

Cite this: *J. Mater. Chem. A*, 2024, 12, 20077

## Electrochemical reduction of nitrate to ammonia on ultra-stable amorphous Co–P electrocatalyst†

Jin-Long Fan,<sup>a</sup> Sheng-Bo Liu,<sup>c</sup> Ming-Liang Chen,<sup>d</sup> Zhangxiong Wu,<sup>a</sup> Sheng-Peng Sun<sup>\*a</sup> and Yao-Yin Lou<sup>†ab</sup>

Electrocatalytic reduction of nitrate ( $\text{NO}_3^-$ ) to ammonia ( $\text{NH}_3$ ) is garnering increasing interest due to its potential to reduce  $\text{CO}_2$  emissions as a substitute for the Haber-Bosch process, while also mitigating  $\text{NO}_3^-$  pollution. However, it remains a challenge to achieve a current density exceeding  $300 \text{ mA cm}^{-2}$  while maintaining the stability of catalysts. Additionally, the anodic oxygen evolution reaction, characterized by slow kinetics and high energy barriers, severely impedes the widespread adoption of  $\text{NH}_3$  formation from  $\text{NO}_3^-$  reduction. Therefore, in this study, we introduce amorphous phosphorus-doped cobalt catalysts (Co–P@NF) prepared via a facile electrodeposition process for efficient  $\text{NO}_3^-$  reduction and hydrazine oxidation. The incorporation of phosphorus in Co–P@NF facilitates electron migration from phosphorus to cobalt, enhancing  $^*\text{H}$  provision for efficient hydrogenation of the intermediate  $^*\text{NO}_2^-$ . This results in a current density of  $2 \text{ A cm}^{-2}$  at  $-0.3 \text{ V}$ , with a faradaic efficiency for  $\text{NH}_3$  of 91% in an electrolyte containing  $1 \text{ M NO}_3^-$ . Moreover, the Co–P@NF catalyst exhibits remarkable long-term stability, maintaining an  $\text{NH}_3$  faradaic efficiency exceeding 90% and a current density of  $799 \text{ mA cm}^{-2}$  after 82 hours of electrolysis. Furthermore, Co–P@NF displays high catalytic activity in promoting the rate-determining step of hydrazine oxidation, from  $^*\text{N}_2\text{H}_2$  to  $^*\text{N}_2\text{H}$ . The incorporation of the HzOR (hydrazine oxidation reaction)-assisted  $\text{NO}_3^-$ -RR (nitrate reduction reaction) unit significantly reduces the cell voltage to  $0.34 \text{ V}$  at  $300 \text{ mA cm}^{-2}$ .

Received 4th April 2024  
Accepted 13th June 2024

DOI: 10.1039/d4ta02299h

rsc.li/materials-a

<sup>a</sup>School of Chemical and Environmental Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China. E-mail: shepsun@suda.edu.cn; yyilou@iue.ac.cn

<sup>b</sup>CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, P. R. China

<sup>c</sup>Jiangsu Key Laboratory of Environmental Science and Engineering, School of Environmental Science and Engineering, Suzhou University of Science and Technology, Suzhou 215009, China

<sup>d</sup>Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, Delft, 2629HZ, the Netherlands

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ta02299h>



Yao-Yin Lou

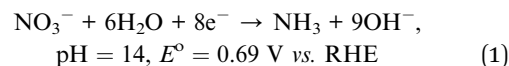
Yao-Yin Lou earned his PhD degree in 2019 from Ecole Nationale Supérieure de Chimie de Rennes, France, where he received joint training from Université de Rennes 1. From 2020 to 2022, he served as an associate researcher at Xiamen University and subsequently worked as an associate professor at Soochow University. Presently, he is a professor at the Institute of Urban Environment, Chinese Academy of Sciences. His research focuses on the development of novel environmental electrocatalysts and electro-reduction methods for the elimination of environmental contaminations. Dr Lou has authored over 30 papers in renowned international journals such as *Nature Communications*, *ACS Catalysis*, *Environmental Science & Technology*, *Water Research*, and *Chemical Engineering Journal*.

# 1. Introduction

Ammonia (NH<sub>3</sub>) is a vital chemical utilized in various industrial applications, such as chemical production, fuel synthesis, and as a fertilizer. Approximately 50% of global food production depends on NH<sub>3</sub> fertilizers.<sup>1</sup> The industrial-scale production of NH<sub>3</sub> predominantly relies on the Haber-Bosch process, which operates at high temperatures (400–600 °C) and high pressures (200–350 atm).<sup>2</sup> This production process is responsible for approximately 1.2% of annual global CO<sub>2</sub> emissions, surpassing emissions from other industrial chemical processes.<sup>3</sup> To address decarbonization challenges in the ammonia sector, an alternative approach known as the dinitrogen reduction reaction has been developed [4]. However, the dinitrogen reduction reaction exhibits a significantly low reaction rate (<10 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>),<sup>2</sup> which is two to three orders of magnitude lower than that of the Haber-Bosch process. In marked contrast, nitrate anions (NO<sub>3</sub><sup>-</sup>) require only 204 kJ mol<sup>-1</sup> of energy to break the N=O bond, a significantly lower energy requirement compared to the N≡N bond in dinitrogen gas (941 kJ mol<sup>-1</sup>). Additionally, NO<sub>3</sub><sup>-</sup> anions exhibit excellent solubility in aqueous solutions.<sup>4</sup> Consequently, the electrochemical reduction reaction of NO<sub>3</sub><sup>-</sup> (NO<sub>3</sub><sup>-</sup>RR) for NH<sub>3</sub> production has garnered increasing attention.

NO<sub>3</sub><sup>-</sup> pollution is a pressing environmental issue, resulting from agricultural runoff, wastewater discharge, and industrial processes. It poses risks to human health and ecosystems, making the development of effective NO<sub>3</sub><sup>-</sup> removal strategies critical. The electroreduction of NO<sub>3</sub><sup>-</sup> aims to produce ammonia, serving the dual purpose of recycling waste materials and mitigating the adverse environmental and ecological impacts of excessive NO<sub>3</sub><sup>-</sup> discharge.<sup>5</sup> Thanks to these advantages, various metal-based electrocatalysts, including Cu, Ru, Ag, Fe, Pd, and Co, have been developed to facilitate the reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>.<sup>2,6,7</sup> However, the reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> is a complex eight-electron reaction (eqn (1)), inevitably resulting in the formation of undesired byproducts such as nitrogen oxyanions and dinitrogen.<sup>8,9</sup> Due to significant progress in electrocatalyst development, achieving high faradaic efficiencies towards NH<sub>3</sub> (FE<sub>NH<sub>3</sub></sub> > 90%) is feasible at pseudo-ampere-level current densities. Nevertheless, the long-term stability of catalysts operating at currents exceeding 300 mA cm<sup>-2</sup> with FE<sub>NH<sub>3</sub></sub> > 90% remains challenging, falling short of the standards set by the U.S. Department of Energy.<sup>10</sup> Meanwhile, the anodic oxygen evolution reaction (OER, 2OH<sup>-</sup> → H<sub>2</sub>O + 1/2 O<sub>2</sub> + 2e<sup>-</sup>, 1.23 V vs. RHE), suffers from slow reaction kinetics and high energy barriers, necessitating an applied potential exceeding 1.6 V.<sup>11</sup> The high voltage requires substantial energy expenditure thereby significantly restricting the widespread application of NH<sub>3</sub> formation from NO<sub>3</sub><sup>-</sup> reduction. Substituting sluggish reactions with thermodynamically favorable ones, such as hydrazine oxidation reaction (HzOR, N<sub>2</sub>H<sub>4</sub> + 4OH<sup>-</sup> → N<sub>2</sub> + 4H<sub>2</sub>O + 4e<sup>-</sup>, -0.33 V vs. RHE), to assist NO<sub>3</sub><sup>-</sup>RR could greatly lower the electricity consumption for NH<sub>3</sub> formation. Moreover, the employment of HzOR-assisted NO<sub>3</sub><sup>-</sup>RR offers environmental benefits, converting toxic, carcinogenic N<sub>2</sub>H<sub>4</sub> in wastewater into dinitrogen and water.

Developing bifunctional electrocatalysts toward anodic HzOR and cathodic NO<sub>3</sub><sup>-</sup>RR with high activity and durability is pivotal to promote the practical applications.



