

Vapor-Phase Synthesis of Electrocatalytic Covalent Organic Frameworks

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The inability to process many covalent organic frameworks (COFs) as thin films plagues their widespread utilization. Herein, a vapor-phase pathway for the bottom-up synthesis of a class of porphyrin-based COFs is presented. This approach allows integrating electrocatalysts made of metal-ion-containing COFs into the electrodes' architectures in a single-step synthesis and deposition. By precisely controlling the metal sites at the atomic level, remarkable electrocatalytic performance is achieved, resulting in unprecedentedly high mass activity values. How the choice of metal atoms, i.e., cobalt and copper, can determine the catalytic activities of POR-COFs is demonstrated. The theoretical data proves that the Cu site is highly active for nitrate conversion to ammonia on the synthesized COFs.

1. Introduction

Most natural enzymes exploit metal ions to enable organisms to carry out their essential functions, such as photosynthesis, respiration, and nitrogen fixation. Drawing inspiration from these metalloenzymes, electrocatalysis on organometallic compounds, such as organic heterocycles and macrocyclic structures, has become an active field.^[1] Among macrocyclic structures, a powerful motif is the porphyrin structure, with four pyrrolic nitrogen atoms in a planar geometry that can chelate metal ions.

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This exquisite design captured the interest of materials scientists studying single-atom catalysts,^[2] and many studies were devoted to the electrocatalytic activity of porphyrins.^[3] However, the chemical instability of porphyrins on the electrodes decorated with these molecules presented a challenge to their applications as electrocatalysts. To that end, tethering and covalently bonding these molecules to the surface became the mainstream approach. With the advent of metal-organic and covalent organic frameworks (MOFs and COFs), new possibilities emerged for creating chemically stable porphyrin-based electrocatalysts.^[4]

COFs and MOFs, polymers of reticular chemistry, are primarily prepared from solution and isolated as powders.^[5,6] However, progress in processing these materials as thin films using conventional solvents and thermal-based techniques has been fairly slow.^[7] To address this challenge and facilitate the integration of these materials into device and electrode architectures, the synthesis and integration steps can be combined by pursuing the synthesis of frameworks on the substrate. One possible pathway is to evaporate the precursors to the substrate and adjust the conditions to induce a reaction.^[8] This path has already shown promising results for the synthesis of Zeolitic imidazolate frameworks,^[9] porphyrin conjugated polymer thin films,^[10] and MOFs.^[11–13] Although taking this pathway and processing COFs via the vapor phase is feasible,^[14] processing thin films of COFs on the substrate has been more focused on transferring the film, synthesized in the liquid phase and via interfacial assemblies,^[15] to the desired substrates. Vapor-phase synthesis is a route that facilitates the integration of materials into complex geometries, enabling the use of COFs for niche applications, e.g., ion-permeable passivation layers,^[16] active layers in composite membranes,^[17] and most importantly, electrocatalytic coatings.^[18]

To that end, herein a process analogous to the oxidative molecular layer deposition^[19] is developed to synthesize cobalt- and copper-containing porphyrin-based COFs (MPOR-COFs). The developed process allows the bottom-up synthesis of COFs that carry pyrrole-N₄ motifs, well known for their electrocatalytic properties.^[20] We show that by changing the metal center, we can tune the selectivity and activity of our electrocatalysts for electrochemical nitrate reduction reaction (eNRR) and oxygen reduction and evolution reactions (ORR/OER) in an aprotic medium, rivaling^[21] the reported performance of catalysts used for these reactions^[22–26]

