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To replace the energy-intensive and polluting traditional ammonia synthesis process, in this study, we designed two polyoxometalate (POM)-based nickel/cobalt metal-organic composite catalysts, namely (HNCP)₂[Ni(H₂O)₄]₂[NiMo₁₂(HPO₄)₄(PO₄)₄O₃₀] (Ni-P₄Mo₆) and (HNCP)₂[Co(H₂O)₄]₂[CoMo₁₂(HPO₄)₄(PO₄)₄O₃₀] (Co-P₄Mo₆). These catalysts utilized {P₄Mo₆} as the structural unit, nickel/cobalt as the metal node, and π -conjugated organic ligands as the linkers, and they were loaded onto graphene oxide (GO) to enhance the conductivity and reaction contact area. Experimental results showed that in acidic electrolytes, Ni-P₄Mo₆/GO achieved an ammonia yield of 2.62 mg h⁻¹ mg⁻¹_{cat.} at -0.6 V (vs. RHE) with a faradaic efficiency (FE) of 83.9% at -0.5 V, outperforming Co-P₄Mo₆/GO (1.63 mg h⁻¹ mg⁻¹_{cat.} at -0.7 V; FE 85.3% at -0.3 V). Under neutral conditions, both the catalysts exhibited significantly improved performances (Ni-P₄Mo₆/GO: 11.6 mg h⁻¹ mg⁻¹_{cat.} yield, 88.4% FE; Co-P₄Mo₆/GO: 11.1 mg h⁻¹ mg⁻¹_{cat.} yield, 78.5% FE), surpassing most comparable catalysts. This work provides a novel strategy for developing efficient electrocatalysts for nitrate reduction to ammonia (e-NO₃RR).

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1. Introduction

As an important carrier and energy storage intermediate in the carbon neutralization industry, ammonia is considered to be a future fuel substitute and plays a vital role in various industries such as leather, papermaking and agricultural fertilizer production.^{1–6} The production of ammonia has been mainly dependent on a macroscale synthesis technology using the Haber-Bosch technique since 1913; however, its thermodynamic constraints—requiring extreme conditions (400–500 °C, 15–25 MPa) to overcome the high activation energy barrier of N≡N bond dissociation—result in massive energy consumption.^{7–11} In contrast, the electrocatalytic nitrate reduction reaction (e-NO₃RR) for the synthesis of ammonia uses renewable electricity to drive the eight-electron reduction process, which can operate at room temperature and atmospheric pressure, and it is more thermodynamically

inclined to choose nitrate rather than inert N₂ as the nitrogen source.^{12–16} The electrocatalytic reduction of NO₃⁻ to NH₃ is an efficient process for transforming nitrate into the more valuable compound, NH₃. The conversion of NO₃⁻ can not only directly mitigate the problem of NO₃⁻ water pollution but also realize the green synthesis of ammonia. As a result, this reaction is regarded as one of the most potential methods for the eco-friendly and continuous production of ammonia in the future.^{17–22} However, the e-NO₃RR faces enormous challenges such as reduced catalytic activity, low selectivity, and low ammonia production rate.²³ Therefore, developing cost-effective catalysts with high efficiency is crucial for overcoming these bottlenecks.^{24–27}

So far, various catalysts have been developed for the e-NO₃RR. Among them, non-metallic catalysts have the characteristics of cost-effectiveness, strong electronic structure, adjustability and durability. However, the catalytic activity of non-metallic catalysts used in the e-NO₃RR is not satisfactory.²⁸ Noble metal catalysts are the most common high-activity electrocatalysts including ruthenium (Ru), rhodium (Rh) and platinum (Pt).^{29–32} Nevertheless, the high cost and scarcity of resources have limited their further application. In contrast to noble metals, transition metal catalysts, along with their various compounds, such as oxides, sulfides, carbides, phosphides, and nitrides, provide unique performance advantages.^{33–35} These materials have gained significant atten-

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tion, especially in the field of e-NO₃RR.^{36–38} For example, Cu/2D-CuO_x, Co/TiO₂ NSs and Ni(OH)₂@Ni show excellent electrocatalytic performance.^{39–42}

Polyoxometalates (POMs) are a prominent category of inorganic compounds composed of numerous metal atoms interconnected through oxygen bridges, which are usually composed of highly oxidized transition metals (mainly W, V and Mo) with d⁰ or d¹ electronic configurations.^{43–47} Because of its reversible redox properties, diverse and controllable structural composition, it has great potential in catalysis, photochemistry, nanotechnology, medicine and other fields.^{48,49} Nevertheless, the limited conductivity, tendency to agglomerate, and poor water solubility of POMs restrict their use in electrocatalysis. The construction of POMs-based metal-organic complexes can effectively ameliorate the aforementioned problems.⁵⁰ The Khalaji-Verjani team synthesized a PMo₁₁-Ru (acac)₃ electrocatalyst, showing high HER activity and stability.⁵¹ Yang *et al.* developed two novel polyoxometalate-based metal-organic complexes through a self-assembly approach to link polyoxometalate clusters with CuCTC, which served as purpose catalysts, enabling both the electrochemical sensing and photocatalytic conversion of Cr(vi). The rates of Cr(vi) photoreduction achieved with these complexes outperformed those of Cu₃ and most other reported catalysts.⁵²

