

Cite this: *Chem. Sci.*, 2025, 16, 378

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# Enhanced electrocatalytic nitrate-to-ammonia performance from Mott–Schottky design to induce electron redistribution†

Ruikai Qi,<sup>‡a</sup> Qiuling Jiang,<sup>‡bd</sup> Li Deng,<sup>a</sup> Xianqiang Yu,<sup>a</sup> Bingyan Shi,<sup>a</sup> Mengxiao Zhong,<sup>\*c</sup> Ying Wang<sup>\*b</sup> and Xiaofeng Lu<sup>ib</sup> <sup>\*a</sup>

Constructing highly efficient electrocatalysts *via* interface manipulation and structural design to facilitate rapid electron transfer in electrocatalytic nitrate-to-ammonia conversion is crucial to attaining superior NH<sub>3</sub> yield rates. Here, a Mott–Schottky type electrocatalyst of Co/In<sub>2</sub>O<sub>3</sub> with a continuous fiber structure has been designed to boost the electrocatalytic nitrate-to-ammonia performance. The optimized Co/In<sub>2</sub>O<sub>3</sub>-1 catalyst exhibits an impressive NH<sub>3</sub> yield rate of 70.1 mg cm<sup>-2</sup> h<sup>-1</sup> at -0.8 V vs. the reversible hydrogen electrode (RHE), along with an NH<sub>3</sub> faradaic efficiency (FE) of 93.34% at 0 V vs. RHE, greatly outperforming the single-component Co and In<sub>2</sub>O<sub>3</sub> samples. The yield rate of Co/In<sub>2</sub>O<sub>3</sub>-1 is also superior to that of most currently reported Co-based catalysts and heterostructured ones. Evidence from experiments and theoretical results confirms the formation of a Mott–Schottky heterojunction, which achieves a Co site enriched with electrons, coupled with an In<sub>2</sub>O<sub>3</sub> facet enriched with holes, inducing an electron redistribution to promote the utilization of electroactive sites. Consequently, the reaction energy barrier for nitrate-to-ammonia conversion is significantly reduced, further enhancing its yield efficiency.

Received 8th October 2024  
Accepted 16th November 2024

DOI: 10.1039/d4sc06818a

rsc.li/chemical-science

## 1. Introduction

NH<sub>3</sub> serves a variety of purposes, including fertilization, chemical production, and fuel.<sup>1</sup> In recent years, scientific research on electrocatalytic nitrate-to-ammonia conversion has gained extensive interest due to its advantages of safety, energy conservation, and eco-friendliness for NH<sub>3</sub> production.<sup>2–10</sup> However, the electrocatalytic nitrate-to-ammonia process involves complex multiple electron transfer and pathways, posing a great challenge to rational design and fabrication of efficient catalysts for electrochemical NH<sub>3</sub> generation.<sup>11–19</sup> Fortunately, some cost-effective transition metal-based materials hold promise as nitrate-to-ammonia electrocatalysts,

particularly cobalt-based catalysts such as FeCoNiAlTi,<sup>20</sup> Co<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> (ref. 21) and Ru<sub>15</sub>Co<sub>85</sub> (ref. 22) due to their superior intrinsic activities. Despite significant improvement in NH<sub>3</sub> faradaic efficiency (FE) that has been achieved at lower potentials, the NH<sub>3</sub> yield rates of those electrocatalysts are still unsatisfactory because of the low current density. Therefore, researchers relentlessly strive for exploring efficient nitrate reduction catalysts with high NH<sub>3</sub> yield.

Heterojunction structures significantly optimize the electronic structure and energy bands at catalyst interfaces, essential for rapid electron transfer. Consequently, at heterojunction interfaces, the adsorption of reactants, desorption of products, and the activity of active sites are promoted.<sup>23–25</sup> Typically, according to the Mott–Schottky effect, electrons in metal/semiconductor heterojunctions tend to spontaneously traverse interfaces until the work functions on both sides balance. This continuous adjustment at the interfaces alters the work function of the Mott–Schottky barrier, regulates the electron cloud density of the catalyst, and induces negative charge accumulation on the side with a higher work function.<sup>26,27</sup> Hence, creating Mott–Schottky junctions is a reliable strategy for modulating electron density at electrocatalyst interfaces. The construction of metal/semiconductor heterostructures with Mott–Schottky rectification effects holds potential for boosting the efficiency of the nitrate-to-ammonia reaction.

Indium oxide (In<sub>2</sub>O<sub>3</sub>) is a common n-type semiconductor with a wide bandgap, low resistivity, and high catalytic activity,

<sup>a</sup>Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: xflu@jlu.edu.cn

<sup>b</sup>State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China. E-mail: ywang\_2012@ciac.ac.cn

<sup>c</sup>State Key Laboratory of Integrated Optoelectronics, Key Laboratory of Advanced Gas Sensors, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun, Jilin Province, 130012, P. R. China. E-mail: zhongmx@jlu.edu.cn

<sup>d</sup>School of Applied Chemistry and Engineering, University of Science and Technology of China, Hefei, 230026, China

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4sc06818a>

‡ These authors contributed equally to this work.



which is widely used in electrocatalysis.<sup>28–30</sup> Therefore, we have demonstrated the clever construction of a continuous fibrous Mott–Schottky type Co/In<sub>2</sub>O<sub>3</sub> heterostructure by combining Co with In<sub>2</sub>O<sub>3</sub> through a simple electrospinning-calcination-partial reduction strategy. The experimental results demonstrate that the long-range ordered fiber network presents numerous active sites, and the formation of a Co/In<sub>2</sub>O<sub>3</sub>-1 heterojunction with the Mott–Schottky effect induces an electron redistribution at the interface, benefitting to reduce the reaction barrier of the catalytic process. Density functional theory (DFT) analysis indicates an augmentation of the density of states (DOS) near the Fermi level for the Co/In<sub>2</sub>O<sub>3</sub>-1 catalyst, and the d-band center ( $\epsilon_d$ ) of Co in Co/In<sub>2</sub>O<sub>3</sub>-1 aligns nearer to the Fermi level compared to Co (111). Therefore, Co/In<sub>2</sub>O<sub>3</sub>-1 exhibits the smallest thermodynamic reaction energy barrier ( $\Delta G(\text{PDS})$ ) for the potential-determining step with the formation of NH<sub>3</sub><sup>\*</sup> from NH<sub>4</sub><sup>+</sup> protonation, suggesting that the Mott–Schottky type Co/In<sub>2</sub>O<sub>3</sub> heterostructure significantly enhances the electrocatalytic nitrate-to-ammonia activity. Therefore, the optimized Co/In<sub>2</sub>O<sub>3</sub>-1 catalyst presents a high NH<sub>3</sub> yield rate of 70.1 mg cm<sup>-2</sup> h<sup>-1</sup> at -0.8 V vs. RHE, outperforming most currently reported nitrate-to-ammonia electrocatalysts.

