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Strong d-p Orbital Hybridization in Cobalt Porphyrin Cages Promotes Electrochemical Nitrate Reduction to Ammonia

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Abstract: The electrocatalytic reduction of nitrate (NO₃RR) to ammonia presents a viable solution for addressing nitrate pollution and offers an environmentally-friendly, energy-efficient alternative for industrial ammonia synthesis. However, the absence of efficient electrocatalysts impedes its industrial application. In this study, we constructed a porphyrin organic cage (PB-2) through the covalent-bonded self-assembly. Subsequently, metalized porphyrin organic cages PB-M (M = Co, Ni, Cu) were synthesized via post-modification of PB-2. These PB-M were utilized to elucidate the reaction pathway and intrinsic structure-performance relationship of the NO₃RR. Experimental results indicate that PB-Co exhibits the highest activity and ammonia selectivity (FE_{NH₃} = 95.8 ± 1.06%, NH₃ yield rate = 995.5 ± 28.4 μmol h⁻¹ mg_{cat}⁻¹). Theoretical calculations reveal that the d-p orbital hybridization between the Co 3d orbital in PB-Co and the NO₃⁻ 2p orbital is the strongest one. PB-Co with a high d-band center of -0.97 eV and high adsorption energy for NO₃⁻ and H₂O, promoting charge transfer and the production of active hydrogen, thereby reducing the activation energy barrier of NO₃⁻. This research illuminates the intrinsic structure-activity relationship of metalized PB-M for the NO₃RR, potentially providing valuable insights for the design of efficient electrocatalysts.

Introduction

Ammonia serves as a fundamental component in contemporary industry and agriculture, primarily owing to its pivotal role in fertiliser production, which is indispensable for global food production.¹⁻³ Prior to the advent of the 20th century, manure constituted the primary source of nitrogen fertilizer required for agricultural production, thereby posing a severe constraint on food production.⁴ The emergence of the Haber-Bosch process made large-scale industrial synthesis of ammonia a reality, markedly increasing food production and protecting billions of people from hunger.⁵⁻⁷ Nevertheless, this process is characterized by high energy intensity, profound dependence on fossil fuels, and significant greenhouse gas emissions.⁸⁻¹⁰ Consequently, the development of a clean and sustainable technology for NH₃ synthesis becomes imperative. In the past few years, electrochemical N₂ reduction to ammonia (NRR) has received increasing attention.¹¹⁻¹⁴ However, utilizing N₂ as a nitrogen source presents several challenges, including its high N≡N dissociation energy, limited solubility, and the potentially competing hydrogen evolution reaction, resulting in the much lower efficiency of NRR comparing to commercial requirements.¹⁵⁻¹⁹ The development of industry and agriculture has led to a significant increase in the generation of nitrate pollutants. These contaminants, often inadequately treated, permeate groundwater and surface water, posing grave threats to both human health and ecosystem equilibrium.^{20,21}

The electrocatalytic reduction of nitrate (NO₃RR) provides an environmentally friendly, energy-saving, and potentially scalable

solution to address nitrate pollution. NO₃RR employs renewable and clean electrical energy to drive the reduction reaction, thereby effectively decoupling ammonia synthesis from fossil fuels. This innovative technology not only curtails greenhouse gas emissions but also addresses the critical challenge of nitrate contamination in water bodies.²²⁻²⁴ Due to the complexity of the NO₃RR process and intermediate products, poses a significant challenge to the development of highly efficient and selective electrocatalysts.²⁵⁻²⁷ Efficient NO₃RR requires highly active, selective, and stable electrocatalysts. Porphyrin serves as the active center in numerous biological enzymes and acts as a significant biomimetic catalyst, possessing high catalytic efficiency and selectivity during the catalytic reaction process.^{28,29} The utilization of porphyrin molecules in NO₃RR has been extensively documented over the years.³⁰⁻³² However, the low density of active sites and the tendency to aggregate have hindered the practical application of porphyrin molecule catalysts. The integration of porphyrins into porous materials, such as covalent organic frameworks (COFs), metal-organic frameworks (MOFs) and Porous organic cages (POC) has become a trend.³³⁻³⁸ POC are an emerging sub-class of crystalline porous materials that have garnered significant attention in recent years due to their exceptional properties. In 2015, Kim et al. reported two porphyrin boxes (PB-1 and PB-2) through dynamic imine condensation reactions.³⁹ These two porphyrin boxes are covalent organic cages with a rhombic cuboctahedral geometry, constructed from six porphyrin units and eight triamine linkers. The hollow characteristics of octahedral porphyrin boxes and the excellent chemical properties of porphyrin units have enabled Kim et al. to apply them in the fields such as electrocatalysis and photocatalysis.⁴⁰⁻⁴³ Due to the open intrinsic and inter-cage pores of porphyrin organic cages, when metal ions coordinate with porphyrin, small molecules can readily diffuse to the metal ion sites, thereby facilitating the occurrence of catalytic reactions. The porphyrin organic cages have the structural characteristics of enzyme catalysts, providing valuable insights for the study of supramolecular catalysts and potential avenues for the research of biomimetic catalysts.

