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In situ Electropolymerized 3D Microporous Cobalt-Porphyrin Nanofilm for Highly Effective Molecular Electrocatalytic Reduction of Carbon Dioxide

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Electrocatalytic CO₂ reduction reaction (CO₂RR) based on molecular catalysts, for example, cobalt porphyrin, is promising to enhance the carbon cycle and mitigate current climate crisis. However, the electrocatalytic performance and accurate evaluations remain problems because of either the low loading amount or the low utilization rate of the electroactive CoN₄ sites. Herein a monomer is synthesized, cobalt(II)-5,10,15,20-tetrakis(3,5-di(thiophen-2-yl)phenyl)porphyrin (CoP), electropolymerized onto carbon nanotubes (CNTs) networks, affording a molecular electrocatalyst of 3D microporous nanofilm (EP-CoP, 2–3 nm thickness) with highly dispersed CoN₄ sites. The new electrocatalyst shortens the electron transfer pathway, accelerates the redox kinetics of CoN₄ sites, and improves the durability of the electrocatalytic CO₂RR. From the intrinsic redox behavior of CoN₄ sites, the effective utilization rate is obtained as 13.1%, much higher than that of the monomer assembled electrode (5.8%), and the durability is also promoted dramatically (>40 h) in H-type cells. In commercial flow cells, EP-CoP can achieve a faradic efficiency for CO (FE CO) over 92% at an overpotential of 160 mV. At a higher overpotential of 620 mV, the working current density can reach 310 mA cm⁻² with a high FE CO of 98.6%, representing the best performance for electrodeposited molecular porphyrin electrocatalysts.

1. Introduction

The excessive emission of greenhouse gases has triggered a serious worldwide environmental and climate crisis.[1] With respect to the dilemma, the developments of highly efficient artificial carbon circles provide promising economic solutions, among which the electrocatalytic CO₂ reduction reactions (CO₂RR) in aqueous solution is a prospective approach to mitigate the greenhouse effect and meanwhile produce value-added chemicals and fuels.[2] With half a century’s efforts, a consensus that exposing electroactive sites remarkably enhances the total catalytic performance has been reached, and hence porous materials, in which inherent pores ensure mass transport, have acquired great mark afterward.[3]

Therein, crystalline metal-organic frameworks and covalent organic frameworks have widely been applied in CO₂RR and offer unique opportunities for designing electrocatalysts with tailored reactivity,
selectivity, and stability,[4] despite some issues such as OH− coordination with Zr4+ and Al3+ in alkaline solution,[5] ligand replacement,[6] and hydrolysis in acid.[7] On the other side, amorphous phosphors, which lack crystalline order, have also emerged as promising materials for CO2RR. Typically, electropolymerization (EP) method has been applied to fabricate amorphous 2D polymer films onto electrode from amino, vinyl, thiophene, or carbazole functionalized metal complexes.[8] For example, Hamuryudan et al. modified graphite electrode via the EP of 5,15-bis(thienyl) functionalized cobalt porphyrin, which recorded an optimal CO production of 86.97% with constant current density at 0.42 mA cm−2 within ~2 h.[8] Similarly, the EP of bithiienyl-substituted Co(II)-phthalocyanine on carbon paper gave an effective electrocatalyst for the reduction of CO2 to CO, corresponding to a Faradaic efficiency (FE) of 94% and turnover frequency (TOF) of 0.29 s−1.[8] Although their activities have been demonstrated in CO2RR, there are few with a thorough product analysis, resulting in a lack of detailed studies focused on CO2RR and its underlying mechanism. In addition, those cases mentioned exclude the CO2RR performances in gas-diffusion-electrode (GDE) based flow cells. Theoretically, the EP method can simultaneously perform fast polymerization and direct film deposition, taking advantage of metal-free green synthesis, mild reaction conditions, precise control of film thickness, etc. More importantly, this electrodeposition method is very promising for the fabrication of large-scale GDE with a minimal amount of materials.[9]

