

Electron-sponge polyoxometalate for interfacial electron and hydrogen regulation toward nitrate to ammonia reduction

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ABSTRACT: Electrocatalytic nitrate reduction to ammonia (ENRA) offers a sustainable strategy for simultaneously mitigating nitrate pollution and producing green ammonia under ambient conditions. However, its efficiency is severely limited by sluggish multi-electron transfer kinetics and the competing hydrogen evolution reaction (HER), particularly due to insufficient regulation of interfacial active hydrogen species (H^*). Polyoxometalates (POMs) feature abundant oxygen-rich sites capable of reversible protonation, thereby serving as an effective source of H^* . Here, we report a POMs-modulated $\text{Cu}_2\text{O}-\text{Cu}$ catalysts that enables synergistic regulation of interfacial electron distribution and H^* availability. X-ray photoelectron spectroscopy confirms pronounced electron transfer between POMs and $\text{Cu}_2\text{O}-\text{Cu}$, while electrochemical analyses reveal that POMs modification significantly enhances the adsorption and storage capacity of H^* , thereby promoting nitrate activation and hydrogenation. Density functional theory (DFT) calculations further reveal that POMs-induced interfacial charge redistribution optimizes nitrate intermediate adsorption and lowers the energy barrier of key proton-coupled electron transfer steps, thereby accelerating the ENRA pathway. As a result, the optimized catalyst delivers a high ammonia yield of $36.5 \text{ mg h}^{-1} \text{ mg}_{\text{cat}}^{-1}$ and excellent Faradaic efficiency of 97.4%. This work provides a general strategy for constructing POMs-based electrocatalysts via interfacial electron and hydrogen regulation, offering new insights into the rational design of selective ENRA systems.

KEYWORDS: polyoxometalates, electrocatalytic nitrate reduction, polyoxometalate derivatives, active hydrogen regulation

1 Introduction

Ammonia is a key chemical commodity widely used in agriculture, chemical manufacturing, and emerging energy systems.[1-5] Industrial ammonia synthesis relies primarily on the Haber-Bosch process, which operates under harsh conditions and is responsible for substantial energy consumption and CO_2 emissions. These limitations highlight the urgent need for sustainable and energy-efficient alternatives for ammonia production.[6-9] Electrocatalytic nitrate reduction to ammonia (ENRA) has emerged as a promising route, enabling the conversion of nitrate-containing wastewater into ammonia under ambient conditions using renewable electricity.[10-12] This approach offers a dual benefit of sustainable ammonia synthesis and environmental remediation. However, the complex multi-electron transfer process is often accompanied by competitive side reactions, such as nitrite formation and nitrogen evolution, resulting in limited selectivity and efficiency.[13-17]

Copper-based catalysts have attracted significant attention for ENRA due to their favorable electronic structure and strong nitrate adsorption capability.[18-20] Nevertheless, their performance is constrained by insufficient in situ generation of active hydrogen species (H^*), which are essential for subsequent hydrogenation steps, thereby limiting reaction kinetics and

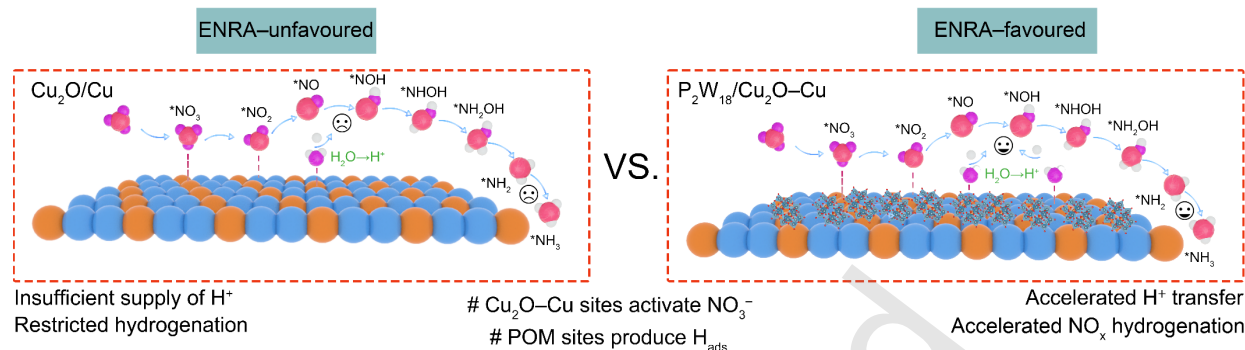
ammonia selectivity.[21-24]

Polyoxometalates (POMs), well-defined metal-oxygen clusters with reversible multielectron redox properties, are often regarded as electron sponges.[25-30] Their ability to reversibly store and shuttle electrons enables efficient proton-coupled electron transfer (PCET), thereby promoting continuous H^* generation. In addition, POMs function as electron reservoirs that facilitate interfacial charge transfer and lower reaction energy barriers, providing a sustained driving force for hydrogenation processes.[6, 31-33] This dual electron-proton regulation enables efficient conversion of nitrogen-containing intermediates toward ammonia.

Inspired by this, we developed a POM-modulated $\text{Cu}_2\text{O}-\text{Cu}$ catalysts ($\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$) to regulate interfacial electron and proton transfer for efficient ENRA (Scheme 1). X-ray photoelectron spectroscopy (XPS) confirms interfacial electronic interaction between P_2W_{18} and $\text{Cu}_2\text{O}-\text{Cu}$, resulting pronounced electronic redistribution at Cu active sites. Furthermore, density functional theory (DFT) calculations reveal the optimized reaction energetics at the $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ interface, providing theoretical insights into the promoted nitrate reduction pathway. The resulting catalyst demonstrates exceptional ENRA performance, with an ammonia yield rate of $36.5 \text{ mg h}^{-1} \text{ mg}_{\text{cat}}^{-1}$ and a Faradaic efficiency of 97.4%. Systematic electrochemical analysis further confirms that the enhanced

performance originates from the synergistic effect between P_2W_{18} -induced electron buffering and Cu_2O -Cu active sites, which jointly promote nitrate activation and $^*H$ -mediated hydrogenation. This work not only demonstrates the

effectiveness of POM-assisted interfacial regulation strategy but also provides a general and rational design principle for constructing high-performance Cu-based electrocatalysts for selective nitrate-to-ammonia conversion.



