

Enhancing NO reduction to ammonia via porous aromatic frameworks: Co-modified PAF-TPP for efficient mass transfer and electrocatalytic performance

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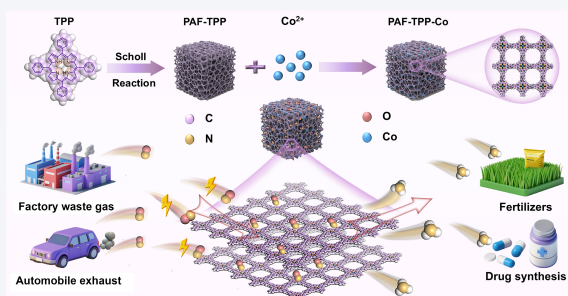
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ABSTRACT: The electrocatalytic reduction of nitric oxide (NO) to ammonia (NH₃) (NORR) provides a sustainable solution for pollutant remediation and value-added chemical synthesis. In this study, we introduce porous aromatic frameworks (PAFs) into the NORR system for the first time, exploiting their unique channel structures to enhance gas adsorption and mass transport. By incorporating Co²⁺ ions into the PAF-TPP material, constructed from tetraphenylporphyrin (TPP), we created the PAF-TPP-Co catalyst, which offers active coordination sites. The PAF structure effectively regulates the interfacial enrichment of NO molecules and promotes mass transport, while the synergistic effect between the Co-N₄ active sites and the PAF framework optimizes both electronic structure and material transport. Through the combined action of microporous structure and active sites, PAF-TPP-Co significantly improves NO adsorption and transport efficiency, facilitating the multi-electron conversion of NO to NH₃. At a potential of −0.6 V vs. RHE, this catalyst achieves an ammonia production rate of 914.2 μg·h^{−1}·mg_{cat}^{−1} and a Faradaic efficiency of 71.3%. Moreover, we propose a “adsorption-transport-catalysis” synergistic mechanism that not only enhances NO activation but also suppresses the competitive hydrogen evolution reaction. *In situ* infrared spectroscopy, Raman spectroscopy, and density functional theory (DFT) calculations were employed to further elucidate the catalytic mechanism. This study offers a new mechanistic perspective on NO electrocatalytic reduction based on PAF materials and provides an effective solution for the “waste-to-resource” conversion of industrial NO emissions.

KEYWORDS: porous aromatic frameworks (PAFs), electrocatalytic reduction, ammonia synthesis, NO adsorption, NO mass transfer



1 Introduction

Ammonia (NH₃), as a pivotal carbon-free chemical, plays an indispensable role in chemical manufacturing, agricultural production, and energy storage [1]. At present, industrial ammonia synthesis predominantly relies on the Haber–Bosch process, which converts nitrogen and hydrogen under harsh conditions of elevated temperature and pressure [2, 3]. However, this process is highly energy-intensive and accompanied by substantial CO₂ emissions,

rendering it incompatible with the imperatives of sustainable development [4]. Accordingly, the development of green and efficient alternative routes for ammonia synthesis is of considerable significance.

In recent years, photocatalytic [5] and electrocatalytic nitrogen reduction reactions (NRR) [6, 7] have been extensively explored as sustainable pathways for ammonia production. Nevertheless, their practical implementation remains severely hindered by the exceptionally high dissociation energy of the N≡N bond and the intrinsically complex multi-electron transfer processes, which collectively lead to sluggish reaction kinetics and unsatisfactory selectivity [8, 9]. In contrast, the electrocatalytic nitric oxide reduction reaction (NORR) has emerged as a promising alternative [10–12]. As a major pollutant originating from industrial emissions and fossil fuel combustion, nitric oxide (NO) can be valorized into ammonia, thereby simultaneously mitigating environmental

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pollution [13, 14] and enabling ammonia synthesis via energetically more favorable pathways [15–17].

To date, a wide spectrum of NORR catalysts has been developed, including noble metals, transition metals, and metal-free materials [15–23]. However, in practical systems, the hydrogen evolution reaction (HER) [24] often acts as a dominant competing process, significantly suppressing ammonia selectivity, particularly under conditions of low NO concentration. Moreover, the inherently low solubility of NO in aqueous electrolytes, together with interfacial mass transport limitations, further constrains the overall reaction efficiency [25, 26]. Therefore, achieving efficient NO enrichment, accelerated mass transport, and synergistic regulation of reaction pathways represents a central challenge for advancing NORR performance.

Current research has primarily focused on modulating the electronic structure of active sites and optimizing interfacial engineering. For instance, molecular structure design has been employed to tune the adsorption energetics of key intermediates, thereby lowering reaction barriers and accelerating kinetics [27]. Engineering interfacial electric fields and proton transport pathways has also been demonstrated to facilitate proton-coupled electron transfer (PCET) while suppressing the HER [28]. In addition, strategies such as metal-support interactions and spin-state regulation have been utilized to tailor the electronic configuration and reaction pathways [9, 29]. Furthermore, heterointerface engineering can enhance reaction selectivity by modulating local charge distributions [3]. Despite these advances, the prevailing strategies remain largely centered on the intrinsic regulation of active sites, with comparatively limited attention paid to the interfacial enrichment and mass transport behavior of NO during the reaction. In practical systems, where NO solubility is low and diffusion is inherently constrained, this factor often becomes a critical bottleneck limiting overall reaction efficiency. Therefore, a central challenge in NORR lies in achieving a synergistic optimization that simultaneously enhances the intrinsic reactivity of active sites while enabling efficient NO enrichment and rapid interfacial transport.

Porous organic polymers, characterized by high specific surface areas and tunable pore architectures, offer distinct advantages in gas adsorption and mass transport regulation [30–32]. These features can effectively increase the local concentration of NO at the catalytic interface and shorten diffusion pathways, thereby accelerating reaction kinetics [33]. Consequently, embedding catalytic active sites within porous frameworks to realize a synergistic design integrating electronic structure modulation with mass transport enhancement represents a promising strategy for advancing NORR performance. Among various candidates, porous aromatic frameworks (PAFs) have attracted considerable attention owing to their high specific surface areas, robust structural stability, and tunable pore architectures and coordination microenvironments. In particular, the incorporation of porphyrin units to construct Co-N₄ moieties not only enables efficient adsorption and activation of NO molecules but also provides well-defined and stable single-atom active centers [34]. Meanwhile, the interconnected porous network of PAFs facilitates effective NO enrichment and rapid diffusion, while offering low-resistance pathways for electron and ion transport, thereby collectively enhancing reaction kinetics and interfacial utilization efficiency [35].

Furthermore, within NORR systems, the inherently low solubility of NO in aqueous media renders isolated porphyrin

molecules insufficient for sustained capture and conversion [36]. In contrast, the PAF architecture establishes an integrated “adsorption-transport-reaction” microenvironment, which markedly alleviates this limitation. As such, these materials hold significant promise for achieving efficient ammonia synthesis via NORR through the synergistic regulation of NO enrichment and electrocatalytic conversion processes.

Despite these advantages, the application of cobalt porphyrin-based PAFs in NORR remains largely unexplored. In particular, porphyrin-based PAFs constructed via the Scholl reaction have received little attention in this context. Compared with other synthetic approaches, the Scholl reaction offers notable merits, including procedural simplicity, the use of cost-effective catalysts, and high synthetic efficiency, while simultaneously preserving the intrinsic porous architecture and adsorption-catalysis functionality of PAF materials.