## 2. Results and discussion

### 2.1 Synthesis and characterization of the Mott–Schottky type Co/In<sub>2</sub>O<sub>3</sub> heterostructure

The nanofibrous Co/In<sub>2</sub>O<sub>3</sub> heterostructure is synthesized using an electrospinning, calcination, and partial reduction process (Fig. 1a). Initially, a poly(vinylpyrrolidone) (PVP)/Co<sup>2+</sup>/In<sup>3+</sup>

precursor nanofibrous membrane is prepared *via* an electrospinning technique and then immediately calcined in air to yield continuous and uniform Co<sub>3</sub>O<sub>4</sub>/In<sub>2</sub>O<sub>3</sub> nanofibers with a rough surface and an average diameter of 144 nm (Fig. 1b and c). After being reduced in a H<sub>2</sub>/Ar atmosphere at 400 °C for 4 h, Co<sub>3</sub>O<sub>4</sub> can be selectively reduced, and then Co/In<sub>2</sub>O<sub>3</sub> is obtained, and its fibrous morphology remains basically unchanged (Fig. 1d). However, the diameter of the Co/In<sub>2</sub>O<sub>3</sub> nanofibers slightly decreases due to oxygen elimination (Fig. 1e). The transmission electron microscopy (TEM) image shows that Co/In<sub>2</sub>O<sub>3</sub> nanofibers are composed of particles stacked together and have obviously porous characteristic (Fig. 1f). The high-resolution TEM (HRTEM) image (Fig. 1g) reveals 0.197 and 0.411 nm periodicities, corresponding to the (111) plane of Co and (211) plane of In<sub>2</sub>O<sub>3</sub>, respectively, and discernible grain boundaries can be observed, demonstrating the successful formation of the Co/In<sub>2</sub>O<sub>3</sub> heterostructure. Fig. 1h exhibits the selected area electron diffraction (SAED) pattern, presenting legible rings attributed to the crystal planes of Co and In<sub>2</sub>O<sub>3</sub>, suggesting a polycrystalline characteristic of Co and In<sub>2</sub>O<sub>3</sub>. Moreover, the energy dispersive X-ray (EDX) spectrum presents strong Co, In and O signals in Co/In<sub>2</sub>O<sub>3</sub>-1 (Fig. S1, ESI<sup>†</sup>). Elemental mapping displays homogeneous distribution of these elements throughout the Co/In<sub>2</sub>O<sub>3</sub>-1 nanofiber (Fig. 1i). In addition, a series of control catalysts with diverse contents of Co are prepared using the same synthesis method, named In<sub>2</sub>O<sub>3</sub>-H, Co/In<sub>2</sub>O<sub>3</sub>-0.5, and Co/In<sub>2</sub>O<sub>3</sub>-2 (Fig. S2 and S3, ESI<sup>†</sup>), which exhibit similar nanofibrous morphologies and average diameters. And the inductively coupled plasma-optical emission spectrometry (ICP-OES) results confirm that