Scheme 1. Schematic illustration of the tandem catalytic mechanism of P_2W_{18}/Cu_2O-Cu for nitrate reduction. Within this bifunctional architecture, the Cu_2O-Cu sites selectively activate nitrate, while POM sites facilitate water dissociation to generate $^*H$. The synergy between the dual sites optimizes H^+ supply, thereby accelerating the successive hydrogenation steps and ultimately driving ammonia formation.

2 Experiment Section

2.1 Synthesis of $K_6[P_2W_{18}O_{62}]$

The polyoxometalate $K_6[P_2W_{18}O_{62}]$ was synthesized according to a previously reported literature method.[34]

2.2 Synthesis of P_2W_{18}/Cu_2O-Cu

In a typical procedure, $K_6[P_2W_{18}O_{62}]$ (20 μ mol, 61.2 mg) and $CuSO_4$ (0.50 mmol, 80.0 mg) were dissolved in 10 mL deionized (DI) water under stirring (Solution A). Separately, $NaBH_4$ (0.50 mmol, 18.9 mg) was dissolved in 10 mL DI water to form a freshly prepared reducing solution (Solution B). The Solution A was first stirred in an ice bath for 10 min to ensure complete coordination. Subsequently, Solution B was added to the above solution dropwise under vigorous stirring. The reaction was maintained for 10 min and a dark precipitate was formed. The product was collected by centrifugation (10000 rpm, 5 min), washed three times with DI water, and dried at 60 $^{\circ}C$ overnight, denoted as P_2W_{18}/Cu_2O-Cu .

2.3 Synthesis of Cu_2O-Cu

The process was carried out following the same protocol as that of P_2W_{18}/Cu_2O-Cu , without the addition of $K_6[P_2W_{18}O_{62}]$.

2.4 Characterizations

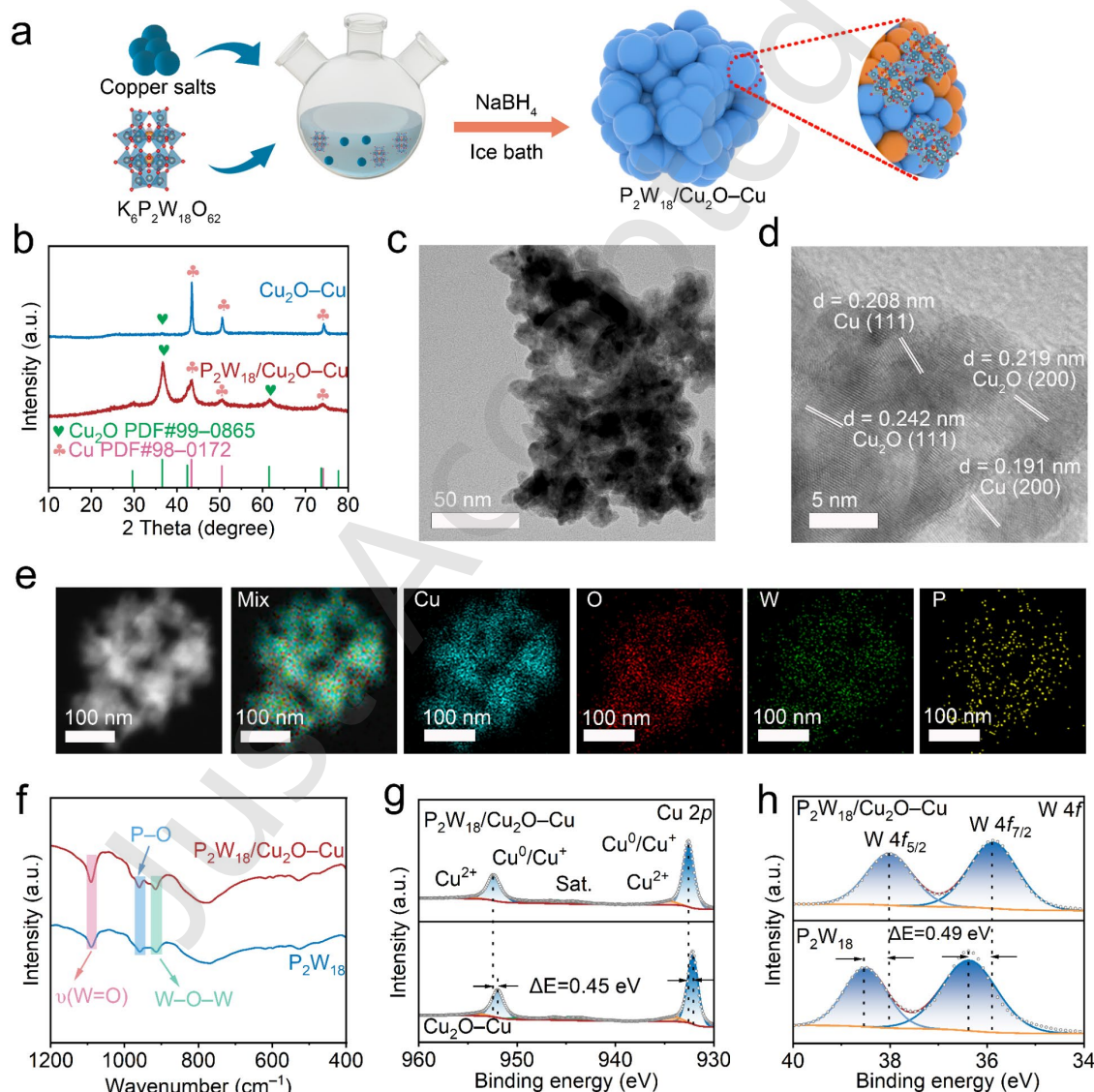
Powder X-ray diffraction (XRD, Rigaku SmartLab, $Cu K\alpha$, $\lambda = 1.5406 \text{ \AA}$) was employed to analyze the crystallinity of the as-prepared samples. Morphological features and elemental distributions were investigated via scanning electron microscopy (SEM, JEOL JSM-7800F) and transmission electron microscopy (TEM, JEM-2100F) integrated with an energy-dispersive X-ray (EDX) spectrometer. Surface chemical states were determined using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific 250Xi). In situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, Hefei in situ technology Co. Ltd.) measurements were conducted in an H-cell using a DH7000C DongHua Analytical electrochemical workstation.