NO<sub>3</sub><sup>-</sup>RR is a typical hydrodeoxygenation reaction. Electrocatalysts, like the first-row transition metal phosphides, with good performance in hydrogen evolution and hydrogenation reactions have been reported to have good NO<sub>3</sub><sup>-</sup>RR catalytic activities.<sup>2,6</sup> Javier Vela *et al.*<sup>12</sup> found that over 96% selectivity of NH<sub>3</sub> from NO<sub>3</sub><sup>-</sup> reduction was achieved on Ni<sub>2</sub>P, which was previously reported as a good electrocatalyst for hydrogen evolution reaction (HER).<sup>13</sup> Yang *et al.*,<sup>14</sup> found that the Co nanocrystals that could generate plenty of \*H had an exceptional performance of electrochemical NO<sub>3</sub><sup>-</sup>RR to NH<sub>3</sub>. Li *et al.*<sup>15</sup> also proved that the generated \*H with moderate adsorption energy on the catalyst can behave as important reactive species for the hydrogenation of reaction intermediates to NH<sub>3</sub> and suppress the competing HER. Notedly, the good modulation of the adsorption energy of \*H and \*NO<sub>3</sub> on the catalyst surface is critical for the improvement of the catalytic activity and product selectivity.<sup>16</sup> Meanwhile, a synergistic benefit was also proposed by Simpson and Johnson for the CuNi alloys: the Ni sites acted as the active sites for the adsorption of \*H, and the Cu sites facilitated the adsorption of NO<sub>3</sub><sup>-</sup> intermediates on these binary alloy electrodes.<sup>17</sup>

On the other hand, amorphous materials with long-range disordered structures have exhibited superior electrocatalytic performance and durability compared to their crystalline counterparts.<sup>18,19</sup> The coordination of surface atoms on amorphous materials is highly unsaturated. Also, amorphous alloy has a high degree of structure flexibility, both of which benefit catalysis. Due to the advanced properties, the amorphous-structure catalysts were widely used in oxygen reduction,<sup>20</sup> carbon dioxide reduction,<sup>21</sup> and hydrogen evolution reaction.<sup>22</sup> However, to our best knowledge, few literature reports exist on the amorphous catalysts for the NO<sub>3</sub><sup>-</sup>RR process. Inspired by the exceptional performance of the Co-based catalyst for HER and hydrodeoxygenation reaction,<sup>23</sup> the amorphous Co-P was prepared *via* a facile one-step electrodeposition procedure for HzOR-assisted NO<sub>3</sub><sup>-</sup>RR. The as-prepared amorphous Co-P exhibited superior catalytic performances, which is one of the most advanced NO<sub>3</sub><sup>-</sup>RR catalysts so far, as (1) a high partial current density for NH<sub>3</sub> formation (*j*<sub>NH<sub>3</sub></sub>) was observed at 2 A cm<sup>-2</sup>, along with a faradaic efficiency (FE<sub>NH<sub>3</sub></sub>) of 91% at -0.3 V *versus* RHE. The corresponding yield of NH<sub>3</sub> production was 2.9 mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, which is almost 11-fold higher than that achieved by the Haber-Bosch process (200 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>); (2) a good stability for NH<sub>3</sub> formation with FE<sub>NH<sub>3</sub></sub> over 90% at current density around 800 mA cm<sup>-2</sup> for more than 82 h electrolysis; (3) the cell voltage of HzOR-assisted NO<sub>3</sub><sup>-</sup>RR at 300 mA cm<sup>-2</sup> over Co-P@NF||Co-P@NF was only 0.34 V. Electrochemical *in situ* shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS) was conducted to clarify the pathways and mechanisms of NO<sub>3</sub><sup>-</sup>RR.

## 2. Materials and methods

### 2.1. Materials

Nickel foam (NF) used as electrode substrate was supplied from Suzhou JiaShide Foam Metal Co., Ltd. Trisodium citrate dihydrate ( $C_6H_5Na_3O_7 \cdot 2H_2O$ ) and sodium hypophosphite ( $NaH_2PO_2 \cdot H_2O$ ) were obtained from Meryer Chemical Technology Co., Ltd.  $CoCl_2 \cdot 6H_2O$ , KOH and  $(NH_4)_2SO_4$  were purchased from Sinopharm Chemical Reagent Co., Ltd.  $NaNO_3$  and  $NaNO_2$  were bought from Aladdin Co., Ltd. All reagents were analytical grade without any further purification and all solution were prepared by Milli-Q water (MQ).

### 2.2. Synthesis of Co@Ni foam and Co-P@Ni foam

Phosphorus doped cobalt on the Ni foam substrate (Co-P@NF) was prepared by a simple constant-potential electrodeposition method in a three-electrode system, where Ni foam, Pt foil, and saturated calomel electrode (SCE) were applied as the working electrode, counter electrode and reference electrode, respectively. Before the electrodeposition process, Ni foam ( $0.5 \times 1.0 \text{ cm}^2$ ) was ultrasonically cleaned in acetone solution, ethanol solution and deionized (DI) water several times. An aqueous solution (55 mL) containing 0.2 M  $C_6H_5Na_3O_7$ , 0.5 M  $(NH_4)_2SO_4$ , 0.6 M  $NaH_2PO_2$  and 0.1 M  $CoCl_2 \cdot 6H_2O$  were used as the electrolyte. Co-P was deposited on the Ni foam at  $-2.0 \text{ V}$  vs. SCE in the above electrolyte saturated with  $N_2$  at room temperature for 45 min. The preparation of Co@NF followed the same process but without the addition of  $NaH_2PO_2$ .

### 2.3. Assembly of Zn-nitrate flow battery

The Zn-nitrate flow battery was assembled in a membrane electrode assembly flow reactor wherein Co-P@NF ( $2 \text{ cm} \times 2 \text{ cm}$ ) was used as both the anode and cathode, respectively. The anodic and cathodic chambers were separated by a Nafion N115 proton exchange membrane. Bipolar plates were high-purity titanium plates with a single serpentine flow field and guard plates were Perspex sheets. The catholyte was 1 M NaOH/0.1 M  $KNO_3$  while the anolyte was 6 M NaOH, and their flow rates were controlled to be  $150 \text{ mL min}^{-1}$  by a peristaltic pump. Chronopotentiometry was recorded to plot the polarization curves. The power density ( $P$ ) was calculated by the following equation:  $P = j \times E$ , where  $j$  is the current density and  $E$  is the cell voltage.

### 2.4. Electrochemical measurements

The electrocatalytic performances of Co@NF and Co-P@NF were investigated in a three-electrode system connected to a DH7000C electrochemical workstation (Donghua, Jiangsu) in an H-type cell with a Nafion 115 membrane as a separator. The Co@NF and Co-P@NF with the same size ( $0.5 \times 0.5 \text{ cm}^2$ ) were used as working electrodes, while a platinum foil and a saturated calomel electrode were used as the counter electrode and reference electrode. 1 M KOH aqueous solution (30 mL) containing different  $NaNO_3$  concentrations (*i.e.*, 10, 20, 50, 100 and 1000 mM) and 1.0 M  $N_2H_4$  were used as the cathodic and anodic

electrolyte, respectively. The electrochemical linear voltammetry (LSV) analysis was carried out in a single undivided electrochemical cell. The Tafel slope was obtained by fitting the linear part of the Tafel plots according to the Tafel equation ( $\eta = a + b \times \log(j)$ ). The electrochemical impedance measurement was performed in a frequency range of 0.01 Hz to 1000 Hz with an amplitude of 5 mV. The double layer capacitance ( $C_{dl}$ ) of the obtained samples was calculated from CV curves at different scan rates of 10–100  $\text{mV s}^{-1}$  in the non-Faraday area. The current density was normalized to the geometric electrode area ( $0.25 \text{ cm}^2$ ) unless otherwise specified. All recorded electrode potentials vs. Hg/HgO were transformed to potentials against the reversible hydrogen electrode (RHE) according to the calibration equation expressed as  $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.0591 \times \text{pH}$ .

## 3. Results and discussions

### 3.1. Catalyst composition and microstructure

The Co-P@NF exhibits a much rougher surface than Co@NF (Fig. 1a and b), as indicated by the irregular nanograins formed on the surface of Co-P@NF (Fig. 1c), compared to the flat surface of Co@NF (Fig. 1d). As shown in the high-resolution transmission electron microscopy (HRTEM) images, the nanograins on Co-P@NF were amorphous (Fig. 1e), while the lattice fringe of Co@NF was observed (Fig. 1f). There was also no diffraction pattern for Co-P@NF, demonstrating the amorphous feature of this catalyst (Fig. S1†). The lattice distance of 1.91 Å was well ascribed to the (101) plane of metallic Co. The element mapping analysis (Fig. 1g) indicated that Co and P were evenly dispersed in the nanograins of Co-P@NF. The different structure morphologies of Co-P@NF and Co@NF were also confirmed by the XRD pattern (Fig. 1h). There was no crystalline peak observed in the XRD pattern of Co-P@NF, except the two peaks belonging to the Ni substrate. In comparison, two small peaks at  $41.6^\circ$  and  $44.5^\circ$  were observed in the XRD pattern of Co@NF, which were assigned to Co(100) and Co(101). The elemental compositions and electronic structure of Co-P@NF were determined using XPS (Fig. 1i and j). For Co-P@NF, P 2p showed a doublet with a binding energy of 128.3 (P 2p<sub>3/2</sub>) and 130.2 eV (P 2p<sub>1/2</sub>), assigned to elemental P (P<sup>0</sup>) and oxidized P (P<sup>5+</sup>), while Co 2p depicted two peaks at 781.8 eV (Co 2p<sub>3/2</sub>) and 797.6 eV (Co 2p<sub>1/2</sub>) assigned to oxidation of Co resulting from the exposition of the catalyst to air. There was no P 2p peaks found in the Co@NF spectra. It was well-fitted with the results from the HRTEM-EDS analysis. There were about 13 at% P in Co-P nanograins (Fig. S2 and Table S1†). Compared to Co-P@NF, the Co 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks of Co@NF exhibited a small shift towards higher binding energies (Fig. 1i). This shift indicated that the introduction of P promotes electron migration from the P to the Co, which makes Co electron-rich and becomes more favorable for the  $NO_3^-$ RR processes. The electron-rich property of Co-P@NF was also demonstrated by EIS analysis (Fig. S3†). Thanks to the electron transfer from P to Co, the impedance of Co-P@NF (0.32 Ω) was lower than that of the Co@NF (0.52 Ω).