Building on this rationale, we introduce porous aromatic frameworks into the NORR system. Specifically, tetraphenylporphyrin (TPP) was employed as the monomer to construct PAF-TPP, followed by metallation to incorporate Co-N₄ active centers, yielding the PAF-TPP-Co catalyst. This material integrates a high specific surface area with a stable microporous architecture, enabling efficient NO adsorption and interfacial enrichment, while the Co centers promote the selective activation and hydrogenation of NO molecules. At −0.6 V vs. RHE, the catalyst delivers an NH₃ yield rate of 914.2 μg·h^{−1}·mg_{cat}^{−1} and a Faradaic efficiency of 71.3%, demonstrating outstanding NORR performance. Moreover, the robust M-N₄ coordination structure effectively suppresses the HER, thereby enhancing reaction selectivity. This work provides a new design paradigm for the application of porous organic frameworks in NORR and offers a viable strategy for the valorization of NO-containing exhaust gases.

2 Experimental

2.1 Materials

The chemical reagents used in this study include anhydrous aluminum chloride, tetraphenylporphyrin, anhydrous cobalt chloride, sodium sulfate, sodium hydroxide, sodium hypochlorite (purchased from Macklin), sodium nitroprusside, sodium citrate, and salicylic acid (purchased from Sigma-Aldrich), as well as trichloromethane, hydrochloric acid, and anhydrous ethanol (purchased from Beijing Chemical Plant). Unless otherwise stated, these reagents were used without further purification. Prior to use, trichloromethane was dried over 4A molecular sieves to remove excess moisture.

2.2 Synthesis of PAF-TPP

A mixture of 0.2 g of TPP monomer, 1.5 g of anhydrous aluminum chloride (AlCl₃) catalyst, and chloroform solvent was thoroughly blended. The resulting mixture was transferred to a stainless-steel reaction vessel lined with polytetrafluoroethylene (PTFE) and sealed. The reaction was carried out in an oven at 120 °C for 18 h under anhydrous conditions. After cooling, the powder was filtered and washed three times with a mixture of 1 mol·L^{−1} hydrochloric acid and anhydrous ethanol. Subsequently, the sample was subjected to continuous washing for 8 h each with anhydrous ethanol, acetone, and dichloromethane. The purified powder was then dried in an oven at 80 °C to yield the PAF-TPP material with a

yield of 93%. A schematic diagram of the sample is shown in Fig. 1(a).

2.3 Synthesis of PAF-TPP-Co

0.1 g of PAF-TPP sample was added to 50 mL of methanol solution and sonicated for 30 min to ensure complete dispersion of the sample in the solvent. Separately, 0.3 g of the metal salt (CoCl_2) was dissolved in 20 mL of methanol solution. The two solutions were then mixed and stirred at room temperature for one day to allow the coordination of PAF-TPP with the metal ions via a co-precipitation method. After stirring, the mixture was washed with methanol, filtered, and dried to yield the metal-ion coordinated product, denoted as PAF-TPP-Co.

2.4 Electrochemical experiments

Electrochemical experiments were conducted using a CHI series electrochemical workstation (Shanghai Chenhua), with the testing system constructed in an H-type dual-chamber electrolysis cell. A three-electrode setup was employed, with a platinum sheet electrode as the counter electrode, an Ag/AgCl electrode as the reference electrode, and a carbon paper electrode loaded with the catalyst as the working electrode. Since NO gas is hazardous to both human health and the environment, the electrolysis system was strictly sealed, and exhaust gases were treated by passing through two wash bottles—one containing an acidic solution and the other

containing potassium permanganate solution. Additionally, to ensure the purity of the NO gas, two wash bottles filled with KOH solution were placed at the gas inlet to remove excess gases. Both the cathode and anode compartments of the electrolysis cell were filled with 80 mL of 0.5 M sodium sulfate electrolyte. A pretreated Nafion 117 proton exchange membrane was used as the separator. To ensure the purity of the NORR testing system, argon gas was passed through the system for 20 min prior to the experiment to completely purge any residual gases. After purging, the working electrode was activated by 12 cycles of cyclic voltammetry (CV), followed by linear sweep voltammetry (LSV) testing. Subsequently, NO gas (with a concentration of 10%) was introduced for 10 min, and LSV tests were repeated. The current signals under Ar and NO conditions were compared to select the appropriate potential. Chronoamperometric tests were then performed at the chosen potential for 1 h. At the end of the experiment, argon gas was passed through the system for another 10 min to remove excess NO gas. After purging, the electrolyte was collected for ammonia yield analysis. All operations were carried out within a sealed fume hood. The potential values in the electrochemical tests, referenced to the Ag/AgCl electrode, were converted to the reversible hydrogen electrode (RHE) according to the Nernst equation

$$E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.22 \text{ V} + 0.059 \times \text{pH}$$