3 Results and Discussion

A polyoxometalate-modified Cu_2O-Cu catalyst, denoted as P_2W_{18}/Cu_2O-Cu , was synthesized via a chemical reduction strategy (Fig. 1a). A series of catalysts were prepared by tuning the molar ratio of Cu precursor to $NaBH_4$ ($CuSO_4/NaBH_4 = 2:1, 1:1, 1:2$, and $1:3$, denoted as $P_2W_{18}/Cu_2O-Cu-1$, P_2W_{18}/Cu_2O-Cu , $P_2W_{18}/Cu_2O-Cu-2$, and $P_2W_{18}/Cu_2O-Cu-3$, respectively) to optimize the reduction process. X-ray diffraction (XRD) was employed to determine the crystalline structure of the obtained samples. As shown in Figs. 1b and S1, P_2W_{18}/Cu_2O-Cu exhibits characteristic diffraction peaks corresponding to Cu_2O (PDF#99-0865) and metallic Cu (PDF#98-0172). Specifically, the diffraction peaks at 36.5° , 61.4° , and 73.9° are indexed to the (111), (220), and (311) planes of Cu_2O , while the peaks at 43.4° and 50.4° correspond to the (111) and (200) planes of metallic Cu, confirming the coexistence of both crystalline phases. Compared with P_2W_{18}/Cu_2O-Cu , the Cu_2O-Cu control sample exhibits stronger diffraction peaks associated with metallic Cu and weaker Cu_2O reflections, indicating a higher reduction degree of Cu species by $NaBH_4$ in the control sample. Conversely, in the P_2W_{18}/Cu_2O-Cu sample, the presence of P_2W_{18} regulates the reduction process by accepting electrons, thereby suppressing excessive reduction toward metallic Cu and favoring the formation of the Cu_2O-Cu heterostructure. Transmission electron microscopy (TEM) reveals that P_2W_{18}/Cu_2O-Cu consists of interconnected nanoparticles (Fig. 1c). High-resolution TEM (HR-TEM) further resolves lattice fringes with spacings of 0.208 and 0.191 nm, attributable to the Cu (111) and Cu (200) planes, respectively, as well as 0.242 and 0.219 nm, assigned to the Cu_2O (111) and Cu_2O (200) planes, respectively (Fig. 1d). Energy-dispersive X-ray spectroscopy (EDS) mapping demonstrates a homogeneous distribution of Cu, O, W, and P throughout the particles (Fig. 1e), indicating successful surface anchoring of the P_2W_{18} species on Cu_2O-Cu . In contrast, the Cu_2O-Cu control exhibits relatively larger particles (Figs. S2 and S3), and HR-TEM similarly confirms the coexistence of Cu and Cu_2O phases.

Fourier transform infrared (FT-IR) spectroscopy further confirms the structural integrity of P_2W_{18} within the composite. As shown in Fig. 1f, P_2W_{18}/Cu_2O-Cu displays characteristic vibrational bands at 1080, 960, 910 and 780 cm^{-1} , corresponding to P-O, terminal W=O, and bridging W-O-W vibrations, respectively.[35, 36] The preservation of these features indicates that the Dawson-type P_2W_{18} structure remains intact after integration. X-ray photoelectron spectroscopy (XPS) was performed to investigate the interfacial electronic interaction. In the Cu 2p spectra (Fig. 1g), P_2W_{18}/Cu_2O-Cu shows Cu 2p_{3/2} and Cu 2p_{1/2} peaks at 932.8 and 952.4 eV, respectively, with a positive shift of 0.45 eV compared with Cu_2O-Cu . This shift can be attributed to the combined effects of the modified Cu oxidation-state distribution and interfacial electronic interaction between

exhibit overlapped Cu 2p signals, their coexistence is further confirmed by Cu LMM Auger spectroscopy (Figs. S4 and S5), which reveals the presence of both Cu^+ and Cu^0 species in P_2W_{18}/Cu_2O-Cu . The W 4f_{7/2} and W 4f_{5/2} peaks are observed at 35.8 and 38.1 eV, corresponding to the +6 oxidation state of W (Fig. 1h). Compared with pristine P_2W_{18} , these peaks shift towards lower binding energies by 0.49 eV, which is consistent with electron enrichment at W centers. In contrast, negligible shifts are observed in the O 1s and P 2p spectra (Fig. S6), suggesting that charge redistribution is primarily confined to Cu-W interactions. Collectively, these results demonstrate the successful construction of P_2W_{18} -functionalized Cu_2O-Cu nanoparticles and reveal a pronounced interfacial electron transfer from Cu species to W centers, which is expected to play a key role in modulating the



Cu species and $P_2W_{18}O_{62}$, suggesting the regulation of the Cu electronic structure by $P_2W_{18}O_{62}$. Since Cu^+ and Cu^0 species

catalytic properties.

Figure 1. (a) Schematic illustration of the synthesis of P_2W_{18}/Cu_2O-Cu composites. (b) XRD pattern of P_2W_{18}/Cu_2O-Cu and Cu_2O-Cu . (c) TEM and (d) HRTEM image of P_2W_{18}/Cu_2O-Cu . (e) EDS images of P_2W_{18}/Cu_2O-Cu . (f) FT-IR spectra of P_2W_{18} and P_2W_{18}/Cu_2O-Cu . (g) High-resolution XPS spectra of Cu 2p for P_2W_{18}/Cu_2O-Cu and Cu_2O-Cu . (h) High-resolution XPS spectra of W 4f for P_2W_{18}/Cu_2O-Cu and P_2W_{18} .