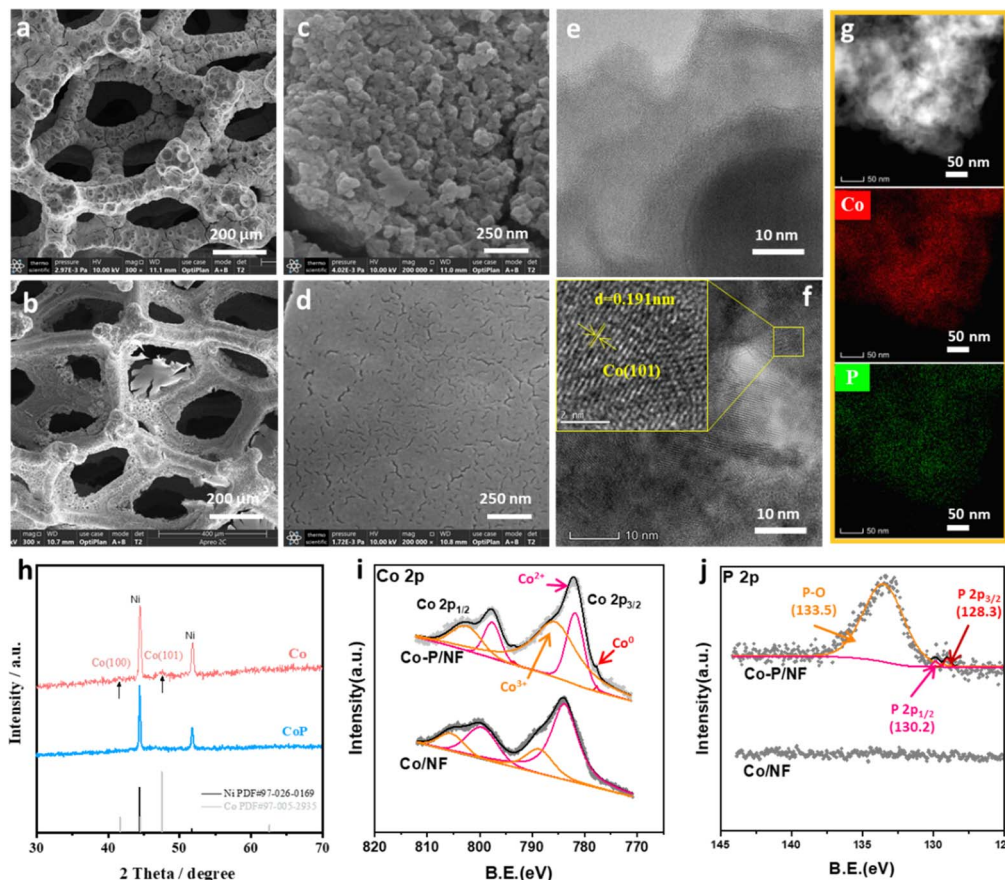
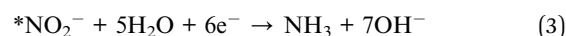


Fig. 1 SEM images of Co-P@NF (a and c) and Co@NF (b and d). HR-TEM images of Co-P@NF (e) and Co@NF (f). TEM-EDS mapping of Co-P@NF (g). (h) XRD pattern of Co-P@NF and Co@NF. XPS spectra: Co 2p (i) and P 2p (j) of Co-P@NF and Co@NF.

### 3.2. Electrocatalytic performances of $\text{NO}_3^-$ RR

The linear sweeping voltammetry was firstly applied to investigate the catalytic activity over Co-P@NF and Co@NF during  $\text{NO}_3^-$ RR (Fig. 2a). In the absence of  $\text{NO}_3^-$ , Co-P@NF has a smaller onset potential ( $\eta_{\text{HER}}$ ) and a much higher current density ( $j_{\text{HER}}$ ) of hydrogen evolution reaction than that of Co@NF ( $\eta_{\text{HER}}$ :  $-0.05$  V vs.  $-0.15$  V;  $j_{\text{HER}}$  at  $-0.1$  V:  $69$  mA  $\text{cm}^{-2}$  vs.  $12$  mA  $\text{cm}^{-2}$ ), indicating the superior catalytic activity of HER on Co-P@NF. The Tafel slope of HER over Co-P@NF ( $136$  mV  $\text{dec}^{-1}$ ) was also smaller than that of Co@NF ( $164$  mV  $\text{dec}^{-1}$ ) (Fig. 2b), demonstrating that Co-P@NF had a faster kinetic for HER and provided more \*H for  $\text{NO}_3^-$  reduction, according to Volmer step ( $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{*H} + \text{OH}^-$ ). In the presence of  $\text{NO}_3^-$ , increased current densities ( $j$ ) were observed on both Co-based electrodes, since Co was a good candidate for  $\text{NO}_3^-$ RR. The larger  $j$  on Co-P@NF indicated the enhanced catalytic activity of  $\text{NO}_3^-$  reduction after the incorporation of P into Co. Two current reduction peaks were appearing after the addition of  $\text{NO}_3^-$ ,  $0.09$  V and  $-0.03$  V on the curve of Co-P@NF, and  $0.01$  V and  $-0.15$  V on the curve of Co. According to previous studies,<sup>24,25</sup> the first peak was assigned to  $\text{NO}_3^-$  reduction into  $\text{*NO}_2^-$  following a 2-electrons transfer process (eqn (2)), while the second peak was allocated to the  $\text{*NO}_2^-$  reduction into  $\text{NH}_3$  following a 6-electrons transfer process (eqn (3)).



Co-P@NF displayed positive shifts of  $80$  mV for the  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  peak and  $120$  mV for the  $\text{NO}_2^- \rightarrow \text{NH}_3$  peak, compared to Co@NF, suggesting a drop of the energy barrier of  $\text{*NO}_3^-$  reduction to  $\text{NH}_3$  on Co-P@NF. According to the Tafel slope in the  $\text{NO}_3^-$ -containing electrolyte, Co-P@NF ( $32$  mV  $\text{dec}^{-1}$ ) had a higher kinetic activity for  $\text{NO}_3^-$ RR than that of Co ( $160$  mV  $\text{dec}^{-1}$ ). EIS results also revealed the incorporation of P into Co would decrease the electron transfer resistance that was beneficial to facilitate  $\text{NO}_3^-$ RR process. The constant-potential electrolysis was performed and the partial current density of  $\text{NH}_3$  formation ( $j_{\text{NH}_3}$ ) at different applied potential was obtained (Fig. 2c). The concentration of  $\text{NH}_3$  and  $\text{NO}_2^-$  formed was detected by colorimetric methods using a UV-vis absorbance spectrophotometer (DR3900) and ion chromatography (ICS-600), respectively (Text S1, Text S2, Fig. S4 and S5<sup>†</sup>). The substrate of NF was relatively inactive for  $\text{NO}_3^-$ RR (Fig. S6<sup>†</sup>), since the  $j_{\text{NH}_3}$  on Ni foam was only  $7$  mA  $\text{cm}^{-2}$ , compared with the electrodeposited Co-based catalysts ( $1296$  mA  $\text{cm}^{-2}$  on Co-P@NF and  $212$  mA  $\text{cm}^{-2}$  on Co@NF). Significantly higher  $j_{\text{NH}_3}$  was obtained with Co-P@NF, surpassing  $1$  A  $\text{cm}^{-2}$  at potential