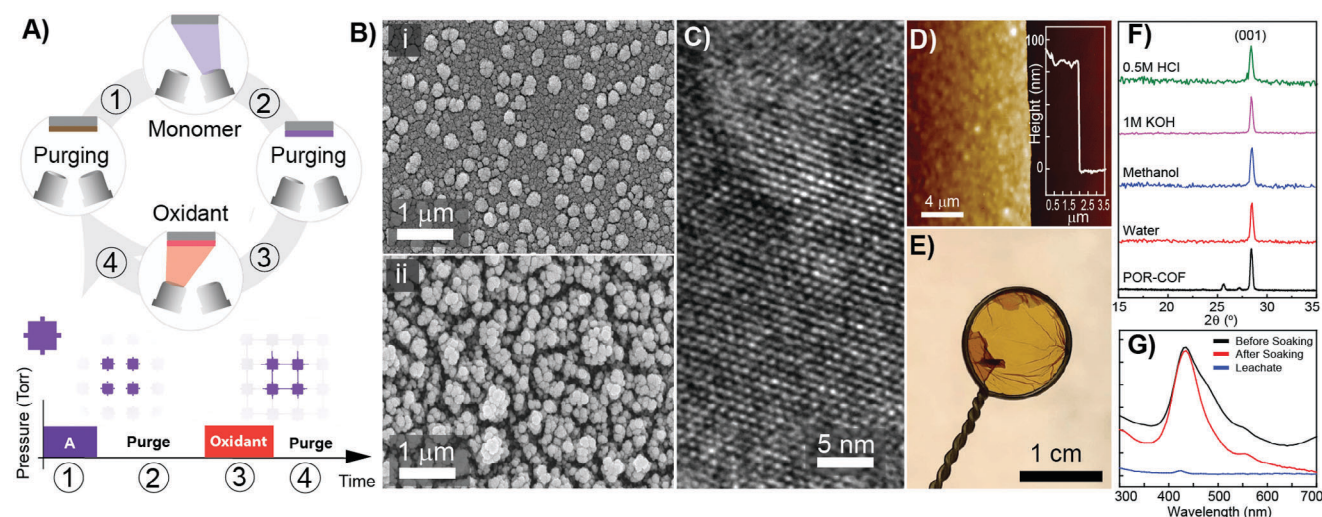


Figure 1. Synthesis of Porphyrin-based COF (POR-COF): A) Schematics of vapor-phase synthesis of POR-COF and the reactor pressure-time trajectory. In the first step, a pulse of TAPP (monomer) was given. Thereafter, the reactor was pumped down and purged to reach the base pressure. In the third step, an oxidant pulse was given to polymerize the TAPP to form POR-COF via oxidative polymerization. Subsequently, the reactor was purged again, and the cycle was repeated. B) i and ii) SEM top surface images of the samples formed by operating the reactor with two different sets of processing parameters (scale bars are 1 μm) and C) HRTEM image of POR-COF (scale bar is 5 nm). D) AFM height image (scale bar 4 μm , inset: height profile image) of POR-COF film and E) digital photographic image of POR-COF film transferred to a wire loop. F) PXRD of POR-COF and POR-COF washed with water, methanol, 1 M KOH and 0.5 M HCl. G) The UV-Vis absorption spectra of POR-COF before and after being soaked in chloroform along with the spectrum of chloroform solution after the experiment.

2. Results and Discussion

2.1. Vapor-Phase Synthesis of MPOR-COF

A schematic representation of the process is shown in **Figure 1A**. This process involves the sequential delivery of oxidant and porphyrin molecules to the reaction zone, separated with a nitrogen purge cycle to remove the excess materials and reaction byproducts. Porphyrin molecules, 5,10,15,20-tetra(4-aminophenyl) porphyrin (TAPP) or its transition-metal complexes (M-TAPP, $M = \text{Co}^{2+}$, Cu^{2+}) were prepared, purified, and used as the main precursors. Various substrates, including silicon (100), sapphire (C-cut), glassy carbon, gas diffusion layer, quartz, gold, and platinum, were used to evaluate the material's properties. The details of characterization, the synthetic approach, and the preparation of materials are reported in Sections 1 and 2 (Supporting Information). The reaction between TAPP and the halogenated metalloid, antimony pentachloride (SbCl_5), leads to the formation of a thin film on various substrates. Although the reaction pathway was not validated experimentally, a plausible reaction mechanism, adapted from Wamser's work,^[27] is shown in Section 2 (Scheme S1) (Supporting Information). Briefly, the terminal amine group interacts with the Lewis acid, SbCl_5 , and forms an adduct. Subsequently, SbCl_5 carries out two-electron oxidation via $\text{SbCl}_5 + 2e^- \rightarrow \text{SbCl}_3 + 2\text{Cl}^-$, thereby oxidizing M-TAPP to form radical cation (M-TAPP $^{\cdot+}$). The as-formed intermediate is readily stabilized by the removal of two protons by Cl^- ions, and these radical cations undergo coupling reactions via dihydrophenazine or phenazine linkage, where two neighboring radical cations react with each other, resulting in the formation of dimers or higher oligomers. The polymerization process continues as the dimers or oligomers react further, propagating the polymer chain. The

process continues until termination occurs, leading to the formation of the final polymer product. The reaction byproducts, hydrogen chloride (HCl) and antimony trichloride (SbCl_3) are removed during the purge cycle. **Figure 1Bi** presents the microscopy images of the particulate materials synthesized on sapphire. Details of the processing conditions are presented in Section 2 (Supporting Information). When the film thickness increases above 300 nm, shown in **Figure 1Bii**, the particulate-like nature of the materials becomes evident. The number density of these particulate domains seems to be correlated with the nucleation rate of MPOR-COFs. Here, to demonstrate these phenomena and create a more uniform film, random nucleation is suppressed by introducing pyridine as separate pulses into the reaction chamber. Pyridine, as a weak base, neutralizes the reaction byproduct (HCl) and shifts the reaction equilibrium.^[28] Consequently, a higher conversion of the monomer is achieved, which results in an increased degree of polymerization and the formation of a polymeric film. The details of experimental section, evaporation condition, pulse, and purge sequences are outlined in Sections 2 and 3 (Supporting Information) (Figures S1–S10, Supporting Information). The use of pyridine pulses in the synthesis of POR-COF resulted in the formation of ordered domains that extend up to 30 nm in size, as evidenced by transmission electron microscopy (TEM). **Figure 1C** shows one crystallite domain, which is ≈ 25 by 30 nm in size. The materials synthesized with pyridine pulses formed films that could be easily lifted off and transferred onto other substrates. The atomic-force microscopy (AFM), **Figure 1D**, shows the thickness of these films, transferred to a silicon substrate. The POR-COF film synthesized is stable and flexible. **Figure 1E** shows an image of a representative thin film sample on a wire loop; while the film thickness is ≈ 90 nm, it covers the whole 1.0 cm diameter of the wire loop, presenting the