In the family of POMs, the [P₄Mo^V₆O₃₁]^{12–} ({P₄Mo₆}) anion has a stable structure with minimal steric hindrance and a rich array of active oxygen atoms. It can have a good synergistic effect with metal active sites and organic ligands, which gives {P₄Mo₆} good topological scalability. Notably, the molybdenum in the structure is in pentavalent reduced state (Mo^V), which is an excellent electron donor. This unique characteristic can be leveraged as a potential “electron-donating unit” to pair with catalytically active species.^{53–55} Therefore, the integration of {P₄Mo₆} with composite materials could potentially establish an optimized catalytic framework, enhancing electron transport dynamics while improving both reaction efficiency and product specificity in nitrate reduction (NO₃RR) for ammonia synthesis.

Based on the above analysis, we selected the {P₄Mo₆}-type anion as the basic structural unit, nickel (Ni) and cobalt (Co) metal ions as nodes, and 2-(4-(4-carboxyphenyl)phenyl)imidazo(4,5-*f*)-(1,10)-phenanthroline (HNCP) with a large π -conjugated system as the organic ligand to construct two {P₄Mo₆} polyoxometalate-based metal-organic complexes, (HNCP)₂[Ni(H₂O)₂]₂[NiMo₁₂(H₂PO₄)₆(PO₄)₂(OH)₆O₂₄] (Ni-P₄Mo₆) and (HNCP)₂[Co(H₂O)₂]₂[CoMo₁₂(H₂PO₄)₆(PO₄)₂(OH)₆O₂₄] (Co-P₄Mo₆), which was anchored onto functionalized graphene oxide (GO) substrates to obtain Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO composites. The structural integration of graphene within the composite architecture significantly boosts the electrical conductivity and surface area, enhances the charge transfer kinetics for improved composite dispersion, and optimizes active site utilization to maximize the electrocatalytic performance.^{56–59} Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO composites show superior electrocatalytic efficacy in nitrate-to-ammonia conversion and stability, reaching the apex of NH₃ yield of

11.6 mg h^{–1} mg^{–1}_{cat} and 11.1 mg h^{–1} mg^{–1}_{cat} and Faraday efficiency of 88.4% and 78.5% at –1.0 V in neutral electrolytes, respectively. Our findings propose a rational design framework for polyoxometalate-integrated catalytic systems, achieving unprecedented faradaic efficiency in sustainable ammonia synthesis *via* nitrate electroreduction.

2. Experimental section

2.1 Preparation of (HNCP)₂[Ni

(H₂O)₄]₂[NiMo₁₂(HPO₄)₄(PO₄)₄O₃₀] (Ni-P₄Mo₆)

A mixture of [(NH₄)₆Mo₇O₂₄·4H₂O] (0.85 g), (NiCl₂·6H₂O) (0.40 g), HNCP (0.05 g) and CH₃CH₂OH (10 mL) was stirred for 10 min, and then deionized water (40 mL) and H₃PO₄ were added, respectively, with continuous stirring for 60 min. The pH value was adjusted to 1.0–1.5 with 1.0 M HCl or NaOH, and then the suspension was transferred to a 20 mL Teflon-lined autoclave and kept at 180 °C for 5 days. After slow cooling to room temperature at a rate of 10 °C h^{–1}, yellow diamond crystals were obtained (yield 65% based on Mo).

2.2 Preparation of (HNCP)₂[Co

(H₂O)₄]₂[CoMo₁₂(HPO₄)₄(PO₄)₄O₃₀] (Co-P₄Mo₆)

The compound Co-P₄Mo₆ was prepared following the same procedure as that of compound Ni-P₄Mo₆ except that NiCl₂·6H₂O (0.40 g) was replaced with CoCl₂·6H₂O. Following gradual cooling at a rate of 10 °C h^{–1} until reaching room temperature, yellow-brown rhombic crystals of Co-P₄Mo₆ were obtained (yield 55% based on Mo).

2.3 Preparation of Ni-P₄Mo₆/GO

A mixture of Ni-P₄Mo₆ (0.50 g) and 50 mL deionized water was ultrasonicated for 3 h. Then, GO (0.25 g) and polyethyleneimine (C₂H₅N) (10 μ L) were added and stirred for 30 min. The dispersion was washed with deionized water and centrifuged at 8000 rpm. After vacuum freeze-drying, a black fluffy powder was obtained (yield 40% based on Mo).

2.4 Preparation of Co-P₄Mo₆/GO

Co-P₄Mo₆/GO was prepared following the same procedure as that of Ni-P₄Mo₆/GO except that Ni-P₄Mo₆ (0.50 g) was replaced with Co-P₄Mo₆ (0.50 g). After vacuum freeze-drying, a black fluffy powder was obtained (yield 40% based on Mo).