To systematically evaluate the electrocatalytic nitrate reduction performance, a series of electrochemical measurements were conducted in 0.01 M phosphate-buffered saline (PBS) containing nitrate. Linear sweep voltammetry (LSV) was first employed to

probe the electrochemical behavior of the catalyst (Fig. 2a). The presence of nitrate (NO_3^- , 0.1 M) induces a pronounced increase in cathodic current density relative to the nitrate-free electrolyte, indicating the activation of ENRA at negative potentials. Product

distribution was quantified using calibrated colorimetric methods for NH_4^+ , NO_3^- , and NO_2^- (Figs. S7–S9). The effect of nitrate concentration on catalytic activity was then systematically investigated (Fig. 2b and Fig. S10). Both ammonia yield rate and Faradaic efficiency (FE) increase with NO_3^- concentration and reach a maximum at 100 mM, suggesting an optimal balance between substrate availability and interfacial reaction kinetics. To optimize catalyst composition, a series of control catalysts with different component ratios were further evaluated (Fig. 2c and Fig. S11). Among all samples, $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ exhibits the highest ammonia yield rate and FE. Consistently, LSV and Tafel slope analysis (Fig. S12) reveal that $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ possesses the lowest Tafel slope (83 mV dec^{-1}), indicating its superior reaction kinetics for nitrate reduction. To further verify the electrochemical redox behavior of Dawson-type P_2W_{18} species,

cyclic voltammetry (CV) measurements were conducted in an extended cathodic potential range (Figure S13). The observed reduction features are assigned to the stepwise $\text{W(VI)}/\text{W(V)}$ transitions of P_2W_{18} , demonstrating that the POM units retain their electrochemical activity after integration with the $\text{Cu}_2\text{O}-\text{Cu}$ substrate. Subsequently the origin of the enhanced activity, electrochemical surface area (ECSA) and charge-transfer properties were further analyzed (Fig. S14). CV indicate that $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ exhibits the highest double-layer capacitance (0.810 mF cm^{-2}), reflecting the largest ECSA and the highest density of accessible active sites. Electrochemical impedance spectroscopy (EIS) further confirms the smallest charge-transfer resistance, indicating accelerated interfacial electron transport (Fig. S15).

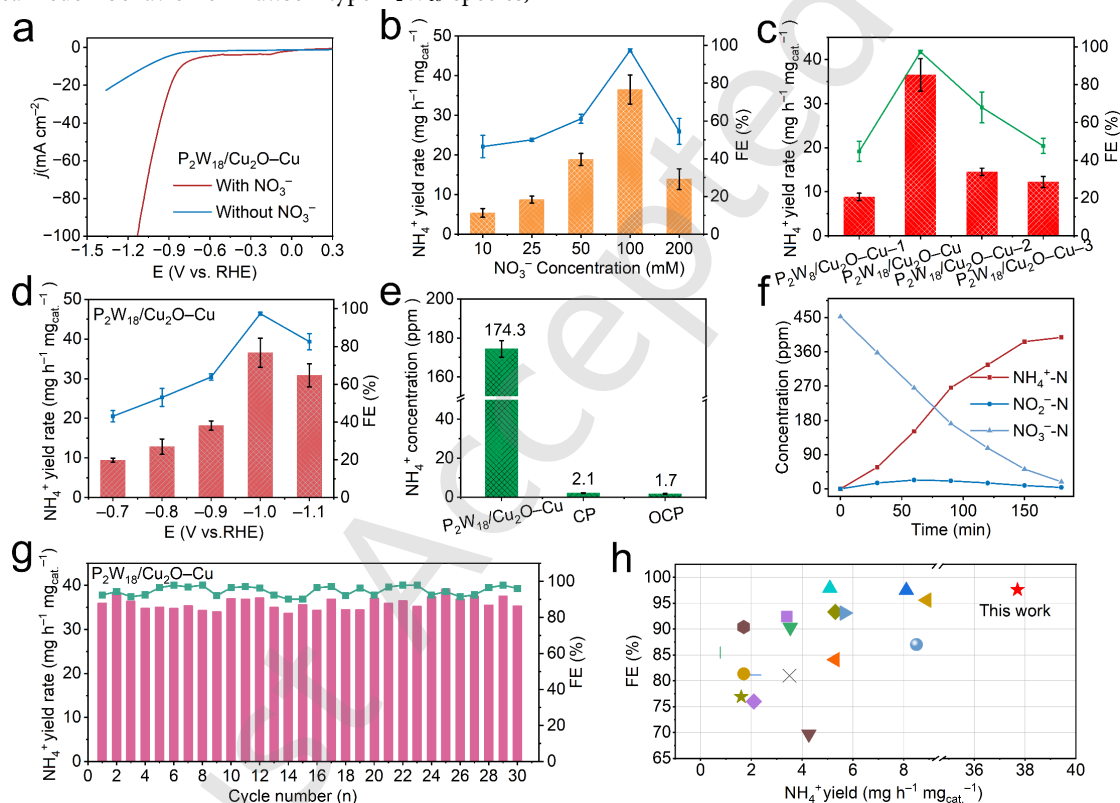


Figure 2. (a) LSV curve of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ in 0.01 M PBS with and without nitrate. (b) Ammonia yields and FE for $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ at different concentration of nitrate. (c) Ammonia yields and FE of different comparison samples. (d) Ammonia yields and FE at varying potentials for $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$. (e) Concentration profiles of NO_3^- , NO_2^- and NH_3 during long-term electrolysis. (f) Control experiments showing ammonia yield under different conditions, including open-circuit potential (OCP), carbon paper (CP) electrode and $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$. (g) Cycling stability test of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ over 30 consecutive cycles. (h) Comparison of ENRA performance of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ with representative reported catalysts.

Controlled potential electrolysis performed from -0.7 to -1.1 V vs. RHE shows that $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ exhibits optimal performance at -1.0 V vs. RHE, delivering an ammonia yield of $36.5 \text{ mg h}^{-1} \text{ mg}_{\text{cat}}^{-1}$ and an FE of 97.4% (Fig. 2d and Fig. S16). Time-resolved monitoring of nitrogen species (Fig. 2e) shows a continuous decrease in NO_3^- concentration, accompanied by a corresponding increase in NH_4^+ , while NO_2^- remains at a consistently low level, indicating a highly selective NO_3^- to NH_4^+ conversion pathway. Furthermore, rigorous control experiments were conducted to exclude non-electrochemical ammonia formation and external nitrogen contamination (Fig. 2f). No detectable NH_4^+ was observed under open-circuit potential (OCP)

after 1 h, and bare carbon paper (CP) shows negligible activity under identical conditions, confirming that ammonia originates exclusively from electrocatalytic ENRA on $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$. Long-term stability was evaluated through 30 consecutive electrolysis cycles (Fig. 2g), during which both ammonia yield rate and FE remain nearly unchanged, demonstrating excellent durability. Finally, comparison with previously reported catalysts (Fig. 2h) shows that this system delivers superior performance in both activity and selectivity, highlighting its competitive advantage for electrocatalytic nitrate to ammonia conversion.[3, 37–52]