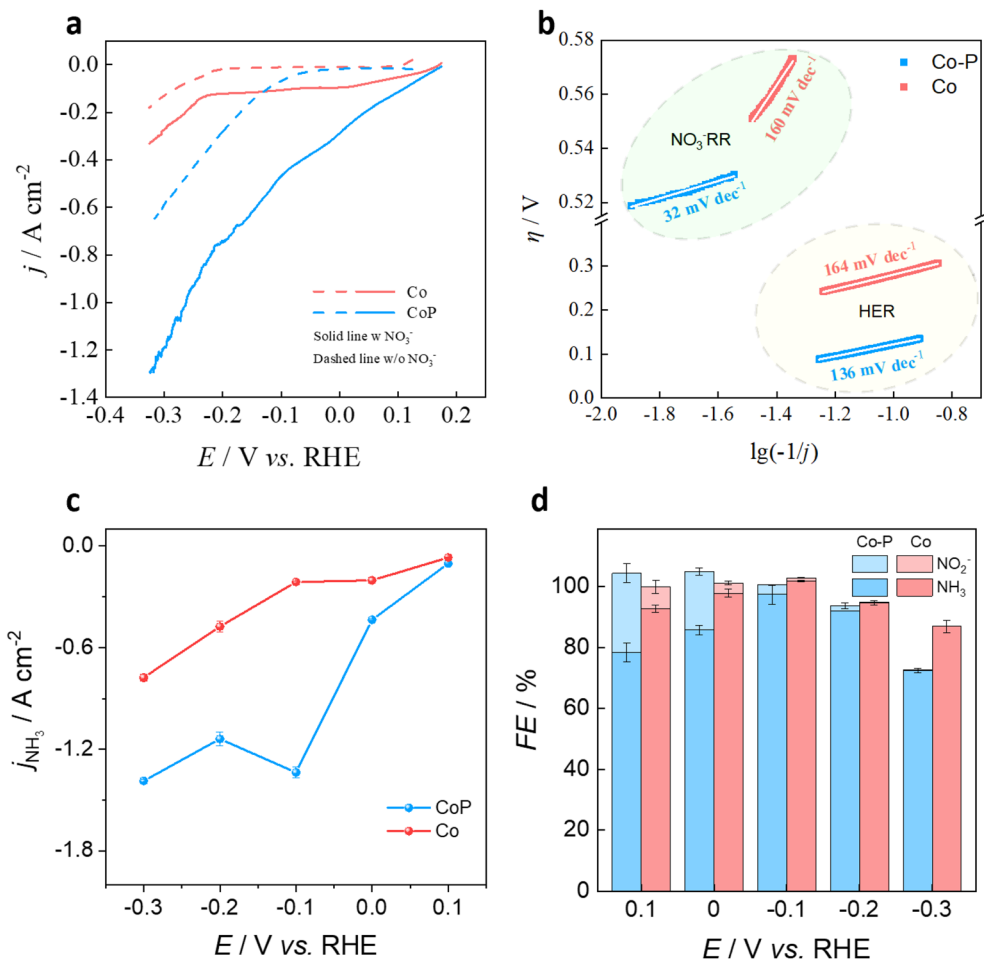


Fig. 2 (a) Linear sweeping voltammetry over Co@NF and Co-P@NF in the electrolyte of  $1 \text{ mol L}^{-1} \text{ KOH}$  with or without  $100 \text{ mmol L}^{-1} \text{ NO}_3^-$ . (b) Tafel slope of Co@NF and Co-P@NF in the presence of  $\text{NO}_3^-$ . (c) Partial current density of  $\text{NH}_3$  production over Co@NF and Co-P@NF. (d) FE of  $\text{NH}_3$  and  $\text{NO}_2^-$  over Co-P@NF and Co@NF in the potential range of  $0.1$ – $-0.3 \text{ V}$ .

below  $-0.1 \text{ V vs. RHE}$ . At this potential, the highest faradaic efficiency for  $\text{NH}_3$  formation ( $\text{FE}_{\text{NH}_3}$ , 97.5%) was achieved with Co-P@NF (Fig. 2d). Consequently, the Co-P@NF electrode shows superior performance with high  $\text{FE}_{\text{NH}_3}$  and  $j_{\text{NH}_3}$  for  $\text{NO}_3^-$  electroreduction to  $\text{NH}_3$  as compared to other reported electrodes, as exhibited in Table S2.† The low  $\text{FE}_{\text{NH}_3}$  over Co-P@NF at the potential of  $0.1 \text{ V}$  and  $0 \text{ V}$ , where the HER did not occur and the  $\theta_{\text{H}}$  coverage ( $\theta_{\text{H}}$ ) was too low to further hydrogenation of  $\text{NO}_2^-$  to  $\text{NH}_3$ . Until the potential negatively shifted to  $-0.1 \text{ V}$ , the  $\theta_{\text{H}}$  increased, based on eqn (4), and therefore the maximum  $\text{FE}_{\text{NH}_3}$  was obtained. As potential continued to decreasing, the  $\text{FE}_{\text{NO}_2^-}$  significantly declined but the slight decreased  $\text{FE}_{\text{NH}_3}$  was also observed due to the strong HER competition on the Co-P@NF (Fig. 2d). The competitive HER also led to a decrease in  $j_{\text{NH}_3}$  from  $1336 \text{ mA cm}^{-2}$  to  $1138 \text{ mA cm}^{-2}$ , when potential was negatively shifted from  $-0.1 \text{ V}$  to  $-0.2 \text{ V}$ . The electrochemically active surface area (ECSA) was also measured (Fig. S7a–c†), revealing that Co@NF and Co-P@NF had comparable ECSA. However, a higher ECSA-normalized current density for  $\text{NH}_3$  production ( $j_{\text{NH}_3}(\text{ECSA})$ ) was observed with Co-P@NF (Fig. S7d†), indicating that this catalyst had higher intrinsic activity for  $\text{NH}_3$

production. To clarify the possible N pollution caused by nitrogen reduction reaction, the electrolysis in the electrolyte free of  $\text{NO}_3^-$  ions was performed and little  $\text{NH}_3$  was produced (Fig. S8†).  $j_{\text{NH}_3}$  in the solution with  $\text{NO}_3^-$  ions was over 133-fold higher than that in the electrolyte free of  $\text{NO}_3^-$ , where the  $\text{FE}_{\text{NH}_3}$  was only about 1%. In addition, the typical two peaks of  $^{15}\text{NH}_4^+$  after the electrolysis of  $^{15}\text{NO}_3^-$  also suggested that the  $\text{NH}_3$  product indeed came from the electrocatalytic reduction of  $\text{NO}_3^-$  (Fig. S9†).

$$\eta = E - E_{\text{eq}} = \frac{RT}{F} \ln \frac{\theta_{\text{H}}}{\theta_{\text{H}}^0} \quad (4)$$

where  $\theta_{\text{H}}$  and  $\theta_{\text{H}}^0$  are the  $\theta_{\text{H}}$  coverage at  $E$  and  $E^0$ , respectively;  $F$  is the Faraday constant,  $96485 \text{ C mol}^{-1}$ ;  $R$  is the gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  $T$  is the kelvin temperature,  $\text{K}$ .

It should be noted that the sum FE of  $\text{NO}_2^-$  and  $\text{NH}_3$  formation was over 100% (Fig. 2d). The  $\text{NO}_3^-$ RR over Co-P@NF and Co@NF were then performed at open circle potential (OCP) and the  $\text{NO}_2^-$  and  $\text{NH}_3$  were both detected in the electrolyte (Fig. 3a and S10†), indicating that there was a spontaneous reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  and  $\text{NH}_3$  on Co-P@NF and Co@NF.

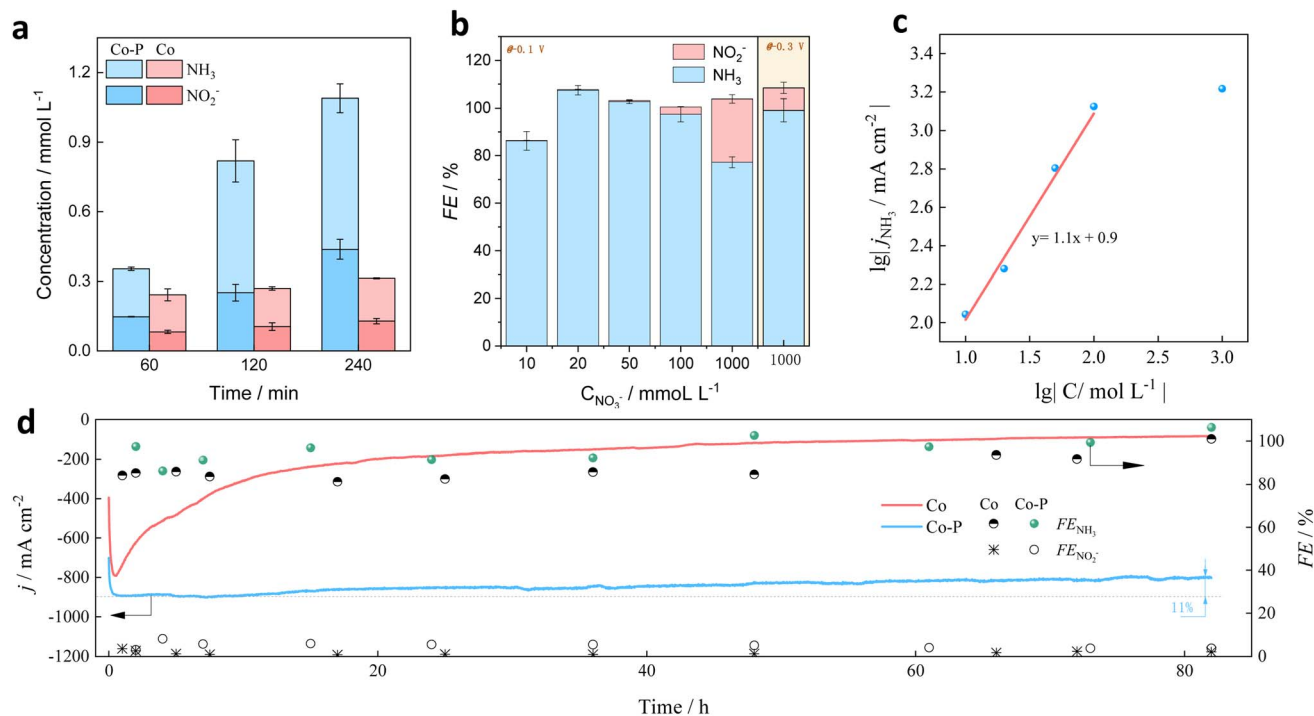
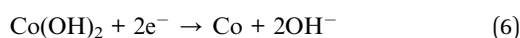


Fig. 3 (a) Concentration of  $\text{NO}_2^-$  and  $\text{NH}_3$  over Co-P@NF and Co@NF at open circle potential. (b) FE of  $\text{NO}_2^-$  and  $\text{NH}_3$  and (c)  $\lg(-j)$  vs.  $\lg C$  plots for Co-P@NF were calculated at  $-0.1 \text{ V}$  vs. RHE. (d) Long-term stability of Co-P@NF in the electrolyte of  $1 \text{ mol L}^{-1}$  with  $100 \text{ mmol L}^{-1}$   $\text{NO}_3^-$  at  $-0.1 \text{ V}$ .