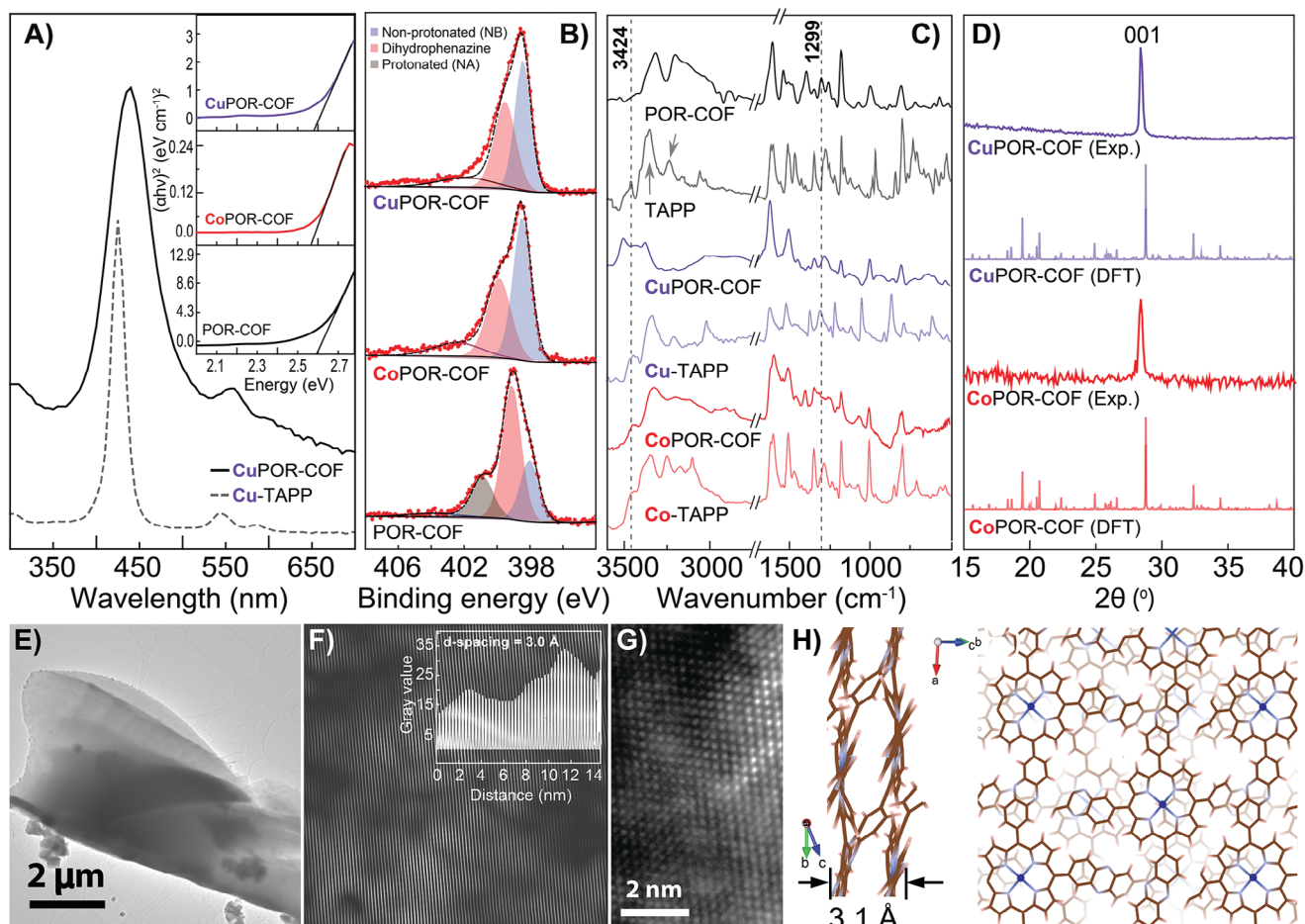


Figure 2. Characterization of MPOR-COF: A) UV-Vis spectra of Cu-TAPP (dotted line) and CuPOR-COF (solid line) deposited on quartz. The inset presents the Tauc plots of POR-COF, CoPOR-COF, and CuPOR-COF. B) High-resolution XPS spectra corresponding to N1s for POR-COF, CoPOR-COF, and CuPOR-COF samples. The blue peak represents the non-protonated pyrrolic N (N_B), red peak indicates the dihydrophenazine N and the brown peak designates the protonated pyrrolic N (N_A). C) FT-IR spectra of TAPP (light black), POR-COF (black), Co-TAPP (light red), CoPOR-COF (red), Cu-TAPP (light violet) and CuPOR-COF (violet). D) Experimental and DFT calculated PXRD of CoPOR-COF and CuPOR-COF. E) TEM images of CoPOR-COF. F) Inverse fast Fourier transform (IFFT) image of (E) (inset shows the line profile). G) HRTEM image of CuPOR-COF. The TAPP, Co-TAPP and Cu-TAPP deposition rates were 10, 5 and 7.5 nm⁻¹s respectively. H) Side and top views of DFT-derived AB stacking crystal structure of CuPOR-COF. The blue dot in the top view structure represents the Cu²⁺ ion.

mechanical stability of the thin films. The films were also chemically stable. The result of chemical stability studies on these materials is shown in Figure 1F. The film exhibited no change in crystallinity after being submerged in water, methanol, 1 M KOH or 0.5 M HCl for 24 h, indicating that the as-synthesized POR-COF is stable in different environments. The stability of the POR-COF film in organic solvent was also evaluated using UV-Vis spectroscopy (Figure 1G). The UV-Vis spectra of POR-COF samples deposited on sapphire were collected before and after submerging in chloroform. The spectra exhibit no difference in the position of maximum intensity wavelength ($\lambda_{\max}$), and the intensity of the peaks are comparable. A peak appears in the UV-Vis spectrum corresponding to the solvent, indicating the presence of unreacted precursors leaching out of the film.

Following the synthesis of a thin film of POR-COF, metal-TAPP (M-TAPP, M = Cu²⁺, Co²⁺) precursors were employed to synthesize metal-porphyrin-COFs (MPOR-COFs). Because both Co- and Cu-porphyrin-based frameworks are reported to have re-

markable electrocatalytic activities,^[29] herein Co-TAPP and Cu-TAPP are used as precursors and films of MPOR-COFs are synthesized and deposited on the electrodes. Figure 2A illustrates the UV-Vis absorption of Cu-TAPP, CuPOR-COF, and the Tauc plot for MPOR-COFs (inset). Compared to Cu-TAPP (which exhibits the Soret band at 425 nm and Q bands at 544 and 586 nm) CuPOR-COF shows red-shift in the Soret band to 436 nm. This red-shift is attributed to the extended π conjugation over the 2D skeleton of the COFs.^[30] From the Tauc plot, shown in the inset of Figure 2A, the estimated optical bandgap is $\approx$ 2.57 eV. Further details on the optical properties, variation of the band gap as a function of processing conditions, and stability are discussed in Figures S11–S14 (Supporting Information).

