

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 ($ZrCl_4$, $\geq 99.5\%$, Sigma Aldrich); meso-Tetra(4-carboxyphenyl)porphine (TCPP, Frontier Scientific); *N,N*-dimethylformamide (DMF; spectrophotometric grade, Spectrum); formic acid (reagent grade, $\geq 99.5\%$, Sigma Aldrich); nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 99.3% Alfa Aesar); fluorine-doped tin oxide (FTO, cleaned via sonication in Alconox/ H_2O , isopropanol, acetone, then H_2O with rinsing with H_2O and drying in between, Hartford Glass); acetonitrile (distilled before use, HPLC grade, Spectrum); sodium perchlorate ($NaClO_4$; 99+%, Aldrich); tetrabutylammonium hexafluorophosphate ($TBAPF_6$; recrystallized $\times 4$ from ethanol, electrochemical grade, Fluka Analytical).

Synthesis of Ni(II)TCPP: Free-base 5,10,15,20-(4-carboxymethoxyphenyl)-porphyrin, $H_2TMeCPP$, 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.^{2,3} The crimson product was precipitated out by addition of water then filtered, washed with water, and allowed to dry: ¹H NMR (400 MHz, *d*₆-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 MOF³ 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(K α) radiation (Cu–K α = 1.5418 Å). The PXRD experiments were carried out over a 2 θ 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 μ m 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 μ m 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 μ M), 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 $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$, where the expected $E_{1/2}$ is +560 mV vs. NHE.⁴ For all aqueous electrochemical experiments, 18.3 m Ω -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 NaClO₄ 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 NaClO₄ electrolyte in the standard three-electrode arrangement described above. Overpotentials ($\eta = V - E^{\circ}$) 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 H_2O_2 indicator strips were used and immersed into the electrolyte solution after the CPE experiment. The color code was used to estimate the H_2O_2 concentration.

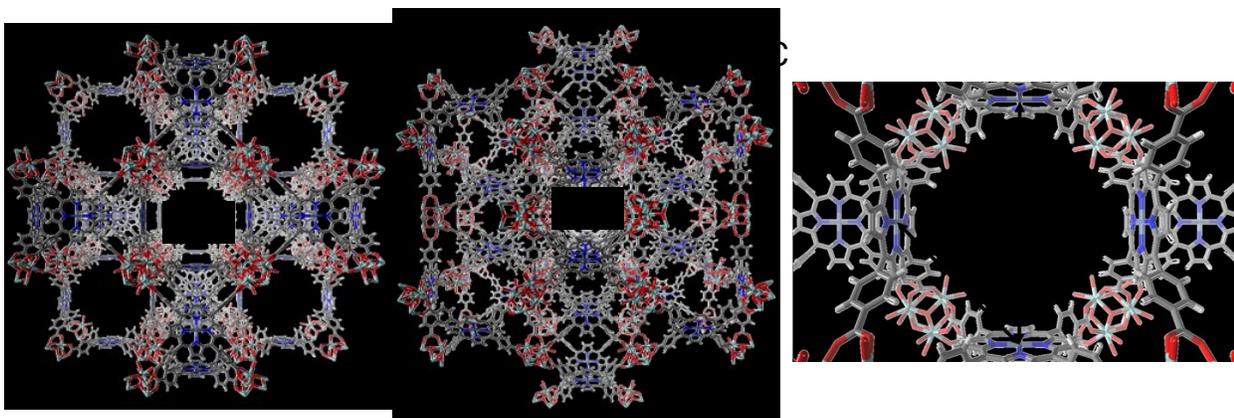


Figure S1. The distances between Zr nodes of PCN-224-Ni shown in (A) and (B). (C) The distances between Ni(II)-to-Ni(II) metal centers of co-facial and orthogonal porphyrins within the same channel.³