This spontaneous reduction process may explain the over-100% FE. A similar phenomenon was reported by Han and his colleagues:<sup>26</sup> oxidation of Co to  $\text{Co}(\text{OH})_2$  by  $\text{NO}_3^-$  (eqn (5)) and the electroreduction of  $\text{Co}(\text{OH})_2$  to Co (eqn (6)) proceed simultaneously during the  $\text{NO}_3^-$  RR (eqn (2) and (3)), and a dynamic Co valence cycle was achieved. The OCP over Co-P@NF was obviously lower than that of Co@NF (Fig. S11†), indicating that Co-P@NF had a superior ability of the spontaneous reduction of  $\text{NO}_3^-$ , thanks to the electron-rich of Co atom in Co-P@NF, giving that the  $\text{NO}_2^-$  and  $\text{NH}_3$  formation on Co-P@NF was approximate 3-times higher than that of Co@NF at OCP.



The concentration of  $\text{NO}_3^-$  in real wastewater can vary from  $1 \text{ mmol L}^{-1}$  to  $2000 \text{ mmol L}^{-1}$ .<sup>27</sup> Therefore,  $\text{NO}_3^-$  RR on Co-P@NF was performed in a wide  $\text{NO}_3^-$  concentration range. The  $\text{FE}_{\text{NH}_3}$  was maintained above 95% in the range of  $20 \text{ mmol L}^{-1}$  to  $100 \text{ mmol L}^{-1}$  at  $-0.1 \text{ V}$  (Fig. 3b). The low  $\text{FE}_{\text{NH}_3}$  in the solution of  $10 \text{ mmol L}^{-1}$  and  $1000 \text{ mmol L}^{-1}$  was due to the competitive adsorption between  $*\text{H}$  and  $*\text{NO}_3^-$ . For example, in the case of  $10 \text{ mmol L}^{-1}$ ,  $\text{NO}_3^-$  concentration was so low that catalytic sites were occupied by  $*\text{H}$  which would be formed into  $\text{H}_2$  via Volmer-Tafel or Volmer-Heyrovsky mechanism and decrease the  $\text{FE}_{\text{NH}_3}$ . When the  $\text{NO}_3^-$  concentration increased, the HER would be gradually hindered so that the  $\text{FE}_{\text{NO}_2^-}$  increased.  $\text{FE}_{\text{NO}_2^-}$  was about 27% in the case of  $1000 \text{ mmol L}^{-1}$

$\text{NO}_3^-$ , where  $*\text{H}$  was insufficient for  $*\text{NO}_2^-$  reduction (eqn (3)), leading to the accumulation of  $*\text{NO}_2^-$  on the catalytic surface. A quasi-first-order reaction relationship between  $j$  and the  $\text{NO}_3^-$  concentration was obtained (Fig. 3c), revealing that the rate-determining step of  $\text{NO}_3^-$  RR ( $\text{RDS}_{\text{NO}_3^- \text{RR}}$ ) was  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  step. Therefore, supplement of sufficient  $*\text{H}$  was significant for efficient reduction of  $\text{NO}_2^-$ . When a potential of  $-0.3 \text{ V}$  was applied in the solution of  $1000 \text{ mmol L}^{-1}$ , an increase in  $\text{FE}_{\text{NH}_3}$  and a decrease in  $\text{FE}_{\text{NO}_2^-}$  were observed, respectively. This is attributed to a higher  $\theta_{\text{H}}$  (according to eqn (4)) and a stronger affinity of  $*\text{H}$  at more negative potentials,<sup>28</sup> which promotes further hydrogenation of  $\text{NO}_2^-$  to  $\text{NH}_3$ . Meanwhile,  $j_{\text{NH}_3}$  increased to  $2 \text{ A cm}^{-2}$  with the  $\text{FE}_{\text{NH}_3}$  as 91% (Fig. S12†). The corresponding  $\text{NH}_3$  yield rate was  $2.9 \text{ mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$  that was almost 11-fold higher than that of Haber-Bosch route ( $200 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ). Long-term stability tests at  $-0.1 \text{ V}$  vs. RHE assessed the durability of Co-P@NF against Co@NF (Fig. 3d). For Co-P@NF,  $\text{FE}_{\text{NH}_3}$  (>90%) remained stable after the 82 h electrolysis. The  $j_{\text{NH}_3}$  experienced a slight decrease from  $890 \text{ mA cm}^{-2}$  to  $799 \text{ mA cm}^{-2}$  (about 89% of the initial  $j_{\text{NH}_3}$ ), which still exceeded U.S. Department of Energy's standard requirement by more than two fold ( $300 \text{ mA cm}^{-2}$ ). For Co@NF, the  $j_{\text{NH}_3}$  quickly decayed from  $798 \text{ mA cm}^{-2}$  to  $198 \text{ mA cm}^{-2}$  after 20 h electrolysis and its  $\text{FE}_{\text{NH}_3}$  was also lower than that of Co-P@NF. To further check the stability of the Co-P@NF catalyst, the cyclic electrolysis was also conducted for  $\text{NO}_3^-$  reduction. The results demonstrated that the faradaic efficiency of  $\text{NH}_3$  formation remained consistently at 100% throughout the 11 electrolysis cycles. Moreover, the yield of  $\text{NH}_3$  formation

of the 11th was still two-times higher than that of Haber-Bosch route ( $200 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) (Fig. S13†). Above stability test results indicated the amorphous-structured Co@P indeed had a satisfactory durability during  $\text{NO}_3^-$ RR. According to the TEM analysis, the morphology of Co-P was well kept after the consecutive recycling tests (Fig. S14†). Furthermore, XRD (Fig. S15†) and XPS (Fig. S16†) analysis was also performed on the samples after the consecutive recycling tests, and the results demonstrated negligible changes in the chemical compositions and oxidation states. The excellent stability of the catalysts was possibly ascribed to amorphous feature of the Co-P catalysts.

Tert-butanol (TBA), used as a specific  $^*H$  radical quenching reagent, was added during the process to evaluate the role of active  $^*H$  (Fig. 4a). Upon the addition of TBA, the  $j$  decreased sharply from  $546 \text{ mA cm}^{-2}$  to  $373 \text{ mA cm}^{-2}$  on Co@NF and from  $886 \text{ mA cm}^{-2}$  to  $628 \text{ mA cm}^{-2}$  on Co-P@NF. Meanwhile, the  $FE_{\text{NH}_3}$  also decreased from 96% to 88% on Co@NF and from 106% to 100% on Co-P@NF. The quenching test results demonstrated that the  $^*H$  radicals truly improved the reaction rate and  $FE_{\text{NH}_3}$ . We further used dimethyl-1-pyrroline-*N*-oxide

(DMPO) as the radical trapping reagent to monitor the formation of  $^*H$  radicals with and without using  $\text{NO}_3^-$  (Text S3). As shown in Fig. 4b, the ESR spectra display typical 9 signals with intensity ratios of 1 : 1 : 2 : 1 : 2 : 1 : 2 : 1 : 1 without adding  $\text{NO}_3^-$  in the catholyte, which confirms the formation of DMPO-H. When  $\text{NO}_3^-$  was added, the typical 9 signals nearly disappeared, indicating that the produced  $^*H$  is consumed by the intermediates in the  $\text{NO}_3^-$ RR process. These results strongly prove the key role of the  $^*H$  radicals in  $\text{NO}_3^-$  reduction into  $\text{NH}_3$ . The electrochemical *in situ* Raman spectra of Co-P and Co catalysts depicted in Fig. 4c and d, were recorded across a potential window of  $-0.7$ – $-1.13 \text{ V}$  versus the RHE with increments of 50 mV. Three distinct peaks, corresponding to  $A_{1g}$ ,  $E_g$  and  $F_{2g}$  vibrations models of Co-O band, were visible on Co-P and Co catalysts at around  $686.9$ ,  $480.5$  and  $524.9 \text{ cm}^{-1}$ .<sup>29</sup> The formation of Co-O band was ascribed to the oxygen vacancies over the two catalysts. The coordination of surface atoms on amorphous materials is highly unsaturated.<sup>30</sup> According to the electron paramagnetic resonance (EPR) analysis (Fig. S17†), the Co-P@NF had a much higher density of