In this study, we successfully synthesized a porphyrin porous organic cage (PB-2), which can be utilized as a support for Single

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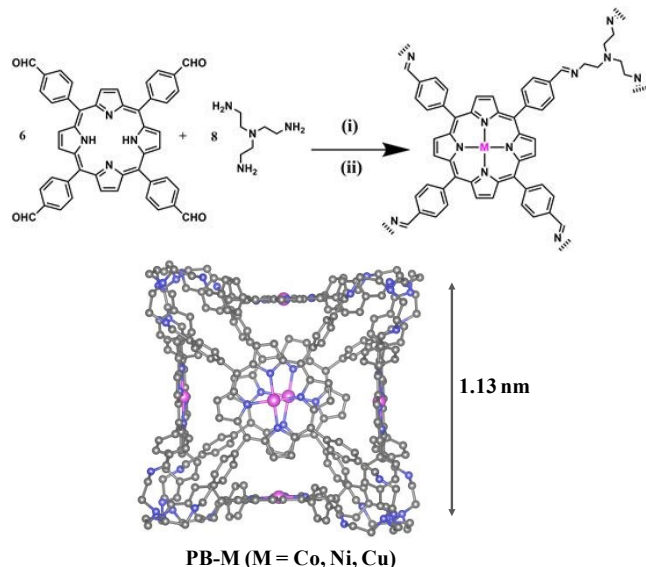
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Metal Atoms (SACs). The incorporation of metal atoms into PB-2 significantly enhances its electrocatalytic activity for NO₃RR. Specifically, PB-Co demonstrates an excellent electrocatalysis efficiency for NO₃RR with FE_{NH₃} of 95.8 ± 1.06% and corresponding NH₃ yield of 995.5 ± 28.4 μmol h⁻¹ mg_{cat}⁻¹. The d-band center of PB-Co is -0.97 eV, which is closer to the fermi level, DFT analysis show that the d-p orbital hybridization between the Co 3d orbital in PB-Co and the NO₃⁻ 2p orbital is the most robust. The experimental and theoretical results also suggest that PB-Co adsorbs H₂O more easily and produces active hydrogen (*H). Furthermore, PB-Co exhibits the lowest reaction barrier, thereby facilitating the reduction of NO₃⁻.



Scheme 1. (a) Synthesis of PB-2 and PB-M (M = Co, Ni, Cu). (i) TFA, o-dichlorobenzene, 80 °C, 5d; (ii) THF, Co²⁺/Ni²⁺/Cu²⁺ salt, 70 °C, 24 h.

Results and discussion

The cage used in our work was PB-2, first reported by the Kim group.³⁹ PB-2 was synthesized through dynamic imine condensation between meso-tetrakis(4-formylphenyl)porphyrin (p-Por-CHO) and tris(2-aminoethyl)amine (TREN), achieving a [6+8] architecture as designed (Scheme 1). Structural validation through MALDI-TOF and ¹H NMR spectroscopy confirmed the successful assembly of PB-2. The mass spectral profile revealed a prominent molecular ion peak at m/z 5097.3 correlating with the proposed six-porphyrin/eight-TREN stoichiometry (Figure S1). ¹H NMR spectroscopy showed that the imine proton signal at around 8.44 ppm (H_e-C=N) of PB-2 (Figure S2).⁴⁴ Then, the metal atom (Co, Ni, Cu) was incorporated into PB-2 by refluxing the mixture of PB-2 and corresponding metal salts. The successful metallization of PB-2 in the presence of different metal salts was verified using MALDI-TOF mass spectrometry (Figure S1). Powder X-ray diffraction was employed to characterize the crystal structure of PB-2 and PB-M (Figure S3). The similar characteristic peaks of PB-2 and PB-M were observed, indicating that the crystal

structure of PB-2 was not destroyed by chelating metals. The Fourier transform infrared (FT-IR) spectroscopy of PB-2 and PB-M (M = Co, Ni, Cu) were also studied (Figure 1a). Specifically, the peak at 1640 cm⁻¹ can be assigned to the C=N bond, the disappeared peak at 3332 cm⁻¹ corresponds to the stretching of N-H on the porphyrin ring and the newly appeared peak at 1000 cm⁻¹ (M-N-C) confirm the successful metallization of PB-2.⁴⁵ The UV-vis spectra of PB-2 displayed a strong Soret band around 420 nm and four Q-bands between 500 and 670 nm (Figure 1b). The Soret band are due to the a_{1u}(π)→e_g(π*) transition whereas the Q bands correspond to a_{2u}(π)→e_g(π*) transition, respectively. The reduction in the number of Q bands in PB-Co, PB-Ni, and PB-Cu is attributed to the increased symmetry of porphyrin upon coordination of metal ions, indicating the coordination of metal ions within the PB-2.⁴⁶

X-ray photoelectron spectroscopy (XPS) tests were conducted to investigate the surface chemical states as well as the elemental composition of these samples. The C 1s XPS spectrum of PB-2 revealed four distinct peaks at 284.8, 285.6, 286.7 eV, and 289.4 eV, which can be attributed to C-C, C-N, C=O, and N-C=O bonds, respectively (Figure S4). In the N 1s XPS of PB-M (Figure 1c), three distinct peaks attributable to imine nitrogen, metal-coordinated nitrogen and pyrrolic N, respectively.⁴⁷ PB-Co exhibited characteristic Co²⁺ signatures in its 2p spectrum with satellite peaks (Figure 1d). PB-Ni showed analogous divalent characteristics (Figure S5). In the case of PB-Cu, peaks for both divalent and monovalent copper were observed, and the ratio of Cu⁺/(Cu²⁺+Cu⁺) in the PB-Cu samples is 30.9%.⁴⁸ The loading amount of metal atoms were by inductively coupled plasma optical emission spectrometry analysis (ICP-OES), with Co, Ni, and Cu contents of 6.04 %, 6.27 %, and 7.18 % respectively (Table S1).