More detailed synthetic procedures, characterization conditions,

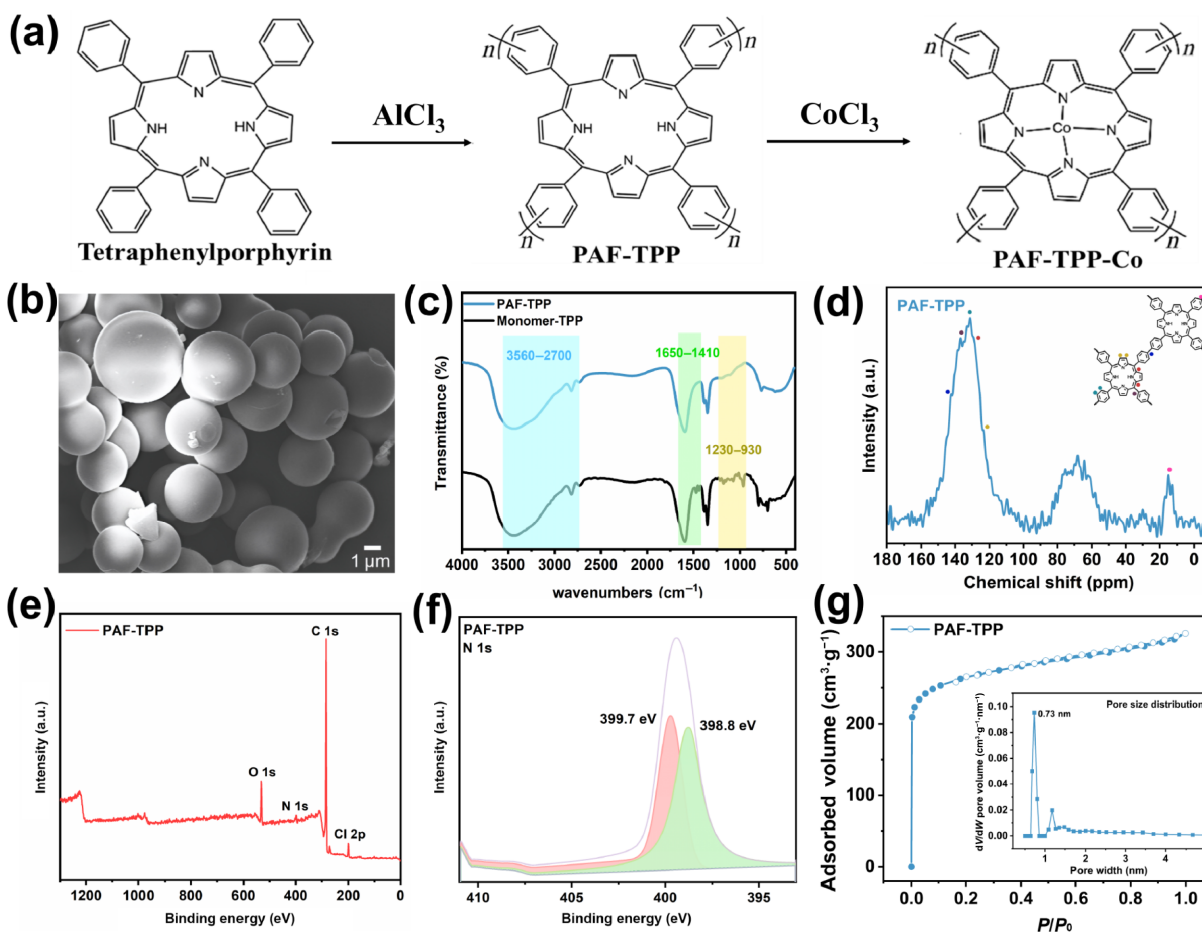


Figure 1 (a) Schematic diagram of the preparation of PAF-TPP and PAF-TPP-Co. (b) SEM image of PAF-TPP. (c) FTIR spectra of TPP and PAF-TPP. (d) Solid-state ^{13}C CP/MAS NMR spectrum of PAF-TPP. (e) XPS full spectrum of PAF-TPP. (f) High-resolution XPS spectrum of N 1s for PAF-TPP. (g) Nitrogen adsorption/desorption isotherms and pore size distribution of PAF-TPP.

and additional electrochemical analyses are provided in the Electronic Supplementary Material (ESM).

3 Results and discussion

The PAF-TPP material was synthesized via the Scholl reaction, using AlCl_3 as a Lewis acid catalyst in chloroform solvent, as illustrated in Fig. 1(a). Detailed synthesis procedures are described in Section 2. Macroscopically, the PAF-TPP material appears as a black powder (Fig. S1 in the ESM). To investigate the microscopic morphology of the synthesized PAF-TPP material, we characterized its surface using scanning electron microscopy (SEM). As shown in Fig. 1(b), the SEM images reveal that PAF-TPP predominantly exhibits a spherical morphology with a relatively uniform distribution. The particle size is approximately 3 μm .

To examine the polymerization sites during the synthesis of PAF-TPP, Fourier-transform infrared (FTIR) spectroscopy was employed to compare PAF-TPP with its precursor monomer. As shown in Fig. 1(c), the FTIR spectra of PAF-TPP and the monomer are highly similar within the 4000 to 400 cm^{-1} range, indicating that the basic chemical structure of the monomer is retained during polymerization. However, compared to the monomer, the PAF-TPP spectrum exhibits significant changes in several wavenumber regions.

The broad peak between 3560–2700 cm^{-1} is attributed to the stretching vibrations of C–H in unsaturated carbon and N–H bonds [37, 38]. The strong peak at 1660–1410 cm^{-1} , indicated by the green shading, corresponds to the C=C stretching vibration in the aromatic ring [39]. After polymerization, a significant reduction in the number of absorption peaks in the green-highlighted region was observed, likely due to the extended conjugation of the π -system and the conjugate effects, resulting in a more uniform energy distribution and greater stability of the C=C stretching vibration peaks [40]. The peaks in the yellow-highlighted region, associated with the in-plane deformation vibrations of the benzene ring, disappear after polymerization, suggesting that the polymerization reaction predominantly occurred at the benzene ring, and the coupling polymerization process inhibited the in-plane deformation vibrations of the benzene rings [40, 41].

These differences in the FTIR spectra indicate that a coupling polymerization reaction occurred between the benzene rings during the synthesis, consistent with the Scholl reaction mechanism. In this process, the reaction polymerization sites randomly appear at vacant positions on the benzene rings, resulting in the formation of the new PAFs material.

The ^{13}C solid-state NMR spectrum of PAF-TPP (Fig. 1(d)) further confirms the formation of the framework. The broad peaks observed in the 100–150 ppm range are attributed to the carbon atoms in the porphyrin and benzene rings of PAF [42–44].

To further confirm the successful incorporation of nitrogen-containing groups into the synthesized porous aromatic framework material, X-ray photoelectron spectroscopy (XPS) analysis was performed on the synthesized PAF-TPP material. As shown in Fig. 1(e), the XPS full spectrum exhibits a prominent nitrogen peak. High-resolution N 1s spectra (Fig. 1(f)) further reveal two distinct characteristic peaks at 398.8 and 399.7 eV. The former corresponds to the characteristic binding energy of pyridine-type nitrogen (=N–) in the porphyrin ring (typically found at 398.3–398.9 eV) [41], while the latter is associated with the pyrrole-type nitrogen (–NH–) in the porphyrin structure (approximately 399.6–400.2 eV)

[45, 46]. The porphyrin molecular framework consists of four pyrrole units linked by methylene bridges, with two nitrogen atoms in the pyridine form and two in the pyrrole form. Therefore, the N 1s spectrum typically shows a main peak split into these two peaks, with an area ratio close to 1:1. The overall peak shape is symmetric with no significant splitting. The peak positions, types, and relative intensities observed in the PAF-TPP sample are highly consistent with the reported characteristics of porphyrin-based ligands, and combined with the synthetic route, it is reasonable to conclude that the material's framework successfully incorporates the targeted structure.

Additionally, the elemental composition of PAF-TPP was analyzed by CHN elemental analysis, and the results are summarized in Table S1 in the ESM. The material exhibits a high carbon content (56.45 wt.%), consistent with the aromatic framework structure. Nitrogen and hydrogen contents were determined to be 4.03 wt.% and 2.805 wt.%, respectively. The presence of nitrogen further confirms the successful incorporation of porphyrin units into the PAF network. Moreover, the elemental composition is in good agreement with the XPS results, collectively verifying the formation of the nitrogen-containing porous aromatic framework.

To gain a deeper understanding of the specific surface area and pore size distribution of the PAF-TPP material, N_2 adsorption–desorption experiments were conducted at 77 K. Prior to the experiments, the sample was heated under vacuum at 423 K for at least 4 h to remove moisture and other volatile impurities. The specific surface area, pore volume, and pore size distribution were then calculated using the Brunauer–Emmett–Teller (BET) theory. The experimental results, as shown in Fig. 1(g), reveal that PAF-TPP exhibits a typical type I adsorption isotherm with a minimal hysteresis loop. At low relative pressures ($P/P_0 < 0.1$), the adsorption volume increases sharply, indicating that the material possesses a microporous structure. The specific surface area measurement is summarized in Table S2 in the ESM, with PAF-TPP showing a surface area of 733.13 $\text{m}^2\cdot\text{g}^{-1}$ and a total pore volume of 0.45 $\text{cm}^3\cdot\text{g}^{-1}$. The pore size distribution further indicates that the pore size of PAF-TPP is approximately 0.73 nm, confirming its microporous nature.

After the synthesis of the PAF-TPP material, metal cobalt ions were introduced to obtain the PAF-TPP-Co material (Fig. 1(a)). To confirm the successful coordination of the metal ions to the framework of the PAF material, XPS was used to characterize both PAF-TPP and PAF-TPP-Co. Figure 2(a) shows the full spectra of PAF-TPP and PAF-TPP-Co in the range of 1200 to 0 eV. Compared to PAF-TPP, the PAF-TPP-Co spectrum exhibits a distinct cobalt (Co) peak, confirming the successful preparation of PAF-TPP-Co.

