphenyl)-porphyrin, H₂TMeCPP, was synthesized by the Adler method.¹ Briefly, a 1 L round bottom flask was charged
with 500 mL of propionic acid, 9.3 mL pyrrole, and 21.8 g methyl 4-formylbenzoate, and the mixture refluxed for 12 h under N₂. After cooling to room temperature, the product was filtered and washed with acetone. Saponification of H₂TMeCPP to yield free-base 5,10,15,20-(4-carboxyphenyl)-porphyrin, H₂TCPP, was done by stirring 1.0 g H₂TMeCPP in THF (25 mL) and MeOH (25 mL) followed by the addition of aqueous KOH (2.63 g in 25 mL H₂O). The reaction mixture was refluxed for 16 h. After cooling to room temperature, the solvent was reduced under vacuum followed by the addition of 50 mL H₂O. This solution was acidified with 1 M HCl until no further precipitate was formed. The H₂TCPP solid was filtered and washed with H₂O. The metalloporphyrin, Ni(II)TCPP, was prepared by refluxing H₂TCPP (0.8 g) in 100 mL DMF with excess NiCl₂·6H₂O (2.5 g) for 6 h. The crimson product was precipitated out by addition of water then filtered, washed with water, and allowed to dry: ¹H NMR (400 MHz, d₆-DMSO) δ – 8.11 (d, 8H), 8.29 (d, 8H), 8.73 ppm (s, 8H).

**Synthesis of potassium salt of Ni(II)TCPP:** 5,10,15,20-(4-carboxymethoxyphenyl)-porphyrin (H₂TMeCPP) (0.83 g, 0.918 mmol) was dissolved and THF (25 mL) and MeOH (25 mL) followed by the addition of aqueous KOH (2.63 g in 25 mL H₂O) The reaction mixture was refluxed for 16 h. After cooling to room temperature, the solvent was removed under vacuum resulting in a dark brown residue which was suspended in EtOH (100 mL). The precipitate was isolated by vacuum filtration, washed with copious amounts of EtOH and THF and dried under vacuum giving a bright red solid: ¹H NMR (400 MHz, D₂O) δ – 7.33 (s, 8H), 7.93 (s, 8H), 8.06 ppm (s, 8H).

**Synthesis of PCN-224 films:** Films of the PCN-224 MOF were prepared solvothermally. In a 6 dram glass vial, 30 mg ZrCl₄ and 10 mg Ni(II)TCPP (for PCN-224-Ni) or H₂TCPP (for PCN-224-fb) were dissolved in 10 mL DMF followed by the addition of 2 mL formic acid. A clean FTO slide was placed in the vial and heated to 120 °C for 16-18 h, after which time the vials were
removed from the oven and allowed to cool to room temperature. The films were rinsed with fresh DMF and acetone and allowed to dry.

