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

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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 NH₃ yield rates. Here, a Mott–Schottky type electrocatalyst of Co/In₂O₃ with a continuous fiber structure has been designed to boost the electrocatalytic nitrate-to-ammonia performance. The optimized Co/In₂O₃-1 catalyst exhibits an impressive NH₃ yield rate of 70.1 mg cm^{−2} h^{−1} at −0.8 V vs. the reversible hydrogen electrode (RHE), along with an NH₃ faradaic efficiency (FE) of 93.34% at 0 V vs. RHE, greatly outperforming the single-component Co and In₂O₃ samples. The yield rate of Co/In₂O₃-1 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 In₂O₃ 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.

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1. Introduction

NH₃ serves a variety of purposes, including fertilization, chemical production, and fuel.¹ 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 NH₃ production.^{2–10} 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 NH₃ generation.^{11–19} Fortunately, some cost-effective transition metal-based materials hold promise as nitrate-to-ammonia electrocatalysts,

particularly cobalt-based catalysts such as FeCoNiAlTi,²⁰ Co₂Mo₆S₈ (ref. 21) and Ru₁₅Co₈₅ (ref. 22) due to their superior intrinsic activities. Despite significant improvement in NH₃ faradaic efficiency (FE) that has been achieved at lower potentials, the NH₃ 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 NH₃ 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.^{23–25} 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.^{26,27} 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 (In₂O₃) is a common n-type semiconductor with a wide bandgap, low resistivity, and high catalytic activity,

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which is widely used in electrocatalysis.^{28–30} Therefore, we have demonstrated the clever construction of a continuous fibrous Mott–Schottky type Co/In₂O₃ heterostructure by combining Co with In₂O₃ 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/In₂O₃-1 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/In₂O₃-1 catalyst, and the d-band center (ϵ_d) of Co in Co/In₂O₃-1 aligns nearer to the Fermi level compared to Co (111). Therefore, Co/In₂O₃-1 exhibits the smallest thermodynamic reaction energy barrier ($\Delta G(\text{PDS})$) for the potential-determining step with the formation of NH₂^{*} from NH^{*} protonation, suggesting that the Mott–Schottky type Co/In₂O₃ heterostructure significantly enhances the electrocatalytic nitrate-to-ammonia activity. Therefore, the optimized Co/In₂O₃-1 catalyst presents a high NH₃ yield rate of 70.1 mg cm^{−2} h^{−1} 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/In₂O₃ heterostructure

The nanofibrous Co/In₂O₃ heterostructure is synthesized using an electrospinning, calcination, and partial reduction process (Fig. 1a). Initially, a poly(vinylpyrrolidone) (PVP)/Co²⁺/In³⁺

precursor nanofibrous membrane is prepared *via* an electrospinning technique and then immediately calcined in air to yield continuous and uniform Co₃O₄/In₂O₃ nanofibers with a rough surface and an average diameter of 144 nm (Fig. 1b and c). After being reduced in a H₂/Ar atmosphere at 400 °C for 4 h, Co₃O₄ can be selectively reduced, and then Co/In₂O₃ is obtained, and its fibrous morphology remains basically unchanged (Fig. 1d). However, the diameter of the Co/In₂O₃ nanofibers slightly decreases due to oxygen elimination (Fig. 1e). The transmission electron microscopy (TEM) image shows that Co/In₂O₃ 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 In₂O₃, respectively, and discernible grain boundaries can be observed, demonstrating the successful formation of the Co/In₂O₃ heterostructure. Fig. 1h exhibits the selected area electron diffraction (SAED) pattern, presenting legible rings attributed to the crystal planes of Co and In₂O₃, suggesting a polycrystalline characteristic of Co and In₂O₃. Moreover, the energy dispersive X-ray (EDX) spectrum presents strong Co, In and O signals in Co/In₂O₃-1 (Fig. S1, ESI†). Elemental mapping displays homogeneous distribution of these elements throughout the Co/In₂O₃-1 nanofiber (Fig. 1i). In addition, a series of control catalysts with diverse contents of Co are prepared using the same synthesis method, named In₂O₃-H, Co/In₂O₃-0.5, and Co/In₂O₃-2 (Fig. S2 and S3, ESI†), which exhibit similar nanofibrous morphologies and average diameters. And the inductively coupled plasma-optical emission spectrometry (ICP-OES) results confirm that