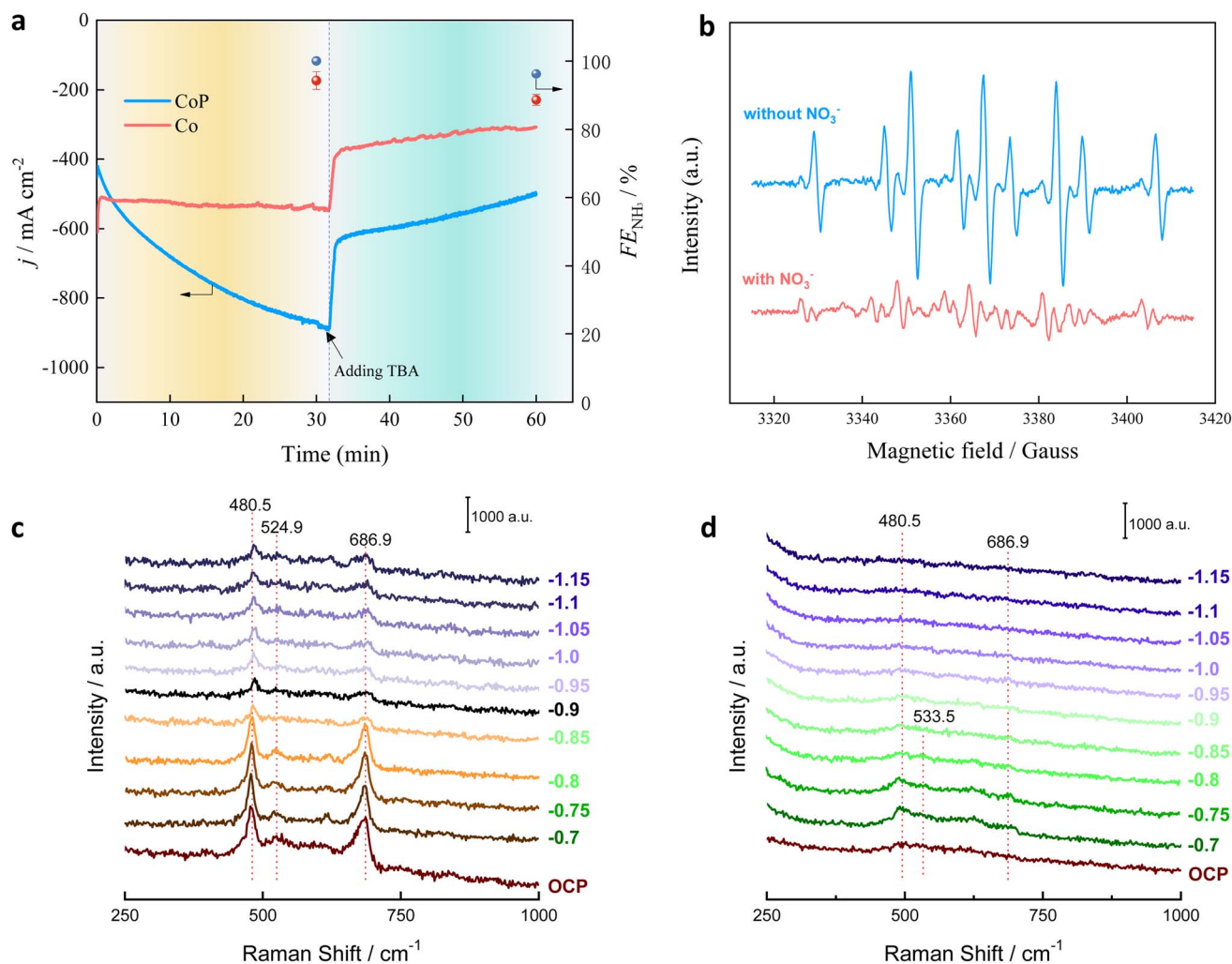


Fig. 4 (a)  $j$  and  $FE_{\text{NH}_3}$  over Co-P@NF and Co@NF at potential of  $-0.1 \text{ V}$  vs. RHE. (b) The DMPO-H\* obtained on Co-P@NF after 5 min of electrocatalysis at  $-0.1 \text{ V}$  vs. RHE in 1 M KOH solution with 0.1 M  $\text{NO}_3^-$  (bottom) or (b) without  $\text{NO}_3^-$  (top). *In situ* electrochemical-Raman on Co-P (c) and Co (d) in the potential of  $-0.7 \text{ V}$ – $-1.15 \text{ V}$  vs. Hg/HgO.

oxygen vacancies. The intensity of Co–O bands on Co–P was much higher than that Co. The Raman spectra were well fitting with the EPR results that the Co–P with amorphous structure had a higher density of oxygen vacancies. As the potential negatively shifted, the Co–O bands gradually decreased. For Co–P catalyst, the Co–O band could be preserved, revealing that the amorphous structure had more stable oxygen vacancies; while no signal could be observed on Co catalyst after the potential lower than  $-0.9$  V. The oxygen vacancies can be used as the adsorption site for the charge transfer, which is conducive to the adsorption/desorption of the reaction intermediates speeding up the  $\text{NO}_3^-$ RR.<sup>31</sup>

### 3.3. Electrocatalytic performances of HzOR

The HzOR electrochemical performance of Co–P@NF was then evaluated in  $1.0$  M KOH +  $1$  M  $\text{N}_2\text{H}_4$  electrolyte, compared to Co@NF and NF. Co–P@NF showed a higher HzOR catalytic activity with small overpotentials of  $-67$ ,  $-16$  and  $486$  mV to reach  $10$ ,  $100$  and  $1000$   $\text{mA cm}^{-2}$  (Fig. 5a), respectively, compared to Co@NF and NF. The smallest Tafel slope of  $24.2$   $\text{mV dec}^{-1}$  was obtained in Co–P@NF, indicating the favorable catalytic oxidation kinetics toward HzOR (Fig. 5b). This ultra-low Tafel slope also indicated that the rate-determining step over Co–P@NF was the dehydrogenation

from  $^*\text{N}_2\text{H}_2$  to  $^*\text{N}_2\text{H}$ . In addition, a comparison between the OER and HzOR performances over Co–P@NF was performed (Fig. 5c and d). Much lower potentials of  $16$  and  $207$  mV were needed in HzOR than those in  $\text{N}_2\text{H}_4$ -free electrolyte ( $1.66$  and  $1.95$  V) to reach the current densities of  $100$  and  $500$   $\text{mA cm}^{-2}$ , respectively, indicating the potential application to replace OER for HzOR-assisted  $\text{NO}_3^-$ RR. Therefore, thanks to the excellent  $\text{NO}_3^-$ RR and HzOR catalytic performances on Co–P@NF, an HzOR-assisted  $\text{NO}_3^-$ RR unit with two-electrode system was assembled by employing Co–P@NF as both anode and cathode. As shown in Fig. 5e, the HzOR-assisted  $\text{NO}_3^-$ RR unit exhibits significantly enhanced catalytic activity compared to the stand alone  $\text{NO}_3^-$ RR unit, only requiring voltages of  $93$ ,  $308$ , and  $516$  mV to achieve current densities of  $100$ ,  $300$ , and  $500$   $\text{mA cm}^{-2}$ , respectively. These values are  $1.45$ ,  $1.53$ , and  $1.67$  V lower than those required by the OER-assisted  $\text{NO}_3^-$ RR system. The cell voltage of Co–P@NF||Co–P@NF at  $300$   $\text{mA cm}^{-2}$  dramatically dropped from *ca.*  $2.0$  V to *ca.*  $0.34$  V after addition of  $\text{N}_2\text{H}_4$  in the electrolyte containing  $\text{NO}_3^-$  ions (Fig. 5f). For comparison, NF as electrodes for the HzOR-assisted  $\text{NO}_3^-$ RR unit was also assembled (Fig. S18†). For a current density of  $300$   $\text{mA cm}^{-2}$ , and the cell voltage of NF||NF ( $2.40$  V) are much higher than that of Co–P@NF||Co–P@NF ( $0.34$  V), indicating the greatly reduced electricity consumption over Co–P catalysts.