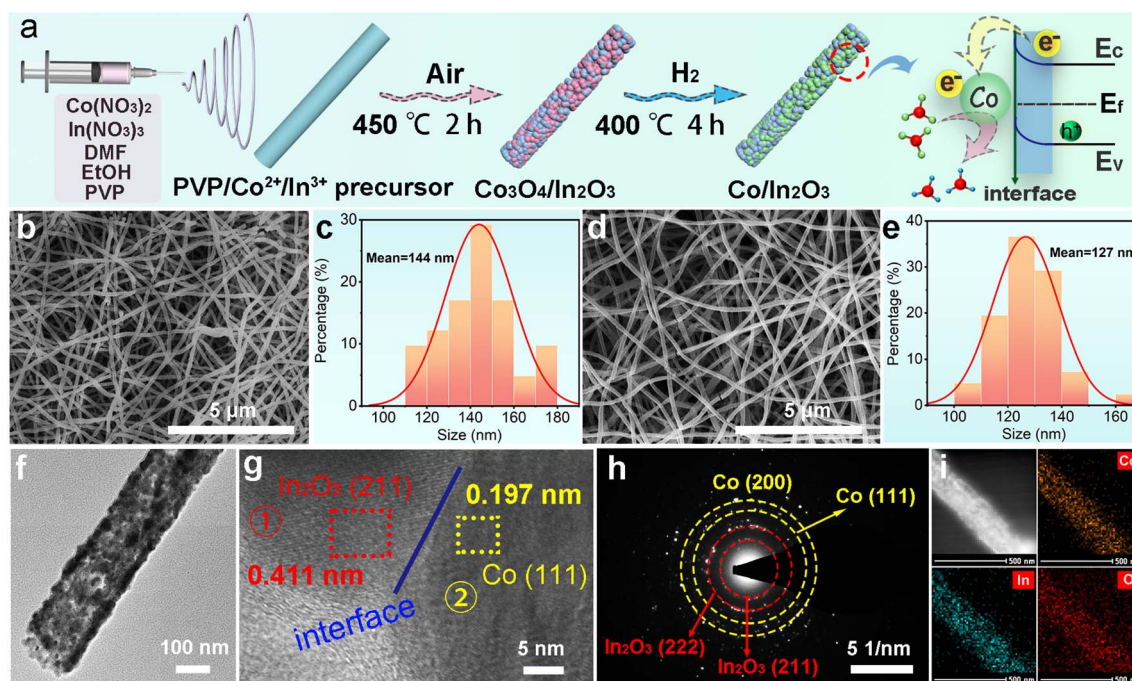
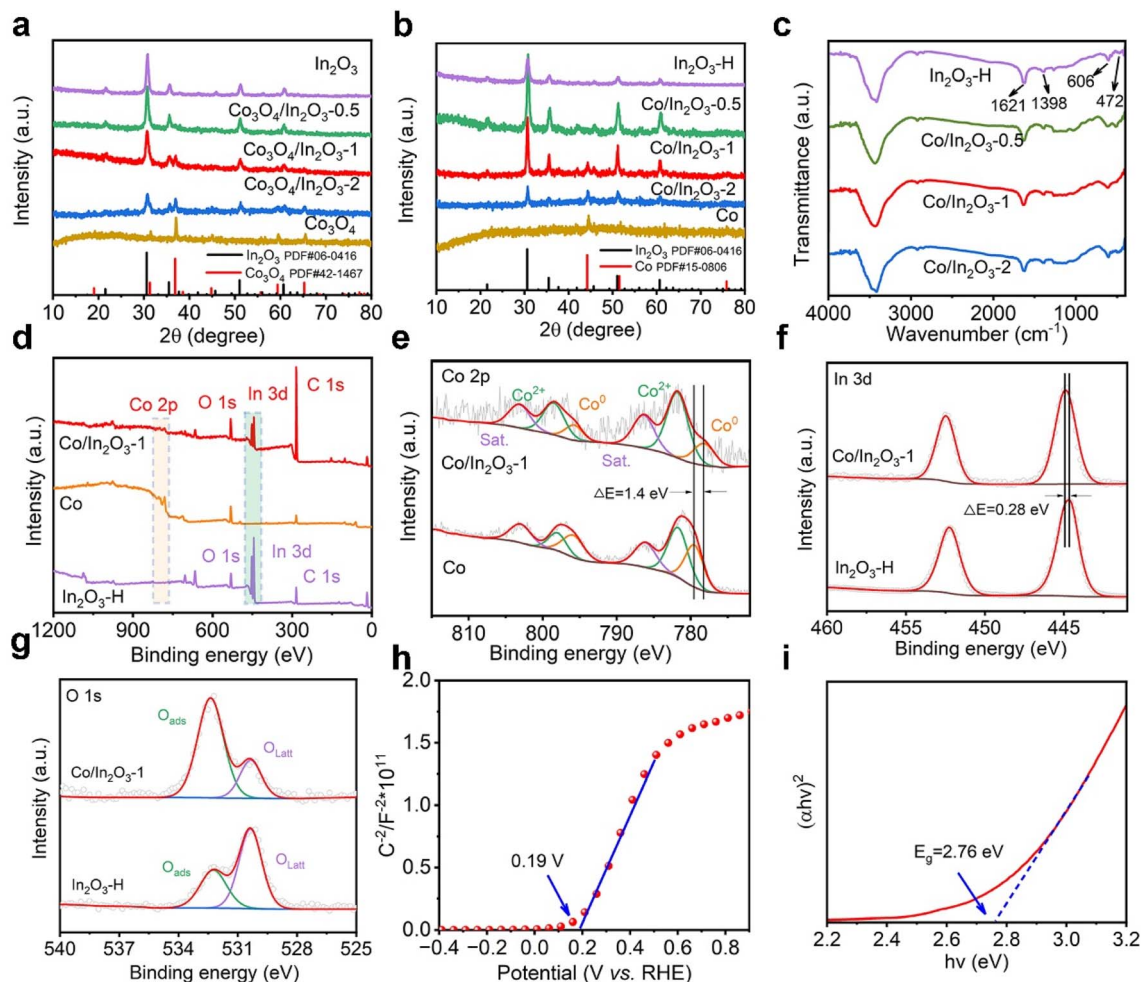


Fig. 1 (a) Synthesis procedure of Co/In<sub>2</sub>O<sub>3</sub>. (b) SEM image and (c) diameter distribution of Co<sub>3</sub>O<sub>4</sub>/In<sub>2</sub>O<sub>3</sub> nanofibers. (d) SEM image and (e) diameter distribution of Co/In<sub>2</sub>O<sub>3</sub> nanofibers. (f) TEM, (g) HRTEM and (h) SAED images of Co/In<sub>2</sub>O<sub>3</sub>. (i) HAADF-STEM image and EDX element mappings of Co–K, In–L, and O–K.





**Fig. 2** (a) XRD profiles of  $\text{In}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4/\text{In}_2\text{O}_3$ -0.5,  $\text{Co}_3\text{O}_4/\text{In}_2\text{O}_3$ -1,  $\text{Co}_3\text{O}_4/\text{In}_2\text{O}_3$ -2 and  $\text{Co}_3\text{O}_4$ . (b) XRD profiles of  $\text{In}_2\text{O}_3$ -H,  $\text{Co}/\text{In}_2\text{O}_3$ -0.5,  $\text{Co}/\text{In}_2\text{O}_3$ -1,  $\text{Co}/\text{In}_2\text{O}_3$ -2 and Co. (c) FTIR spectra of  $\text{In}_2\text{O}_3$ -H,  $\text{Co}/\text{In}_2\text{O}_3$ -0.5,  $\text{Co}/\text{In}_2\text{O}_3$ -1 and  $\text{Co}/\text{In}_2\text{O}_3$ -2. (d) XPS survey spectra of  $\text{Co}/\text{In}_2\text{O}_3$ -1, Co, and  $\text{In}_2\text{O}_3$ -H. Typical narrow-scan (e) Co 2p, (f) In 3d and (g) O 1s XPS spectra of different catalysts. (h) Mott–Schottky plot and (i) Tauc plot of  $\text{In}_2\text{O}_3$ -H.

the molar ratio and feeding amount of Co and In are almost the same (Table S1, ESI<sup>†</sup>). After bare  $\text{Co}_3\text{O}_4$  is reduced to Co metal, the fiber morphology collapses, reflecting that the presence of  $\text{In}_2\text{O}_3$  can maintain the stability of the structure (Fig. S4, ESI<sup>†</sup>).