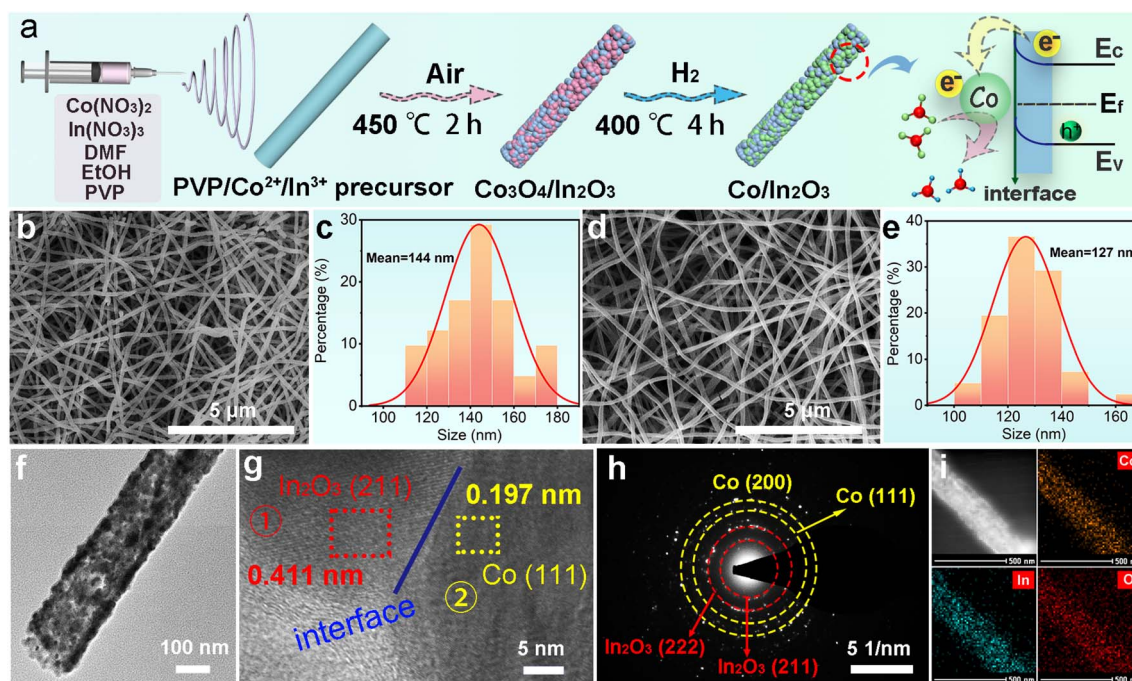


Fig. 1 (a) Synthesis procedure of Co/In₂O₃. (b) SEM image and (c) diameter distribution of Co₃O₄/In₂O₃ nanofibers. (d) SEM image and (e) diameter distribution of Co/In₂O₃ nanofibers. (f) TEM, (g) HRTEM and (h) SAED images of Co/In₂O₃. (i) HAADF-STEM image and EDX element mappings of Co–K, In–L, and O–K.