Herein, we reported the facile and fast fabrication of 3D microporous cobalt(II)-porphyrin nanofilm via EP on the crosslinked carbon nanotubes (CNTs) networks with highly dispersed electroactive CoN4 sites, and its application as electrocatalyst for CO2RR with excellent performances. We purposely designed and synthesized the monomer cobalt(II)-5,10,15,20-tetrakis(3,5-di(thiophen-2-yl)phenyl)porphyrin (CoP). Upon EP, the eight peripheral thiophene units on the porphyrin ring are highly active in coupling with each other, yielding 3D microporous CoP nanofilm (EP-CoP) on the crosslinked CNTs network composite electrode. EP-CoP nanofilm is uniformly dispersed on the CNTs surface with a thickness of 2–3 nm, leading to more abundant easily-accessible CoN4 electroactive sites, modulated electronic structure, and higher stability. Accordingly, a 13.1% utilization ratio and over 40-hours duration of the electroactive CoN4 sites are obtained in standard H-type cells. More importantly, EP-CoP exhibits a working current density of ~310 mA cm−2 with 98.6% selectivity to CO at an overpotential of 0.62 V in GDE-based flow cells, indicating a broad prospect for industrial applications.

2. Results and Discussion

The synthesis and characterizations of CoP were illustrated (Scheme S1, Figures S1–S4, Tables S2,S3, Supporting Information). Moreover, the 3D geometrical structure of the CoP monomer was confirmed by the single-crystal X-ray crystallography (CCDC 2241056), in which the CoN4 adopts a square planar geometry, with the average Co–N bond distance of 1.978 Å (Figure 1a). As expected, the dihedral angles between the peripheral opposite phenylene linkers and porphyrin ring are 66.7° and 64.2° (Figure 1b). Moreover, the dihedral angles between thiienyls from S1 to S4 and phenylene moieties are 3.1°, 23.7°, 21.2°, and 21.8°, respectively. In addition, the adjacent thiienyls appear as a staggered conformation. The unique 3D geometry of CoP with eight thiienyl moieties is essential to form 3D microporous polymer films upon the EP process. Cyclic voltammetry was carried out on a glassy carbon electrode in an anhydrous dimethyl formamide (DMF) solution containing 1 mm CoP and 100 mm tetraethylammonium perchlorate (TBAP) with a scan rate of 0.1 V s−1 (Figure S5, Supporting Information). Three pairs of quasi-reversible redox waves were unambiguously observed with experimental reduction peak potentials at 0.12, −0.69, and −1.75 V (vs Ag-wire reference electrode), corresponding to Co(III)/Co(II), Co(II)/Co(I) and the Co(I) complex anion, respectively.[10] Since the peak current is in proportion to the square root of the scan rate (ν1/2) (Figure S6, Supporting Information), the redox behaviors of CoP are considered as the mass-transfer-controlled electrode progresses. Figure 1c illustrates the formation of EP-CoP via EP from the monomer in a dichloromethane (DCM) solution. It should be noted that the potential higher than 1.15 V is the region for the oxidation polymerization of thienyl groups on CoP (Figure S7, Supporting Information, left). As expected, EP-CoP films were loaded on the crosslinked CNTs network composite electrode after 20 cycles (Figure S7, Supporting Information, right),[11] which is optimized by the experimental results of electrocatalytic CO2RR in H-type cells. For comparison, the polymer powder denoted as CP-CoP, was prepared by the traditional FeCl3-induced oxidative chemical polymerization (CP).[12] Brunauer–Emmett–Teller (BET) measurements based on the N2 adsorption isotherm at 77 K showed that the CP-CoP polymer has a specific surface area of 1400.8 m2 g−1 and two narrow pore size distributions centered at ~5.8 and 8.9 Å, respectively (Figure S8, Supporting Information). As for the CO2 atmosphere, BET surface areas were calculated to be 1040.5 m2 g−1 and 918.8 m2 g−1 at 273 and 298 K, respectively (Figure S9, Supporting Information). Since CoP is better suited for micropore analysis, the pore distribution obtained from CO2 adsorption indicates more elaborate pore structures in the range of 5–6 Å.[13] Because it is difficult to collect a certain amount of EP-CoP for the BET measurements, the experimental results obtained by CP-CoP polymer can provide valuable pore-size information of EP-CoP polymer.