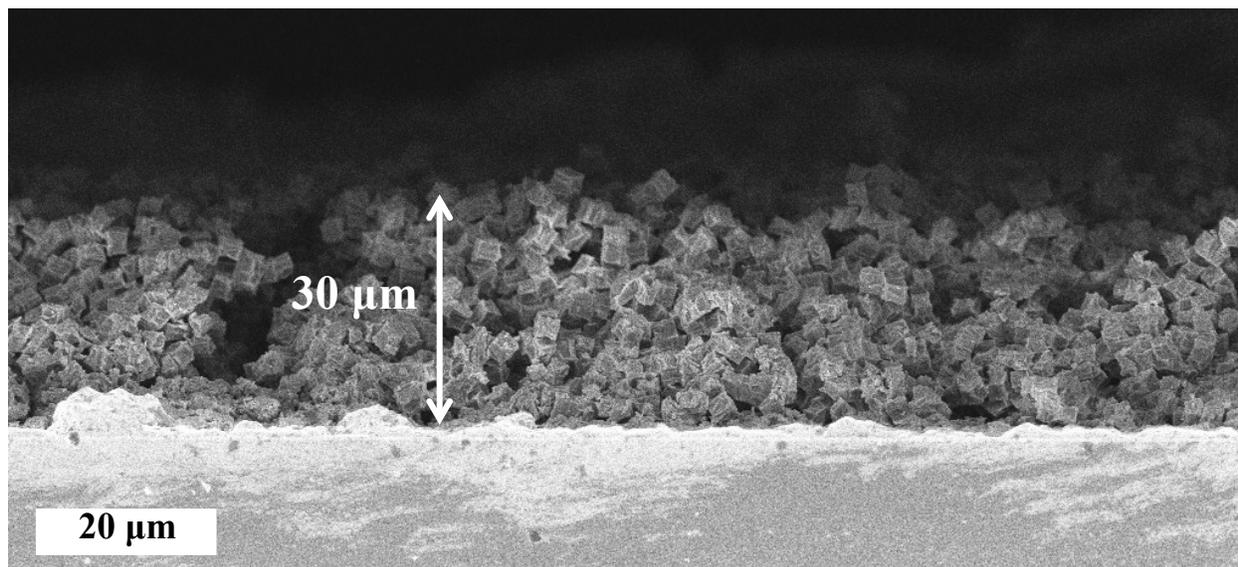


Figure S2. SEM image of solvothermally prepared PCN-224-Ni on FTO showing a film thickness of *ca.* 30 μm .

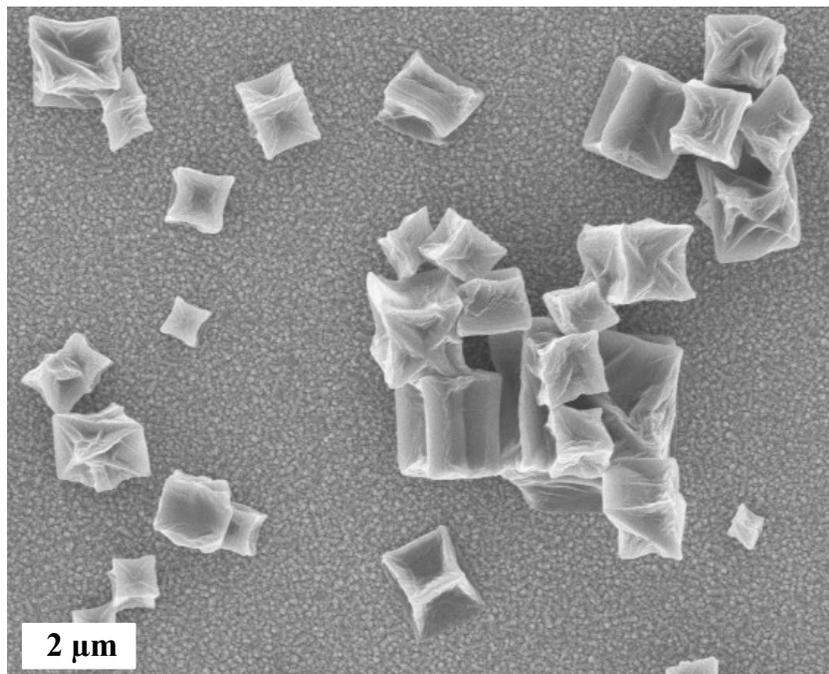


Figure S3. SEM image of PCN-224-fb film.