X-ray diffraction (XRD) analysis identifies the obtained  $\text{Co}_3\text{O}_4/\text{In}_2\text{O}_3$  products (Fig. 2a), exhibiting both  $\text{In}_2\text{O}_3$  (PDF #06-0416) and  $\text{Co}_3\text{O}_4$  (PDF #42-1467) phases. After  $\text{H}_2/\text{Ar}$  reduction treatment at 400 °C, XRD analysis exhibits the disappearance of  $\text{Co}_3\text{O}_4$  peaks, replaced by those of Co (PDF #15-0806), while  $\text{In}_2\text{O}_3$  is still in the oxide phase, demonstrating the formation of the  $\text{Co}/\text{In}_2\text{O}_3$  heterostructure (Fig. 2b). Here, the effect of the  $\text{H}_2/\text{Ar}$  reduction temperature on  $\text{Co}/\text{In}_2\text{O}_3$  synthesis is investigated. From Fig. S5 (ESI),<sup>†</sup> it can be seen that when the temperature is below 400 °C,  $\text{Co}_3\text{O}_4$  cannot be completely reduced, while a high temperature can destroy the  $\text{In}_2\text{O}_3$  crystal structure. Therefore, the temperature of 400 °C is chosen as the optimal experimental condition. Fig. 2c displays the Fourier transform infrared (FTIR) spectra of  $\text{In}_2\text{O}_3$ -H,  $\text{Co}/\text{In}_2\text{O}_3$ -0.5,  $\text{Co}/\text{In}_2\text{O}_3$ -1, and  $\text{Co}/\text{In}_2\text{O}_3$ -2 samples. The peaks at 472 and 606  $\text{cm}^{-1}$  of all the as-prepared

$\text{Co}/\text{In}_2\text{O}_3$  samples correspond to the In–O bond vibration, while those at 1398 and 1621  $\text{cm}^{-1}$  are related to adsorbed water molecules. Due to the metallic properties of Co, the characteristic peaks of  $\text{Co}/\text{In}_2\text{O}_3$  composites are completely consistent with those of  $\text{In}_2\text{O}_3$ -H.<sup>31</sup>

The X-ray photoelectron spectroscopy (XPS) test further assesses valence states of the components in the  $\text{Co}/\text{In}_2\text{O}_3$ -1 sample. Fig. 2d shows that  $\text{Co}/\text{In}_2\text{O}_3$ -1 nanofibers discern the presence of Co, In and O elements. The narrow scan Co 2p XPS spectrum yields six distinct peaks (Fig. 2e),<sup>32,33</sup> notably at 778.1 eV and 795.7 for Co nanoparticles, aligning with the XRD results. The spin–orbit peaks at 781.8 and 798.6 eV correspond to  $\text{Co } 2p_{3/2}$  and  $\text{Co } 2p_{1/2}$ , respectively, and the peaks at 786.3 and 803.2 eV are satellite peaks. In the In 3d core-level spectrum, In  $3d_{5/2}$  and In  $3d_{3/2}$  spin orbit peaks appear at 444.9 and 452.5 eV (Fig. 2f).<sup>34,35</sup> Notably, the  $\text{Co } 2p_{3/2}$  binding energy (BE) of  $\text{Co}/\text{In}_2\text{O}_3$ -1 presents a negative shift of 1.4 eV relative to Co, while In  $2p_{5/2}$  undergoes a positive shift of 0.28 eV compared with  $\text{In}_2\text{O}_3$ -H, signifying electron transfer from  $\text{In}_2\text{O}_3$  to Co in the

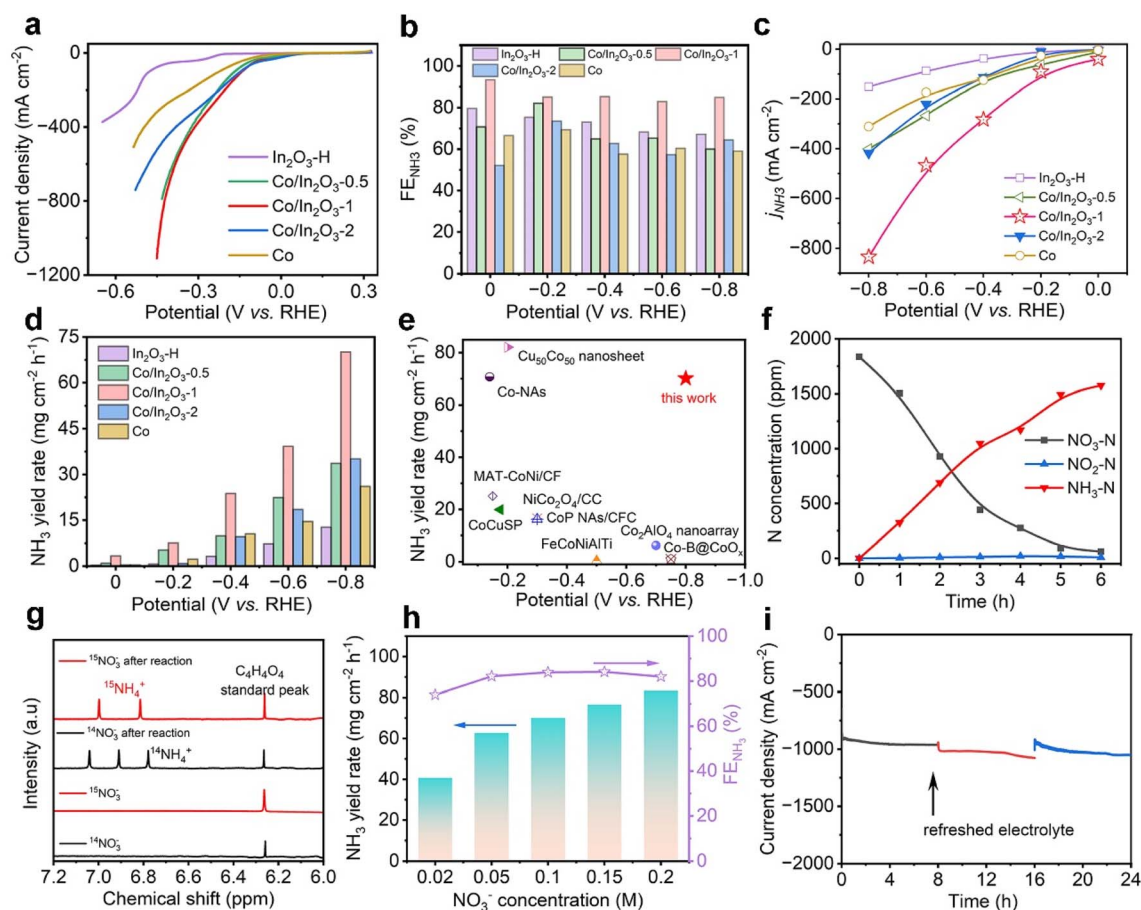


heterostructure. Fig. 2g presents the O 1s XPS spectra of Co/In<sub>2</sub>O<sub>3</sub>-1 and In<sub>2</sub>O<sub>3</sub>-H, identifying two dominant peaks at a BE of 530.4 and 532.2 eV, indicating the lattice (O<sub>latt</sub>) and the surface adsorbed oxygen (O<sub>ads</sub>), respectively. The ratio of O<sub>ads</sub>/(O<sub>ads</sub> + O<sub>latt</sub>) in Co/In<sub>2</sub>O<sub>3</sub>-1 is higher than that in In<sub>2</sub>O<sub>3</sub>-H, suggesting more surface oxygen defects accessible in Co/In<sub>2</sub>O<sub>3</sub>-1.<sup>36</sup>