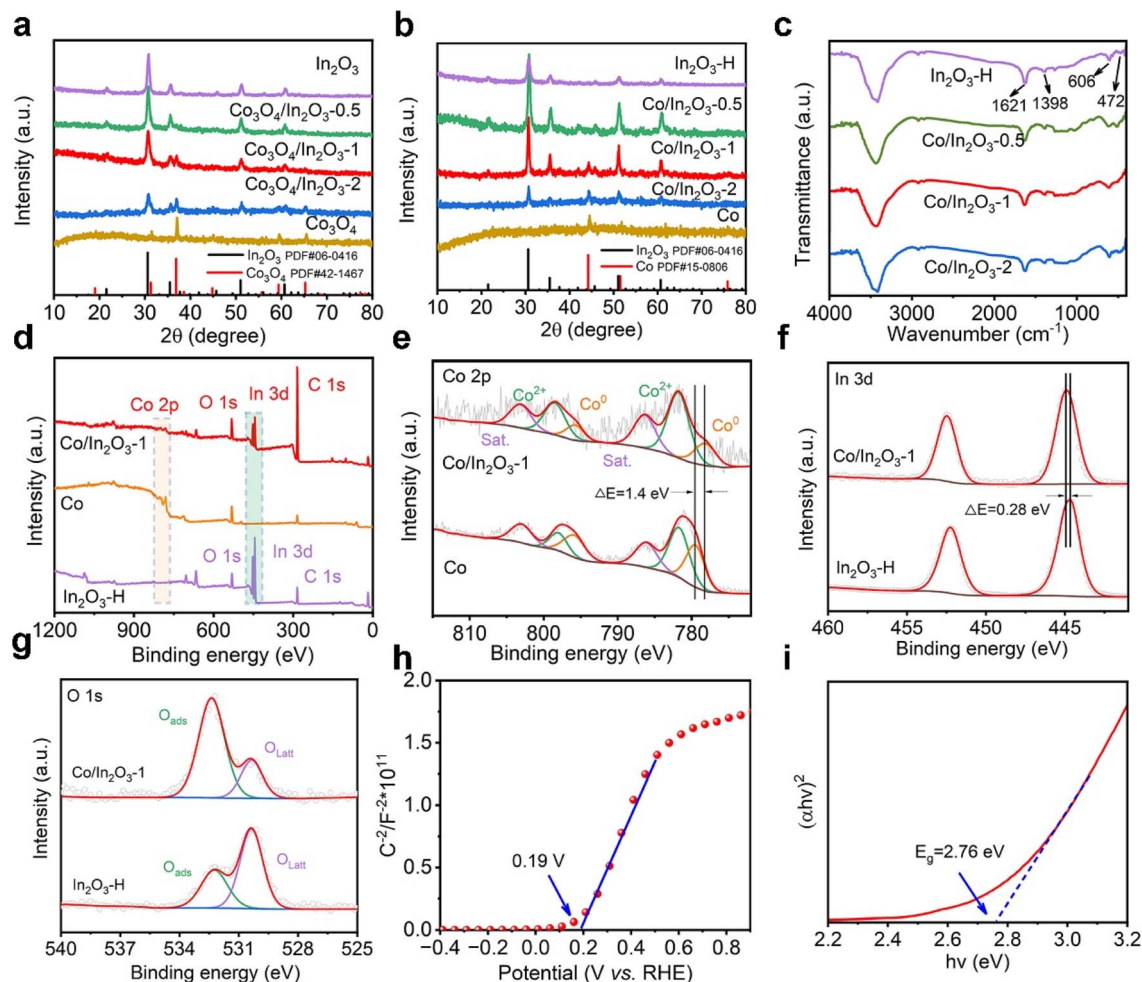


Fig. 2 (a) XRD profiles of In_2O_3 , $\text{Co}_3\text{O}_4/\text{In}_2\text{O}_3$ -0.5, $\text{Co}_3\text{O}_4/\text{In}_2\text{O}_3$ -1, $\text{Co}_3\text{O}_4/\text{In}_2\text{O}_3$ -2 and Co_3O_4 . (b) XRD profiles of In_2O_3 -H, $\text{Co}/\text{In}_2\text{O}_3$ -0.5, $\text{Co}/\text{In}_2\text{O}_3$ -1, $\text{Co}/\text{In}_2\text{O}_3$ -2 and Co. (c) FTIR spectra of In_2O_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 In_2O_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 In_2O_3 -H.

the molar ratio and feeding amount of Co and In are almost the same (Table S1, ESI†). After bare Co_3O_4 is reduced to Co metal, the fiber morphology collapses, reflecting that the presence of In_2O_3 can maintain the stability of the structure (Fig. S4, ESI†).