2.5 Characterization

Fourier transform infrared (FTIR) spectra were recorded using a Bruker Tensor II spectrometer (Bruker, Germany) in the range of 4000–400 cm^{–1} by a KBr tablet method. X-ray powder diffraction (PXRD) was performed using a Rigaku D/max-TTR-III diffractometer with Cu-K α -ray irradiation. The scanning speed was 5° s^{–1} and the measurement range was 5–50°. X-ray photoelectron spectroscopy (XPS) spectra were recorded at room temperature using a 12 kV and 20 mA Al K α X-ray source by VG ESCALAB MK (VK, UK). The surface structure and morphology of the samples were characterized by trans-

mission electron microscopy (TEM) (JEOL, JEM-2010, 200 kV) and field emission scanning electron microscopy (FE-SEM) (Hitachi, SU 8000). Energy-dispersive spectroscopy (EDS) spectra were recorded by ensemble measurements using an SEM and a TEM. Ultraviolet-visible (UV-vis) spectra were recorded using a Shimadzu UV-1601 spectrometer in the wavelength range of 550–800 nm. Electrochemical tests were performed using a three-electrode system in a CHI 760E electrochemical workstation (Shanghai Chenhua).

3. Results and discussion

3.1 Preparation of composite catalyst materials

Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO composite catalysts were synthesized for the e-NO₃RR (Scheme 1). The composite materials were mainly synthesized in two steps. First, crystal materials Ni-P₄Mo₆ and Co-P₄Mo₆ were prepared *via* a one-pot hydrothermal approach, and they were loaded onto graphene oxide (GO) to obtain Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO.

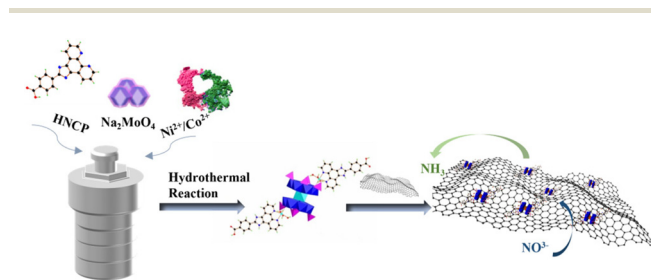
3.2 Morphology and structure characterization of samples

The morphology and composition of the two prepared catalysts were analyzed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The TEM result confirmed that the particles of the complex were distributed on the surface of the lamellar layers (Fig. 1 and Fig. S1†). The SEM images showed that the overall morphologies of Ni-

P₄Mo₆/GO and Co-P₄Mo₆/GO are similar, both showing the lamellar morphology of GO (Fig. S2a and S3a†). The energy-dispersive X-ray spectroscopy (EDS) spectra of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO (Fig. 1 and Fig. S1–S3†) showed that C, P, Mo, N and Ni/Co elements were present and uniformly distributed on the surface of Ni-P₄Mo₆/GO or Co-P₄Mo₆/GO, which indicates that the crystalline materials were successfully loaded onto the surface of GO.

The Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO powders showed the same characteristic peaks in the FT-IR spectrum (Fig. 2a). The characteristic bands in the range of 594–1080 cm⁻¹ were assigned to the $\nu(\text{Mo-O-Mo})$, $\nu(\text{Mo-O})$ and $\nu(\text{P-O})$ stretching vibrations of {P₄Mo₆}, respectively. The characteristic peak at 1200–1400 cm⁻¹ was attributed to the $\nu(\text{C=N})$ stretching vibration in the ligand. The characteristic absorption peaks at 1500–1600 cm⁻¹ and 1693 cm⁻¹ were attributed to the $\nu(\text{C=C})$ stretching vibration and $\nu(\text{C=O})$ stretching vibration of GO and the ligand in the compound, respectively.

Single-crystal X-ray diffraction analysis (Table S1†) showed that Ni-P₄Mo₆ and Co-P₄Mo₆ were isomorphic crystals. Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO were characterized by powder X-ray diffraction (PXRD) (Fig. 2b). The experimental diffraction peak of the composites is consistent with the simulated diffraction peaks of Ni-P₄Mo₆ and Co-P₄Mo₆, respectively, and the characteristic peak at 26.18° was attributed to GO, indicating that the crystalline material was successfully compounded with GO. In addition, the elemental composition and valence state of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO composites were measured by X-ray photoelectron spectroscopy (XPS) (Fig. 3 and Fig. S4†). The XPS full spectra (Fig. 3a) confirmed the presence of Ni/Co, Mo, C, P, O, and N in Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO, respectively. From the XPS fine spectrum of Ni-P₄Mo₆/GO (Fig. 3b), it can be seen that in the Ni 2p spectrum, the 856.5 eV and 873.5 eV peaks were attributed to Ni 2p_{3/2} and Ni 2p_{1/2}, and the 862.5 eV and 880.5 eV characteristic peaks were attributed to Ni 2p_{3/2} and Ni 2p_{1/2} satellite peaks,⁶⁰ indicating that the Ni element in Ni-P₄Mo₆/GO is Ni²⁺. The fine spectrum of Mo 3d in Fig. 3c shows that the characteristic peaks at 231.7 eV and 234.7 eV belong to Mo 3d_{5/2} and Mo 3d_{3/2}, indicating that the Mo element in Ni-P₄Mo₆/GO is Mo⁵⁺.⁶¹ The characteristic peaks at 398.3 eV and 399.5 eV in the N 1s spectrum belonged to the imidazole nitrogen in the organic ligand (Fig. 3d). The C 1s spectrum showed three



Scheme 1 Synthetic procedure for Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO composites.