To elucidate the synergistic role of P_2W_{18} modification in regulating the ENRA pathway and interfacial adsorbed hydrogen ($^*H$) behavior, a series of electrochemical analyses were performed in 1.0 M KOH containing 0.1 M NO_3^- . As shown in Fig. 3a and Fig. S17, the ammonia yield rate and FE of different catalysts were systematically compared. P_2W_{18}/Cu_2O-Cu exhibits the highest activity among all samples, outperforming both Cu_2O-Cu and P_2W_{18} , thereby confirming a pronounced synergistic interaction between P_2W_{18} species and Cu-based active sites in promoting ENRA. Meanwhile, the suppressed HER on P_2W_{18}/Cu_2O-Cu demonstrates its excellent selectivity toward nitrate reduction by effectively inhibiting the competitive proton reduction pathway (Fig. S18). The involvement of $^*H$ was further probed using tert-butanol (TBA) with different concentrations as a $^*H$ scavenger. The LSV results (Fig. 3b) demonstrate that

P_2W_{18}/Cu_2O-Cu delivers the highest cathodic current density in the absence of TBA, indicative of accelerated reaction kinetics. Consistently, Tafel slope analysis reveals a minimum value of 83 $mV\ dec^{-1}$ under TBA-free conditions (Fig. S19). Upon increasing TBA concentration, the cathodic current gradually decreases, suggesting that reaction kinetics are strongly dependent on the availability of surface $^*H$ species. The effect of $^*H$ on catalytic performance was further quantified by comparing ammonia yield rates with and without TBA (Fig. 3c and Fig. S20). Across the potential window of -0.7 to -1.1 V vs. RHE, the ammonia production rate without TBA is consistently higher than that in the presence of TBA. Although both systems reach optimal activity at -1.0 V vs. RHE, the pronounced suppression upon TBA addition indicates that $^*H$ -mediated hydrogenation plays a decisive role in governing ENRA activity and selectivity.

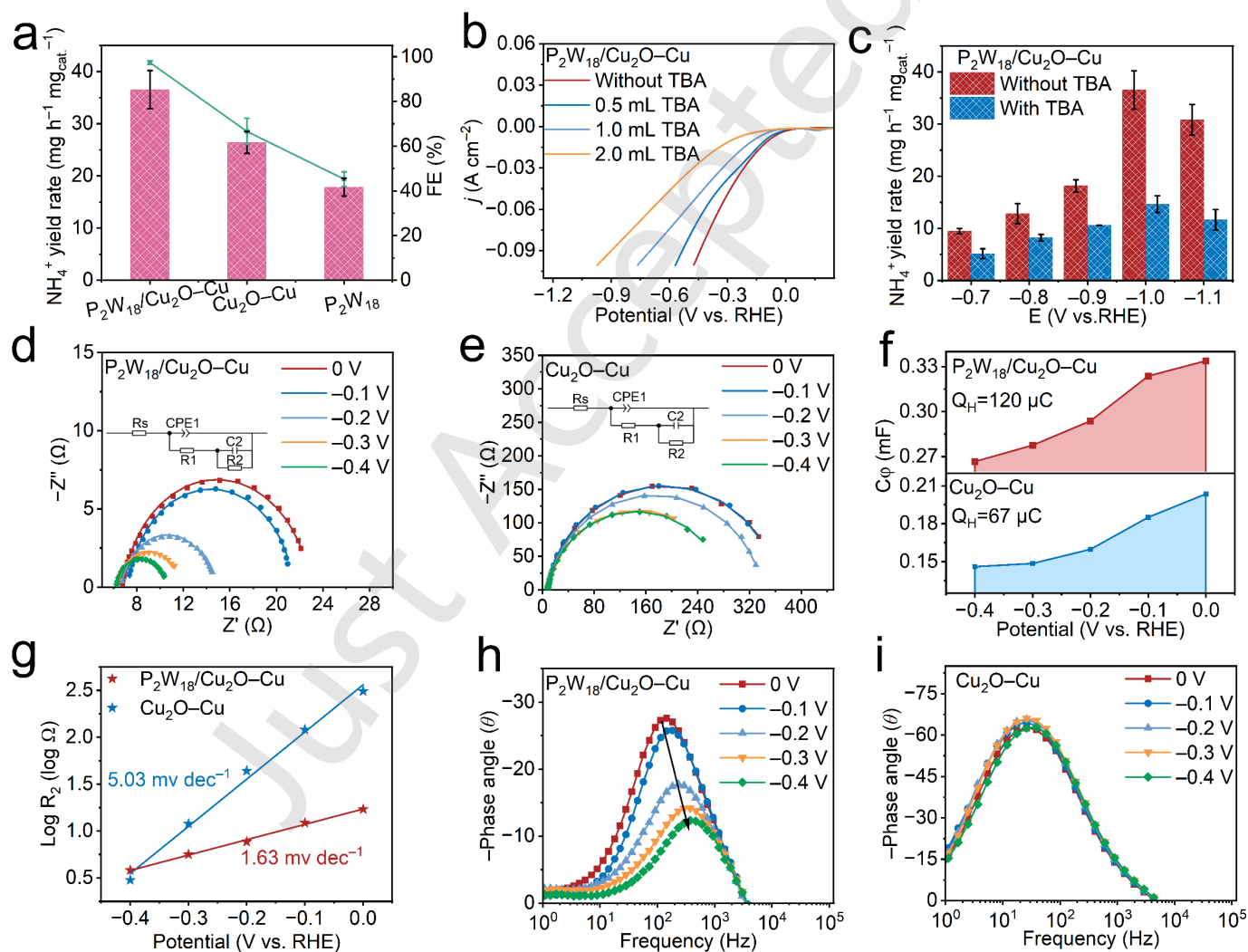


Figure 3. (a) Ammonia yields and FE over P_2W_{18}/Cu_2O-Cu , Cu_2O-Cu , and P_2W_{18} . (b) LSV curves of P_2W_{18}/Cu_2O-Cu under different TBA concentrations. (c) Ammonia yields with and without TBA at various applied potentials. (d, e) Nyquist plots obtained from electrochemical impedance spectroscopy measurements during potential scans from 0 V to -0.4 V vs. RHE for P_2W_{18}/Cu_2O-Cu and Cu_2O-Cu , the inset shows the equivalent circuit model used for fitting. (f) Hydrogen adsorption pseudocapacitance and (g) Tafel slopes for $^*H$ adsorption derived from the EIS data for P_2W_{18}/Cu_2O-Cu and Cu_2O-Cu . (h, i) Corresponding Bode phase plots for P_2W_{18}/Cu_2O-Cu and Cu_2O-Cu .