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 In_2O_3 (PDF #06-0416) and Co_3O_4 (PDF #42-1467) phases. After H_2/Ar reduction treatment at 400°C , XRD analysis exhibits the disappearance of Co_3O_4 peaks, replaced by those of Co (PDF #15-0806), while In_2O_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 H_2/Ar reduction temperature on $\text{Co}/\text{In}_2\text{O}_3$ synthesis is investigated. From Fig. S5 (ESI†), it can be seen that when the temperature is below 400°C , Co_3O_4 cannot be completely reduced, while a high temperature can destroy the In_2O_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 In_2O_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 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 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 In_2O_3 -H.³¹

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),^{32,33} notably at 778.1 eV and 795.7 eV 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).^{34,35} 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 In_2O_3 -H, signifying electron transfer from In_2O_3 to Co in the



heterostructure. Fig. 2g presents the O 1s XPS spectra of Co/In₂O₃-1 and In₂O₃-H, identifying two dominant peaks at a BE of 530.4 and 532.2 eV, indicating the lattice (O_{latt}) and the surface adsorbed oxygen (O_{ads}), respectively. The ratio of O_{ads}/(O_{ads} + O_{latt}) in Co/In₂O₃-1 is higher than that in In₂O₃-H, suggesting more surface oxygen defects accessible in Co/In₂O₃-1.³⁶

Rationally engineered Mott-Schottky interfaces stimulate spontaneous electron transfer, substantially enhancing charge transfer efficiency. The Mott-Schottky data for In₂O₃-H material are depicted in Fig. 2h, where the positive slope and the x-intercept suggest n-type In₂O₃-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 In₂O₃ 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 KNO₃. Initially, a substantial augmentation of current density occurs in the presence of KNO₃, 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/In₂O₃ is also larger than that of individual Co, In₂O₃-H, and Co₃O₄/In₂O₃, 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% *i*R-compensation, it is preliminarily believed that Co/In₂O₃-1 has the highest ammonia production activity due to its largest current density (Fig. 3a). Afterwards, using electrochemical impedance spectroscopy