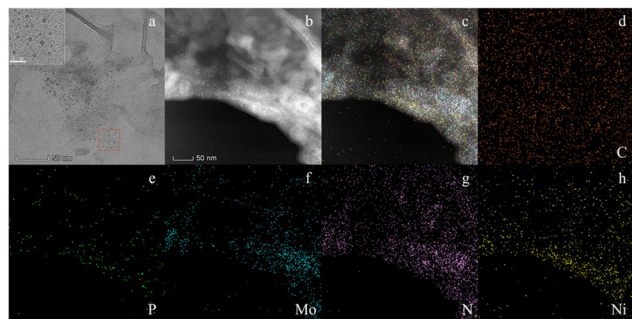


Fig. 1 (a–b) TEM of Ni-P₄Mo₆/GO. (c–h) Element mapping of images of Ni-P₄Mo₆/GO.

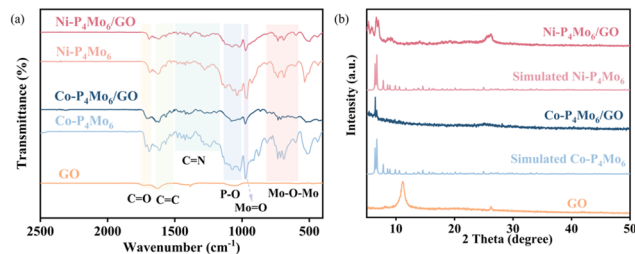


Fig. 2 (a) XRD spectra of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO. (b) FTIR spectra of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO.

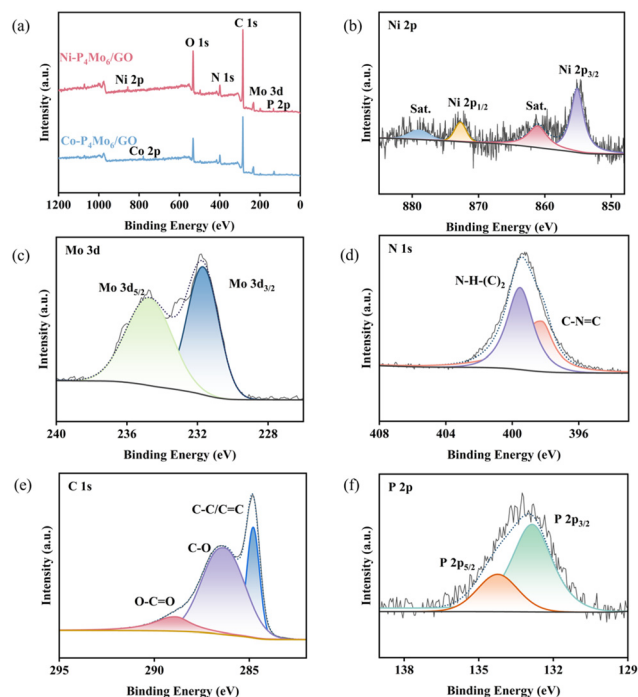


Fig. 3 (a) XPS survey spectra of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO. High-resolution XPS spectra of (b) Ni 2p, (c) Mo 3d, (d) N 1s, (e) C 1s, and (f) P 2p.

peaks, 284.8, 286.4, and 288.9 eV corresponding to C-C/C=C, C-O, and O-C=O, respectively (Fig. 3e). The characteristic peaks of P 2p at 132.8 and 134.2 eV were attributed to P 2p_{3/2} and P 2p_{1/2} (Fig. 3f).

The nitrogen adsorption-desorption isotherms of Ni-P₄Mo₆/GO, Co-P₄Mo₆/GO and GO samples were measured (Fig. 4). The results indicate that the specific surface areas of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO are 23.3 m² g⁻¹ and 18.0 m² g⁻¹, respectively, which are significantly higher than the specific surface area of GO (1.26 m² g⁻¹), which proves the successful loading of the sample. Simultaneously, the higher specific surface area obtained after loading can increase the contact area between the catalyst and the electrolyte, which improves the electrocatalytic performance of the material.⁶²

3.3 Electrochemical e-NO₃RR measurement

The e-NO₃RR study was carried out in a typical three-electrode system with an H-type electrolytic cell. Prior to all measure-

ments, high-purity Ar was continuously purged through the cathode compartment at a flow rate of 150 mL min⁻¹ for a minimum of 30 minutes to eliminate N₂ from both the electrolyte and the reactor. The measured potentials in this study were calibrated to the RHE scale using the following equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 + 0.059 × pH, and all the potentials were referenced to reversible hydrogen electrode (vs. RHE) potentials. Ammonia production was analyzed by indophenol blue spectrophotometry,⁶³ and by-product nitrite was analyzed by naphthalene ethylenediamine hydrochloride spectrophotometry (Fig. S5–S8†).