**Characterization. Powder X-ray diffraction (PXRD):** PXRD measurements were performed on powder samples using a Rigaku MiniFlex 600 with Cu(Kα) radiation (Cu−Kα = 1.5418 Å). The PXRD experiments were carried out over a 2θ range of 3–60° in continuous scanning mode (10.0°/min) and a resolution of 0.1°. **Scanning electron microscopy imaging (SEM) and energy-dispersive X-ray analysis (EDX):** A LEO (Zeiss) 1550 field-emission scanning electron microscope, equipped with an in-lens detector, operating at 5.0 kV was used for high-resolution images of the thin films. EDX was collected using a built in Oxford INCA E2H X-ray Energy Dispersive Spectrometer (EDS) system with a Silicon Drifted detector. **X-ray photoelectron spectroscopy (XPS):** XPS measurements were collected using a PHI 5000 Versa Probe III spectrometer with an aluminum anode X-ray source and photon energy of 1486.6 eV. Survey spectra were collected using a 200 μm beam size at 50 W and 15 kV, scanning a range from 1100 eV to 0 eV at a pass energy of 224.0 eV and a step size of 0.8 eV/step. Elemental peak data were collected using a 100 μm beam size at 25 W and 15 kV with a pass energy of 69.0 eV and a step size of 0.1250 eV/step. The emitted photoelectrons were detected by a 32-channel hemispherical analyzer, and the operating pressure of the main chamber was below 10^{-7} Pa during the time of measurement. **Inductively Coupled Plasma−Mass Spectrometry (ICP-MS).** The PCN-224-Ni thin films were digested in 70% nitric acid and heated to 90 °C for 1 h. After filtration through a syringe filter (<0.2 μM), the solution was diluted with water so that the final concentration of nitric acid was 7% by volume. All samples were analyzed for nickel and zirconium content using a Thermo Electron X-Series inductively coupled plasma mass spectrometer (ICP-MS) in accordance with Standard Method 3125-B.
**Electrochemistry.** Electrochemical experiments were performed on a Basi EC epsilon potentiostat using a Ag/AgCl (aqueous saturated KCl) reference electrode. The Ag/AgCl electrode was calibrated against Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$, where the expected $E_{1/2}$ is $+560$ mV vs. NHE. For all aqueous electrochemical experiments, 18.3 mΩ-cm ultrapure water was obtained using a Barnstead EASYpure UV system. **Cyclic Voltammetry (CV).** CV measurements were collected in a three-electrode arrangement using Pt mesh as a counter electrode, Ag/AgCl reference electrode, and PCN-224-Ni/FTO as working electrode. The scan rate was varied over the range of 25-800 mV/s. **Square-Wave Voltammetry (SWV).** SWV measurements were collected in the electrochemical cell described above with a 1 mV step size, 100 mV amplitude, and 3 Hz frequency. **pH Dependence.** The pH dependence of PCN-224-Ni current density of was performed in the electrochemical cell described above in aqueous 0.1 M NaClO$_4$ electrolyte. Electrodes were immersed in the solution and a potential of 1500 mV vs. NHE was applied. The current density was taken after steady-state current was reached after 5 minutes. **Tafel Analysis.** A potential jump experiment was set up using aqueous 0.1 M NaClO$_4$ electrolyte in the standard three-electrode arrangement described above. Overpotentials ($\eta = V - E^o$) ranging from $\eta = 400$ to 800 mV were applied with 50 mV steps. The current was allowed to equilibrate for 5 min. **Oxygen Evolution.** Controlled potential electrolysis (CPE) experiments were performed in a homemade two-compartment bulk electrolysis glass cell. One compartment housed the PCN-224-Ni/FTO working electrode, Ag/AgCl reference electrode, and dissolved oxygen probe, whereas the counter electrode was housed in the secondary compartment separated by a finely porous glass frit. The cell was purged with Argon and sealed prior to experiments. The evolution of oxygen was monitored in solution using a Unisense OXY-Meter.
**Hydrogen peroxide test.** WaterWorks Peroxide Check \( \text{H}_2\text{O}_2 \) indicator strips were used and immersed into the electrolyte solution after the CPE experiment. The color code was used to estimate the \( \text{H}_2\text{O}_2 \) concentration.

Figure S1. The distances between Zr nodes of PCN-224-Ni shown in (A) and (B). (C) The distances between Ni(II)-to-Ni(II) metal centers of co-facial and orthogonal porphyrins within the same channel.\(^3\)

Figure S2. SEM image of solvothermally prepared PCN-224-Ni on FTO showing a film thickness of *ca.* 30 \( \mu \text{m} \).
Figure S3. SEM image of PCN-224-fb film.

Figure S4. CV (solid blue) and SWV (dash blue) of PCN-224-Ni in aqueous 0.1 M NaClO₄.
Figure S5. pH dependence of steady-state catalytic current density at constant potential ($E_{\text{appl}} = 1500$ mV vs. NHE) for PCN-224-Ni in aqueous 0.1 M NaClO₄.

Figure S6. Tafel plot of PCN-224-Ni in aqueous 0.1 M NaClO₄.
Figure S7. Plot of Current density vs. [H$_2$O] generated from CVs of PCN-224-Ni in 0.1 M TBAPF$_6$/CH$_3$CN with increasing H$_2$O concentrations.
Figure S8. Faradaic efficiencies after electrolysis at 1500 mV vs. NHE in aqueous 0.1 M NaClO$_4$. For NiTCPP, a 1 mM solution of the Ni(II)TCPP potassium salt was used.

Figure S9. The structure of PCN-224-Ni framework showing the distance between the water molecule coordinated to Ni center inside the porphyrin ligand and terminal hydroxyl group on Zr-oxo cluster; (C – grey, H – white, O – red, N – blue, Ni – green and Zr – light blue).
Table S1. Summary of ICP-MS data for digested PCN-224-Ni films and solutions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni (mol)</th>
<th>Zr (mol)</th>
<th>Zr:Ni</th>
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<tbody>
<tr>
<td>PCN-224-Ni as synthesized</td>
<td>$4.63 \times 10^{-7}$</td>
<td>$2.38 \times 10^{-6}$</td>
<td>5.15:1</td>
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<tr>
<td>PCN-224-Ni post-electrolysis</td>
<td>$3.05 (\pm 1.22) \times 10^{-7}$</td>
<td>$1.44 (\pm 0.59) \times 10^{-6}$</td>
<td>4.71:1</td>
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<tr>
<td>Solution post-electrolysis</td>
<td>$2.37 (\pm 1.16) \times 10^{-8}$</td>
<td>$2.62 (\pm 0.74) \times 10^{-8}$</td>
<td>1.23:1</td>
</tr>
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Figure S10. XPS of PCN-224-Ni films pre- (red) and post- (blue) electrolysis experiments displaying (A) Ni2p3 and (B) N1s binding energy; SEM images of PCN-224-Ni films pre- (C) and post- (D) electrolysis.

References