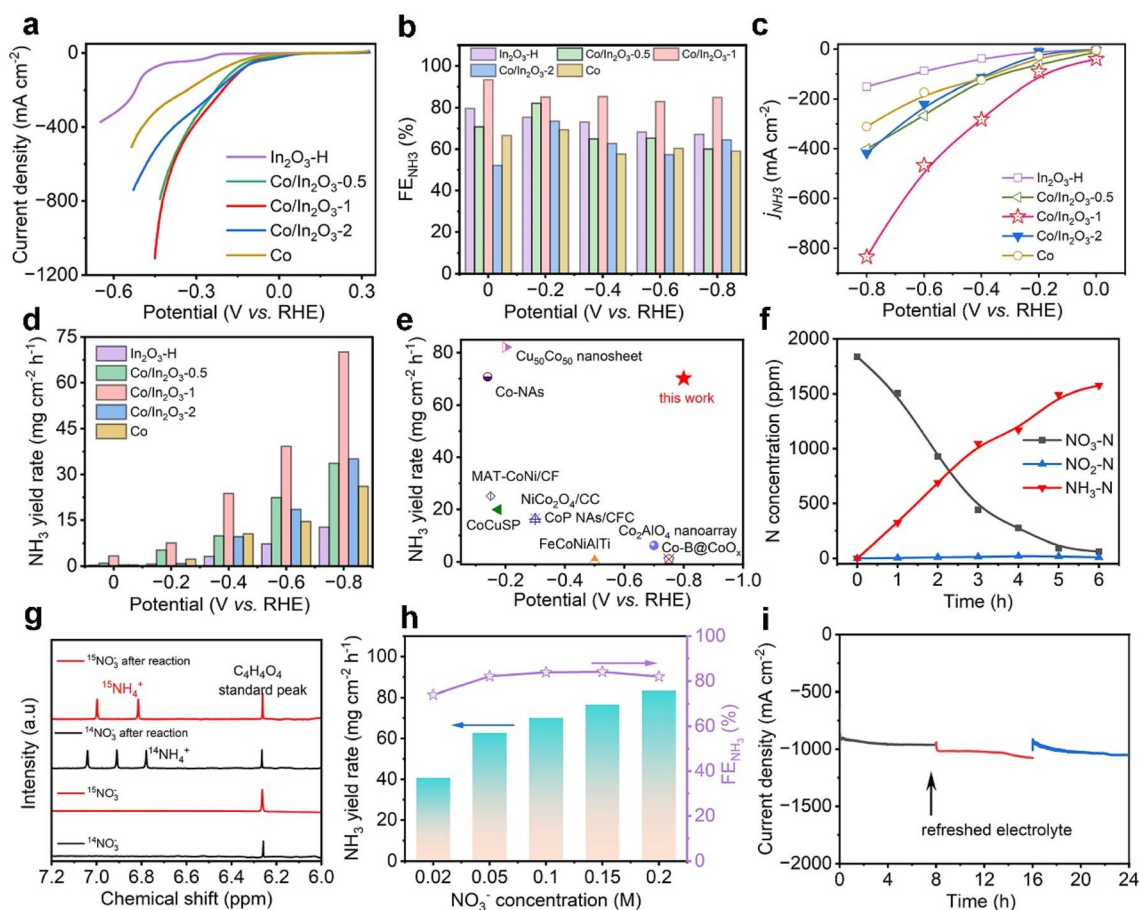


Fig. 3 (a) LSV curves of In₂O₃-H, Co/In₂O₃-0.5, Co/In₂O₃-1, Co/In₂O₃-2 and Co with 80% *i*R-correction. (b) NH₃ FE, (c) *j*_{NH₃} and (d) NH₃ yield rate of In₂O₃-H, Co/In₂O₃-0.5, Co/In₂O₃-1, Co/In₂O₃-2 and Co at varied potentials. (e) Comparison of the NH₃ yield rate of Co/In₂O₃-1 at a potential of −0.8 V for 1 h of electrocatalytic nitrate-to-ammonia conversion with that of other reported catalysts. (f) Time-dependent concentration changes of NO₃-N, NO₂-N and NH₃-N during the electrocatalytic nitrate-to-ammonia reaction by Co/In₂O₃-1 at −0.8 V in 1 M KOH with an initial concentration of 1800 mg L^{−1} of NO₃-N. (g) NMR spectra of the products produced before and after the electrocatalytic nitrate-to-ammonia reaction by Co/In₂O₃-1 in the electrolyte of 1 M KOH with 0.1 M K¹⁵NO₃ and 0.1 M K¹⁴NO₃ at −0.8 V. (h) The NH₃ FEs and NH₃ yield rate of Co/In₂O₃-1 at −0.8 V in the electrolyte of 1 M KOH with varied concentrations of KNO₃. (i) Chronoamperometric curves of Co/In₂O₃-1 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/In₂O₃-1 is calculated to be 6.89 Ω, which is lower than that of other control samples including In₂O₃-H (246 Ω), Co (14.14 Ω), Co/In₂O₃-0.5 (57.67 Ω), and Co/In₂O₃-2 (9.61 Ω). This signifies faster charge transfer and optimal electrocatalytic kinetics of Co/In₂O₃-1, benefitting the enhanced nitrate-to-ammonia performance. Cyclic voltammetry (CV) is executed, with the double-layer capacitance (*C_{dl}*) determined through potential scanning in the non-faraday region (Fig. S9, ESI†). The *C_{dl}* of Co/In₂O₃-1 is 3.2 mF cm⁻², larger than those of In₂O₃-H (1.7 mF cm⁻²), Co/In₂O₃-0.5 (3.1 mF cm⁻²), Co/In₂O₃-2 (1.8 mF cm⁻²) and Co (2.0 mF cm⁻²), showcasing more active sites to boost the nitrate-to-ammonia efficiency (Fig. S10, ESI†).