3.3.1 Electrochemical e-NO₃RR under acidic conditions.

The linear sweep voltammetry (LSV) curves of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO were tested under the conditions of 0.1 M NaNO₃ + 0.05 M H₂SO₄ (with nitrate) and 0.05 M H₂SO₄ (without nitrate) (Fig. S9a†). The LSV curves reveal that Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO exhibit significantly greater current densities when NO₃⁻ is present than those in its absence, indicating that Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO have an e-NO₃RR catalytic activity. The corresponding chronoamperometric (j - t) curves of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO at different potentials were tested (Fig. S9b and S9c†), showing that there is an increase in current density as the potential shifted from -0.3 V to -0.7 V vs. RHE. The reduction products were measured quantitatively by UV-vis spectrophotometry (Fig. S9d and S9e†). From Fig. 5a and b, it can be observed that Ni-P₄Mo₆/GO exhibits the best e-NO₃RR performance, with an NH₃ yield of 2.62 mg h⁻¹ mg⁻¹_{cat.} (-0.6 V vs. RHE) and an FE of 83.9% (-0.5 V vs. RHE). Co-P₄Mo₆/GO also achieved certain e-NO₃RR performance, with the highest NH₃ yield of 1.63 mg h⁻¹ mg⁻¹_{cat.} (-0.7 V vs. RHE) and FE of 85.3% (-0.5 V vs. RHE).

3.3.2 Electrochemical e-NO₃RR under neutral conditions.

The e-NO₃RR test results of the samples under the above-mentioned acidic conditions could be partially affected by the competitive HER. To further explore the catalytic performance of the catalysts, the e-NO₃RR test under neutral conditions was also performed (0.1 M NaNO₃ + 0.1 M Na₂SO₄). The LSV curve test results show that (Fig. 6a), the current density of Ni-P₄Mo₆/GO is higher than that of Co-P₄Mo₆/GO at the same voltage, indicating that its catalytic activity is better. The current density of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO in the electrolyte increases with the increase in potential (Fig. S10a and S10b†). Compared to Co-P₄Mo₆/GO (NH₃ yield: 4.23 mg h⁻¹ mg⁻¹_{cat.} at -1.3 V vs. RHE; FE: 65.1% at -0.9 V vs. RHE), Ni-

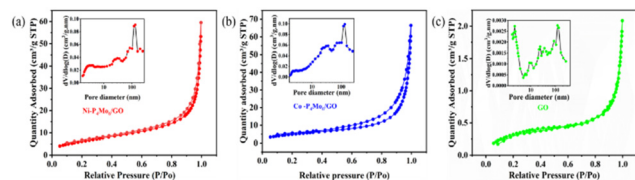


Fig. 4 Nitrogen adsorption-desorption isotherms and corresponding pore-size distribution curves of (a) Ni-P₄Mo₆/GO, (b) Co-P₄Mo₆/GO, and (c) GO.

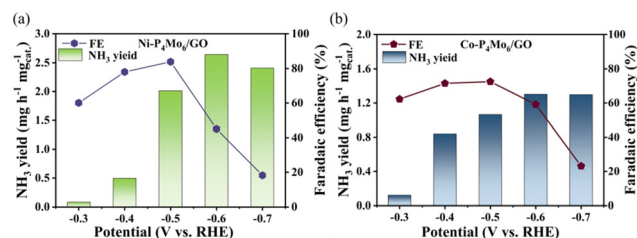


Fig. 5 NH₃ yield rate and FE of (a) Ni-P₄Mo₆/GO and (b) Co-P₄Mo₆/GO.

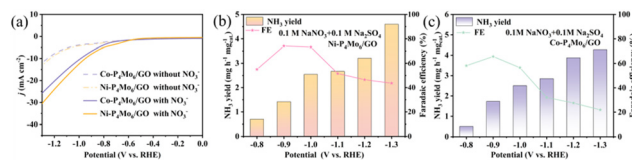


Fig. 6 (a) LSV curves of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO. NH₃ yield and FE of (b) Ni-P₄Mo₆/GO and (c) Co-P₄Mo₆/GO.

P₄Mo₆/GO (NH₃ yield: 4.52 mg h⁻¹ mg⁻¹ cat. at -1.3 V vs. RHE; FE: 74.1% at -0.9 V vs. RHE) exhibits a better catalytic activity (Fig. S10c, S10d† and Fig. 6b, c). In comparison with the electrocatalytic nitrate synthesis ammonia performance under acidic conditions, the performance of catalysts is significantly improved.