Due to the relatively weak adsorption capacity of cages for N₂ at 77 K, the porosity of cage is mostly estimated by CO₂ adsorption at 195 K, which is common in porous molecular materials. As shown in Figure 1e and Figure S6, all of these samples exhibited typical type IV sorption isotherm curves, a characteristic evidence for mesoporous structures. The Brunauer–Emmett–Teller (BET) surface areas were calculated to be 242.8 m² g⁻¹, 48.1 m² g⁻¹, 51.6 m² g⁻¹, and 59.4 m² g⁻¹ for PB-2, PB-Co, PB-Ni, and PB-Cu, respectively. The pore-size distributions of PB-M showed a main peak centered at around 3.4 nm. The microstructure of these samples was characterized using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). SEM (Figure S7) and TEM (Figure S8) images revealed that PB-2 and PB-M (M = Co, Ni, Cu) have similar morphological characteristics. The element mapping image shows the uniform distribution of Co, C, and N in PB-Co (Figure 1f). Additionally, the morphology and element distribution of PB-2, PB-Ni, and PB-Cu are displayed in Figure S9–S11, respectively.

In order to evaluate the electrochemical performance of PB-2 and PB-M (M=Co, Ni, Cu), these samples were dropcast onto a 1 × 1.5 cm² carbon paper (CP) with a mass loading of 0.5 mg cm⁻² and tested in H-type electrolytic cell with a three-electrode system. Figure 2a depicts the linear sweep voltammetry (LSV) curves of the samples in Ar-saturated 0.5 M K₂SO₄ with and without 0.1 M KNO₃.



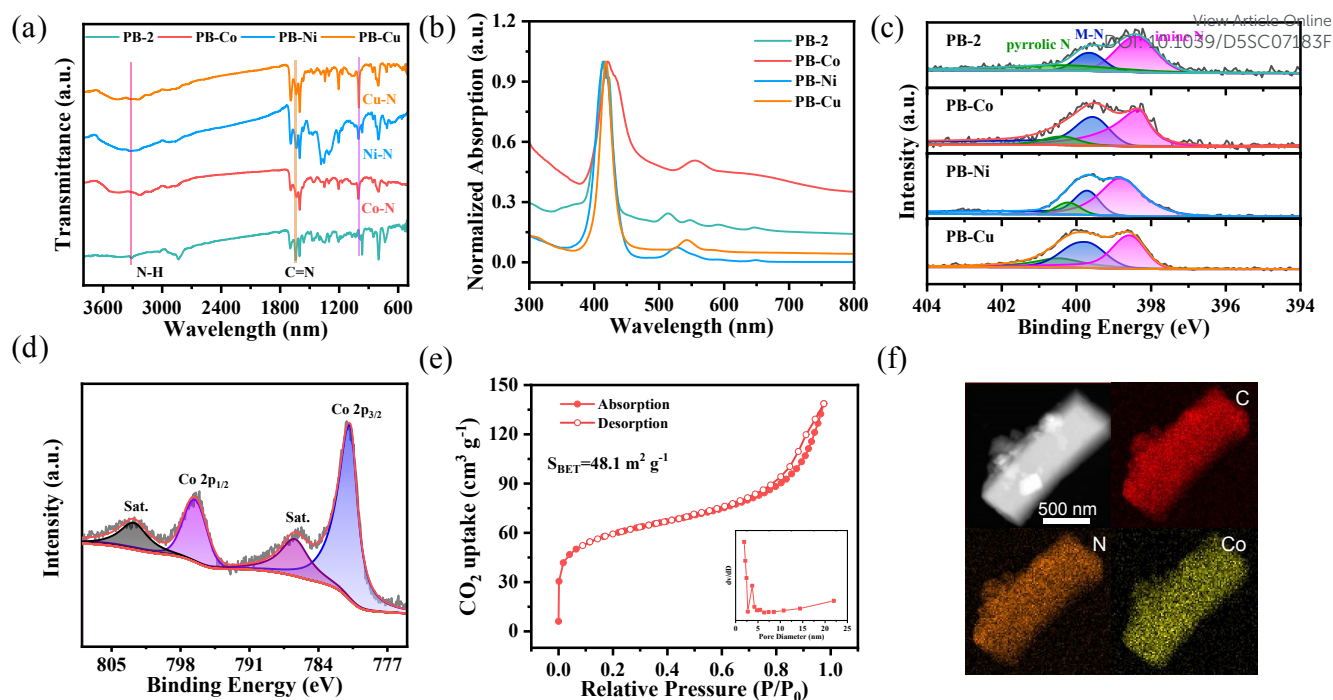


Figure 1. (a) FT-IR spectra of PB-2, PB-Co, PB-Ni and PB-Cu. (b) UV-vis absorption spectra of PB-2, PB-Co, PB-Ni and PB-C. (c) High-resolution N 1s XPS spectra of PB-2, PB-Co, PB-Ni and PB-Cu. (d) High-resolution Co 2p XPS spectra of PB-Co. (e) CO₂ adsorption-desorption curves of PB-Co. (f) TEM mapping image of PB-Co.

In 0.5 M K₂SO₄ electrolyte, only the hydrogen evolution reaction (HER) occurs on the catalyst surface, and the current density of the PB-Co catalyst does not significantly increase until the voltage is lower than -0.25 V (vs.RHE, the same hereinafter). The addition of KNO₃ significantly increased the current density of PB-2 and PB-M (M = Co, Ni, Cu) in the electrolyte. For PB-Co catalysts, the current density starts to take off at -0.25 V and increases to 200 mA cm⁻² at -1.35 V, in contrast, the maximum current density of PB-2 catalyst within the test voltage range is less than 100 mA cm⁻², which is the proof of the great NO₃RR activity for PB-Co. As illustrated in Figure 2b, the Tafel slope of PB-Co (105.6 mV dec⁻¹) is notably smaller than those of PB-2 (426.2 mV dec⁻¹), PB-Ni (294.1 mV dec⁻¹), and PB-Cu (182.5 mV dec⁻¹). This indicates that PB-Co exhibits the fastest reaction kinetics. The analysis results indicate that both PB and PB-M catalysts have potential ability toward NO₃RR. Compared with PB-2 catalyst, metalized PB-2 all showed enhanced catalytic performance.