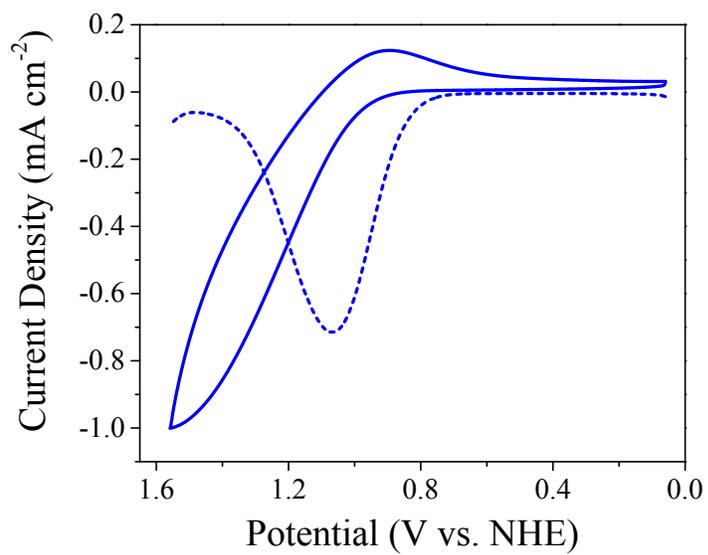


Figure S4. CV (solid blue) and SWV (dash blue) of PCN-224-Ni in aqueous 0.1 M NaClO₄.

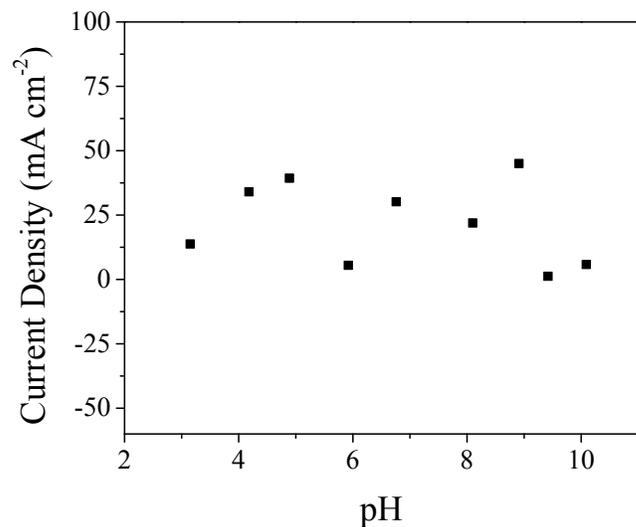


Figure S5. pH dependence of steady-state catalytic current density at constant potential ($E_{appl} = 1500$ mV vs. NHE) for PCN-224-Ni in aqueous 0.1 M NaClO₄.

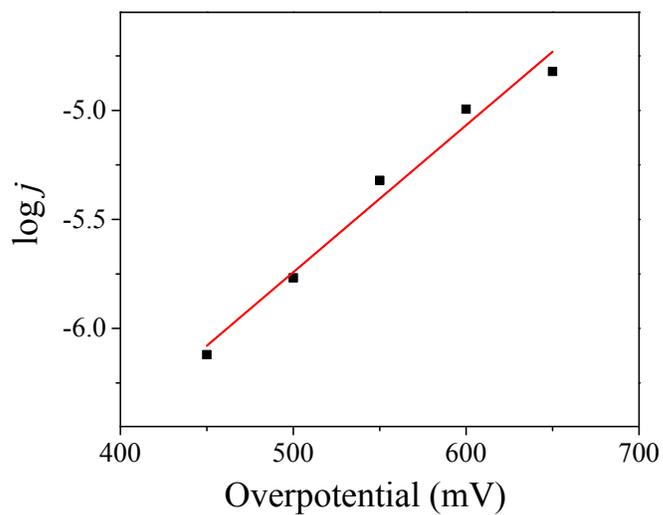


Figure S6. Tafel plot of PCN-224-Ni in aqueous 0.1 M NaClO₄.