Rationally engineered Mott-Schottky interfaces stimulate spontaneous electron transfer, substantially enhancing charge transfer efficiency. The Mott-Schottky data for In<sub>2</sub>O<sub>3</sub>-H material are depicted in Fig. 2h, where the positive slope and the x-intercept suggest n-type In<sub>2</sub>O<sub>3</sub>-H possessing a flat band potential of 0.19 V (vs. RHE). The Tauc plot (Fig. 2i) derived from the UV-vis result (Fig. S6a, ESI†) indicates a bandgap of 2.76 eV. It is generally accepted that the flat band potential of n-type semiconductors is usually employed to approximate the conduction band, typically lying between 0.1 and 0.3 eV below the Fermi level. Therefore, the band relationship suggests that the heterojunction formed by Co and In<sub>2</sub>O<sub>3</sub> conforms to the Mott-Schottky model (Fig. S6b, ESI†).

## 2.2 Evaluation of electrocatalytic nitrate-to-ammonia performances

The electrocatalytic nitrate-to-ammonia performance is evaluated in 1.0 M KOH with 0.1 M KNO<sub>3</sub>. Initially, a substantial augmentation of current density occurs in the presence of KNO<sub>3</sub>, demonstrating that the electrocatalytic nitrate-to-ammonia reaction possesses higher activity than the hydrogen evolution reaction (HER). The current density and onset potential of the obtained Co/In<sub>2</sub>O<sub>3</sub> is also larger than that of individual Co, In<sub>2</sub>O<sub>3</sub>-H, and Co<sub>3</sub>O<sub>4</sub>/In<sub>2</sub>O<sub>3</sub>, demonstrating that the catalyst with the Mott-Schottky heterostructure exhibits a higher catalytic activity (Fig. S7, ESI†). Furthermore, the effect of the feeding ratio of Co to the In precursor on the electrocatalytic activity has also been revealed. By comparing the LSV curves of varied catalysts with 80% *iR*-compensation, it is preliminarily believed that Co/In<sub>2</sub>O<sub>3</sub>-1 has the highest ammonia production activity due to its largest current density (Fig. 3a). Afterwards, using electrochemical impedance spectroscopy



**Fig. 3** (a) LSV curves of In<sub>2</sub>O<sub>3</sub>-H, Co/In<sub>2</sub>O<sub>3</sub>-0.5, Co/In<sub>2</sub>O<sub>3</sub>-1, Co/In<sub>2</sub>O<sub>3</sub>-2 and Co with 80% *iR*-correction. (b) NH<sub>3</sub> FE, (c)  $j_{\text{NH}_3}$  and (d) NH<sub>3</sub> yield rate of In<sub>2</sub>O<sub>3</sub>-H, Co/In<sub>2</sub>O<sub>3</sub>-0.5, Co/In<sub>2</sub>O<sub>3</sub>-1, Co/In<sub>2</sub>O<sub>3</sub>-2 and Co at varied potentials. (e) Comparison of the NH<sub>3</sub> yield rate of Co/In<sub>2</sub>O<sub>3</sub>-1 at a potential of  $-0.8$  V for 1 h of electrocatalytic nitrate-to-ammonia conversion with that of other reported catalysts. (f) Time-dependent concentration changes of NO<sub>3</sub>-N, NO<sub>2</sub>-N and NH<sub>3</sub>-N during the electrocatalytic nitrate-to-ammonia reaction by Co/In<sub>2</sub>O<sub>3</sub>-1 at  $-0.8$  V in 1 M KOH with an initial concentration of 1800 mg L<sup>-1</sup> of NO<sub>3</sub>-N. (g) NMR spectra of the products produced before and after the electrocatalytic nitrate-to-ammonia reaction by Co/In<sub>2</sub>O<sub>3</sub>-1 in the electrolyte of 1 M KOH with 0.1 M K<sup>15</sup>NO<sub>3</sub> and 0.1 M K<sup>14</sup>NO<sub>3</sub> at  $-0.8$  V. (h) The NH<sub>3</sub> FEs and NH<sub>3</sub> yield rate of Co/In<sub>2</sub>O<sub>3</sub>-1 at  $-0.8$  V in the electrolyte of 1 M KOH with varied concentrations of KNO<sub>3</sub>. (i) Chronoamperometric curves of Co/In<sub>2</sub>O<sub>3</sub>-1 at  $-0.8$  V in 3 cycles, and each cycle lasting for 8 h of long-term electrolysis.

(EIS), we evaluate the charge-transfer kinetics (Fig. S8, ESI†). After calculation and fitting, the charge transfer resistance of Co/In<sub>2</sub>O<sub>3</sub>-1 is calculated to be 6.89 Ω, which is lower than that of other control samples including In<sub>2</sub>O<sub>3</sub>-H (246 Ω), Co (14.14 Ω), Co/In<sub>2</sub>O<sub>3</sub>-0.5 (57.67 Ω), and Co/In<sub>2</sub>O<sub>3</sub>-2 (9.61 Ω). This signifies faster charge transfer and optimal electrocatalytic kinetics of Co/In<sub>2</sub>O<sub>3</sub>-1, benefitting the enhanced nitrate-to-ammonia performance. Cyclic voltammetry (CV) is executed, with the double-layer capacitance (*C*<sub>dl</sub>) determined through potential scanning in the non-faraday region (Fig. S9, ESI†). The *C*<sub>dl</sub> of Co/In<sub>2</sub>O<sub>3</sub>-1 is 3.2 mF cm<sup>-2</sup>, larger than those of In<sub>2</sub>O<sub>3</sub>-H (1.7 mF cm<sup>-2</sup>), Co/In<sub>2</sub>O<sub>3</sub>-0.5 (3.1 mF cm<sup>-2</sup>), Co/In<sub>2</sub>O<sub>3</sub>-2 (1.8 mF cm<sup>-2</sup>) and Co (2.0 mF cm<sup>-2</sup>), showcasing more active sites to boost the nitrate-to-ammonia efficiency (Fig. S10, ESI†).