Quantification of NH₃ yields was performed by UV-vis spectrophotometry using the indophenol blue method. The NH₃ yield and corresponding Faradaic efficiency (FE) at different potentials are calculated and shown in Figures 2c-d. Notably, PB-Co exhibited the highest FE toward NH₃ within the -0.70 to -1.10 V, achieving peak Faradaic efficiency (95.8 ± 1.06%) at -0.9 V with a corresponding NH₃ yields of 995.5 ± 28.4 μmol h⁻¹ mg_{cat}⁻¹. We compared the NH₃ yield rates between molecular cobalt porphyrin (Co-TPP) and PB-Co, and found that the NH₃ yield rate of PB-Co was approximately 4 times higher than that of Co-TPP (Figure S14). Therefore, integrating Co onto porphyrin organic cage can effectively enhance the catalytic performance. Interestingly, despite the PB-Cu catalyst showing a relatively high current density in the LSV curve, it exhibited the lowest Faraday efficiency and NH₃

yield among the PB-M catalysts. Therefore, we calculated the yield rate and FE of NO₂⁻, a significant byproduct of nitrate reduction (Figure 2e and Figure S15). The PB-Cu catalyst showed the highest yield rate of NO₂⁻. At -0.7 V, the yield rate and FE of NO₂⁻ were 393.8 ± 36.3 μmol h⁻¹ mg_{cat}⁻¹ and 11.8 ± 0.07 %, respectively. As the potential decreased, the FE of NO₂⁻ also showed a downward trend. In order to visually display the dominant product after the reaction, the yield rate ratio of NH₃ to NO₂⁻ in the product was defined as [NH₃]/[NO₂⁻]. As shown in Figure 2f and Figure S15, for PB-2 catalyst, the values of [NH₃]/[NO₂⁻] were less than 1, indicating that both NO₂⁻ are the main products with low selectivity for NH₃. As for PB-Co and PB-Ni, the values of [NH₃]/[NO₂⁻] were much greater than 1.0, indicating high selectivity for NH₃. As for PB-Cu, within the test potential range, the values of [NH₃]/[NO₂⁻] were much smaller than 1.0, indicating that NO₂⁻ is the main product. The reason for this phenomenon is that *NO₂⁻ is easy to desorb on PB-Cu, and through theoretical calculation, the desorption free energy of NO₂⁻ on PB-Cu is a negative value, indicating that the desorption of NO₂⁻ on PB-Cu is a spontaneous process, resulting in the selectivity of ammonia synthesis on PB-Cu being lower than that of PB-Ni and PB-Co (Figure S16).⁴⁹

To elucidate the primary active centers and mechanism of PB-M in NO₃RR, systematic KSCN poisoning experiments were implemented. This approach leverages the strong affinity of SCN⁻ for metal sites, thereby blocking nitrate adsorption through competitive binding.^{50,51} When introduced into the combined electrolyte system (0.5 M K₂SO₄ + 0.1 M KNO₃), the KSCN additive induced a marked decrease in current densities compared to the KSCN-free control, as evidenced by electrochemical characterization (Figure 2g and Figure S17). Notably, the