Chronoamperometry and UV-vis examinations are performed to determine the NH₃ yield rate and FE (Fig. S11–S14, ESI†). Initially, the NH₃ FE exceeds that of NO₂⁻ across diverse catalyst electrodes at different electrolysis voltages, indicating domination of NH₃ as the electrolysis product (Fig. S15, ESI†). As depicted in Fig. 3b, the NH₃ FE of Co/In₂O₃-1 reaches 93.34% at 0 V, surpassing that of In₂O₃-H (79.67% at 0 V), Co/In₂O₃-0.5 (82.16% at -0.2 V), Co/In₂O₃-2 (73.53% at -0.2 V) and Co (69.41% at -0.2 V). Concurrently, Co/In₂O₃-1 exhibits higher NH₃ partial current densities (*j_{NH₃}*) 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 NH₃ yield rate with a decrease in applied potential for the as-synthesized catalysts. Notably, the NH₃ yield rate of Co/In₂O₃-1 outperforms that of In₂O₃-H, Co/In₂O₃-0.5, Co/In₂O₃-2 and Co over the entire potential range, thanks to its exceptional NH₃ FE and *j_{NH₃}*. Specifically, at a potential of -0.8 V, the NH₃ yield rate of Co/In₂O₃-1 reaches 70.1 mg cm⁻² h⁻¹, superior to that of In₂O₃-H (12.7 mg cm⁻² h⁻¹), Co/In₂O₃-0.5 (33.7 mg cm⁻² h⁻¹), Co/In₂O₃-2 (35.1 mg cm⁻² h⁻¹) and Co (26.1 mg cm⁻² h⁻¹). Additionally, as depicted in Fig. 3e and Table S2 (ESI),† the NH₃ yield rate of Co/In₂O₃-1 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/In₂O₃-1 has the potential for large-scale NH₃ production. To evaluate the efficiency of Co/In₂O₃-1 in nitrate removal, a batch experiment is conducted with an initial NO₃⁻-N concentration of around 1800 ppm to detect the remaining products (Fig. 3f). Remarkably, nearly all NO₃⁻-N sources are reduced within 6 h, with an impressive NH₃-N selectivity of 88.7%. Following 6 h of electrolysis, NO₃⁻ is almost removed and there is nearly no obvious NO₂⁻ formation. These findings demonstrate that Co/In₂O₃-1 achieves an outstanding activity and NH₃ FE, showing potential for nitrate removal/conversion in wastewater. Subsequently, isotope labeling experiments ascertain the source of NH₃ (Fig. 3g). Compared to the negligible peak of NH₄⁺ before electrolysis, the ¹H NMR spectrum of the ¹⁴NO₃⁻ solution reveals three different ¹⁴NH₄⁺ peaks, while the ¹⁵NO₃⁻ solution features a notable ¹⁵NH₄⁺ double peak after 1 h of electrolysis at -0.8 V, demonstrating the origination of the produced ammonia from KNO₃ reduction.