Using the same EP method, the EP-CoP film was also prepared on the indium tin oxide (ITO) substrate for the measurement of UV–vis spectrum (Figure S11, Supporting Information). As for the monomer CoP film spin-coated on the ITO, the maximum absorption wavelength at 433 nm is assigned to Soret band, while the shoulder peak with maximum absorption wavelength at 539 nm is assigned to Q band (Table S4, Supporting Information).[14] Obviously, the EP-CoP film shows a red-shifted Soret band (448 nm) and Q band (561 nm), indicating an extended π-conjugation after EP.[13] In addition, one new absorption shoulder appears at 348 nm for EP-CoP, which indicates the effective formation of thiophene dimers in the process of EP. Compared with the monomer, EP-CoP shows an extra peak at 1103 cm−1 in their Fourier-transform infrared spectra (Figure S12, Table S5, Supporting Information), which can be ascribed to the α-linked C–C stretching of thiophene dimers. Similarly, this α-linked C–C stretching of thiophene dimers was observed at 1108 cm−1 in the CP-CoP.

Further, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) were
performed to investigate the morphology of EP-CoP/CNTs. Particularly, the samples were carefully rinsed several times with different solvents to exclude any monomers, oligomers, and electrolytes. SEM images clearly indicate there is no agglomeration of the polymer films on the crosslinked CNTs networks (Figure 2a). Meanwhile, the HRTEM image shows that the amorphous polymer films with a thickness of 2–3 nm spread uniformly on the highly conductive CNTs networks (Figure 2b, Figure S13, Supporting Information). This was further supported by energy dispersive X-ray spectroscopy (EDX), which reveals a homogeneous distribution of Co, N, and S elements on CNTs (Figure 2c). Contrast, a serious agglomeration was found for CP-CoP film on carbon paper drop-coated from its polymer ink under long-time ultrasonic blending. The agglomeration is composed of some rods packed disorderly and discretely with an approximate length of \( \approx 1 \mu \text{m} \) and width of \( \approx 200 \text{ nm} \) (Figure S14, Supporting Information). It should be noted that, because the CNTs surface provides the initial nucleation sites for the EP of CoP monomers, the EP-CoP nanofilms are homogeneously grown and highly dispersed on the crosslinked CNTs networks.

In order to get insight into the electronic structure, X-ray photoelectron spectroscopy (XPS) was employed, and a benchmark of cobalt(II)-tetraphenylporphyrin (CoTPP) was parallel investigated. As shown in Figure 3a, the binding energy of Co 2p \( ^{3/2} \) decreases from 779.3 eV for CoTPP to 778.4 eV for CoP, which is attributed to the higher electron density of CoN\(_4\) donated by the electron-rich thienyl moieties. However, it returns to 779.0 eV for EP-CoP. A reasonable explanation is that the extended \( \pi \)-electron delocalization in EP-CoP releases the electron density in CoN\(_4\) slightly. To support our hypothesis, X-ray absorption spectroscopy was applied on Co foil, CoP, and CP-CoP, and the Co K-edge X-ray absorption near edge structure (XANES) spectra are shown in Figure S15 (Supporting Information). In comparison to CoP, CP-CoP reveals a similar line size, shape, and position, consistent with its formal Co(II) oxidation state. However, the onset photon energy of 7708.7 eV for CoP increases to 7709.9 eV for CP-CoP polymer, indicating a positive edge shift. Normally, this phenomenon is derived from a higher oxidation state.\(^{[16]}\) Obviously, the polymerization furnishes the Co center with a more delocalized electronic structure, which reduces the electron density in this system.