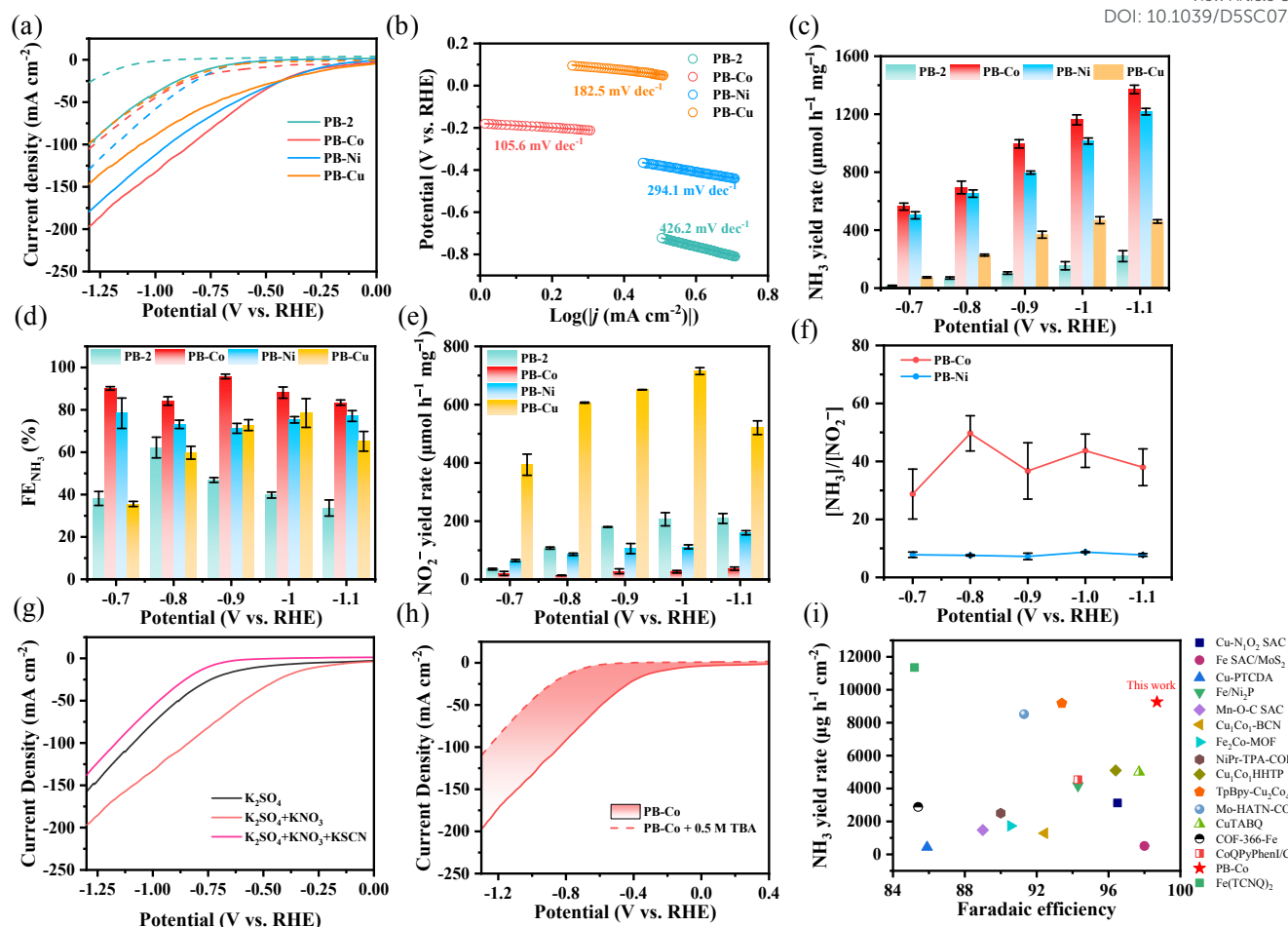


Figure 2. (a) LSV curves of the PB-2 and PB-M in Ar-saturated 0.5 M K_2SO_4 (dashed line) and 0.5 M K_2SO_4 + 0.1 M KNO_3 (solid line) electrolyte. (b) the Tafel plots of the PB-2 and PB-M in 0.5 M K_2SO_4 + 0.1 M KNO_3 . (c) NH_3 yield rate of PB-2 and PB-M at different potential. (d) FE_{NH_3} of PB-2 and PB-M at different potential. (e) NO_2^- yield rate of PB-2 and PB-M at different potential. (f) $[\text{NH}_3]/[\text{NO}_2^-]$ at different potential. (g) LSV curves of PB-Co in 0.5 M K_2SO_4 , 0.5 M K_2SO_4 + 0.1 M KNO_3 , and 0.5 M K_2SO_4 + 0.1 M KNO_3 + 0.1 M KSCN electrolyte. (h) Comparison of current density change by adding 0.5 M TBA into KNO_3 -containing electrolyte. (i) Comparison of NO_3RR performance of PB-Co with other electrocatalysts.

suppressed current levels fell below those observed in nitrate-free conditions, confirming the predominant role of metal centers in PB-M ($M = \text{Co}, \text{Ni}, \text{Cu}$) for NO_3RR . NO_3RR is a process involving the transfer of nine protons, so active hydrogen ($^*\text{H}$) plays an important role in NO_3RR . In order to study the ability of different metals to produce $^*\text{H}$, 0.5 M tert-butanol (TBA) was added to the electrolyte, where TBA acts as a scavenger for $^*\text{H}$. The integral area of current density change after the addition of TBA for PB-Co (68.38) is larger than that of PB-Ni (42.64) and PB-Cu (19.51) (Figure 2h and Figure S18), indicating that PB-Co can produce more $^*\text{H}$. We compared the performance of PB-Co with other recently reported electrocatalysts for NO_3RR , the NH_3 yield rate and FE_{NH_3} of PB-Co exceeds the majority of catalysts reported in previous literature (Figure 2i and Table S2).

The stability of catalysts is a crucial factor in assessing their potential for industrial application. Seven cycles of electrolysis with PB-Co electrode were carried out at -0.9 V, each cycle lasting 1 hour (Figure 3a). It is clear that the FE and yield rate for NH_3 slightly decreased, indicating excellent catalytic stability of PB-Co. Post-electrolysis characterization of PB-Co through FT-IR (Figure S20), XPS (Figure S21), SEM (Figure S22), and XPS analyses demonstrated

minor structural alterations, conclusively verifying the exceptional stability of the catalyst under operational conditions. MALDI-TOF analysis also demonstrated that the molecular structure of PB-Co remained intact (Figure S23). ICP-MS analysis of the electrolyte (after electrocatalysis for 4h) indicated that the leached Co, Ni, and Cu concentrations were below detectable limit ($0.1 \mu\text{g/L}$), therefore, PB-M has great stability during the electrolysis. To corroborate the source of produced ammonia, the NO_3RR performance of carbon paper (CP) were evaluated by the NH_3 yield (Figure 3b). As expected, CP exhibits low NO_3RR activity. The PB-Co was used as the working electrode in 0.1 M K_2SO_4 electrolyte, no NH_3 production was detected. Similarly, with PB-Co as the working electrode and 0.5 M K_2SO_4 + 0.1 M KNO_3 as the electrolyte, no ammonia was detected in the electrolyte under open circuit voltage (OCP). Isotope labeling experiments using K^{14}NO_3 or K^{15}NO_3 as a nitrogen source followed by product identification via $^1\text{H-NMR}$ were performed. As shown in Figure 3c, three peaks were observed in the $^1\text{H-NMR}$ spectrum after 2h of electrolysis when using K^{14}NO_3 as the electrolyte corresponding to $^{14}\text{NH}_4^+$. Only double peaks corresponding to $^{15}\text{NH}_4^+$ are identified in the $^1\text{H-NMR}$ spectrum when using K^{15}NO_3