Next, the concentration of KNO₃ in the electrolyte is adjusted to range from 0.02 M to 0.2 M to evaluate the environmental compatibility of Co/In₂O₃-1 for the electrocatalytic nitrate-to-ammonia reaction. First, as the KNO₃ concentration increases, the onset potential and current density increase as expected (Fig. S16, ESI†), accompanied by a progressive increase in the NH₃ yield rate, reaching 83.3 mg cm⁻² h⁻¹ at a KNO₃ concentration of 0.2 M (Fig. 3h). Second, the NH₃ FE consistently remains above 80%, indicating that Co/In₂O₃-1 maintains efficient electrocatalytic nitrate-to-ammonia activity across a broad concentration range. To assess the stability of Co/In₂O₃-1 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 NH₃ FE and yield rate remain consistent in the different cycles, with average values of 69.24% and 58.3 mg cm⁻² h⁻¹, affording evidence for the ideal durability of the Co/In₂O₃-1 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/In₂O₃-1 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/In₂O₃-1 interface with a relatively enhanced charge density, suggesting these locations as preferential adsorption sites for nitrate reduction. According to the previous study,³⁷ 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), In₂O₃ (211), and Co/In₂O₃-1, 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), In₂O₃ (211), and Co/In₂O₃-1, predominantly arising from the NOH* hydrogenation step. Upon protonating NOH* on the Co (111) surface, we observe its tendency towards forming N* and producing H₂O, with a reaction energy of -1.67 eV. However, on both In₂O₃ (211) and Co/In₂O₃-1, the formation of HNOH* is energetically favored after NOH* protonation. Notably, this process on In₂O₃ (211) is endothermic with an energy requirement of 2.28 eV, and it becomes spontaneous on Co/In₂O₃-1, 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 HNO₂^{*}, with a corresponding reaction energy ($\Delta G(\text{PDS})$) of 0.66 eV. On In₂O₃ (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 In₂O₃ (211) suggest that these two catalysts are unlikely to facilitate nitrate-to-ammonia efficiently. However, on Co/In₂O₃-1, the protonation of NH* to form NH₂^{*} 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/In₂O₃-1 by the strong