Further analysis of the Co 2p high-resolution spectrum (Fig. 2(b)) reveals characteristic peaks at 781.3 and 795.8 eV, corresponding to the Co^{2+} 2p_{3/2} and 2p_{1/2} binding energies, respectively. Satellite peaks for Co^{2+} are observed at 783.9 and 804.8 eV [47]. Additionally, the N 1s high-resolution spectrum (Fig. 2(c)) indicates that upon the introduction of Co^{2+} , the nitrogen peak splits into two separate symmetric peaks, with the pyrrole-type nitrogen peak shifting slightly to higher binding energy (400.1 eV). This shift is consistent with the coordination of the metal center to the pyrrole-type nitrogen atom of the porphyrin ring. In summary, the XPS data confirm that cobalt ions have been successfully anchored to the porphyrin sites of the PAF-TPP framework via

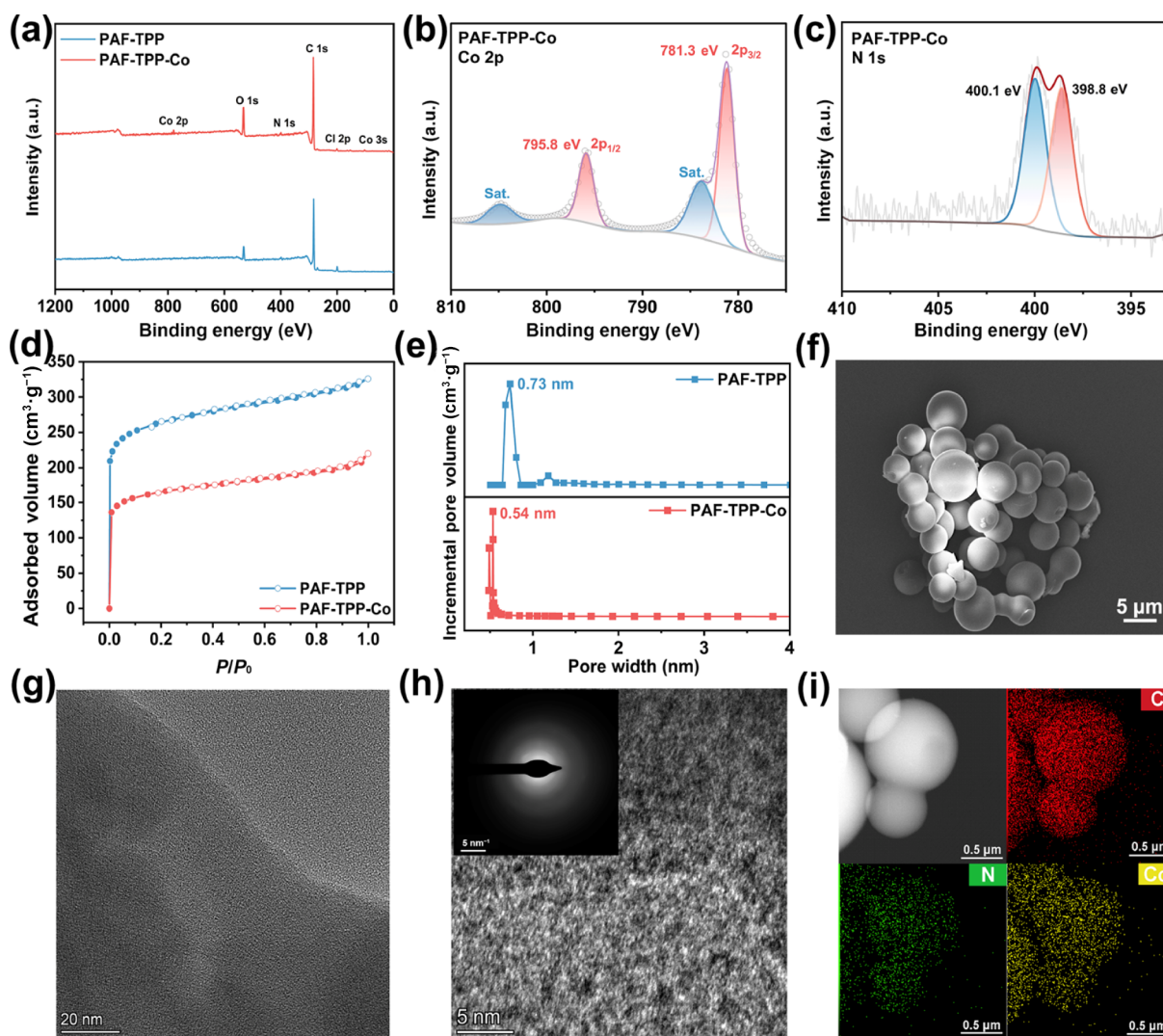


Figure 2 (a) XPS full spectra of PAF-TPP and PAF-TPP-Co. (b) High-resolution XPS spectrum of Co 2p for PAF-TPP-Co. (c) High-resolution XPS spectrum of N 1s for PAF-TPP-Co. (d) Nitrogen adsorption/desorption isotherms of PAF-TPP and PAF-TPP-Co. (e) Pore size distribution curves for PAF-TPP and PAF-TPP-Co. (f) SEM image of PAF-TPP-Co. (g) TEM image of PAF-TPP-Co. (h) HRTEM image and SAED diffraction rings of PAF-TPP-Co. (i) TEM elemental mapping of PAF-TPP-Co.

coordination, leading to the formation of the PAF-TPP-Co material.

To further verify the coordination of the PAF-TPP material with metal ions, inductively coupled plasma optical emission spectroscopy (ICP-OES) was employed to analyze the elemental content of the samples. Table S3 in the ESM presents the ion concentrations in the solution obtained after the incorporation of metal cobalt ions into the PAF-TPP material, along with the corresponding detection limits. As shown in the table, the target metal content in the sample exceeds the detection limit, indicating that metal ions were successfully incorporated into the PAF-TPP framework. Based on the molar amount of porphyrin units, it was calculated that, for PAF-TPP-Co, approximately 6.78% of the porphyrin units were successfully coordinated with the metal. Although this coordination ratio is relatively low, it is sufficient to form recognizable metal active centers within the framework, providing the necessary foundation for subsequent catalytic studies.

To investigate the impact of metal ion incorporation on the specific surface area and pore volume of PAF-TPP, N_2 adsorption-desorption experiments were performed on both PAF-TPP and PAF-TPP-Co at 77 K. As shown in Figs. 2(d) and 2(e),

both samples exhibit typical type I isotherms with negligible hysteresis loops, indicating the dominance of microporous structures. The pore size distribution reveals that PAF-TPP-Co possesses a primary pore size centered at 0.53 nm, retaining distinct microporous characteristics, which suggests that metal coordination does not alter the overall pore structure type.

The calculated specific surface area and pore volume are summarized in Table S2 in the ESM. PAF-TPP-Co shows a BET surface area of $523.00 \text{ m}^2\text{g}^{-1}$ and a total pore volume of $0.34 \text{ cm}^3\text{g}^{-1}$, both of which are significantly lower than those of PAF-TPP ($733.13 \text{ m}^2\text{g}^{-1}$ and $0.45 \text{ cm}^3\text{g}^{-1}$, respectively). This decrease can be primarily attributed to the incorporation of Co species into the framework, which partially occupy the pore channels and reduce the accessible pore volume for N_2 adsorption, thereby leading to diminished surface area and pore volume. Importantly, although the pore size is reduced after Co coordination, the resulting micropores (0.53 nm) remain larger than the kinetic diameter of NO ($\sim 0.317 \text{ nm}$) [48], ensuring molecular accessibility without diffusion limitation. In addition, metal coordination may enhance local framework rigidity or induce slight pore constriction, further influencing the gas adsorption behavior. Such a confined

microporous environment is favorable for NO enrichment and adsorption within the pore channels, thereby facilitating the NORR process [49, 50].