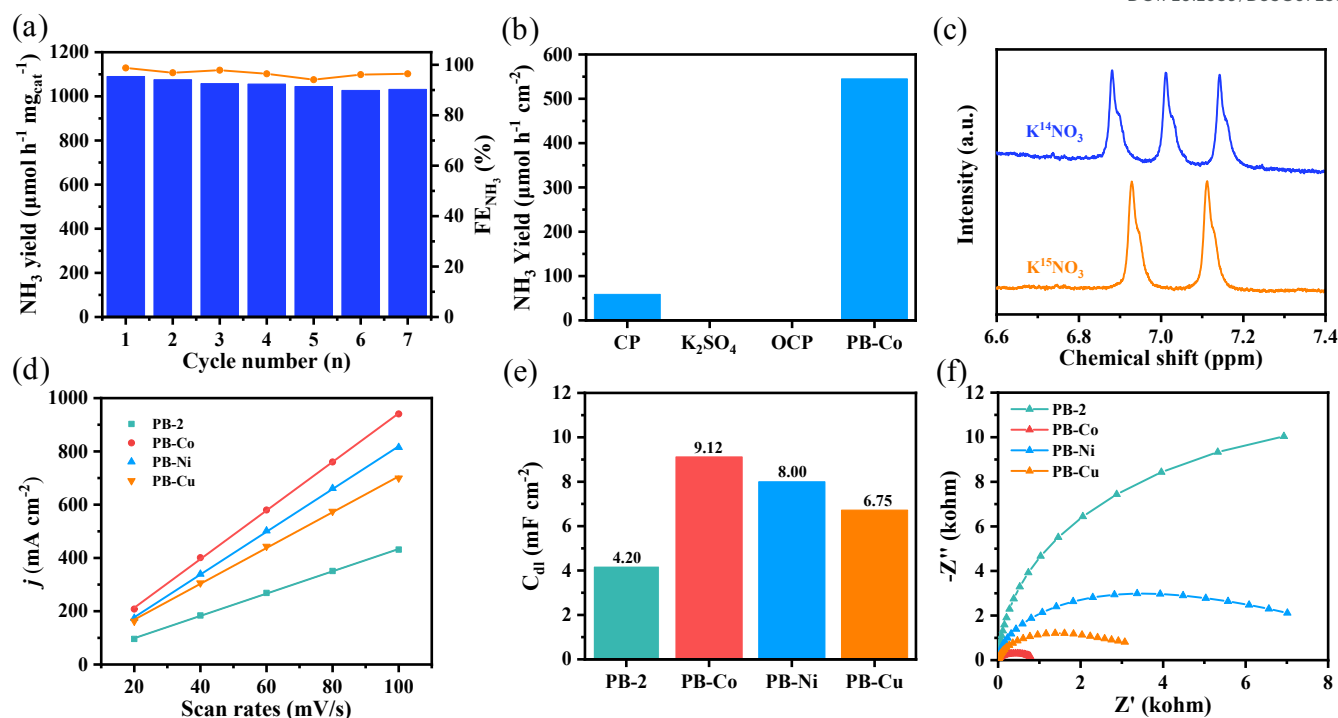


Figure 3. (a) The cycling tests of PB-Co for reduction tests at -0.90 V vs. RHE. (b) NH_3 yield of PB-Co under different test conditions. (c) ^1H NMR spectra of the electrolyte used in the NO_3RR with K^{15}NO_3 or K^{14}NO_3 as nitrogen sources. (d) Current density at different scanning rates. (e) Double layer capacitance of PB-2 and PB-M. (f) Nyquist plots of PB-2 and PB-M.

as the electrolyte, suggesting that the produced ammonia totally originates from electrochemical NO_3RR .

To evaluate the true catalytic performance of samples, it is necessary to obtain electrochemically active surface areas (ECSA), however, we cannot directly calculate the ECSAs. Due to the relationship between double-layer capacitance (C_{dl}) and ECSA, we can roughly calculate the ECSA by calculating the C_{dl} .^{52,53} Cyclic voltammetry measurements were conducted (Figure S24), and fitting the current density Δj at different scanning rates (20 to 100 mV s^{-1}), the C_{dl} of PB-2 and PB-M were obtained (Figure 3d-e). The results revealed that the C_{dl} values for PB-Co is 9.12 mF cm^{-2} , which are notably higher than that for PB-Ni (8.02 mF cm^{-2}), PB-Cu (6.72 mF cm^{-2}), and PB-2 (4.18 mF cm^{-2}). The observed enhancement in NO_3RR performance of PB-M compared to PB-2 reveals a correlation with its enhanced ECSAs. To systematically evaluate catalytic efficacy, we conducted electrochemical impedance spectroscopy (EIS) analysis to probe interfacial charge-transfer characteristics (Figure 3f). PB-Co and PB-Cu demonstrated substantially reduced semicircle diameters relative to PB-2 and PB-Ni, correlating with lower R_{ct} values. This charge-transport optimization mechanism effectively enhances the nitrate-to-ammonia conversion kinetics in cobalt-modified systems.