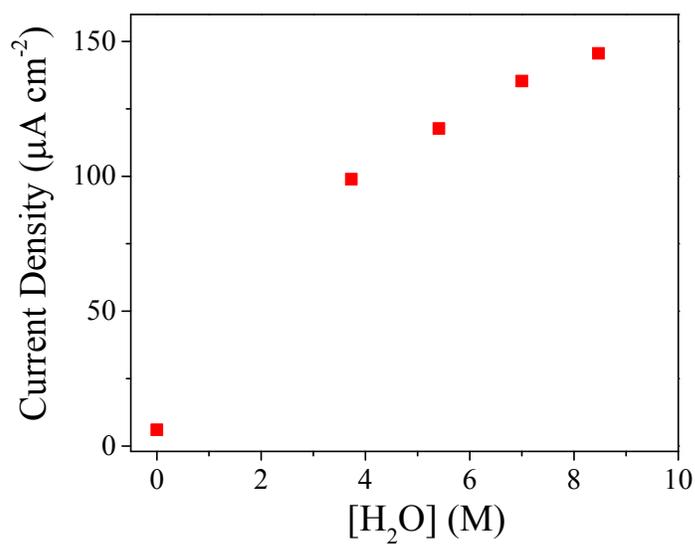


Figure S7. Plot of Current density vs. $[\text{H}_2\text{O}]$ generated from CVs of PCN-224-Ni in 0.1 M TBAPF₆/CH₃CN with increasing H₂O concentrations.

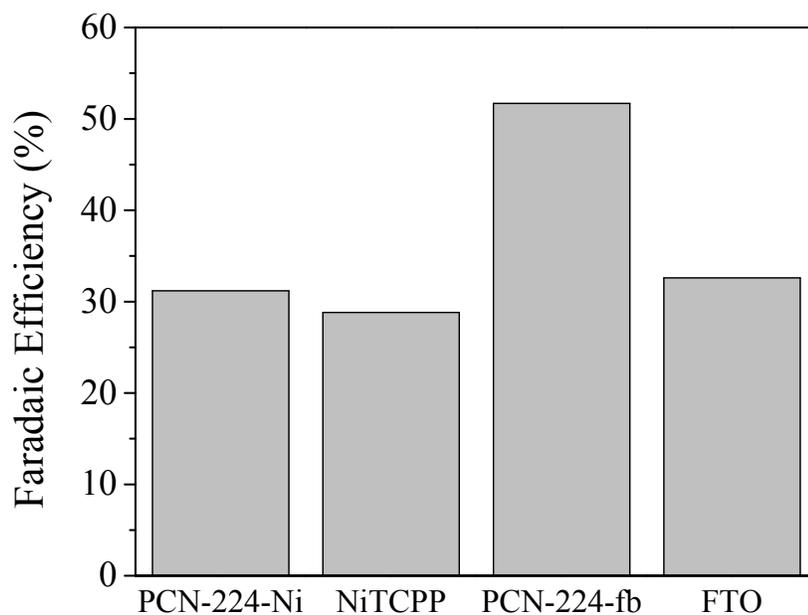


Figure S8. Faradaic efficiencies after electrolysis at 1500 mV vs. NHE in aqueous 0.1 M NaClO₄. For NiTCPP, a 1 mM solution of the Ni(II)TCPP potassium salt was used.

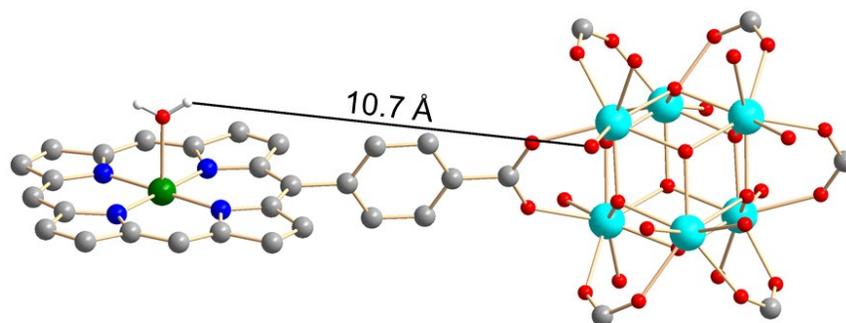


Figure S9. The structure of PCN-224-Ni framework showing the distance between the water molecule coordinated to Ni center inside the porphyrin ligand and terminal hydroxyl group on Zr-oxo cluster; (C – grey, H – white, O – red, N – blue, Ni – green and Zr – light blue).

Table S1. Summary of ICP-MS data for digested PCN-224-Ni films and solutions.