This result is consistent with the validation of metal incorporation through XPS and ICP-OES, confirming that Co^{2+} ions have been stably anchored to the porphyrin coordination sites within the framework, and have had a considerable impact on the pore structure parameters, while maintaining the overall structural type of the framework.

To investigate the structural impact of metal ion incorporation on the PAF-TPP material, X-ray diffraction (XRD) analysis was performed on both PAF-TPP and PAF-TPP-Co. As shown in Fig. S3 in the ESM, the diffraction patterns of both materials are highly similar, with no sharp diffraction peaks observed, indicating that the materials exhibit a long-range disordered, amorphous structure. This suggests that the introduction of metal ions does not induce any new ordered phases or alter the inherent disordered characteristics of the framework.

From the SEM image (Fig. 2(f)), the morphology of the material remains unchanged after Co incorporation, retaining a uniformly distributed spherical structure. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) mapping (Fig. S4 in the ESM) confirms the homogeneous distribution of Co throughout the framework. The transmission electron microscopy (TEM) image (Fig. 2(g)) shows a uniform morphology without observable metal nanoparticles or aggregation [42]. The high-resolution TEM (HRTEM) image (Fig. 2(h)) exhibits no distinct lattice fringes, and the selected area electron diffraction (SAED) pattern displays diffuse halo rings, indicating an amorphous structure of PAF-TPP-Co. In addition, TEM elemental mapping (Fig. 2(i)) reveals a uniform distribution of C, N, and Co, consistent with SEM results. These results indicate that Co species are atomically dispersed and coordinated within the porphyrin-based framework rather than forming nanoparticles.

To systematically investigate the effect of metal-ion

incorporation on the electrocatalytic activity of PAF-TPP, LSV measurements were performed under both inert (Ar) and reactive (NO) atmospheres. As shown in Fig. 3(a), PAF-TPP exhibits low current responses under both Ar and NO conditions, indicating its limited intrinsic electrochemical activity. In contrast, PAF-TPP-Co displays a pronounced increase in current density upon introduction of NO, suggesting that NO reduction becomes the dominant electrochemical process. This observation highlights the key role of Co incorporation in regulating and enhancing the electrocatalytic performance toward NO reduction. In the chronoamperometric test (Fig. 3(b)), both catalysts maintain stable current densities within 1 h, demonstrating good electrochemical stability.

For NO electroreduction to ammonia, PAF-TPP shows relatively low catalytic activity across all applied potentials, with a maximum NH_3 yield of only $24.5 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$. In contrast, the Co-incorporated PAF-TPP-Co exhibits significantly enhanced catalytic performance. The NH_3 production rate initially increases and then decreases with more negative potentials, reaching an optimal value of $914.2 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$ at -0.6 V vs. RHE, accompanied by a Faradaic efficiency of 71.3% (Fig. 3(c)).

The pronounced performance difference can be attributed to the modulation of active-site electronic structure and reaction pathway. In PAF-TPP, NO is weakly adsorbed on the porphyrin framework through hydrogen bonding or π - π interactions, which is insufficient to effectively activate the N-O bond, resulting in a relatively high reaction barrier. In contrast, Co- N_4 sites can coordinate with NO via a strong metal-adsorbate interaction, where the Co 3d orbitals accept electron density from NO while simultaneously enabling d- π^* back-donation. This interaction effectively weakens the N-O bond strength and facilitates key proton-coupled electron transfer steps (e.g., $^*\text{NO} \rightarrow ^*\text{NOH}$ or $^*\text{NHO}$) [51].

In addition, the markedly enhanced current response of PAF-TPP-Co under NO atmosphere further indicates that its catalytic

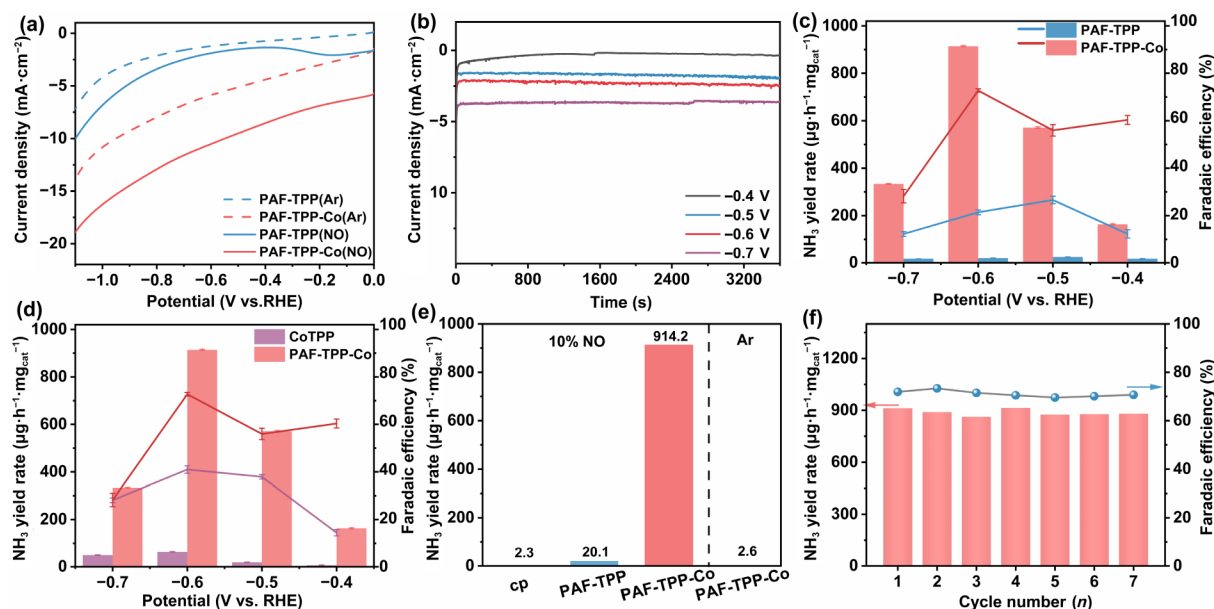


Figure 3 (a) LSV of PAF-TPP and PAF-TPP-Co in Ar- and NO-saturated $0.5 \text{ M Na}_2\text{SO}_4$. (b) i - t curves for electrocatalytic NH_3 synthesis at various applied potential on PAF-TPP-Co. (c) Electrocatalytic NORR performance of PAF-TPP and PAF-TPP-Co in $0.5 \text{ M Na}_2\text{SO}_4$. NH_3 yield rate and Faradaic efficiency represent the mean values of three independent measurements, with error bars indicating the standard deviation (mean $\pm$ SD, $n = 3$). (d) Electrocatalytic NORR performance of CoTPP and PAF-TPP-Co in $0.5 \text{ M Na}_2\text{SO}_4$. NH_3 yield rate and Faradaic efficiency represent the mean values of three independent measurements, with error bars indicating the standard deviation (mean $\pm$ SD, $n = 3$). (e) Control experiments under different conditions. (f) Cycling durability of PAF-TPP-Co.

selectivity originates from preferential NO adsorption and activation. Together with the high Faradaic efficiency (71.3%), these results demonstrate that Co-N₄ sites not only promote NORR but also effectively suppress the competing HER, thereby improving selectivity toward ammonia formation.