The electrocatalytic CO\(_2\)RR was investigated in a three-electrode system and all potentials were converted into the reversible hydrogen electrode (RHE) with \( i_R \) compensation. Initially in a H-cell separated by proton exchange membrane, cyclic voltammetry experiments were performed to study the redox behaviors of electroactive CoN\(_4\) sites. Typically, the experiments were performed in 0.2 M phosphate buffer solution (PBS, pH = 7.4) saturated with argon, in which the electrocatalytic CO\(_2\)RR would be excluded while only the hydrogen evolution reaction (HER) possibly involved. Three pairs of reversible redox waves were clearly observed in Figure 3b, corresponding to the

![Figure 1](https://www.advancedsciencenews.com/)

**Figure 1.** a) Top view and b) side view of the single crystal structure of CoP, and c) synthetic diagram for EP-CoP.
Figure 2. a) SEM image of EP-CoP/CNTs. b) HRTEM image of EP-CoP/CNTs. c) EDX images of C (red), N (yellow), S (cyan), and Co (violet) on EP-CoP/CNTs.

Redox reactions of Co$^{2+}$/Co$^+$ couples in CoTPP, CoP, and EP-CoP. Compared with CoTPP, this redox potential shifts negatively by 137 mV for CoP and 81 mV for EP-CoP, which is consistent with the results of XPS and XANES spectra. As expected, the lower electron density of Co$^{2+}$ improves the electron affinity of CoN$_4$ sites, resulting in the shift of their peak potentials in the cyclic voltammograms. To eliminate the effect of the loading method on the loading amount,$^{[17]}$ we controlled the total catalyst loadings in the same order of magnitude, which were evaluated as 2.16 $\times$ 10$^{-8}$ mol cm$^{-2}$ for EP-CoP and 2.29 $\times$ 10$^{-8}$ mol cm$^{-2}$ for CoP by inductively coupled plasma (ICP) analysis. In a CO$_2$-saturated 0.5 m KHCO$_3$ electrolyte, bare CNTs exhibited a negligible cathodic current as observed from linear-sweep voltammetry (Figure 3c), while CoP showed an appreciable current density,

Figure 3. a) Co 2p XPS spectra of CoP (top), EP-CoP (middle), and CoTPP (bottom). b) Cyclic voltammograms of CoTPP (purple), CoP (blue), and EP-CoP (pink), scan rate: 0.1 V s$^{-1}$. c) Linear scan voltammograms of bare CNTs (black), CoP (blue), and EP-CoP (pink) in 0.5 m KHCO$_3$ under CO$_2$, at a scan rate of 0.1 V s$^{-1}$. d) Potential-dependent FE of CO and H$_2$ of CoP (blue) and EP-CoP (pink) in the H-cell (0.5 m KHCO$_3$). e) TOF$_{CO}$ of CoP (blue) and EP-CoP (red) calculated from the electroactive CoN$_4$ amount (top, solid) and the ICP-measured total Co amount (bottom, dash). f) Potential-dependent FE$_{CO}$ (green) and current density (red) of EP-CoP in the flow cell (1 m KOH).
with an onset potential of \(-0.40 \text{ V}\). By contrast, an abrupt increase in the current density was observed for EP-CoP with an onset potential of \(-0.37 \text{ V}\), indicating an effective CO\(_2\) reduction process. Afterward, potentiostatic electrolysis was performed from \(-0.45 \text{ to } -0.87 \text{ V}\) to investigate the electrocatalytic CO\(_2\)RR activity, and only mixed gaseous H\(_2\) and CO products were detected without any liquid products in the electrolyte solution (Figure 3d). Both CoP and EP-CoP showed a FE\(_{\text{CO}}\) higher than 90% between \(-0.54 \text{ to } -0.79 \text{ V}\), with a maximum FE\(_{\text{CO}}\) of 95% for EP-CoP. Under more negative potentials (e.g., \(-0.87 \text{ V}\)), HER gradually prevailed due to its more favorable kinetics. Moreover, the most prominent difference appears at \(-0.45 \text{ V}\), where a higher FE\(_{\text{CO}}\) of 84.9% was recorded for EP-CoP than that of 72.3% for CoP. Obviously, the polymer films of EP-CoP showed an improved selectivity under low overpotentials, which can be ascribed to the positive shifting of CoN\(_4\) redox waves. For comparison, the drop-coated CP-CoP was studied for CO\(_2\)RR under the same conditions. As plotted in Figure S16 (Supporting Information), the FE\(_{\text{CO}}\) slightly increased from 40.7% at \(-0.5 \text{ V}\) to 54.6% at \(-0.58 \text{ V}\), and then sharply decreased to 9.6% at \(-0.87 \text{ V}\), indicating that HER dominated during the whole operation potentials. The inferior performance of CP-CoP can be attributed to the insufficient electron transfer resulting from its agglomeration and uneven dispersion on the surface of CNTs. On the contrary, the highly dispersed EP-CoP nanofilm grown on the crosslinked CNTs networks shortens the electron transfer distance between the CNTs and the CoN\(_4\) electroactive sites and enhances the kinetics of CO\(_2\)RR. Consequently, we achieved excellent performances with a ultralow total loading amount (Figure S23, Table S7, Supporting Information). It should be noted that the nanometer-scaled thickness and the highly exposed CoN\(_4\) sites are crucial because the polymer is actually insulated at the working potential for CO\(_2\)RR.[18]