3.3.3 Electrochemical e-NO₃RR at different concentrations of NO₃⁻ electrolytes. To explore how varying nitrate concentrations influence the catalytic activity, Ni-P₄Mo₆/GO, which exhibited better performance in the aforementioned measurement results, was used as the catalyst for further study. The LSV curves of Ni-P₄Mo₆/GO at different concentrations of the NO₃⁻ electrolyte (10 mM, 0.1 M, 0.2 M, 0.3 M, 0.4 M, 0.5 M and 0.6 M) were further compared (Fig. S11†). The findings show that higher NO₃⁻ levels lead to a gradual increase in current density, and the initial potential of the reaction shifts to the positive direction, which demonstrates enhanced kinetic accessibility of the nitrate hydrodeoxygenation pathway, facilitating efficient ammonia generation through optimized proton-coupled electron transfer processes.⁶⁵

The best NH₃ yield rate and FE of Ni-P₄Mo₆/GO in electrolyte with different NO₃⁻ concentrations are shown in Fig. 7 and Table S2.† At a nitrate concentration of 10 mM, an NH₃ yield of Ni-P₄Mo₆/GO is 1.05 mg h⁻¹ mg⁻¹ cat. (-1.2 V vs. RHE) and the FE is only 45.2% (-0.9 V vs. RHE) (Fig. 7a). This may be attributed to the fact that when the concentration of nitrate is too low, the e-NO₃RR is inhibited and the performance of the catalyst is reduced.

Then, the electrocatalytic test of Ni-P₄Mo₆/GO was further compared in an electrolyte containing 0.1 to 0.6 M of nitrate (Fig. 7b–g). It is important to highlight that as the nitrate concentration increases, the ammonia production rate and FE of Ni-P₄Mo₆/GO show a trend of gradually increasing first (0.1 M to 0.5 M) and then decreasing (0.6 M). When the nitrate concentration is 0.5 M, the highest NH₃ yield is 11.6 mg h⁻¹ mg⁻¹ cat. (-1.3 V vs. RHE), and the best FE is 88.4% (-1.1 V vs. RHE), which is at a high level in the current reported electrocatalytic nitrate reduction yield (Table S3†). When the nitrate concentration is 0.6 M, ammonia production and FE all decrease (Fig. 7g), because the concentration of NO₃⁻ in the solution continues to increase, the current density increases, but the adsorption ability of Ni-P₄Mo₆/GO for NO₃⁻ tends to saturate. Meanwhile, the transfer of hydrogen is somewhat limited, resulting in a decrease in NH₃ production and FE.⁶⁶

For comparison, the e-NO₃RR tests of Co-P₄Mo₆/GO and GO were also conducted in 0.5 M NaNO₃/Na₂SO₄ electrolyte

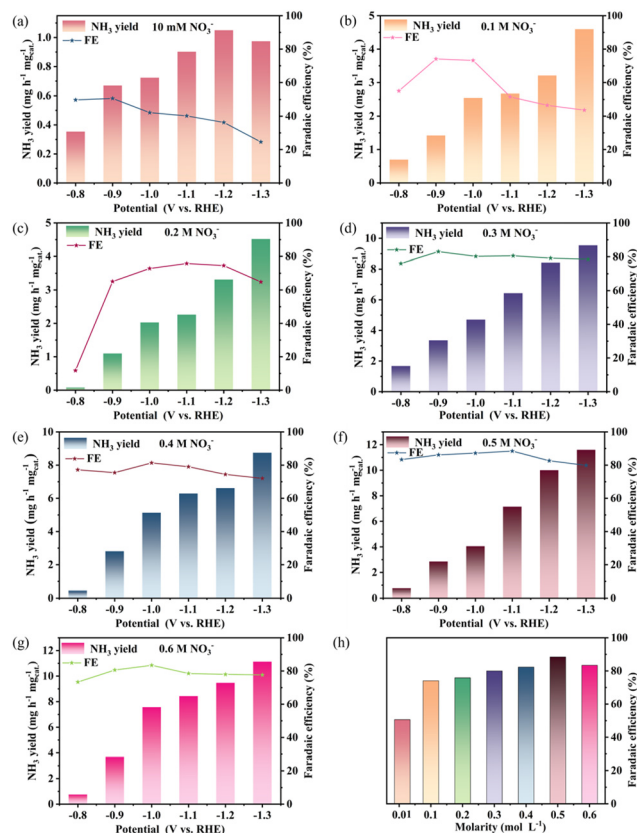


Fig. 7 (a–g) NH₃ yield rate and FE of Ni-P₄Mo₆/GO with different NO₃⁻ concentrations. (h) FE corresponding to the optimal voltage of Ni-P₄Mo₆/GO at each concentration.

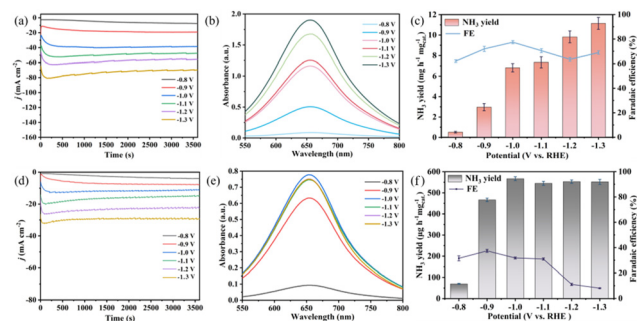


Fig. 8 (a) Chronoamperometric (*j*-*t*) curves of Co-P₄Mo₆/GO. (b) UV-vis absorption spectra of Co-P₄Mo₆/GO. (c) NH₃ yield rate and FE of Co-P₄Mo₆/GO. (d) Corresponding chronoamperometric (*j*-*t*) curves of GO. (e) UV-vis absorption spectra of GO. (f) NH₃ yield rate and FE of GO.