To gain atomistic insight into the origin of hydrogen evolution reaction suppression and ENRA selectivity, the generation, adsorption, and utilization behavior of $^*\text{H}$ species was further investigated. In ENRA, the catalyst must continuously generate $^*\text{H}$ to drive hydrogenation steps. The $^*\text{H}$ generation and adsorption behavior were first evaluated using in situ electrochemical impedance spectroscopy (EIS). EIS measurements were performed under continuous potential scanning from 0 to -0.4 V vs. RHE (Figs. 3d and e). Nyquist plots for all catalysts exhibit a single capacitive semicircle, whose radius decreases with increasingly negative potential, indicating accelerated interfacial charge transfer. Using an equivalent circuit model incorporating adsorption processes, the hydrogen adsorption pseudocapacitance (C_{H}) and charge-transfer resistance (R_2) were extracted.[53] Integration of C_{H} over potential yields the hydrogen adsorption charge (Q_{H}), which reflects the surface $^*\text{H}$ adsorption capacity.[54] The Q_{H} value of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ ($120 \mu\text{C}$) is significantly higher than that of $\text{Cu}_2\text{O}-\text{Cu}$ (Fig. 3f), indicating an enhanced ability to accommodate reactive hydrogen species.

Furthermore, the $^*\text{H}$ generation kinetics were evaluated via the relationship between R_2 and potential. $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ exhibits a Tafel slope of 1.63 mV dec^{-1} , substantially lower than that of $\text{Cu}_2\text{O}-\text{Cu}$ (Fig. 3g), demonstrating faster $^*\text{H}$ formation kinetics and a reduced energetic barrier for hydrogenation steps. Phase angle-frequency analysis (Figs. 3h and i) provides further kinetic insight. For $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$, the phase angle peak shifts toward higher frequencies and decreases in intensity with increasingly negative potential, reflecting increased surface $^*\text{H}$ coverage and rapid consumption of $^*\text{H}$ in ENRA. In contrast, $\text{Cu}_2\text{O}-\text{Cu}$ shows minimal variation, indicating limited $^*\text{H}$ adsorption and inefficient utilization of generated hydrogen species. Collectively, these results demonstrate that P_2W_{18} modification simultaneously enhances interfacial charge transfer, accelerates $^*\text{H}$ generation kinetics, and increases $^*\text{H}$ adsorption capacity, thereby establishing a synergistic catalytic system that efficiently promotes $^*\text{H}$ -mediated ENRA to ammonia while suppressing competing hydrogen evolution.