X-ray photoelectron spectroscopy (XPS) was used to analyze the elemental composition and chemical bonding in MPOR-COF (M = H₂, Cu²⁺, Co²⁺). The N1s high-resolution spectrum of POR-COF, displayed in Figure 2B, exhibits four distinct peaks at 398 (blue), 399.1 (red), 400.8 (brown), and 403.9 eV, which are

attributed to non-protonated pyrrolic N (N_B), dihydrophenazine N, protonated pyrrolic N (N_A), and satellite peaks, respectively.^[31–33] The unchanged difference in binding energy ($N_A - N_B = 2.8$ eV) and atomic ratio ($N_B/N_A = 1.3$) of N_A and N_B when comparing the precursors and deposited films suggests that the stoichiometry of the parent monomer is preserved in the product. Unlike the POR-COF spectrum, the N1s spectra for CuPOR-COF and CoPOR-COF, Figure 2B, exhibit three peaks centered at 398.4 (blue), 399.8 (red), and 402.4 eV. The absence of protonated pyrrolic species at ≈ 401 eV indicates metal hybridization in the porphyrin structure. The chemical properties of the films were further analyzed with FT-IR. As shown in Figure 2C, the TAPP spectrum exhibits primary amine ($-NH_2$) asymmetric and symmetric stretching and N-H bending vibration at 3424, 3323, and 1616 cm^{-1} , respectively. Additionally, the N-H stretching of the pyrrole is observed at 3218 cm^{-1} . Furthermore, characteristic porphyrin vibrational bands corresponding to C-H out-of-plane and in-plane bending were observed at 709, 731, 799, and 965, 982, 1015 cm^{-1} , respectively.^[34] The pyrrole skeletal vibrations were spotted at 1399, 1347, and 1464 cm^{-1} .^[34] However, after oxidative polymerization, the characteristic asymmetric stretching of the primary amine ($-NH_2$) was not observed in POR-COF. Similarly, CoPOR-COF and CuPOR-COF displayed all the characteristic porphyrin FT-IR absorptions, with slight shifts due to metalation. Notably, in CuPOR-COF, the primary amine asymmetric stretching almost vanished, while in CoPOR-COF, some primary amine asymmetric stretching was still visible, indicating an incomplete reaction in the latter case. The presence of a new peak at 1299 cm^{-1} in POR-COF was assigned to the newly formed dihydrophenazine (C-NH-C) bending vibration.^[28] Here, we note that the fingerprint of the phenazine moiety is not present. The latter can be attributed to the formed hydrochloric acid, the byproduct of the reaction, hindering the formation of phenazine linkage.^[28] When pyridine pulses are included, the phenazine linkage becomes apparent in the FT-IR data (Figure S15, Supporting Information); the data detailing the MPOR-COFs synthesized with pyridine pulses are presented in Figures S15–S17 (Supporting Information).

The as-synthesized MPOR-COF exhibits crystallinity, as evidenced by the X-ray diffraction studies. The diffractograms, shown in Figure 2D, exhibit a peak at $\approx 28^\circ$, which is assigned to the (001) plane. The d -spacing corresponding to the (001) plane for MPOR-COFs is ≈ 0.3 nm. The HRTEM and inverse fast Fourier transform (IFFT) images of CoPOR-COF are presented in Figures 2E,F. The inset in Figure 2F presents the line profile of Figure 2E. The HRTEM image of CuPOR-COF is presented in Figure 2G. The bright spots in Figure 2G are the locations of the copper atoms. Detailed microscopy data are presented in Figure S18 (Supporting Information). The d -spacing of POR-COF, CoPOR-COF, and CuPOR-COF calculated from inverse fast Fourier transform (IFFT) images are found to be ≈ 0.3 , ≈ 0.29 , and ≈ 0.31 nm, respectively. The obtained values are aligned with the values obtained from the diffractograms (Figure 2D; Figure S19A, Supporting Information). Furthermore, these numbers are matched with the DFT simulated AB stacking (Figure 2H; Figure S19B, Supporting Information). Herein, the formation of AB stacking is expected because the charge repulsion between nitrogen atoms disfavors AA stacking. Hence, for POR-COFs, the AB stacking structure with space group P1 was

modeled; the values for the unit cells are reported in Section 3 and Table S1 (Supporting Information). Besides the charge repulsion, it is possible that factors such as molecular size, edge disorder, and the reaction irreversibility suppress the crystallinity of the synthesized MPOR-COF.^[35–39] For instance, our experiments done using pyridine pulses during the reaction and its impact on the structural parameter of the synthesized COFs, presented in Figures S20–S24 (Supporting Information), highlight the significance of the reaction dynamics on the structural properties of MPOR-COF. We also evaluated the effect of different substrates on the formation of POR-COF and noted that the formation of COFs appears to be substrate-independent. Figure S25 (Supporting Information) presents example diffractograms taken from samples deposited on different substrates.