(Fig. 8). The results indicate that Co-P₄Mo₆/GO also has positive e-NO₃RR performance (the NH₃ yield of 11.1 mg h⁻¹ mg⁻¹ cat. (-1.1 V vs. RHE) and FE of 78.5% (-1.0 V vs. RHE)) (Fig. 8c). The NH₃ yield of 0.55 mg h⁻¹ mg⁻¹ cat. (-1.1 V vs. RHE) and the FE of 39.2% (-0.9 V vs. RHE) are obtained for GO, which exhibits almost minor e-NO₃RR activity compared with the composite (Fig. 8f).

Since the $\text{e-NO}_3\text{RR}$ to NH_3 is an intricate process requiring an eight-electron transfer, the by-products include NO_2^- , which is also studied by hydrochloric acid naphthalene ethylenediamine spectroscopy analysis (Fig. S12†). We observe that the FE values for NO_2^- are below 10% (Fig. 9a), with the maximum yield reaching only $0.3 \text{ mg h}^{-1} \text{ mg}^{-1}_{\text{cat}}$, suggesting that $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ demonstrates strong selectivity during the nitrate-to-ammonia conversion process.

Electrochemical impedance spectroscopy (EIS) is widely acknowledged as an effective approach for investigating catalytic kinetics. The Nyquist plots⁶⁷ and Bode plots of $\text{Ni-P}_4\text{Mo}_6/\text{GO}$, $\text{Co-P}_4\text{Mo}_6/\text{GO}$ and GO were performed (Fig. 9b and Fig. S13†). From the Nyquist plots, the linear slope of GO itself is the smallest, indicating that the diffusion resistance of GO is large, which is not conducive to the $\text{e-NO}_3\text{RR}$ dynamic process. After the crystal material was loaded, the slope increases and the diffusion resistance decreases, which is consistent with the high $\text{e-NO}_3\text{RR}$ performance of $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ and $\text{Co-P}_4\text{Mo}_6/\text{GO}$. $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ demonstrates minimal charge transfer resistance and optimal electron transport efficiency, confirming that the Faraday process between it and the electrolyte interface was faster. The C_{dl} value of $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ is 3.7 mF cm^{-2} , and the C_{dl} value of $\text{Co-P}_4\text{Mo}_6/\text{GO}$ is 3.1 mF cm^{-2} , indicating that $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ has better electrochemical performance (Fig. S14†).

Good stability is essential for catalysts. After 24 hours of continuous electrolysis, the XRD pattern, FTIR spectrum and XPS spectra of the $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ composite showed that the structure of the material did not change (Fig. 10a, b and Fig. S15†). This reveals that the material structure did not change. Under the optimal conditions for ammonia synthesis (-1.1 V vs. RHE, $0.5 \text{ M NaNO}_3 + 0.1 \text{ M Na}_2\text{SO}_4$ electrolyte), the current density of the catalyst remained basically unchanged during continuous electrolysis for 24 h (Fig. 10). The NH_3 yield and FE of $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ changed in a small range after 24 cycles of electrocatalytic tests under the same conditions, which indicates that the catalyst $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ exhibits good stability.

A set of control experiments were conducted to verify the origin of the produced NH_3 : (1) $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ served as the working electrode in an Ar-saturated blank solution lacking NaNO_3 , and can hardly detect ammonia after electrolysis (Fig. 11a); (2) using bare carbon cloth as the working electrode, very little ammonia was produced after electrolysis for 1 h in a

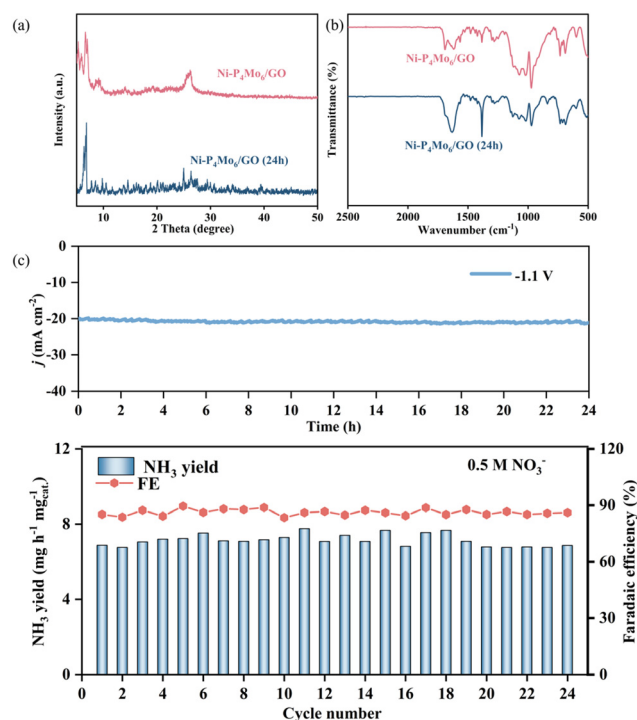


Fig. 10 (a) Comparison of the XRD patterns of $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ after continuous electrolysis for 24 hours. (b) FT-IR spectra of $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ before and after continuous electrolysis for 24 hours. (c) Corresponding chronoamperometric (j - t) curves for 24 h continuous electrolysis at -1.1 V vs. RHE and NH_3 yield rate and FE with different cycles.