Notably, the faradic current density of the CO\(_2\)-to-CO conversion of EP-CoP is greater than that of CoP (Figure S17, Supporting Information), which might originate from the difference between either the intrinsic electroactivity or the loading amount of CoN\(_4\) sites. To clarify this issue, cyclic voltammetry was performed at a series of scan rates. The peak potentials move little with the scan rate, and the peak current are proportional to the scan rates, indicating that the redox behaviors of the electroactive CoN\(_4\) sites in both CoP monomer and EP-CoP are pretty reversible (Figures S18,S19, Supporting Information). The relationship between the peak current and the scan rate abides by the following equation:[19] 

\[
i_p = \frac{n^2 F^2}{4RT} \Gamma \nu \tag{1}
\]

where \(n\) is the electron transfer number, \(F\) is Faraday constant (96,485 C mol\(^{-1}\)), \(R\) is the gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \(T\) is the temperature (298.15 K), \(A\) is electrode area (cm\(^2\)), \(\Gamma\) is the surface coverage (mol cm\(^{-2}\)), and \(\nu\) is the scan rate (V s\(^{-1}\)). From the slope of the \(i_p\) versus \(\nu\) curve, the electroactive amount of CoN\(_4\) sites (i.e., \(\Gamma\)) was calculated as 2.83 \(\times\) 10\(^{-9}\) mol for EP-CoP and 1.32 \(\times\) 10\(^{-9}\) mol for CoP. Note that the electroactive amount or the effective loading amount, is the product of electrode area and surface concentration of CoN\(_4\) sites, it’s not necessary to know the exact area of the composite electrode and the coverage of CoN\(_4\) sites.

The TOF calculated from ICP and cyclic voltammetry were shown in Figure 3e. The intrinsic TOFs of CoP and EP-CoP obtained from the electroactive amount of CoN\(_4\) sites are comparable, that is, at the limiting steady-state 71.4 s\(^{-1}\) for EP-CoP and 63.1 s\(^{-1}\) for CoP, indicating that the electrochemical activities of CoN\(_4\) sites are similar with each other. However, the TOF values are much higher than those calculated from the total amount of Co by the ICP measurements. The results show that the TOFs obtained by ICP measurements were largely underestimated, indicating that most of the CoN\(_4\) sites are not electroactive even in the ultrathin EP-CoP nanofilm. Thus, the utilization rate of the CoN\(_4\) sites in the EP-CoP nanofilm can be obtained as 13.1%, much higher than that of the drop-coated CoP film (5.8%). It becomes clear that the difference in the catalytic current densities between CoP and EP-CoP arises not from the intrinsic activity but from the utilization rate of the CoN\(_4\) sites. In view of the inevitable aggregation and low conductivity of molecular metalloporphyrin catalysts, 3D microporous EP-CoP nanofilm prepared by in situ EP method have been demonstrated as a better choice to create a robust electron transfer pathway for CO\(_2\)RR than its analogs.