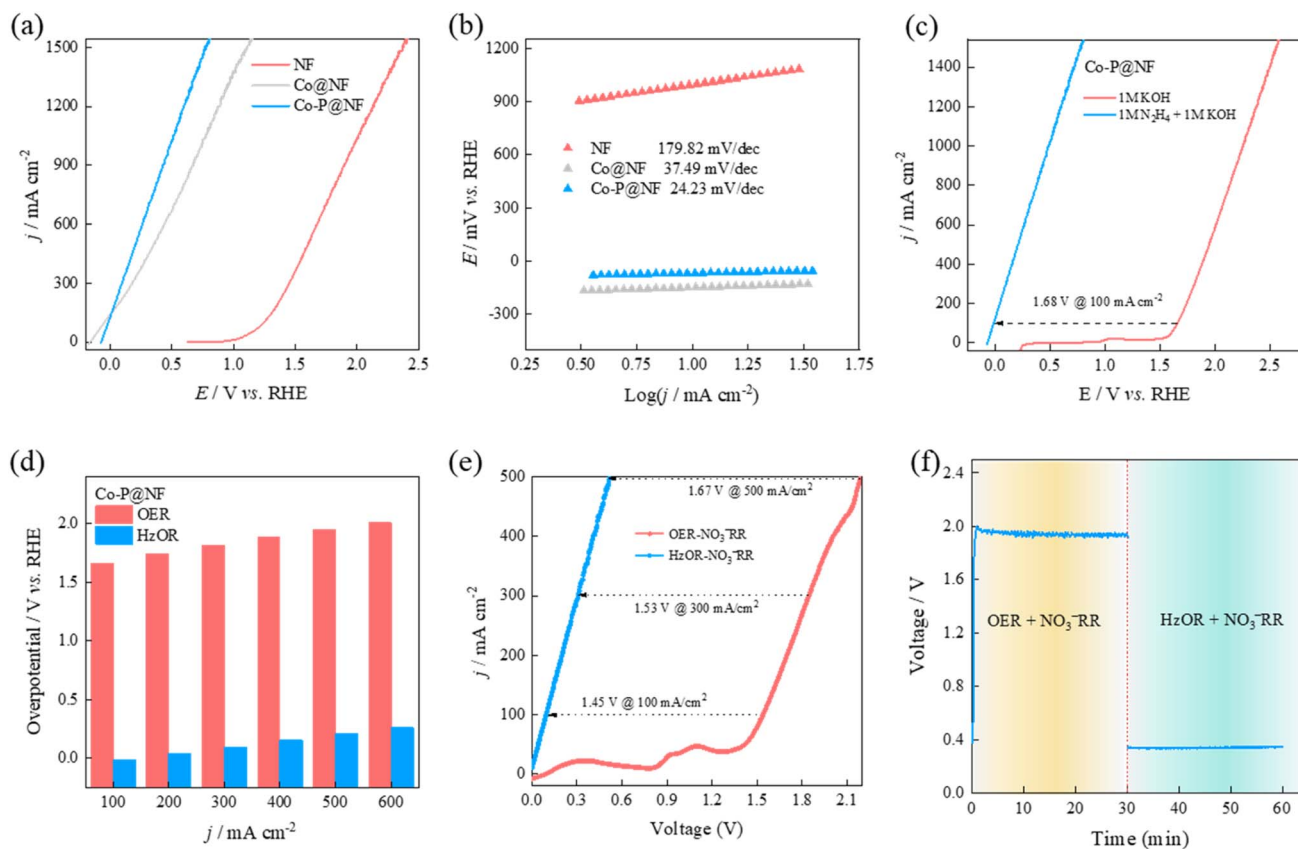


Fig. 5 HzOR performance in  $1.0$  M KOH +  $1.0$  M  $\text{N}_2\text{H}_4$  electrolyte. (a) Linear sweep voltammetry analysis on NF, Co@NF and Co–P@NF catalysts and the corresponding (b) Tafel slopes. (c) Compared LSV curves of Co–P@NF between OER ( $1.0$  M KOH) and HzOR ( $1.0$  M KOH and  $1.0$  M  $\text{N}_2\text{H}_4$ ), and (d) the corresponding histogram catalytic performance comparison. (e) Comparison LSV curves of Co–P@NF between OER- $\text{NO}_3^-$ RR and HzOR- $\text{NO}_3^-$ RR. (f) Cell voltage of Co–P@NF||Co–P@NF at  $300$   $\text{mA cm}^{-2}$  in OER- $\text{NO}_3^-$ RR and HzOR- $\text{NO}_3^-$ RR system.

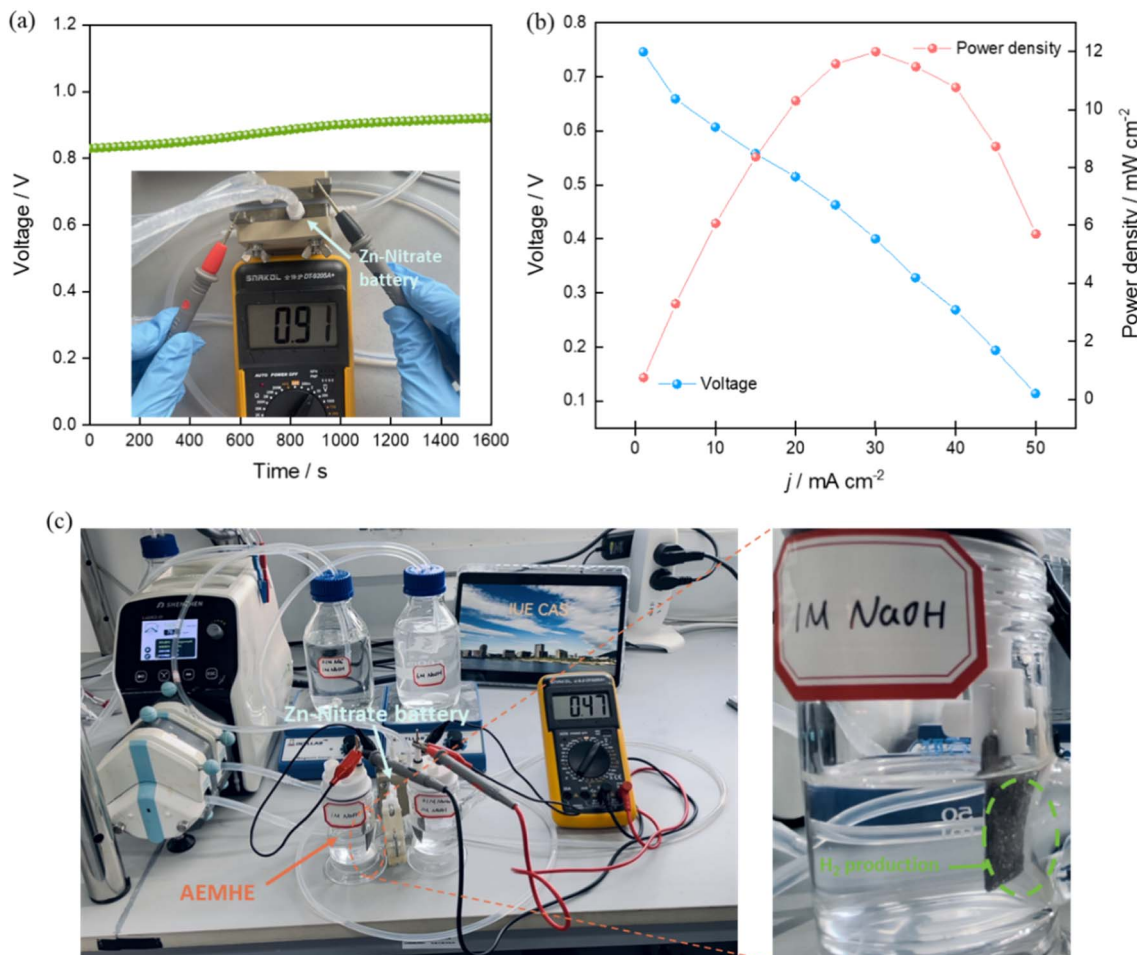


Fig. 6 Zn-nitrate flow battery application. (a) The open circuit voltage. The cathodic and anodic electrolytes used in Zn-nitrate flow battery were 0.1 M  $\text{NO}_3^- + 1 \text{ M NaOH}$  and 6 M NaOH, respectively. (b) Polarization and power density curves. (c) The digital photograph of the tandem Zn-nitrate flow battery and AEMHE devices for hydrogen production.

The Zn-nitrate flow battery was assembled with an open circuit voltage over 0.8 V (Fig. 6a). The polarization curves by steady-state chronopotentiometry were obtained. The Zn-nitrate flow battery is practically feasible with the discharging power density up to  $12 \text{ mW cm}^{-2}$  (Fig. 6b). To confirm the efficacy of the electricity supply of this battery, the low-voltage-driven anion exchange membrane hydrazine electrolyzer (AEMHE), which used the bimetallic Co-P@NF as both the anode and cathode for the HzOR and HER, respectively (Fig. 6c). The Zn-nitrate flow battery can well drive the AEMHE with only a cell voltage of 0.47 V and give high current density over  $35 \text{ mA cm}^{-2}$  for  $\text{H}_2$  production (Fig. S19<sup>†</sup>), the corresponding  $\text{H}_2$  production rate as  $0.64 \text{ mmol h}^{-1} \text{ cm}^{-2}$ . This result shows that the Zn-nitrate flow battery possesses great potential in electricity generation.

## 4. Conclusions

In summary, an amorphous P doped Co (Co-P@NF) was prepared *via* a facile electrodeposition process. Co-P@NF with a higher density oxygen vacancies sites showed high catalytic activities for both  $\text{NO}_3^-$  RR and HzOR. They show a high current density over  $2 \text{ A cm}^{-2}$  for  $\text{NH}_3$  formation and high FE up to 91%

at  $-0.3 \text{ V versus RHE}$  in the electrolyte of  $1 \text{ M NO}_3^-$ . Thanks to the amorphous structure, the Co-P could preserve the oxygen vacancies sites and give a high stability for  $\text{NO}_3^-$  reduction over 82 h electrolysis with the current density over  $799 \text{ mA cm}^{-2}$  and the FE over 90%. A low cell voltage of HzOR-assisted  $\text{NO}_3^-$  RR at  $300 \text{ mA cm}^{-2}$  was also obtained over Co-P@NF||Co-P@NF and was only 0.34 V. A Zn-nitrate flow battery was assemble using Co-P@NF as electrodes can deliver a peak power density of  $12 \text{ mW cm}^{-2}$  and well drive an AEMHE, accompanied with an  $\text{H}_2$  yield rate of *ca.*  $0.64 \text{ mmol h}^{-1} \text{ cm}^{-2}$ . This work demonstrates the feasibility for boosting the activity and stability toward  $\text{NO}_3^-$  RR by constructing the amorphous structure.

## Data availability

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

## Author contributions

Jin-Long Fan: conceptualization, investigation, writing – original draft. Sheng-Bo Liu: investigation. Ming-Liang Chen:

writing – review & editing. Zhangxiong Wu: writing – review & editing. Sheng-Peng Sun: investigation, supervision. Yao-Yin Lou: conceptualization, investigation, supervision, writing – review & editing.