2.2. Electrochemical Nitrate Reduction Reaction (eNRR)

The electrocatalytic properties of our MPOR-COFs in nitrate reduction were investigated by applying thin films of MPOR-COF to carbon-based electrodes. The eNRR experiments were performed in a typical two-compartment, three-electrode cell, where Ag/AgCl and a platinum mesh were used as the reference and counter electrodes, respectively, and the two compartments were separated by a Nafion-115 cation exchange membrane. The concentration of the generated ammonia during eNRR is evaluated using optical spectrophotometry; the calibration curve for ammonia quantification is given in Figure S26 (Supporting Information). To establish these experiments, controlled Linear sweep voltammetry (LSV) experiments were performed, and the activity of the CuPOR-COF and CoPOR-COF catalysts in the absence and presence of nitrate in alkaline electrolyte were compared (Figure S27, Supporting Information). As shown in Figure 3A, when KNO_3 is added to 1 M KOH electrolyte, CuPOR-COF provides increased current density and a shift in onset potential, which we attribute to nitrate reduction to ammonia. For CoPOR-COF, a similar trend was observed (Figure S27, Supporting Information); However, upon estimating the ammonia yield, we noted that the values are nearly half of that of CuPOR-COF. We measured the ammonia partial current density, Faradaic efficiency (F.E.), and ammonia yield of CuPOR-COF under various potentials at pH 14 (Figures S28 and S29, Supporting Information and Figure 3B). Our results indicate that CuPOR-COF at a voltage window of -1.4 to -1.8 V versus Ag/AgCl presents a maximum F.E. of $\approx 86\%$ and a yield of 6.0 $mg\ h^{-1}\ cm^{-2}$ (Figure 3B). This areal yield, with loading of $100\ \mu g\ cm^{-2}$, translates to a per-mass yield of $60\ mg\ h^{-1}\ mg^{-1}$, threefold higher than previously reported values.^[35–41] Compared with similar COFs prepared by a solution phase technique,^[21] our CuPOR-COF catalyst's performance presents a 20-fold higher yield. The F.E.% declines at higher potentials due to the competing hydrogen evolution on the electrodes (Figure 3B). Similarly, at pH 7, our electrocatalyst shows a yield of $\approx 5.6\ mg\ h^{-1}\ cm^{-2}$ and a maximum F.E. of $\approx 80\%$, only slightly lower than the values observed at pH 14 (Figure 3B). For Co-POR-COF, the measured ammonia F.E.% never exceeded more than $\approx 42\%$ (Figure S30A, Supporting Information), proving the significance of the metal atom in defining the reaction selectivity. The eNRR done on POR-COF as a control experiment in alkaline electrolyte had an insignificant ammonium yield, an