Chronoamperometry and UV-vis examinations are performed to determine the NH<sub>3</sub> yield rate and FE (Fig. S11–S14, ESI†). Initially, the NH<sub>3</sub> FE exceeds that of NO<sub>2</sub><sup>-</sup> across diverse catalyst electrodes at different electrolysis voltages, indicating domination of NH<sub>3</sub> as the electrolysis product (Fig. S15, ESI†). As depicted in Fig. 3b, the NH<sub>3</sub> FE of Co/In<sub>2</sub>O<sub>3</sub>-1 reaches 93.34% at 0 V, surpassing that of In<sub>2</sub>O<sub>3</sub>-H (79.67% at 0 V), Co/In<sub>2</sub>O<sub>3</sub>-0.5 (82.16% at -0.2 V), Co/In<sub>2</sub>O<sub>3</sub>-2 (73.53% at -0.2 V) and Co (69.41% at -0.2 V). Concurrently, Co/In<sub>2</sub>O<sub>3</sub>-1 exhibits higher NH<sub>3</sub> partial current densities (*j*<sub>NH<sub>3</sub></sub>) across various potentials, suggesting its superior electrocatalytic nitrate-to-ammonia activity over the entire potential range (Fig. 3c). Fig. 3d reveals an augmentation in the NH<sub>3</sub> yield rate with a decrease in applied potential for the as-synthesized catalysts. Notably, the NH<sub>3</sub> yield rate of Co/In<sub>2</sub>O<sub>3</sub>-1 outperforms that of In<sub>2</sub>O<sub>3</sub>-H, Co/In<sub>2</sub>O<sub>3</sub>-0.5, Co/In<sub>2</sub>O<sub>3</sub>-2 and Co over the entire potential range, thanks to its exceptional NH<sub>3</sub> FE and *j*<sub>NH<sub>3</sub></sub>. Specifically, at a potential of -0.8 V, the NH<sub>3</sub> yield rate of Co/In<sub>2</sub>O<sub>3</sub>-1 reaches 70.1 mg cm<sup>-2</sup> h<sup>-1</sup>, superior to that of In<sub>2</sub>O<sub>3</sub>-H (12.7 mg cm<sup>-2</sup> h<sup>-1</sup>), Co/In<sub>2</sub>O<sub>3</sub>-0.5 (33.7 mg cm<sup>-2</sup> h<sup>-1</sup>), Co/In<sub>2</sub>O<sub>3</sub>-2 (35.1 mg cm<sup>-2</sup> h<sup>-1</sup>) and Co (26.1 mg cm<sup>-2</sup> h<sup>-1</sup>). Additionally, as depicted in Fig. 3e and Table S2 (ESI),† the NH<sub>3</sub> yield rate of Co/In<sub>2</sub>O<sub>3</sub>-1 also surpasses that of many Co-based and other heterostructured nitrate-to-ammonia catalysts reported so far, suggesting that this cost-effective and efficient Co/In<sub>2</sub>O<sub>3</sub>-1 has the potential for large-scale NH<sub>3</sub> production. To evaluate the efficiency of Co/In<sub>2</sub>O<sub>3</sub>-1 in nitrate removal, a batch experiment is conducted with an initial NO<sub>3</sub><sup>-</sup>-N concentration of around 1800 ppm to detect the remaining products (Fig. 3f). Remarkably, nearly all NO<sub>3</sub><sup>-</sup>-N sources are reduced within 6 h, with an impressive NH<sub>3</sub>-N selectivity of 88.7%. Following 6 h of electrolysis, NO<sub>3</sub><sup>-</sup> is almost removed and there is nearly no obvious NO<sub>2</sub><sup>-</sup> formation. These findings demonstrate that Co/In<sub>2</sub>O<sub>3</sub>-1 achieves an outstanding activity and NH<sub>3</sub> FE, showing potential for nitrate removal/conversion in wastewater. Subsequently, isotope labeling experiments ascertain the source of NH<sub>3</sub> (Fig. 3g). Compared to the negligible peak of NH<sub>4</sub><sup>+</sup> before electrolysis, the <sup>1</sup>H NMR spectrum of the <sup>14</sup>NO<sub>3</sub><sup>-</sup> solution reveals three different <sup>14</sup>NH<sub>4</sub><sup>+</sup> peaks, while the <sup>15</sup>NO<sub>3</sub><sup>-</sup> solution features a notable <sup>15</sup>NH<sub>4</sub><sup>+</sup> double peak after 1 h of electrolysis at -0.8 V, demonstrating the origination of the produced ammonia from KNO<sub>3</sub> reduction.

Next, the concentration of KNO<sub>3</sub> in the electrolyte is adjusted to range from 0.02 M to 0.2 M to evaluate the environmental compatibility of Co/In<sub>2</sub>O<sub>3</sub>-1 for the electrocatalytic nitrate-to-ammonia reaction. First, as the KNO<sub>3</sub> concentration increases, the onset potential and current density increase as expected (Fig. S16, ESI†), accompanied by a progressive increase in the NH<sub>3</sub> yield rate, reaching 83.3 mg cm<sup>-2</sup> h<sup>-1</sup> at a KNO<sub>3</sub> concentration of 0.2 M (Fig. 3h). Second, the NH<sub>3</sub> FE consistently remains above 80%, indicating that Co/In<sub>2</sub>O<sub>3</sub>-1 maintains efficient electrocatalytic nitrate-to-ammonia activity across a broad concentration range. To assess the stability of Co/In<sub>2</sub>O<sub>3</sub>-1 during nitrate-to-ammonia electrocatalysis, we conducted three cycle tests with a total 24-h electrocatalysis at -0.8 V (Fig. 3i). The catalytic current density remains steady throughout the test. Moreover, the NH<sub>3</sub> FE and yield rate remain consistent in the different cycles, with average values of 69.24% and 58.3 mg cm<sup>-2</sup> h<sup>-1</sup>, affording evidence for the ideal durability of the Co/In<sub>2</sub>O<sub>3</sub>-1 catalyst for electrocatalytic nitrate-to-ammonia conversion (Fig. S17, ESI†).