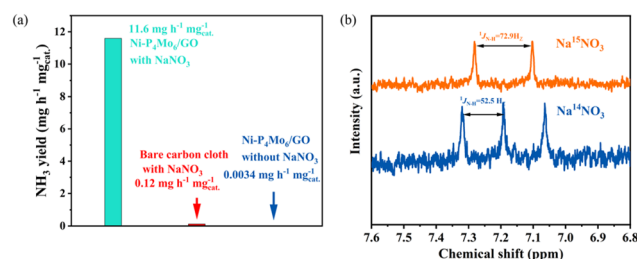


Fig. 11 (a) NH_3 yield rate of $\text{Ni-P}_4\text{Mo}_6/\text{GO}$ in $0.1 \text{ M Na}_2\text{SO}_4$ with or without NaNO_3 , respectively, and blank carbon paper in $0.1 \text{ M Na}_2\text{SO}_4$ solution with NaNO_3 . (b) ^1H NMR spectra of the electrolyte after 1 h of NO_3RR testing at -1.1 V vs. RHE with $^{14}\text{NO}_3^-$ and $^{15}\text{NO}_3^-$ as the N source, respectively.

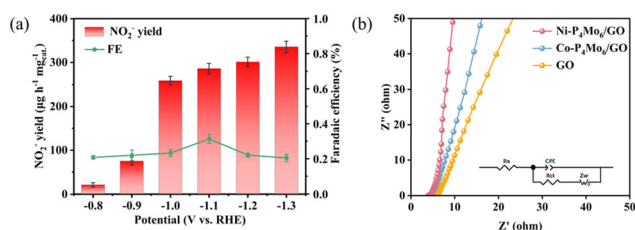


Fig. 9 (a) NO_2^- yield rate and FE of $\text{Ni-P}_4\text{Mo}_6/\text{GO}$. (b) Electrochemical impedance spectra of $\text{Ni-P}_4\text{Mo}_6/\text{GO}$, $\text{Co-P}_4\text{Mo}_6/\text{GO}$ and GO .

$0.1 \text{ M Na}_2\text{SO}_4$ solution with NaNO_3 . To verify the origin of NH_3 , N-isotope labeling experiments were conducted. When $\text{Na}^{14}\text{NO}_3$ served as the nitrogen source, the ^1H NMR spectrum of the electrolyte exhibited three distinct characteristic peaks of $^{14}\text{NH}_4^+$ following the $\text{e-NO}_3\text{RR}$ test. When $\text{Na}^{15}\text{NO}_3$ was used as the nitrogen source, the ^1H NMR spectrum of the electrolyte after the electrocatalytic test showed two characteristic peaks of $^{15}\text{NH}_4^+$ (Fig. 11b).⁶⁸ The above-mentioned findings provide strong evidence that all the ammonia is derived from the conversion of NO_3^- on $\text{Ni-P}_4\text{Mo}_6/\text{GO}$.

4. Conclusions

In this work, two crystalline materials were synthesized using a one-pot mode and loaded with GO to obtain two composites (Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO). The systematic optimization of electrolyte composition and nitrate feed concentrations was conducted to elucidate their synergistic influence on electrocatalytic activity, selectivity, and stability metrics in the nitrate reduction reaction. In the neutral electrolyte, the catalytic activity of Ni-P₄Mo₆/GO and Co-P₄Mo₆/GO was significantly improved and superior to some similar catalysts owing to the combined influence of the electron-donating capacity of the {P₄Mo₆} unit, good catalytic activity of Ni/Co, and the excellent charge transport ability of the graphene substrate. It is worth noting that the NH₃ yield (11.6 mg h⁻¹ mg⁻¹_{cat.}) and FE (88.4%) of Ni-P₄Mo₆/GO are higher than those of Co-P₄Mo₆/GO (NH₃ yield of 11.1 mg h⁻¹ mg⁻¹_{cat.}, FE of 78.5%). This work establishes a transformative design paradigm for polyoxometalate-derived electrocatalysts, offering mechanistic insights and synthetic protocols that advance the frontier of e-NO₃RR technologies.

Author contributions

Nan Zhao: data curation, formal analysis, investigation methodology, software, writing – original draft. Xinming Wang: conceptualization, data curation, formal analysis, funding acquisition, methodology, resources, supervision, writing – review & editing. Shuang Rong: software, validation. Qiushuang Jiang: conceptualization, methodology. Haoyun Li: data curation, formal analysis. Haijun Pang: funding acquisition, software, validation. Huiyuan Ma: conceptualization, data curation, formal analysis, methodology, resources, supervision.

Data availability

All relevant data are available within the manuscript and its additional files.

Conflicts of interest

There are no conflicts to declare.

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