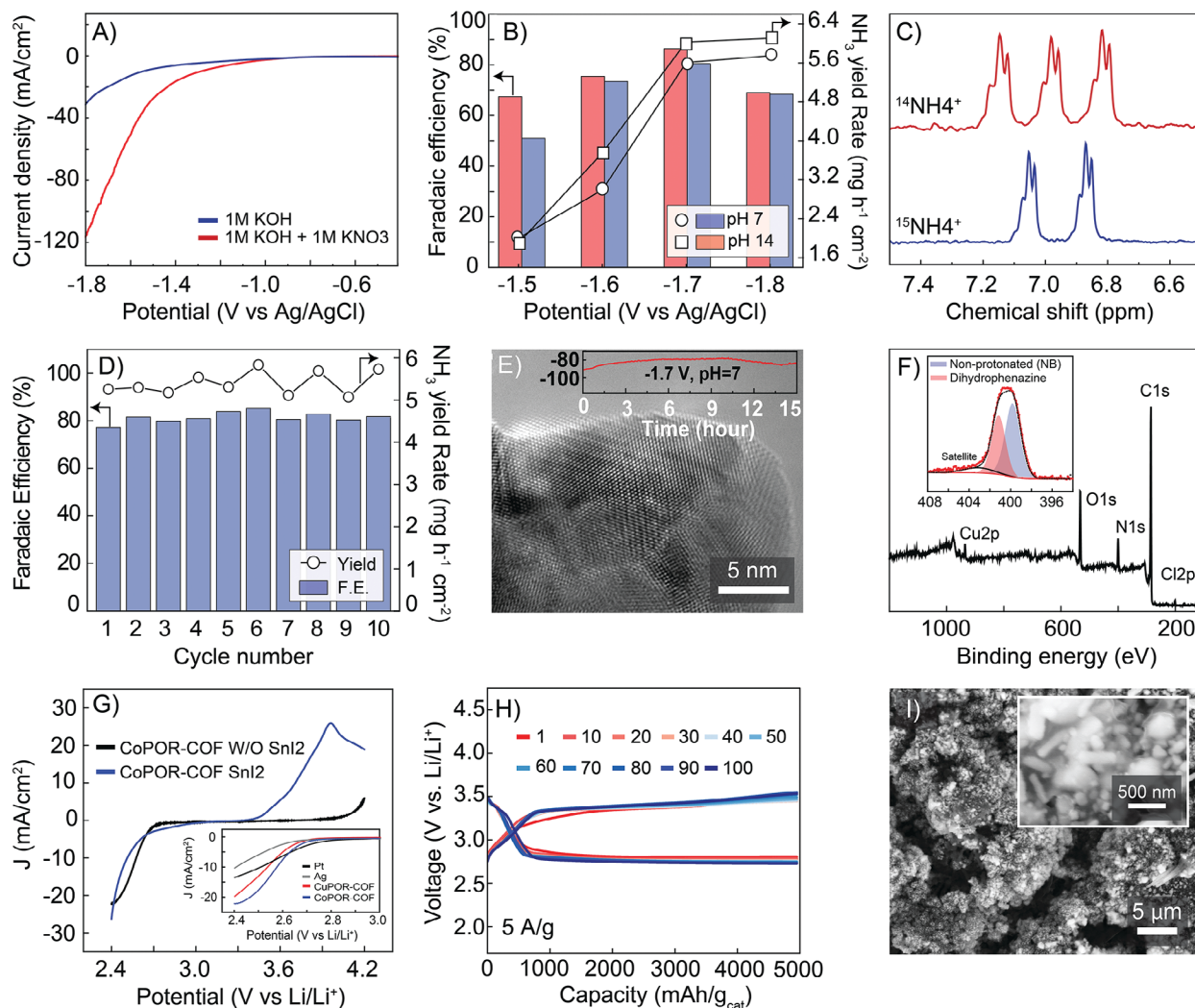


Figure 3. Electrocatalytic performance of MPOR-COF: A) Linear sweep voltammetry (LSV) of CuPOR-COF in 1 M KOH and 1 M KOH + 1 M KNO₃. B) Ammonia Faradaic efficiencies and yield rates at different applied potentials and pH. C) ¹H NMR spectra of the electrolyte after electrocatalysis using K¹⁵NO₃ and K¹⁴NO₃ as the nitrate sources. D) Cycling stability of CuPOR-COF during 10 consecutive electroreduction cycles at -1.7 V versus Ag/AgCl and pH ≈ 7. E) HRTEM image of CuPOR-COF after nitrate reduction for 10 hours at -1.7 V versus Ag/AgCl at pH ≈ 7. The inset shows the long-term chronoamperometry for 15 h under -1.7 V versus Ag/AgCl at pH ≈ 7. F) XPS survey and N1s high-resolution spectra (inset) of CuPOR-COF@carbon paper after nitrate reduction for 10 hours at -1.7 V versus Ag/AgCl at pH ≈ 7. G) LSV results of CoPOR-COF with and without the presence of SnI₂ as a redox mediator. The inset plot compares the reduction current density of CoPOR-COF and CuPOR-COF with that of Ag and Pt nanoparticles. H) Lithium-oxygen battery cycling for CoPOR-COF catalyst. I) SEM image of discharged cathode illustrating the bright spots, lithium peroxides, covering the cathode surface (inset).

order of magnitude lower than that of CuPOR-COF (Figure S30B, Supporting Information).

To validate that the ammonia obtained was derived from nitrate ions (NO₃⁻) in the electrolyte, two control experiments were conducted. First, chronoamperometry was performed in a nitrate-free electrolyte (1 M KOH) at -1.7 V versus Ag/AgCl. The results revealed low ammonia production (0.053 mg h⁻¹ cm⁻²) in the electrolyte, as shown in Figure S31A (Supporting Information). However, in the presence of nitrate, the ammonia yield was ≈6.0 mg h⁻¹ cm⁻². Second, nuclear magnetic resonance (NMR) spectroscopy was employed to verify NO₃⁻ as the primary source of ammonia generation. Isotopically labeled 1 M K¹⁵NO₃ and 1 M K¹⁴NO₃ were utilized, with electrolysis conducted at -1.7 V ver-

sus Ag/AgCl. Figure 3C illustrates the ¹H NMR spectra, where ¹⁴NH₄⁺ exhibited three peaks at 6.84, 6.97, and 7.10 ppm with a coupling constant of 52 Hz, while two distinct ¹⁵NH₄⁺ peaks were observed at 6.88 and 7.06 ppm with a coupling constant of 72 Hz, respectively.^[42] The obtained results provide confirmation that the generated ammonia is the result of eNRR, and it is not a contaminant. To further evaluate the stability of the catalyst, we tested the catalyst under ten consecutive, 15-min cycles of eNRR in a neutral electrolyte at an applied potential of -1.7 V versus Ag/AgCl, with the electrolyte being replenished at the end of each cycle. As shown in Figure 3D, the F.E. remains stable, and the average ammonia yield is estimated to be 5.5 mg h⁻¹ cm⁻². An electrode used for measuring electrocatalytic stability

for 10 h is further characterized with XPS and TEM. As shown in Figure 3E, the HRTEM image indicates that the crystallinity of CuPOR-COF is preserved, and materials appear stable. The XPS data, shown in Figure S31B (Supporting Information) and Figure 3F, present the spectrum of CuPOR-COFs before and after being used in the eNRR experiments, respectively; there is no indication of degradation or change in the stoichiometry of materials. Further, the high-resolution N1s spectrum (Figure 3F inset) suggests that there is no change in the structure of the porphyrin units. The presented data on the activity of our COFs in eNRR show the robustness of the developed electrocatalysts.

2.3. Li-O₂ Battery Performance

As shown above, the selectivity of the designed electrocatalysts hinges on the identity of the chelated metal ions. Given the reports on the Co- and Fe-porphyrin outstanding performance in ORR,^[43,44] our synthesized MPOR-COFs were tested as catalysts in the cathode of a Li-O₂ battery. The discharge/charge efficiency in the Li-O₂ system was evaluated by LSV experiments (ORR/OER) conducted in between 2.4 and 4.2 V, measured versus Li/Li⁺.^[45,46] The experiment is conducted in a three-electrode electrochemical cell (Section 5, Supporting Information) including an oxygen-saturated electrolyte of 1 M LiTFSI salt dissolved in a mixture of dimethyl sulfoxide (DMSO) and ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) in a 9:1 volumetric ratio. The LSV traces, shown in the inset of Figure 3G, indicate that both MPOR-COFs can effectively catalyze ORR with current densities of 20 mA cm⁻² (CuPOR-COF) and 22.5 mA cm⁻² (CoPOR-COF). These values exceed the current density of Pt nanoparticles (14 mA cm⁻²) and Ag nanoparticles (10 mA cm⁻²), as shown in the inset of Figure 3G. Considering the reports on Co atoms, coordinated with pyridinic and pyrrolic structures, catalyzing OER,^[47] we further tested the OER performance of our electrocatalysts, in the presence of 65 mM bifunctional SnI₂ additive (with Sn²⁺ for the Li anode protection and I⁻ as a redox mediator).^[48] We observed a synergy between the COF catalyst and the SnI₂ and recorded a high current density of ≈ 27 mA cm⁻² at the applied potential of ≈ 3.9 V. Figures 3G,H illustrate a stable galvanostatic cycling result of a battery loaded with our CoPOR-COF catalyst and tested for 100 cycles under a high current density of 5 A g⁻¹ and a capacity of 5000 mAh g⁻¹. These numbers are by far the highest gravimetric current density and capacity reported for Li-O₂ batteries. After 100 cycles, the discharge potential remained stable at 2.7 V, and the charge potential remained at a low charge potential of 3.6 V. Also, no noteworthy capacity loss was observed during the discharge process. The discharge products were characterized to investigate the performance of the electrocatalysts further. Details of the experiment and the quantification procedures are provided in Figure S32 (Supporting Information). Using UV-Vis and Raman spectroscopy (Figures S33 and S34, Supporting Information), the discharged product, shown as bright spots in Figure 3I, was identified as lithium peroxide (Li₂O₂). Figure S35A (Supporting Information) shows a representative SEM image of an electrode surface after a charge cycle, where the discharged products disappear, providing macroscopic evidence of the stability of our synthesized electrodes. The two electrocata-