### 2.3 The investigations of the nitrate-to-ammonia reaction mechanism

Owing to the multiple reactive sites on the Co/In<sub>2</sub>O<sub>3</sub>-1 catalyst, the charge density difference is determined prior to investigating the nitrate-to-ammonia reaction mechanism. The red circle in the charge density difference in Fig. S18 (ESI)† highlights the Co/In<sub>2</sub>O<sub>3</sub>-1 interface with a relatively enhanced charge density, suggesting these locations as preferential adsorption sites for nitrate reduction. According to the previous study,<sup>37</sup> the possible reaction pathways of the nitrate reduction process are illustrated in Fig. 4a. Fig. S19–S21 (ESI)† illustrate the optimal structures of reaction intermediates on Co (111), In<sub>2</sub>O<sub>3</sub> (211), and Co/In<sub>2</sub>O<sub>3</sub>-1, respectively, along the most conductive reaction pathway. The free energy diagrams for nitrate reduction are depicted in Fig. 4b, revealing varied favorable pathways for nitrate reduction on Co (111), In<sub>2</sub>O<sub>3</sub> (211), and Co/In<sub>2</sub>O<sub>3</sub>-1, predominantly arising from the NOH\* hydrogenation step. Upon protonating NOH\* on the Co (111) surface, we observe its tendency towards forming N\* and producing H<sub>2</sub>O, with a reaction energy of -1.67 eV. However, on both In<sub>2</sub>O<sub>3</sub> (211) and Co/In<sub>2</sub>O<sub>3</sub>-1, the formation of HNOH\* is energetically favored after NOH\* protonation. Notably, this process on In<sub>2</sub>O<sub>3</sub> (211) is endothermic with an energy requirement of 2.28 eV, and it becomes spontaneous on Co/In<sub>2</sub>O<sub>3</sub>-1, exhibiting an exothermic reaction energy of -0.69 eV. The PDS analysis reveals the catalytic potential for nitrate-to-ammonia conversion on the three catalysts. On Co (111), the PDS is identified as the formation of HNO<sub>2</sub><sup>\*</sup>, with a corresponding reaction energy ( $\Delta G(\text{PDS})$ ) of 0.66 eV. On In<sub>2</sub>O<sub>3</sub> (211), NOH\* hydrogenation is regarded as the PDS, exhibiting the highest  $\Delta G(\text{PDS})$  value of 2.28 eV. The high thermodynamic energy barriers on both Co (111) and In<sub>2</sub>O<sub>3</sub> (211) suggest that these two catalysts are unlikely to facilitate nitrate-to-ammonia efficiently. However, on Co/In<sub>2</sub>O<sub>3</sub>-1, the protonation of NH\* to form NH<sub>2</sub><sup>\*</sup> appears as the PDS, with a  $\Delta G(\text{PDS})$  of merely 0.15 eV. This remarkably small  $\Delta G(\text{PDS})$  signifies the significant synergistic enhancement of nitrate-to-ammonia catalytic activity of Co/In<sub>2</sub>O<sub>3</sub>-1 by the strong



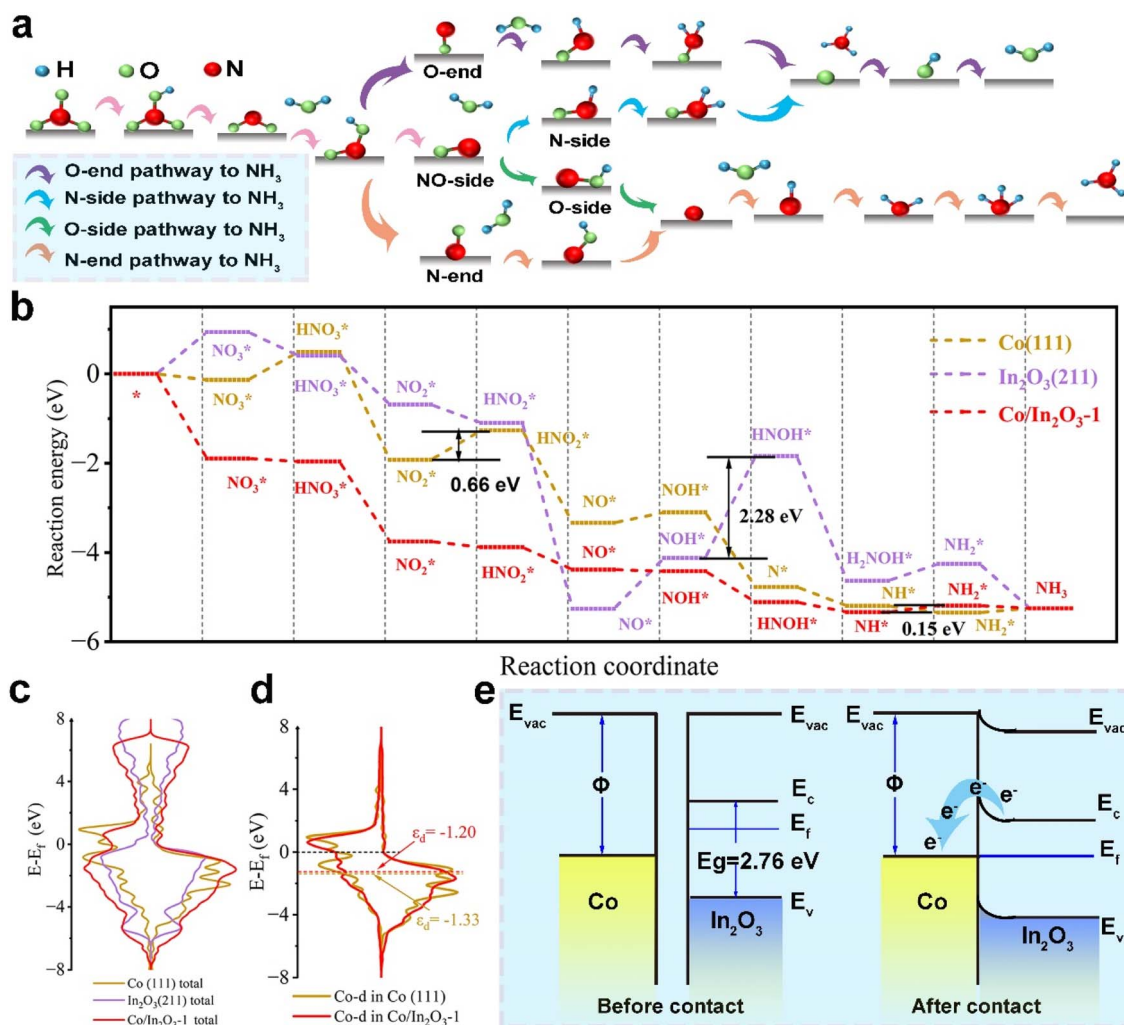


Fig. 4 (a) Illustration of potential reaction pathways of electrocatalytic nitrate-to-ammonia conversion. (b) Free energy diagrams for electrocatalytic nitrate-to-ammonia conversion on Co (111), In<sub>2</sub>O<sub>3</sub> (211), and Co/In<sub>2</sub>O<sub>3</sub>. (c) Total density of states (TDOS) of Co (111), In<sub>2</sub>O<sub>3</sub> (211), and Co/In<sub>2</sub>O<sub>3</sub>. (d) Projected density of states (PDOS) of the Co d orbital in the Co (111) and Co/In<sub>2</sub>O<sub>3</sub>. (e) The energy band diagrams of metallic Co and semiconductor In<sub>2</sub>O<sub>3</sub> before and after the formation of a Mott-Schottky heterojunction.