In situ FT-IR spectrometry was conducted to explore the reaction mechanism of PB-M for NO_3RR . As shown in Figure 4a, the band at $\sim 1335 \text{ cm}^{-1}$ was attributed to the N-O asymmetric stretching vibration of adsorbed NO_3^- . The bands located at $\sim 1100 \text{ cm}^{-1}$ and $\sim 1269 \text{ cm}^{-1}$ were assigned to the intermediates $^*\text{NO}$ and $^*\text{NO}_2^-$, respectively. The band located at $\sim 1465 \text{ cm}^{-1}$ belonged to N-H bending vibration of $^*\text{NH}_4^+$, indicating the conversion of NO_3^- to

NH_3 on the catalyst surface under applied potentials. More importantly, we monitored the characteristic peaks of the adsorbed $^*\text{NH}_2\text{OH}$ species at $\sim 1178 \text{ cm}^{-1}$.⁵⁴⁻⁵⁶ According to the above results, the NO_3RR on PB-Co satisfies the NHO pathway ($^*\text{NO}_3^- \rightarrow ^*\text{NO}_2^- \rightarrow ^*\text{NO} \rightarrow ^*\text{NHO} \rightarrow ^*\text{NHOH} \rightarrow ^*\text{NH}_2\text{OH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3$).

Density functional theory (DFT) calculation was carried out to get deep insight into the great NO_3RR performance of PB-Co. The electronic configuration of metal d orbitals is an important factor affecting catalytic activity. The projected density of states (PDOS) and spatial spin density of PB-Co, PB-Ni, and PB-Cu are plotted in Figure 4b. It was found that the DOS for spin-up and down is more asymmetric for PB-Co than PB-Ni and PB-Cu, and the spatial spin density also indicates that PB-Co has the largest spin density. The calculated d-band centers (ϵ_d) for PB-Co, PB-Ni, and PB-Cu are -0.971 eV , -1.176 eV , and -2.656 eV , respectively. Previous researches have shown that the more positive the d-band center, the stronger the adsorption energy of NO_3^- , therefore, the adsorption of NO_3^- on PB-Co is the strongest.⁵⁷ The interaction between metal d orbitals and NO_3^- 2p orbitals can be explained by the acceptance-donation mechanism:^{58,59} on the one hand, the occupied d orbitals of metal atoms transfer electrons to the empty π^* orbitals of NO_3^- , on the other hand, the unoccupied d orbitals of metal atoms accept electrons from NO_3^- . To further probe the mechanism, the bader charge and charge density differences were calculated. The bader charge analysis of PB-M indicates that Co atom in PB-Co have more positive charges, which is beneficial to the adsorption of NO_3^- molecules (Figure S25). Based on the bader charge and charge density difference of $^*\text{NO}_3^-$, PB-Co and PB-Ni



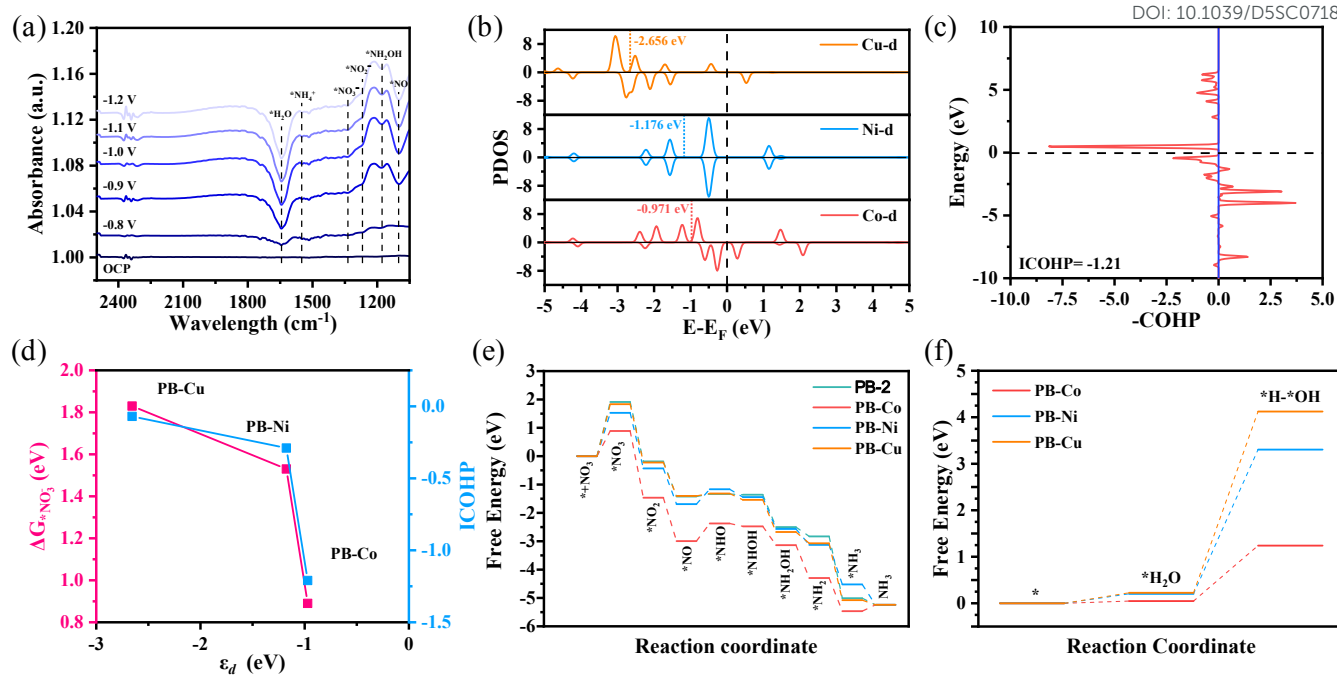


Figure 4. (a) Projected densities of states (PDOS) of the M (Co, Ni, Cu) 3d states. (b) PDOS of the M 3d states and NO_3^- 2p states. (c) COHP between the Co and NO_3^- . (d) The adsorption free energy and ICOHP versus d-band center. (e) The calculated Gibbs free energy diagram of NO_3^- to NH_3 conversion over PB-2 and PB-M. (f) The reaction energies of *H formation over PB-M through H_2O electrolysis