To further investigate the catalytic efficiency of the Co centers in PAF-TPP-Co materials, we established a baseline with 6.78% Co ion content. The ammonia production rate of PAF-TPP-Co was then normalized, and the corrected ammonia yield is shown in Fig. S12 in the ESM. The optimal ammonia yield was achieved at −0.6 V, reaching 13,480 μg·h^{−1}·mg_{Co}^{−1}.

To further elucidate the role of the microporous structure in the electrocatalytic NORR process, a non-porous CoTPP catalyst with a similar Co-N₄ coordination environment was selected as a control. As shown in Fig. 3(d) and Fig. S6 in the ESM, CoTPP exhibits significantly lower NH₃ yield and Faradaic efficiency within the same potential range, indicating inferior catalytic performance. Given the similar nature of the Co-N₄ active sites in both systems, the observed performance difference is primarily attributed to their distinct structural features.

In contrast, the microporous framework of PAF-TPP-Co effectively facilitates NO adsorption and enrichment, thereby increasing the local reactant concentration at the electrode–electrolyte interface and improving mass transport within the catalyst. Moreover, the porous architecture enhances the exposure and accessibility of active sites, leading to improved utilization efficiency. Overall, these results demonstrate that the microporous structure plays a critical role in enhancing NORR performance by simultaneously promoting reactant transport and maximizing active site utilization.

To clarify the source of ammonia and validate the intrinsic activity of the catalyst, control experiments were conducted (Fig. 3(e)). In a NO atmosphere, the bare carbon paper electrode showed negligible ammonia production. Similarly, in an Ar atmosphere, the PAF-TPP-Co catalyst did not exhibit significant ammonia generation, effectively ruling out interference from environmental nitrogen contamination or other non-NO sources. Through blank and non-metal catalyst controls, it was confirmed that the generated ammonia indeed originates from the electrocatalytic reduction of NO and is closely related to the presence of active sites in the catalyst.

To evaluate the reusability of the PAF-TPP-Co catalyst, a series of seven consecutive cycles were performed in a saturated NO 0.5 M Na₂SO₄ solution at −0.6 V (vs. RHE). As shown in Fig. 3(f), the variations in Faradaic efficiency (FE%) and ammonia production rate during each cycle were negligible, demonstrating that the catalyst retained its initial activity and selectivity throughout all cycles.

After NORR, combined TEM, XRD, XPS, and ICP-OES analyses (Figs. S13–S16 and Table S6 in the ESM) indicate that the catalyst retains its structural and chemical integrity, with no detectable Co leaching. These results demonstrate that PAF-TPP-Co exhibits excellent structural and chemical stability under electrochemical conditions, which originates from the Co-N₄ coordination anchoring rather than Co dissolution or framework reconstruction.

The electrolyte solution plays a crucial role in the mass transport and transformation processes during the NORR reaction, and its pH value significantly influences both ammonia production and Faradaic efficiency. Whether under acidic, neutral, or alkaline conditions, the electrocatalytic NORR reaction at the working

electrode involves H⁺ or OH[−]. Thus, we investigated ammonia production and Faradaic efficiency under seven different pH conditions (0, 3, 5, 7, 9, 11, 14) at −0.6 V (vs. RHE). As shown in Figs. 4(a) and 4(b), the best ammonia yield and Faradaic efficiency were achieved under neutral conditions. This is because the NORR mechanism for ammonia production involves several steps, including *NO → *NOH → *NH₂OH. Under acidic conditions, an excess of H⁺ promotes the HER as a side reaction, and overly acidic conditions exacerbate hydrogen evolution. In contrast, under alkaline conditions, the insufficient availability of H⁺ hinders the hydrogenation steps required for ammonia production, leading to a reduced ammonia yield and ultimately making it difficult to generate NH₃.

To investigate the electrochemically active surface characteristics of PAF-TPP and PAF-TPP-Co, CV measurements were conducted in the non-Faradaic region (Fig. S17 in the ESM). The capacitive current density was plotted against the scan rate to estimate the double-layer capacitance (*C_{dl}*) [52]. As shown in Fig. 4(c), PAF-TPP-Co exhibits a higher *C_{dl}* value (3.81 mF·cm^{−2}) than PAF-TPP (2.67 mF·cm^{−2}), indicating a larger electrochemically accessible surface area. This enhancement is attributed to the introduction of Co sites, which increases the exposure of active sites and promotes charge accumulation at the electrode–electrolyte interface.

Additionally, after normalizing the ammonia production rate and current density under NO atmosphere [27, 36] for PAF-TPP and PAF-TPP-Co, the normalized activity of PAF-TPP-Co remained higher than that of PAF-TPP (Fig. S18 in the ESM). This indicates that the performance difference between the two PAF materials is primarily due to the incorporation of Co active sites, which effectively enhances the intrinsic catalytic activity of the catalyst.

To evaluate the catalyst's reaction kinetics, electrochemical impedance spectroscopy (EIS) was employed to measure the charge transfer resistance (*R_{ct}*). As shown in Fig. 4(d), PAF-TPP exhibited the highest charge transfer resistance, with an *R_{ct}* value of 2.794 Ω, while PAF-TPP-Co showed a lower impedance, with an *R_{ct}* of 1.426 Ω. This suggests that the introduction of cobalt ions facilitates electron transfer during the electrocatalytic process, thereby accelerating the reaction kinetics. These findings are consistent with the results obtained from the electrocatalytic NO reduction experiments, where PAF-TPP-Co exhibited superior electrocatalytic performance compared to PAF-TPP.

To elucidate the reaction pathway and side reactions in the electrocatalytic reduction of NO by PAF-TPP-Co, we performed quantitative analysis of hydrazine and hydroxylamine in the products. As shown in Fig. S19 in the ESM, the concentrations of both by-products at different applied potentials are close to the detection limit, and no detectable by-products were observed.

To further evaluate the competition between the NORR and the HER, the H₂ Faradaic efficiency (FE) of both catalysts was systematically assessed at different applied potentials. As shown in Fig. S20 in the ESM, the PAF-TPP-Co catalyst exhibits significantly lower H₂ FE compared to the PAF-TPP counterpart over the entire potential range, while maintaining a higher Faradaic efficiency toward NO reduction. This result clearly demonstrates that the introduction of Co active sites effectively suppresses the HER and promotes the NORR pathway.