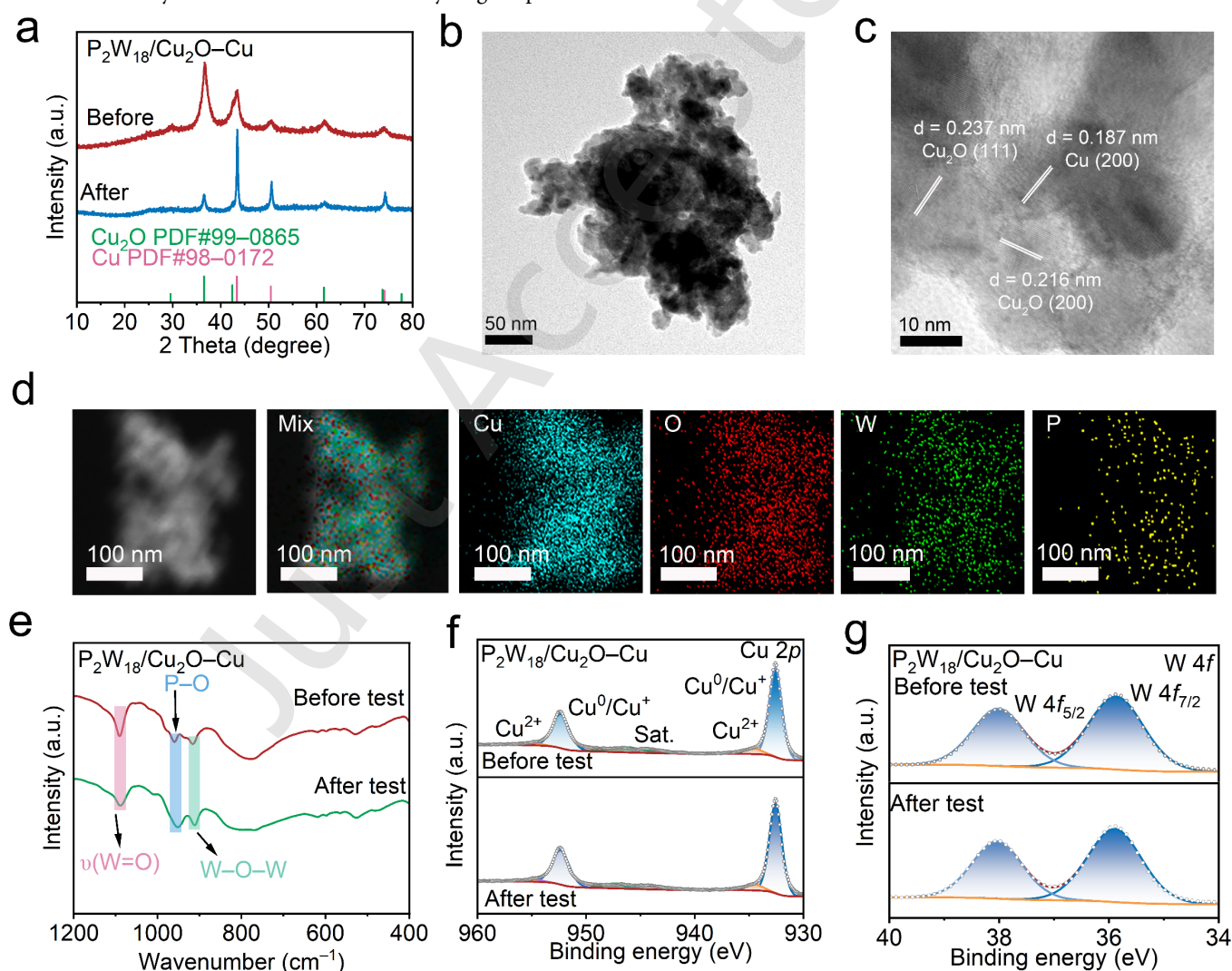


Figure 4. (a) XRD pattern of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ before and after ENRA. (b) TEM image, (c) HRTEM image, and (d) EDS images of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ after ENRA. (e) FT-IR spectra of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ before and after ENRA. (f, g) High-resolution XPS spectra of Cu 2p and W 4f for $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ before and after ENRA.

The structural and chemical stability of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ was evaluated under continuous ENRA conditions. XRD patterns before and after electrolysis are nearly identical, with all peaks

indexed to Cu_2O and Cu , indicating unchanged bulk crystal structure (Fig. 4a). TEM shows that the aggregated nanoparticle morphology is well preserved after reaction (Fig. 4b), while HR-

TEM confirms the retention of lattice fringes corresponding to Cu_2O and Cu (Fig. 4c). EDS mapping reveals uniform distributions of Cu, O, W, and P, indicating no significant leaching (Fig. 4d). FT-IR spectra show that P-O and W-O-W vibrations are retained after reaction, confirming structural stability of the POM component (Fig. 4e). XPS shows negligible shifts in Cu 2p and W 4f after electrolysis, indicating stable oxidation states of Cu^0/Cu^+ and W^{6+} (Figs. 4f and g). Cu LMM, P 2p and O 1s further

confirm preservation of Cu^+ and structural integrity of P_2W_{18} (Figs. S21 and S22). XPS reveals the coexistence of Cu^+ and Cu^0 species after electrolysis, indicating that partial reduction of Cu_2O occurs while Cu^+ species remain stabilized under ENRA conditions. Collectively, $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ exhibits excellent structural and chemical stability under ENRA conditions, confirming its robustness for long-term operation.

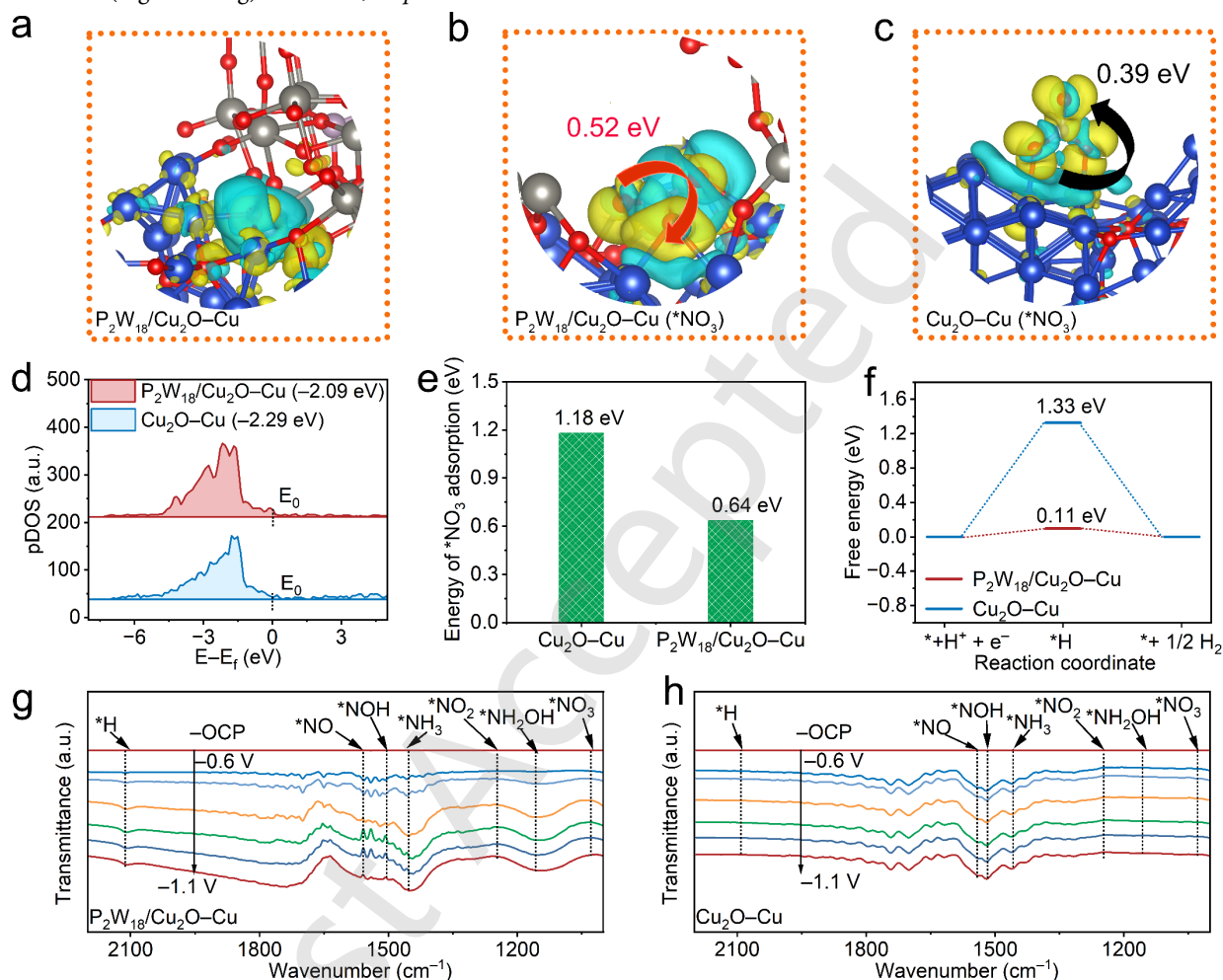


Figure 5. (a) Charge density difference distribution of P_2W_{18} and $\text{Cu}_2\text{O}-\text{Cu}$ for $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$. Charge density difference and Bader charge analysis for NO_3^- adsorption on (b) $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ and (c) $\text{Cu}_2\text{O}-\text{Cu}$. (d) pDOS profiles of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ and $\text{Cu}_2\text{O}-\text{Cu}$. (e) Calculated NO_3^- adsorption energies on $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ and $\text{Cu}_2\text{O}-\text{Cu}$. (f) Gibbs free energy profiles for $^*\text{H}$ adsorption on $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ and $\text{Cu}_2\text{O}-\text{Cu}$. (g, h) In-situ FT-IR spectra of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ and $\text{Cu}_2\text{O}-\text{Cu}$.