lysts showcased here serve as examples of electrocatalysts that can be produced by utilizing porphyrins as precursors of COFs. We also assessed the structural durability of CoPOR-COF following 100 cycles of OER through XPS analysis. As depicted in Figures S35B,C (Supporting Information), the high-resolution N1s spectrum provides compelling evidence that the porphyrin units' structure remains unaltered after enduring 100 cycles in OER conditions. This observation strongly supports the notion of CoPOR-COF's long-term structural stability under these operating conditions. Furthermore, the OER activity of CoPOR-COF was compared with that of RuO₂. As shown in Figure S35D (Supporting Information), CoPOR-COF demonstrates a remarkable advantage in terms of OER activity when compared with RuO₂. Notably, at 3.9 V, CoPOR-COF showcases an approximately twofold increase in current density compared with that of RuO₂ in the presence of the redox mediator SnI₂. However, it is important to note that above 3.9 V, the current density of CoPOR-COF begins to decline. At 4.2 V, both CoPOR-COF and RuO₂ exhibit comparable current densities (CoPOR-COF ≈ 19 mA cm⁻² and RuO₂ ≈ 17 mA cm⁻²). These findings underscore the diverse electrocatalytic performance of CoPOR-COF relative to RuO₂.

2.4. Theoretical Calculations

As noted, the identity of the porphyrin-chelated metal ions defines the selectivity of the electrocatalysts. Here we shed light on the significance of this selection by explaining the reason behind the observed efficiency of our CuPOR-COF in eNRR. Among the nine H⁺/e⁻ transfer steps of eNRR,^[49,50] the reduction step from *NH₂OH to *NH₂ (Figure 4A) (* denotes chemisorption) was recently determined to be the potential-determining step (PDS) on a similar 2D nickel-centered porphyrin-based COF^[42] (Section 6, Supporting Information). We investigated the ab initio thermodynamics of the PDS (*NH₂OH $\rightarrow$ *NH₂) on CuPOR-COF, CoPOR-COF, and NiPOR-COF electrocatalysts (Figure 4B). The calculated Gibbs free energy for the PDS (*NH₂OH $\rightarrow$ *NH₂) of eNRR of CuPOR-COF ($\Delta G = -0.02$ eV) indicates a nearly spontaneous process, which is more thermodynamically favorable than CoPOR-COF ($\Delta G = 0.07$ eV), NiPOR-COF ($\Delta G = 0.19$ eV), and previously reported Ni porphyrin-based COFs ($\Delta G = 0.28$ eV).^[42] To explain the different catalytic performances of MPOR-COF with different metal atoms, we performed further electronic structure calculations. The band structures of CuPOR-COF, CoPOR-COF, and NiPOR-COF (Figures S36A,D,G, Supporting Information) show that the half-filled flat bands composed of unsaturated Cu-*d*_{xy} and Co-*d*_{z²} orbitals located at the Fermi energy, making them active to accept and release electrons, while the gapped band and fully-filled Ni-*d*_{z²} orbital are inert for the adsorption of reactants. As a result, the molecular NH₂OH (reactant of PDS) can only be physically adsorbed on the central Ni site, which is weaker than the apparent ionic bonding between N (in NH₂OH) and Cu or Co sites. (Figure S36, Supporting Information). In addition, the band structure of CuPOR-COF-NH₂ (Figure 4C, product of PDS) shows that the conduction band maximum (CBM) is hybridized with Cu-*d*_{z²} and Cu-*d*_{xy} orbitals close to the Fermi energy. Therefore, it is feasible to attract NH₂ groups along the directions of Cu-*d*_{z²} orbitals and deliver a low reaction energy for the PDS, which can also be supported by