To investigate the differences in NO adsorption performance between PAF-TPP and PAF-TPP-Co, which incorporates Co²⁺ ions, NO temperature-programmed desorption (NO-TPD) tests were

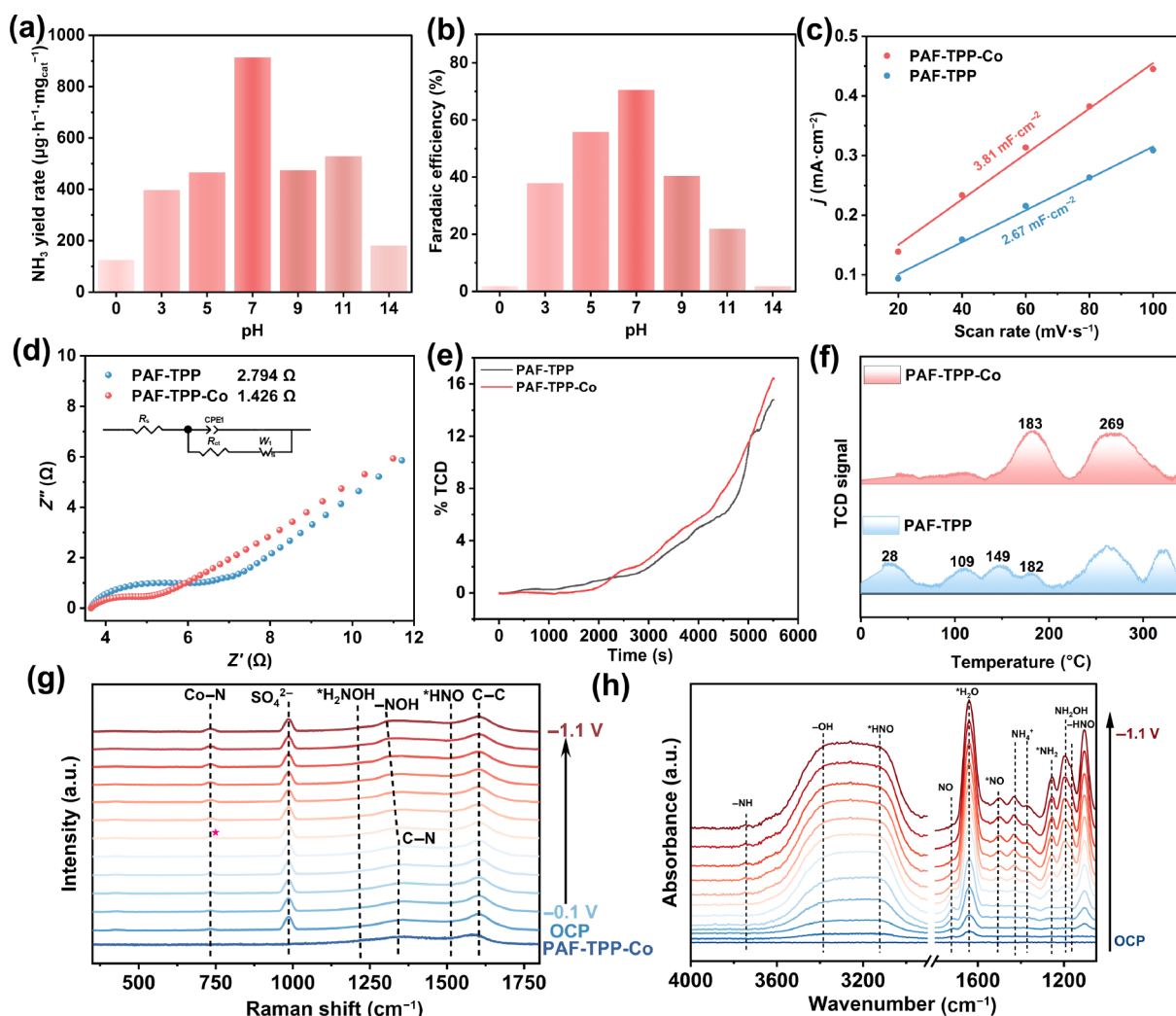


Figure 4 (a) and (b) Testing of PAF-TPP-Co catalyst at a potential of -0.6 V under different pH values. (c) Linear fitting of the capacitive currents versus CV scan rates for PAF-TPP and PAF-TPP-Co. (d) Nyquist plots of PAF-TPP and PAF-TPP-Co in $0.5 \text{ M Na}_2\text{SO}_4$ electrolytes. (e) and (f) NO-TPD. (g) *In-situ* electrochemical Raman spectra of PAF-TPP-Co at different potentials. (h) *In-situ* electrochemical infrared spectra of PAF-TPP-Co at different potentials.

conducted on both materials. As shown in Fig. 4(e), during the first 15 min, PAF-TPP exhibited a distinct NO desorption signal with increasing time and temperature, while PAF-TPP-Co, after the introduction of metal ions, showed no significant change within the initial 10 min. This indicates that the incorporation of metal ions enhances the material's ability to adsorb NO.

To more clearly highlight the differences in NO adsorption between the two materials, the data were subjected to differential treatment. As shown in Fig. 4(f), PAF-TPP-Co displays two prominent NO desorption peaks at approximately 183 and 269 $^{\circ}\text{C}$, with larger peak areas and higher desorption temperatures. In contrast, the PAF-TPP sample exhibited desorption phenomena at much lower temperatures, near room temperature (28 $^{\circ}\text{C}$), 109, and 149 $^{\circ}\text{C}$, with clearly lower peak positions. These results suggest that the introduction of cobalt metal ions significantly strengthens the interaction between the material and NO molecules, making the binding of NO molecules at the framework surface and coordination sites more stable.

The cobalt metal sites in PAF-TPP-Co enhance the adsorption energy barrier by forming coordination bonds or strong interactions with NO molecules, thereby delaying the desorption process. This result is consistent with the observation that PAF-TPP-

Co is able to more effectively capture and activate NO molecules during the electrocatalytic NO reduction reaction, providing higher efficiency and catalytic selectivity for the reaction.

To gain deeper insights into the electrocatalytic reduction of NO by PAF-TPP-Co, we performed *in situ* electrochemical Raman spectroscopy to monitor the reaction process (Fig. 4(g)). All materials exhibited a C-C peak at 1598 cm^{-1} , consistent with the characteristic peak of PAFs. In the absence of NO exposure, no signal was observed at 992 cm^{-1} , which corresponds to the N-O stretching vibration of NO. However, upon exposing the PAF-TPP-Co sample to NO, this peak was clearly observed, confirming the adsorption of NO onto the material. In this study, we monitored the *in situ* Raman spectra of PAF-TPP-Co in an NO atmosphere under applied potentials ranging from open circuit potential to -1.1 V (vs. RHE). Notable changes were observed at 735 cm^{-1} , which is indicative of the interaction between the nitrogen in the NO molecule and the Co center [53] in PAF-TPP-Co. At more negative potentials, starting from -0.5 V (vs. RHE), this signal progressively intensified, suggesting that the interaction between NO and Co requires electrochemical assistance, which aligns with the applied potential settings in our electrocatalytic NO reduction experiments. Additionally, the peak at 1350 cm^{-1} corresponds to the

C–N signal of the raw material. After applying potentials more negative than -0.5 V (vs. RHE), this peak shifted to the left, indicating the gradual emergence of an $-\text{NOH}$ signal. The bands at 1206 and 1515 cm^{-1} were attributed to $^*\text{NH}_2\text{OH}$ and $^*\text{HNO}$ intermediates, respectively [54]. These peaks were relatively weak, consistent with the electrochemical results, suggesting that these species are not the main accumulated products in the electrocatalytic process.