interaction between Co and In<sub>2</sub>O<sub>3</sub>. This result is corroborated by studying the electronic attributes of these three catalysts. As shown in Fig. 4c, the density of states (DOS) near the Fermi level for Co/In<sub>2</sub>O<sub>3</sub>-1 noticeably increases compared to the In<sub>2</sub>O<sub>3</sub> (211) substrate, suggesting improved electrical conductivity of Co/In<sub>2</sub>O<sub>3</sub>. Moreover, as shown in Fig. 4d, the d band center (ε<sub>d</sub>) of Co in Co/In<sub>2</sub>O<sub>3</sub>-1 is -1.20 eV, situated 0.13 eV above the Fermi level compared to the value of Co in Co (111) (-1.33 eV). This shift not only strengthens the catalyst-intermediate interaction, but also further validates the beneficial impact of the Co-In<sub>2</sub>O<sub>3</sub> interaction on the enhanced electrocatalytic activity of Co/In<sub>2</sub>O<sub>3</sub>-1.

Fig. 4e presents the energy band diagram of the Co/In<sub>2</sub>O<sub>3</sub> heterojunction, illustrating the mechanism behind its promoted nitrate-to-ammonia performance. This enhancement is attributed to the prompt and spontaneous electron transfer from In<sub>2</sub>O<sub>3</sub> to Co, facilitated by the elevated Fermi level of In<sub>2</sub>O<sub>3</sub>. Upon intimate contact, the In<sub>2</sub>O<sub>3</sub> band drops, achieving equilibrium between Fermi levels of Co and In<sub>2</sub>O<sub>3</sub>. This forms

a rectifying Schottky junction in the depletion region to generate a charge density gradient and result in an electron-rich zone at the Co side and a hole-rich region at the In<sub>2</sub>O<sub>3</sub> side, creating a built-in electric field to provide a directed electron flow path. This electron reallocation is forecast to augment electroactive site utilization, lower reaction energy thresholds, and speed up the overall reaction kinetics. Therefore, the Co/In<sub>2</sub>O<sub>3</sub>-1 heterojunction electrocatalyst exhibits a superior NH<sub>3</sub> FE and high NH<sub>3</sub> yield rate during the nitrate-to-ammonia process.

#### 2.4 Zn-NO<sub>3</sub><sup>-</sup> battery

Finally, an aqueous Zn-NO<sub>3</sub><sup>-</sup> battery is constructed with Co/In<sub>2</sub>O<sub>3</sub>-1 as the cathode and Zn foil as the anode (Fig. S22a, ESI<sup>†</sup>), achieving both energy production and NH<sub>3</sub> manufacturing. Due to the excellent electrocatalytic nitrate-to-ammonia performance of Co/In<sub>2</sub>O<sub>3</sub>-1, the Zn-NO<sub>3</sub><sup>-</sup> battery exhibits a consistent open circuit voltage of 1.388 V vs. Zn within 1000 s (Fig. S22b,



ESI†). In addition, a peak power density of  $2.15 \text{ mW cm}^{-2}$  is achieved (Fig. S22c, ESI†). Fig. S23a (ESI†) illustrates the discharging curves of the  $\text{Zn-NO}_3^-$  battery at different current densities for 1 h, demonstrating stable battery voltage. An  $\text{NH}_3$  yield rate of  $1.36 \text{ mg h}^{-1} \text{ cm}^{-2}$  at  $20 \text{ mA cm}^{-2}$  is observed (Fig. S23b, ESI†). This suggests that the nitrate-to-ammonia process has outstanding application prospects in practical power generation devices, concurrently producing valuable  $\text{NH}_3$  industrial products.

### 3. Conclusion

In summary, a  $\text{Co/In}_2\text{O}_3$  heterostructure with the Mott–Schottky effect is ingeniously constructed through electrospinning, calcination, and partial reduction techniques. The experimental results reveal the spontaneous electron flow from  $\text{In}_2\text{O}_3$  to Co at the interface, achieving an electron redistribution in the  $\text{Co/In}_2\text{O}_3$  heterojunction to improve the utilization of active sites. Theoretical findings further prove that the  $\varepsilon_{\text{d}}$  of Co in  $\text{Co/In}_2\text{O}_3-1$  is closer to the Fermi level than that of Co in Co (111), with  $\text{Co/In}_2\text{O}_3-1$  exhibiting the smallest  $\Delta G(\text{PDS})$ . This suggests that the remarkable synergistic interaction between Co and  $\text{In}_2\text{O}_3$  significantly boosts the nitrate-to-ammonia catalytic activity of  $\text{Co/In}_2\text{O}_3-1$ . This work offers fresh perspectives for the thoughtful design of efficient Mott–Schottky heterojunction electrocatalysts for electrocatalytic nitrate-to-ammonia conversion.

### Data availability

Data supporting the findings of this study are available within the article ESI.†

### Author contributions

R. Qi and Q. Jiang contributed equally to this work. X. Lu, Y. Wang and M. Zhong conceived the experiments and supervised this project. R. Qi performed the experiments. R. Qi, L. Deng, X. Yu, and B. Shi characterized the catalysts and analyzed the data. Q. Jiang and Y. Wang carried out the theoretical calculation. R. Qi and Q. Jiang wrote the manuscript. All authors have approved the final version of the manuscript.

### Conflicts of interest

The authors declare no conflict of interest.

### Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (52273056 and 22373097) and the Jilin Province Science and Technology Development Program (20220101056JC). Part of the computational time is supported by the High Performance and Computing Center of Jilin Province, Network and Computing Center in Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, and Computing Center in Jilin Normal University.

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