To understand the origin of the enhanced ENRA performance of $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$, density functional theory (DFT) calculations and in situ FT-IR spectroscopy were performed to investigate the interfacial electronic structure, nitrate activation, and reaction pathways (Figs S23–26). Charge density difference analysis reveals evident electron redistribution at the $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ interface (Fig. 5a), demonstrating strong interfacial electronic interaction between P_2W_{18} and $\text{Cu}_2\text{O}-\text{Cu}$. The adsorption behavior of nitrate was further evaluated. Compared with $\text{Cu}_2\text{O}-\text{Cu}$, $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ exhibits a stronger electronic interaction with adsorbed NO_3^- , as evidenced by charge density difference and Bader charge analysis (Figs. 5b and 5c). Moreover, pDOS analysis shows that P_2W_{18} modification introduces more electronic states near the Fermi level (Fig. 5d), favoring a stronger interaction between the catalyst surface and nitrate intermediates. The calculated NO_3^- adsorption energy

decreases from 1.18 eV on $\text{Cu}_2\text{O}-\text{Cu}$ to 0.64 eV on $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ (Fig. 5e), indicating that P_2W_{18} incorporation facilitates nitrate adsorption and activation. The hydrogen adsorption behavior was investigated by calculating the Gibbs free energy of $^*\text{H}$ adsorption (Fig. 5f). $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ exhibits stronger $^*\text{H}$ adsorption than $\text{Cu}_2\text{O}-\text{Cu}$, which promotes the hydrogenation process involved in nitrate reduction while suppressing the competitive hydrogen evolution. In situ FT-IR spectroscopy was employed to identify the reaction intermediates and pathway (Figs. 5g and 5h). During electrolysis, characteristic signals corresponding to nitrate reduction intermediates, including $^*\text{NO}_3$ (1031 cm^{-1}), $^*\text{NO}_2$ (1253 cm^{-1}), $^*\text{NOH}$ (1505 cm^{-1}), and $^*\text{NH}_2\text{OH}$ (1159 cm^{-1}), are detected, confirming the hydroxylamine-mediated pathway. Meanwhile, the stronger $^*\text{H}$ -related signal (2110 cm^{-1}) observed on $\text{P}_2\text{W}_{18}/\text{Cu}_2\text{O}-\text{Cu}$ indicates enhanced generation and adsorption of active hydrogen species, facilitating successive hydrogenation

steps during nitrate reduction. In summary, the theoretical calculations and in situ spectroscopic results demonstrate that P_2W_{18} -induced interfacial electronic regulation optimizes nitrate adsorption, enhances active hydrogen availability, and promotes the hydroxylamine-mediated ENRA pathway, leading to improved catalytic performance.

4 Conclusions

In summary, we have developed a P_2W_{18} -modified Cu_2O -Cu catalyst via a chemical reduction strategy for efficient electrocatalytic nitrate reduction to ammonia. The optimized catalyst delivers a high Faradaic efficiency of 97.4% and an ammonia yield rate of $36.5 \text{ mg h}^{-1} \text{ mg}_{\text{cat}}^{-1}$ at -1.0 V vs. RHE, outperforming the control samples. Mechanistic analyses reveal that P_2W_{18} modification enhances interfacial charge transfer and promotes $^*H$ generation and utilization, thereby facilitating efficient $^*H$ -mediated nitrate to ammonia conversion while suppressing competing hydrogen evolution. DFT calculations further demonstrate that P_2W_{18} incorporation optimizes nitrate intermediate adsorption and reduces the energy barrier of key proton-coupled electron transfer steps. This work provides a simple strategy for regulating interfacial hydrogen chemistry to improve selective nitrate reduction toward ammonia.

Data availability

The data underlying this study are available in the published article.

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Declaration of competing interest

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

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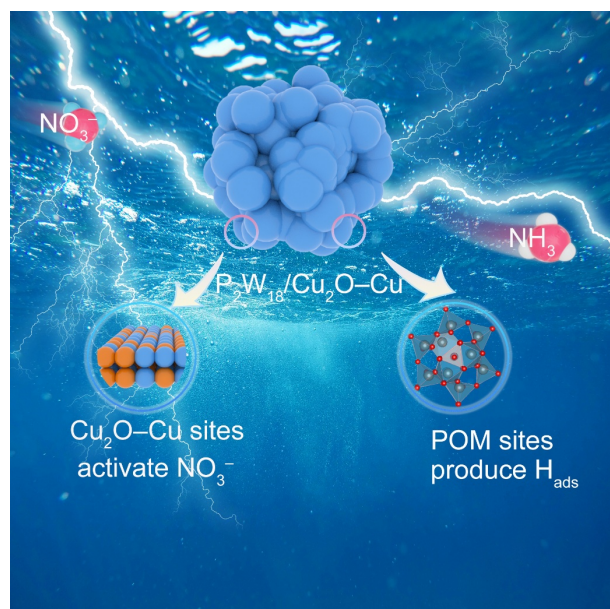
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A P_2W_{18} -driven interfacial engineering strategy is developed to regulate charge redistribution and interfacial $*H$ behavior, effectively suppressing the competing hydrogen evolution reaction while enhancing nitrate reduction activity. The synergistic interaction between P_2W_{18} and Cu-based active sites simultaneously promotes interfacial electron transfer and optimizes $*H$ generation and utilization, leading to markedly improved selectivity and efficiency toward ammonia synthesis.