Previously, CoTPP has been intensively studied toward CO\(_2\)RR with excellent activity and selectivity, although its poor stability and durability limit its further applications.[20] Impressively, in the H-type cell, the EP-CoP showed long durability in CO\(_2\)RR, keeping a constant current density \((-8.5 \text{ mA cm}^{-2}\)\) and FE\(_{\text{CO}}\) (94%) within 40 h of continuous operation at \(-0.62 \text{ V}\) (Figure S20, Supporting Information). As for the drop-coated films, CoP monomers exhibited a higher constant current density \((-3.9 \text{ mA cm}^{-2}\)\) and FE\(_{\text{CO}}\) (90%) than CoTPP at the same operating conditions,[21] but declined after 12 h (Figure S21, Supporting Information). The high durability of EP-CoP should be ascribed to the strong adhesion of polymer nanofilms on the crosslinked CNTs networks during the in situ EP processes. However, the drop-coating polymer-modified electrodes often use polymer binders, suffering from low conductivity, agglomeration, and/or desorption issues.[22]

The current density in H-type cells is usually limited by the low CO\(_2\) solubility in aqueous solution as well as the sluggish mass transport. Thus, we performed the CO\(_2\)RR in a commercial electrolytic flow cell separated by an anion exchange membrane and coupled a gas-diffusion electrode with the EP-CoP nanofilm in 1 m KOH aqueous solution. Starting from \(-0.27 \text{ V}\), the EP-CoP nanofilm presented a FE\(_{\text{CO}}\) of 92.6% with a current density of 2.6 mA cm\(^{-2}\) (Figure 3f). Apparently, the strong alkaline environment decreases the RHE \(\approx\) 389 mV from Co\(^{2+}\)/Co\(^{3+}\) redox potential and thus leads to a low overpotential of 160 mV for CO\(_2\)RR. By tuning the polarization potential, FE\(_{\text{CO}}\) was enhanced from 95.9% at \(-0.37 \text{ V}\) to 98.6% at \(-0.7 \text{ V}\), and the current density reached from \(\approx\) 10 mA cm\(^{-2}\) to \(\approx\) 310 mA cm\(^{-2}\) at \(-0.73 \text{ V}\). The solid/liquid/gas 3-phase interface of the gas-diffusion electrode in the flow cell, can facilitate the mass transfer of CO\(_2\) molecules to the electroactive CoN\(_4\) sites in the microporous EP-CoP nanofilm, accelerate the kinetic rate of CO\(_2\)RR and achieve the high current density and FE\(_{\text{CO}}\). Compared with the previous reports, the CO\(_2\)RR performance based on the EP-CoP shows a more promising application in the industry (Figure S22, Table S6, Supporting Information).
We adopted density functional theory (DFT) calculations to elucidate the high performance of EP-CoP in the flow cell, by using the CoP repeat units. As known, HER always starts with the Volmer step, which involves water adsorption in a neutral/alkaline environment ($\text{H}_2\text{O} + \text{e}^{-} \rightarrow \text{H}_2 + \text{OH}^{-}$).\cite{23} As depicted in Figure 4a, in the absence of an anion, Co(I) binds the O segment of water, with the binding energy of water of $-0.24$ eV. However, in the presence of OH$^-$, Co(I) is primarily prone to adsorb OH$^-$ due to the stronger electrostatic binding ($-1.10$ eV). In this case, Co(I) can only bind the H segment of water due to the strong shielding effect from the OH$^-$ binding which causes nearly thermodynamic-equilibrium adsorption toward water ($-0.04$ eV). On the other hand, due to the binding of OH$^-$, the Gibbs free energy of the key intermediate $\text{H}^*$ ($\Delta G_{\text{H}^*}$) increases from 1.15 to 1.49 eV, further expanding the already high energy barrier toward HER (Figure 4b). In the CO$_2$RR process, the existence of OH$^-$ also significantly raises the free energy barrier for the $\text{COOH}$ intermediate formation (Figure 4c). However, the shielding effect also changes the adsorption mode from the vertical to the parallel, resulting in the more positive CO binding energy (Figure S24, Supporting Information), which is favorable for CO desorption. When only considering the rate-determining step of HER and CO$_2$RR, results are shown in Figure 4d. It is obvious that OH$^-$ is more likely to inhibit HER, and the difference further increases by 0.1 V, which drives the electrons to flow toward CO$_2$RR.