Sample	Ni (mol)	Zr (mol)	Zr:Ni
PCN-224-Ni as synthesized	4.63×10^{-7}	2.38×10^{-6}	5.15:1
PCN-224-Ni post-electrolysis	$3.05 (\pm 1.22) \times 10^{-7}$	$1.44 (\pm 0.59) \times 10^{-6}$	4.71:1
Solution post-electrolysis	$2.37 (\pm 1.16) \times 10^{-8}$	$2.62 (\pm 0.74) \times 10^{-8}$	1.23:1

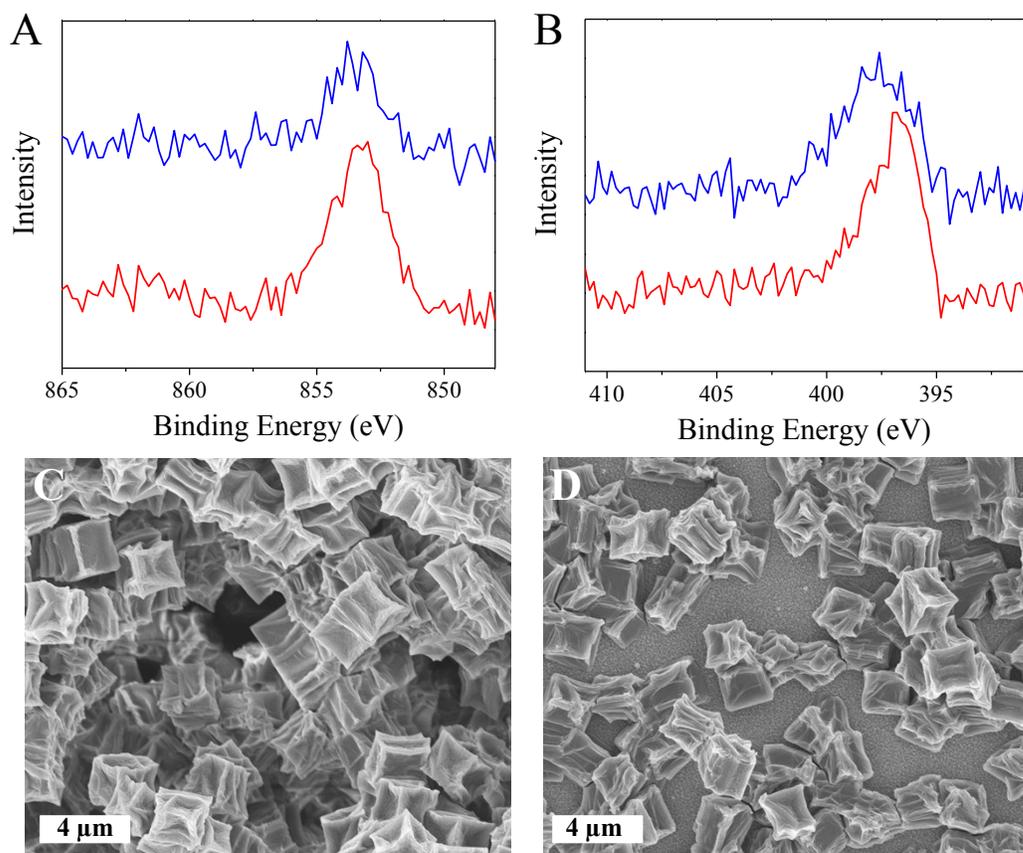


Figure S10. XPS of PCN-224-Ni films pre- (red) and post- (blue) electrolysis experiments displaying (A) Ni_{2p}3 and (B) Ni_{1s} binding energy; SEM images of PCN-224-Ni films pre- (C) and post- (D) electrolysis.

References

- 1 Adler, A. D. *et al.* A simplified synthesis for meso-tetraphenylporphine. *J. Org. Chem.* **32**, 476-476, (1967).
- 2 Adler, A. D., Longo, F. R., Kampas, F. & Kim, J. On the preparation of metalloporphyrins. *J. Inorg. Nucl. Chem.* **32**, 2443-2445, (1970).
- 3 Feng, D. *et al.* Construction of ultrastable porphyrin Zr metal–organic frameworks through linker elimination. *J. Am. Chem. Soc.* **135**, 17105-17110, (2013).
- 4 Bard, A. J. & Faulkner, L. R. *Electrochemical Methods*. 2nd edn, (John Wiley & Sons, Inc., 2001).