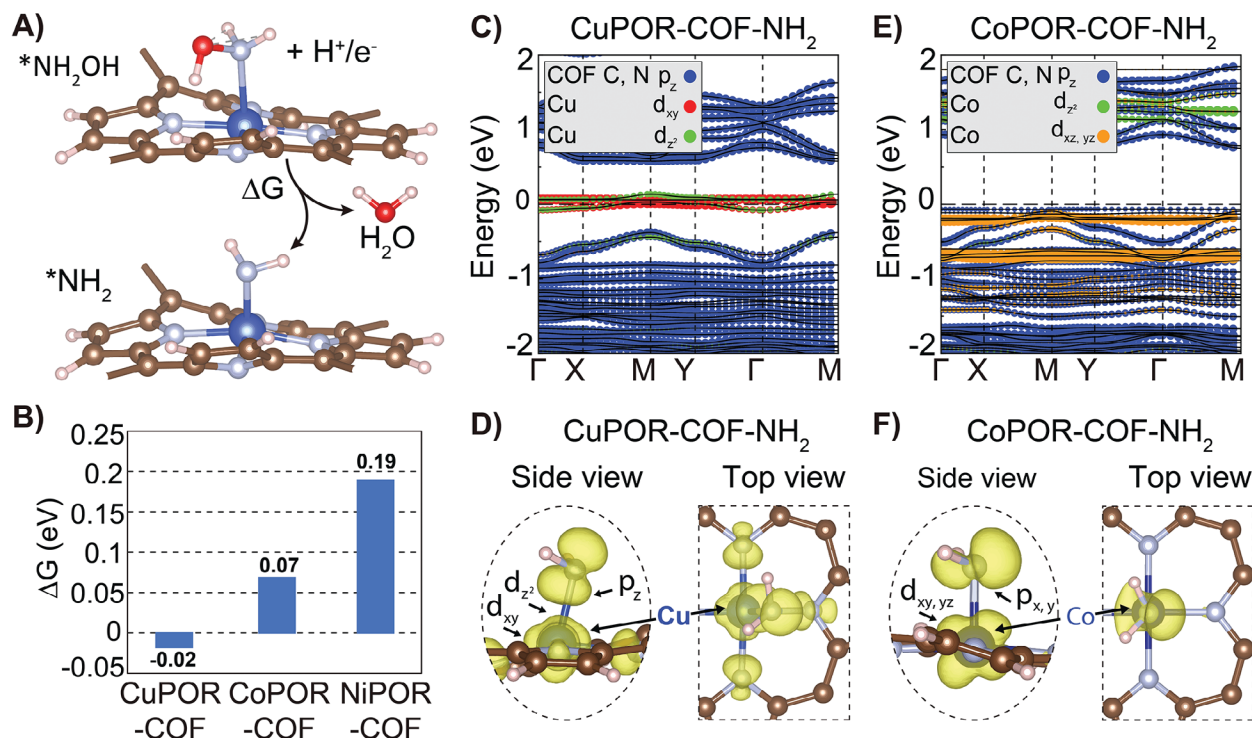


Figure 4. DFT calculations of nitrate electroreduction reaction: A) The ball-and-stick structural sketch of the potential-determining step ($*\text{NH}_2\text{OH} \rightarrow * \text{NH}_2$, * indicates the COF moieties) of electrochemical nitrate reduction reaction (eNRR) on the CuPORA-COF. B) The Gibbs free energies (ΔG) of the PDS of eNRR on CuPORA-COF, CoPORA-COF, and NiPORA-COF. C) The orbital-projected band structures of CuPORA-COF-NH₂. The blue, red, and green dots represent the projectional weight of framework C, N- p_z , Cu- d_{xy} , and Cu- d_{z^2} orbitals, respectively. D) The side/top view of energy-windowed partial charge density around the Fermi energy (from -0.3 to 0.3 eV) with isosurface = $0.01 \text{ e}/\text{\AA}^3$. E, F) The orbital-projected band structures and partial charge density of CoPORA-COF-NH₂. The orange dots represent the projection weight of Co- $d_{xz, yz}$.

the calculated partial charge density around Fermi energy (from -0.3 to 0.3 eV) (Figure 4D) showing bonding dominated by the out-of-plane Cu- d_{z^2} orbital and the vertical N- p_z orbital of NH₂. In comparison, the band structures of CoPORA-COF-NH₂ show gapped bands and fully-filled Co- $d_{xz, yz}$ and d_{yz} orbitals (Figure 4E) near the Fermi energy. The corresponding partial charge density indicates that the weaker attraction between CoPORA-COF and NH₂ is from out-of-plane Co- $d_{xz, yz}$ orbitals, and horizontal N- $p_{x, y}$ orbitals of NH₂. Therefore, our experimental finding of higher product activity toward NH₃ on Cu site than Co site can be understood by the stronger interaction of Cu site with NH₂ as explained from both thermodynamic and electronic perspectives. Moreover, the high activity of Cu active sites toward NH₃ product is also believed to be due to the dual chemical stability in both the more reduced state (Cu¹⁺) and more oxidized state (Cu²⁺) during electrochemical reactions. Such superiority of Cu-based catalysts has been observed in other electrochemical chemical reactions, including eNRR.^[51] Overall, our thermodynamic and electronic analysis has revealed the catalytic efficiency of CuPORA-COF from a microscopic perspective and underpins the significance of the choice of coordinated metal in the porphyrin structure of the synthesized COFs.

3. Conclusion

In conclusion, an appealing pathway for integrating Porphyrin-containing COFs into electrode device architectures is intro-

duced. The developed synthetic pathway offers high-precision coating of COFs as thin films. This bottom-up synthetic method has proven transferable, allowing the emergence of various possibilities for MPORA-COFs. Additionally, we have demonstrated that metal-containing COFs, synthesized with molecular precision, serve as highly effective electrocatalysts in essential electrochemical reactions such as eNRR and ORR/OER. This work introduces a new class of porous catalysts and offers an alternative approach to realize highly efficient electrocatalysis.

4. Experimental Section

The Experimental Section is available in Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Author Contributions

S.I.G.P.M., S.N., and T.Z. equally contributed to this work. Conceptualization: SN. Methodology: SIGPM, SN, SNR, HS, ASK, TZ, ZJ and AMR. Investigation: SIGPM, SNR, SN, HS, TZ and ZJ. Funding acquisition: SN, ASK and AMR. Project administration: SN, ASK and AMR. Supervision: SN, ASK and AMR. Writing – original draft: SIGPM, SN, SNR, HS, TZ and ZJ. Writing – review & editing: SIGPM, SNR, HS, TZ, ZJ, SN, ASK and AMR.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

ammonia, covalent organic frameworks, electrocatalysts, Li-O₂ battery, nitrate reduction, oxygen reduction and evolution reaction, Porphyrins, vapor phase synthesis

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