3. Conclusion

Although those transition metal complexes of porphyrins have excellent performances for electrocatalytic CO$_2$RR, their practical applications are limited because of either the low loading amount or the low utilization rate of the electroactive CoN$_4$ sites. To this end, we designed and synthesized a rigid monomer cobalt(II)-5,10,15,20-tetrakis(3,5-dithiophen-2-yl)phenylporphyrin (CoP), electrodeposited it on the crosslinked CNTs networks by EP method, affording a new electrocatalyst of highly-dispersed 3D microporous EP-CoP nanofilms with 2–3 nm thickness. The functional group, 3,5-dithiophen-2-ylphenyl on the porphyrin ring, as well as the further EP process, can finely tune the electron structure and thus the redox potentials of the CoN$_4$ sites, enabling the accurate calculation of the electroactive loading amount of the molecular electrocatalyst. The uniform ultrathin EP-CoP nanofilm grown on the crosslinked CNTs networks shortens dramatically the electron transfer pathway and enhances the redox potentials of the CoN$_4$ sites, enabling the accurate calculation of the electroactive loading amount of the molecular electrocatalyst. The uniform ultrathin EP-CoP nanofilm grown on the crosslinked CNTs networks shortens dramatically the electron transfer pathway and enhances the redox potentials of the CoN$_4$ sites, enabling the accurate calculation of the electroactive loading amount of the molecular electrocatalyst. The uniform ultrathin EP-CoP nanofilm grown on the crosslinked CNTs networks shortens dramatically the electron transfer pathway and enhances the redox potentials of the CoN$_4$ sites, enabling the accurate calculation of the electroactive loading amount of the molecular electrocatalyst. We found that the intrinsic electroactivity of each CoN$_4$ site in both EP-CoP and CoP change little, but the effective utilization rate of the CoN$_4$ catalytic sites in EP-CoP nanofilm was obtained as 13.1%, much higher than 5.8% of CoP. In the GDE-based flow cell, the working current density reached 310 mA cm$^{-2}$ with a high FECO$_2$ of 98.6%. The excellent performance was elucidated well by the DFT calculations, which reveal that the presence of OH$^-$ strongly inhibits HER and enhances CO$_2$RR. We believe
that the rational design of molecular catalysts via situ EP will provide a prospective assembly method for the fabrication of a large-area electrode for the commercial usage of electrocatalytic CO2 reduction.

4. Experimental Section

Preparations of CoP and CP-CoP Modified Electrodes: CNTs (2 mg) (XF-NANO, XFM13) and 2 mg of CoP or CP-CoP were dispersed in 2 mL ethanol with 20 µL 5% Nafion emulsion by high-power sonication (600 W, Scientz SB-5200DT) to obtain a homogenous ink. Afterward, 200 µL ink was casted onto a carbon paper (Sigracet 28BC, size: 1 cm × 1 cm). The loading amount of CoP was calculated according to the cobalt content from ICP results.

Fabrication of EP-CoP Modified Electrode: The ink containing 2 mg mL⁻¹ CNTs was prepared by high-power sonication (600 W, Scientz SB-5200DT). Ink (200 µL) was then casted onto the carbon paper (Sigracet 28BC, size: 1 cm × 1 cm). The three-electrode system was adopted for the EP, where a silver (Ag) wire served as the reference electrode and a platinum (Pt) foil served as the counter electrode. A DCM solution containing 0.2 mM CoP and 50 mM TBAP was used as the electrolyte. The crosslinked CNTs networks/carbon paper composite electrode emerged into the DCM solution, followed by Ar bubbling for 20 min. After that, cyclic voltammetry was employed to perform EP by potential scan between −0.2 and 1.6 V for 20 cycles with a scan rate of 50 mV s⁻¹. The prepared electrode was rinsed several times with DCM and dried in the air before use. The loading amount of EP-CoP was calculated according to the cobalt content from ICP results.