## Conflicts of interest

No potential conflicts of interest were reported by the authors.

## Acknowledgements

This research was financially supported by National Natural Science Foundation of China (NSFC) (No. 22002131) and China Postdoctoral Science Foundation (Grant No. 2020 M671963).

## References

- 1 L. K. Boerner, Industrial ammonia production emits more CO<sub>2</sub> than any other chemical-making reaction. Chemists want to change that, *Chem. Eng. News*, 2019, **97**, 1–9.
- 2 S. Ye, *et al.*, Elucidating the activity, mechanism and application of selective electrosynthesis of ammonia from nitrate on cobalt phosphide, *Energy Environ. Sci.*, 2022, **15**, 760–770, DOI: [10.1039/D1EE03097C](https://doi.org/10.1039/D1EE03097C).
- 3 X. Liu, A. Elgowainy and M. Wang, Life cycle energy use and greenhouse gas emissions of ammonia production from renewable resources and industrial by-products, *Green Chem.*, 2020, **22**, 5751–5761, DOI: [10.1039/DOGC02301A](https://doi.org/10.1039/DOGC02301A).
- 4 Q. Hu, *et al.*, Reaction intermediate-mediated electrocatalyst synthesis favors specified facet and defect exposure for efficient nitrate–ammonia conversion, *Energy Environ. Sci.*, 2021, **14**(9), 4989–4997, DOI: [10.1039/D1EE01731D](https://doi.org/10.1039/D1EE01731D).
- 5 J. Gao, *et al.*, Electrocatalytic Upcycling of Nitrate Wastewater into an Ammonia Fertilizer via an Electrified Membrane, *Environ. Sci. Technol.*, 2022, **56**, 11602–11613, DOI: [10.1021/acs.est.1c08442](https://doi.org/10.1021/acs.est.1c08442).
- 6 G. Wen, *et al.*, Ambient ammonia production via electrocatalytic nitrite reduction catalyzed by a CoP nanoarray, *Nano Res.*, 2021, **15**(2), 972–977, DOI: [10.1007/s12274-021-3583-9](https://doi.org/10.1007/s12274-021-3583-9).
- 7 R. Zhang, *et al.*, Efficient Ammonia Electrosynthesis and Energy Conversion through a Zn-Nitrate Battery by Iron Doping Engineered Nickel Phosphide Catalyst, *Adv. Energy Mater.*, 2022, 2103872, DOI: [10.1002/aenm.202103872](https://doi.org/10.1002/aenm.202103872).
- 8 J. Zhou, *et al.*, Linear Adsorption Enables NO Selective Electroreduction to Hydroxylamine on Single Co Sites, *Angew. Chem., Int. Ed.*, 2023, e202305184, DOI: [10.1002/anie.202305184](https://doi.org/10.1002/anie.202305184).
- 9 Z. Zhang, *et al.*, Electrochemical-catalytic reduction of nitrate over Pd-Cu/gamma Al<sub>2</sub>O<sub>3</sub> catalyst in cathode chamber: Enhanced removal efficiency and N-2 selectivity, *Chem. Eng. J.*, 2016, **290**, 201–208, DOI: [10.1016/j.cej.2016.01.063](https://doi.org/10.1016/j.cej.2016.01.063).
- 10 G., S. Renewable, Energy to Fuels through Utilization of Energy Dense Liquids (REFUEL) [EB/OL].
- 11 N. K. Oh, *et al.*, Highly efficient and robust noble-metal free bifunctional water electrolysis catalyst achieved via complementary charge transfer, *Nat. Commun.*, 2021, **12**, 4606, DOI: [10.1038/s41467-021-24829-8](https://doi.org/10.1038/s41467-021-24829-8).
- 12 L. Wei, D.-J. Liu, B. A. Rosales, J. W. Evans and J. Vela, Mild and Selective Hydrogenation of Nitrate to Ammonia in the Absence of Noble Metals, *ACS Catal.*, 2020, **10**, 3618–3628, DOI: [10.1021/acscatal.9b05338](https://doi.org/10.1021/acscatal.9b05338).
- 13 P. Liu and J. A. Rodriguez, Catalysts for hydrogen evolution from the [NiFe] hydrogenase to the Ni<sub>2</sub>P (001) surface: the importance of ensemble effect, *J. Am. Chem. Soc.*, 2005, **127**, 14871–14878.
- 14 B. Yang, *et al.*, Electron-deficient cobalt nanocrystals for promoted nitrate electrocatalytic reduction to synthesize ammonia, *Nano Energy*, 2023, **117**, 108901, DOI: [10.1016/j.nanoen.2023.108901](https://doi.org/10.1016/j.nanoen.2023.108901).
- 15 J. Li, *et al.*, Efficient Ammonia Electrosynthesis from Nitrate on Strained Ruthenium Nanoclusters, *J. Am. Chem. Soc.*, 2020, **142**, 7036–7046, DOI: [10.1021/jacs.0c00418](https://doi.org/10.1021/jacs.0c00418).
- 16 J.-Y. Fang, *et al.*, Ampere-level current density ammonia electrochemical synthesis using CuCo nanosheets simulating nitrite reductase bifunctional nature, *Nat. Commun.*, 2022, **13**, 7899.
- 17 B. K. Simpson and D. C. Johnson, Electrocatalysis of Nitrate Reduction at Copper-Nickel Alloy Electrodes in Acidic Media, *Electroanalysis*, 2004, **16**, 532–538.
- 18 Q. Fu, *et al.*, Unraveling and leveraging in situ surface amorphization for enhanced hydrogen evolution reaction in alkaline media, *Nat. Commun.*, 2023, **14**, 6462, DOI: [10.1038/s41467-023-42221-6](https://doi.org/10.1038/s41467-023-42221-6).
- 19 X. Li, *et al.*, Amorphous alloys for electrocatalysis: The significant role of the amorphous alloy structure, *Nano Res.*, 2023, **16**, 4277–4288, DOI: [10.1007/s12274-021-3682-7](https://doi.org/10.1007/s12274-021-3682-7).
- 20 M. Liu, Z. Zhao, X. Duan and Y. Huang, Nanoscale structure design for high-performance Pt-based ORR catalysts, *Adv. Mater.*, 2019, **31**, 1802234.
- 21 Y. X. Duan, *et al.*, Amorphizing of Cu nanoparticles toward highly efficient and robust electrocatalyst for CO<sub>2</sub> reduction to liquid fuels with high faradaic efficiencies, *Adv. Mater.*, 2018, **30**, 1706194.
- 22 Y. C. Hu, *et al.*, A highly efficient and self-stabilizing metallic-glass catalyst for electrochemical hydrogen generation, *Adv. Mater.*, 2016, **28**, 10293–10297.
- 23 J. Wang, *et al.*, Recent progress in cobalt-based heterogeneous catalysts for electrochemical water splitting, *Adv. Mater.*, 2016, **28**, 215–230.
- 24 S.-E. Bae, K. L. Stewart and A. A. Gewirth, Nitrate adsorption and reduction on Cu (100) in acidic solution, *J. Am. Chem. Soc.*, 2007, **129**, 10171–10180.
- 25 E. Molodkina, *et al.*, Electroreduction of nitrate ions on Pt (1 1 1) electrodes modified by copper adatoms, *Electrochim. Acta*, 2010, **56**, 154–165.
- 26 S. Han, *et al.*, Ultralow overpotential nitrate reduction to ammonia via a three-step relay mechanism, *Nat. Catal.*, 2023, **6**(5), 402–414, DOI: [10.1038/s41929-023-00951-2](https://doi.org/10.1038/s41929-023-00951-2).
- 27 P. H. van Langevelde, I. Katsounaros and M. T. M. Koper, Electrocatalytic Nitrate Reduction for Sustainable Ammonia Production, *Joule*, 2021, **5**, 290–294, DOI: [10.1016/j.joule.2020.12.025](https://doi.org/10.1016/j.joule.2020.12.025).

- 28 J.-X. Liu, D. Richards, N. Singh and B. R. Goldsmith, Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals, *ACS Catal.*, 2019, **9**, 7052–7064, DOI: [10.1021/acscatal.9b02179](https://doi.org/10.1021/acscatal.9b02179).
- 29 T. Begildayeva, J. Theerthagiri, S. J. Lee, Y. Yu and M. Y. Choi, Unraveling the Synergy of Anion Modulation on Co Electrocatalysts by Pulsed Laser for Water Splitting: Intermediate Capturing by In Situ/Operando Raman Studies, *Small*, 2022, **18**, 2204309, DOI: [10.1002/smll.202204309](https://doi.org/10.1002/smll.202204309).
- 30 J. Kang, *et al.*, Recent Progress of Amorphous Nanomaterials, *Chem. Rev.*, 2023, **123**, 8859–8941, DOI: [10.1021/acs.chemrev.3c00229](https://doi.org/10.1021/acs.chemrev.3c00229).
- 31 J. Wang, *et al.*, Electrocatalytic Reduction of Nitrate to Ammonia on Low-Cost Ultrathin CoOx Nanosheets, *ACS Catal.*, 2021, **11**, 15135–15140, DOI: [10.1021/acscatal.1c03918](https://doi.org/10.1021/acscatal.1c03918).