transferred 0.53 e and 0.56 e electrons to NO_3^- , respectively, higher than PB-Cu (Figure S26). In order to investigate the orbital interactions between $^*NO_3^-$ and metal atoms, we calculated the DOS (Figure S27) and COHP (Figure 4c and Figure S28). We analyze the PDOS among the 2p orbital of $^*NO_3^-$ and the metal d orbital of PB-M (M = Co, Ni, Cu), the overlaps between Co d orbital in PB-Co and $^*NO_3^-$ 2p orbital are the largest, which effectively forms strongly chemical bonds of Co-O and then boosts the electrons transfer from Co to NO_3^- .^{60,61} The strong adsorption of $^*NO_3^-$ on PB-Co is thus validated by COHP, because a less anti-bonding states are below E_F when NO_3^- adsorbed on PB-Co. Furthermore, we calculated the ICOHP values between metal atoms and O atoms, a more negative ICOHP value for Co-O bond in PB-Co was observed, therefore, the adsorption of NO_3^- on PB-Co is stronger than PB-Ni and PB-Cu.⁶²⁻⁶⁴ As shown in Figure 4d, the closer the d-band center is to the Fermi level, the stronger the adsorption energy for NO_3^- and d-p orbital hybridization, and the better NO_3RR activity. To get deep insight into the superior NO_3RR performance of PB-Co, the DFT calculation was carried out to investigate the reaction pathways for NO_3RR on PB-2 and PB-M. The calculated Gibbs free energy change along with the related intermediates and reaction pathway, are shown in Figure 4e. The first step involves the adsorption of NO_3^- onto the catalysts, the stable adsorption of nitrate molecules on catalysts is the key to determining whether the NO_3RR can occur. The calculated adsorption free energies of PB-2, PB-Co, PB-Ni, and PB-Cu are 1.91, 0.89, 1.53, and 1.83 eV, respectively, indicating that metal atoms can promote the adsorption of NO_3^- . There are two typical reaction pathways in NO_3RR ,⁶⁵ NOH pathway ($^*NO_3^- \rightarrow ^*NO_2^- \rightarrow ^*NO \rightarrow ^*NOH \rightarrow ^*N \rightarrow ^*NH \rightarrow ^*NH_2 \rightarrow ^*NH_3$) and NHO pathway ($^*NO_3^- \rightarrow ^*NO_2^- \rightarrow ^*NO \rightarrow ^*NHO \rightarrow ^*NHOH \rightarrow ^*NH_2OH \rightarrow ^*NH_2 \rightarrow ^*NH_3$), it was found that the NHO pathway is energetically more favorable. The results of

theoretical calculation showed that $\Delta G(NO_3^- \rightarrow ^*NO_3^-)$ was the rate-determining step both PB-2 and PB-M. The energy barrier of NO_3^- required for PB-Co is 0.89 eV, which is the lowest energy barrier, therefore, PB-Co exhibits the best NO_3RR activity and selectivity for NH_3 . NO is an important intermediate in NO_3RR , and the degree of activation of NO determines whether subsequent reactions can proceed smoothly. Therefore, we calculated the N-O bond lengths of NO on different catalysts, which were 1.187 Å (PB-Co), 1.175 Å (PB-Ni), and 1.173 Å (PB-Cu), respectively. The maximum elongation of N-O bond on PB-Co due to the activation effect of the Co atom on *NO , which is beneficial for the subsequent hydrogenation reaction. To further explore the mechanism of PB-M decomposing water to produce active hydrogen, we also calculated the free energy diagram of water decomposition as shown in Figure 4f, Compared with PB-Ni and PB-Cu, H_2O is more easily adsorbed on PB-Co and more easily decomposed to produce active hydrogen. Therefore, PB-Co exhibits excellent NO_3RR activity by promoting the adsorption of NO_3^- and H_2O and producing a large amount of *H .

Conclusions

In summary, we synthesized three metalized porphyrin organic cages by the post-synthetic metalation of PB-2, and investigated their NO_3RR performance. Among the investigated PB-2 with different metal centers, the PB-Co exhibited the highest activity, with the trend following the order PB-Co > PB-Ni > PB-Cu. The PB-Co exhibited the highest FE_{NH_3} of 98.7 %, and Corresponding NH_3 yield rate reached $1089.9 \mu mol h^{-1} mg_{cat}^{-1}$. Density functional theory (DFT) calculations revealed the mechanism underlying this trend, demonstrating that the proximity of the metal d-band center to the Fermi level (-0.97 eV for PB-Co) governs the d-p orbital hybridization



between PB-M and NO₃⁻. This electronic synergy directly correlates with reduced activation barriers, where the enhanced overlap of Co–NO₃⁻ orbitals lowers the reaction energy threshold compared to that of PB-Ni and PB-Cu. The experimental and theoretical results also suggest that PB-Co adsorbs H₂O more easily and produces *H. This work illustrates the intrinsic structure–activity relationship of metalized POCs for the NO₃RR, which may provide useful guidance for designing efficient electrocatalysts.

Data availability

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

Author contributions

You Wu, YangPeng Zhang, Hao Zhao designed the experiments; You Wu synthesized the materials and performed most of the characterization experiments with the help of Yangpeng Zhang, Hao Zhao, Yang Peng and Hailing Ma; You Wu performed the theoretical simulation, interpreted the results and wrote the paper; All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Data availability

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