Electrochemical Measurements: All electrochemical measurements were carried out with a 3-electrode system on either CHI 760D potentiostat (for impedance measurements). As mentioned above, the geometric size of the working electrodes was 1 cm × 1 cm. For iRcompensation, electrolyte resistance between the reference electrode and working electrode was determined by potentiostatic electrochemical impedance spectroscopy analysis at the open-circuit potential with an oscillation amplitude of 5.0 mV and a frequency range from 0.1 to 100 kHz. Considering the iRcompensation, all the potentials were calibrated versus the RHE by the following equations:

\[ E_{\text{vs RHE}} = E_{\text{vs Ag/AgCl}} + 0.059 \times \text{pH} + 0.205 - iR_{\text{comp}} \]  
\[ E_{\text{vs RHE}} = E_{\text{vs Hg/HgO}} + 0.059 \times \text{pH} + 0.098 - iR_{\text{comp}} \]

In the H cell, the counter and reference electrodes were a Pt foil and an Ag/AgCl electrode with an inner solution containing 3.5 m KCl. Proton exchange membrane (DuPont Nafion 117) was used as the separator between the anode and cathodic chambers, and the CO₂ flow rate was 24 sccm. In the commercial flow cell, the gas diffusion electrode, Ni foam, and anion exchange membrane (Fumasep FAA-3-PK-130) were used. The reference electrode was a Hg/HgO electrode with an inner solution containing 1 M KOH, CO₂, catholyte, and anolyte flow rates were 10 sccm, 5, and 80 mL min⁻¹, respectively.

Product Quantifications: The gas outlet of the cathodic chamber was connected to an online gas chromatograph (Shimadzu, GC-2014) with the carrier gas Ar. A flame ionization detector with a methanizer was equipped for quantifying CO₂, and a thermal conductivity detector (TCD) was equipped for quantifying H₂. The gas chromatograph was calibrated by standard gas with the concentration varying from 0.2% to 10% (Figures S25–S27, Supporting Information). The fraction of gaseous product was calculated according to peak areas.

The gaseous product was injected into a gas chromatograph after 12-min’s of electrolysis. The faradic efficiency of H₂ and CO was calculated by the following equation:

\[ FE = \frac{2g_{\text{ppm}}F}{iRT} \]

where g is CO₂ flow rate, x is the fraction of gaseous product detected by gas chromatography, p is atmospheric pressure (101 325 Pa), F is Faraday constant (96 485 C mol⁻¹), i is the current measured by the potentiostat, R is the gas constant (8.314 J mol⁻¹ K⁻¹) and T is 298.15 K. Turnover frequency was calculated by:

\[ \text{TOF} = \frac{\Omega_{\text{CO}}}{2e \cdot N_A \cdot \frac{n_{\text{ele}}}{t}} \]

where \( \Omega_{\text{CO}} \) is the total quantity of electric charge, e is the elementary charge (1.60 × 10⁻¹⁹ C), \( N_A \) is the Avogadro constant (6.022 × 10²³ mol⁻¹), \( n_{\text{ele}} \) is the amount of electroactive CoN₄ sites obtained by cyclic voltammetry or ICP analysis, t is the electrolysis time.

The liquid product was detected in water (H₂O: D₂O, 9:1 in v/v) with the 'H NMR measurement (Figure S28, Supporting Information). DMSO (2 mM) was chosen as the internal reference. The pre-saturation technique was used to reduce the solvent signal. No liquid product was found in the electrolysis.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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3D microporous polymer nanofilms, cobalt porphyrin, electrocatalytic CO₂ reduction, electropolymerization

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