To investigate the reaction mechanism and pathway during the electrocatalytic NORR, *in situ* infrared spectroscopy was employed to track the evolution of reaction intermediates from open circuit potential to -1.1 V (vs. RHE). As shown in Fig. 4(h), the peak at 1506 cm^{-1} is associated with adsorbed NO species, and its intensity increases with more negative potential, indicating the gradual consumption of surface NO [52, 55]. The NO bending mode absorption peak at 1720 cm^{-1} appears at lower potentials, suggesting that the NORR reaction begins to occur at these potentials [56, 57]. The bands at 3371 and 1638 cm^{-1} are attributed to $-\text{OH}$ and H_2O , indicating proton consumption and the occurrence of hydrogenation processes in water [9]. The peaks at 1158 and 3136 cm^{-1} correspond to $^*\text{HNO}$ species [3, 52, 58]. A characteristic peak for NH_2OH is detected at 1200 cm^{-1} [27, 59]. The peaks at 1261 and 3741 cm^{-1} are assigned to $^*\text{NH}_2$ and $-\text{NH}$ [3], which gradually intensify as the potential decreases below -0.5 V. The bands at 1356 and 1424 cm^{-1} are attributed to NH_4^+ , and their intensity increases with more negative potentials, indicating the gradual formation of ammonia products [60]. Based on the *in situ* infrared and Raman spectroscopy results, the NORR reaction pathway for PAF-TPP-Co is confirmed to proceed as follows: $^*\text{NO} \rightarrow ^*\text{HNO} \rightarrow ^*\text{H}_2\text{NO} \rightarrow ^*\text{H}_2\text{NOH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3$.

To elucidate the advantages of Co coordination and the dynamic structural evolution of PAF-TPP-Co during the electrochemical reaction process, density functional theory (DFT) calculations were employed. Based on the constructed model, NO adsorption energies were calculated, revealing that after considering multiple adsorption configurations, including side-on, N-terminal, and O-

terminal orientations, the N-terminal top (TOP) adsorption configuration was the most stable. To investigate the impact of the competing HER during the NORR process, we compared the competitive adsorption of $^*\text{NO}$ and H on PAF-TPP-Co to assess its NORR selectivity. As shown in Fig. 5(a), the strong adsorption energy of PAF-TPP-Co for NO (-1.64 eV) contrasts sharply with its weak adsorption characteristics for H ($G_{\text{H}} = 0.03\text{ eV}$). Combined with the Co d-band center near the Fermi level ($\varepsilon_{\text{d}} = 1.09\text{ eV}$), this not only thermodynamically suppresses the competitive HER reaction but also achieves efficient NORR selectivity through electronic structure modulation [61].

Further analysis of the projected density of states (PDOS) for PAF-TPP-Co (Fig. 5(c)) reveals significant overlap between the 2p orbitals of the four pyrrole N atoms of the tetraphenylporphyrin monomer and the 3d orbitals of the central Co ion near the Fermi level. This confirms the formation of strong electronic coupling and orbital hybridization between the two, which constructs a efficient electron transfer pathway for the catalytic active site. This finding aligns with our previous hypothesis [25, 62]. Further investigation into the NO adsorption system shows that the continuous electronic transfer from the Co center to the framework significantly enhances the overlap between its orbitals and the empty p orbitals of the N atoms in the NO and HNO groups. This dynamically strengthened orbital interaction not only optimizes the binding between Co and the reaction intermediates, but also likely facilitates the proton-coupled electron transfer step by adjusting the electronic cloud density of the active center (Fig. 5(d)) [63, 64].

In terms of selective regulation, these results collectively highlight the structural advantages of porphyrin-based porous materials in electrocatalytic NO reduction, providing a theoretical foundation for designing highly active and selective non-metallic coordination catalysts.

4 Conclusions

This study successfully introduces PAFs into the electrocatalytic

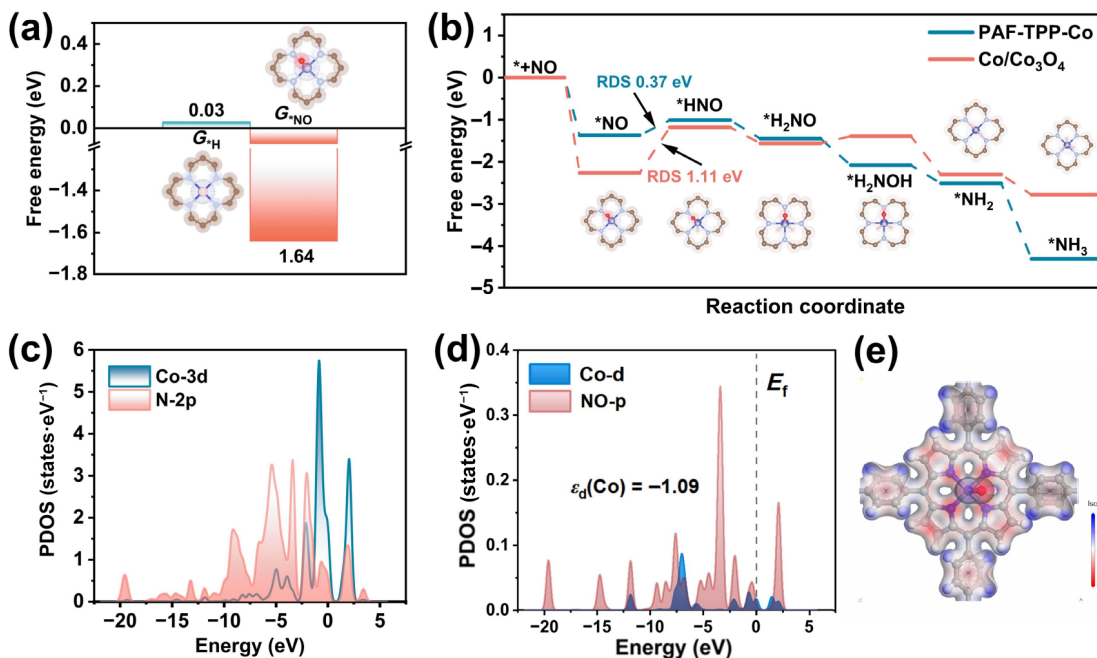


Figure 5 (a) Comparison of the strong adsorption energy of PAF-TPP-Co for NO and its weak adsorption characteristics for H. (b) Free energy landscape for NORR on PAF-TPP-Co and Co/Co₃O₄ [3]. (c) PDOS of N 2p and Co 3d. (d) Local DOS of the adsorbed NO and Co. (e) Optimized molecular structure of PAF-TPP-Co.

NORR, proposing a novel and efficient catalytic strategy. By selecting TPP with numerous active sites, PAF-TPP was synthesized, and cobalt metal ions were incorporated to develop the PAF-TPP-Co catalyst. This catalyst efficiently adsorbs NO molecules and provides ample mass transfer space, thereby promoting the electroreduction of NO. Experimental results show that at -0.6 V vs. RHE, PAF-TPP-Co achieves high-efficiency electroreduction of NO, with an ammonia production rate of $914.2 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$ and a Faradaic efficiency of 71.3%. Theoretical calculations further reveal that the Co^{2+} centers in PAF-TPP-Co, coordinated with the M-N_4 planar structure, effectively facilitate the adsorption and activation of NO, driving the multi-electron transfer conversion of NO to NH_3 while suppressing the competitive HER. This work opens a new direction for the application of porous aromatic frameworks in NORR electrocatalysis and offers a feasible solution for the resource utilization of NO in industrial waste gases.

Electronic Supplementary Material: Supplementary material (morphology and composition analysis diagrams of the comparative samples, supplementary electrochemical performance diagrams of all samples, and supplementary diagrams for the DFT section) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908876>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

N. L. supervised the project. L. N. L. conceived the idea. X. X. Y. and Y. Y. P. performed the experiments. L. Z. carried out the DFT calculations. Y. Y. P., X. X. Y. and L. N. L. wrote and revised the manuscript. H. L. L. and Z. Y. L. joined the discussions and gave useful suggestions. All the authors have approved the final manuscript.

Use of AI statement

None.

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