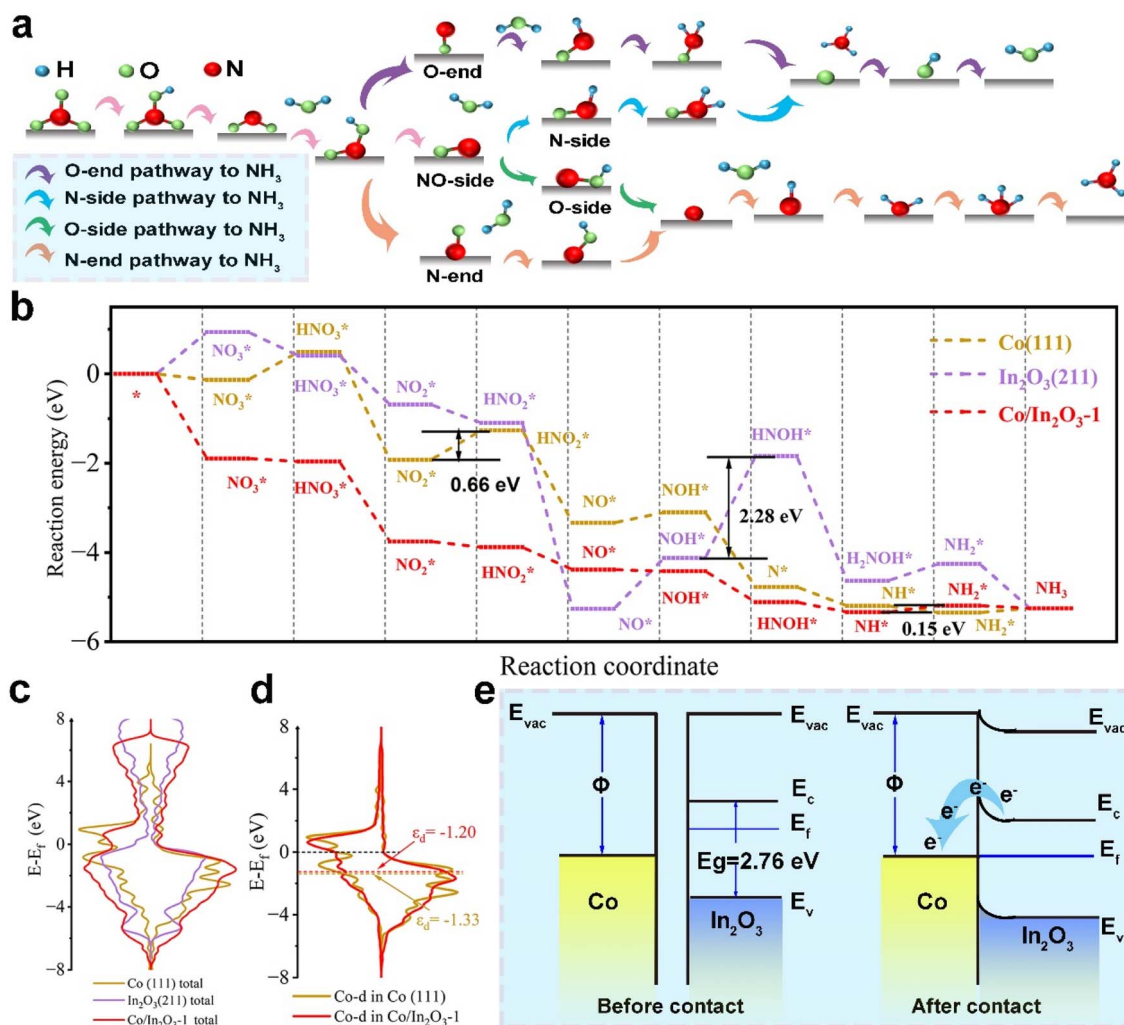


Fig. 4 (a) Illustration of potential reaction pathways of electrocatalytic nitrate-to-ammonia conversion. (b) Free energy diagrams for electrocatalytic nitrate-to-ammonia conversion on Co (111), In_2O_3 (211), and Co/ In_2O_3 . (c) Total density of states (TDOS) of Co (111), In_2O_3 (211), and Co/ In_2O_3 . (d) Projected density of states (PDOS) of the Co d orbital in the Co (111) and Co/ In_2O_3 . (e) The energy band diagrams of metallic Co and semiconductor In_2O_3 before and after the formation of a Mott-Schottky heterojunction.

interaction between Co and In_2O_3 . 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_2O_3 -1 noticeably increases compared to the In_2O_3 (211) substrate, suggesting improved electrical conductivity of Co/ In_2O_3 . Moreover, as shown in Fig. 4d, the d band center (ϵ_d) of Co in Co/ In_2O_3 -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_2O_3 interaction on the enhanced electrocatalytic activity of Co/ In_2O_3 -1.

Fig. 4e presents the energy band diagram of the Co/ In_2O_3 heterojunction, illustrating the mechanism behind its promoted nitrate-to-ammonia performance. This enhancement is attributed to the prompt and spontaneous electron transfer from In_2O_3 to Co, facilitated by the elevated Fermi level of In_2O_3 . Upon intimate contact, the In_2O_3 band drops, achieving equilibrium between Fermi levels of Co and In_2O_3 . 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_2O_3 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_2O_3 -1 heterojunction electrocatalyst exhibits a superior NH_3 FE and high NH_3 yield rate during the nitrate-to-ammonia process.

2.4 Zn- NO_3^- battery

Finally, an aqueous Zn- NO_3^- battery is constructed with Co/ In_2O_3 -1 as the cathode and Zn foil as the anode (Fig. S22a, ESI[†]), achieving both energy production and NH_3 manufacturing. Due to the excellent electrocatalytic nitrate-to-ammonia performance of Co/ In_2O_3 -1, the Zn- NO_3^- 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 mW cm^{-2} is achieved (Fig. S22c, ESI†). Fig. S23a (ESI†) illustrates the discharging curves of the Zn-NO_3^- battery at different current densities for 1 h, demonstrating stable battery voltage. An NH_3 yield rate of $1.36 \text{ mg h}^{-1} \text{ cm}^{-2}$ at 20 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 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 In_2O_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 ε_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 In_2O_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.

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References

- 1 J. Galloway, A. Townsend, J. Erisman, M. Bekunda, Z. Cai, J. Freney, L. Martinelli, S. Seitzinger and M. Sutton, *Science*, 2008, **320**, 889.
- 2 H. Xu, Y. Ma, J. Chen, W. Zhang and J. Yang, *Chem. Soc. Rev.*, 2022, **51**, 2710.
- 3 J. Liang, Z. Li, L. Zhang, X. He, Y. Luo, D. Zheng, Y. Wang, T. Li, H. Yan, B. Ying, S. Sun, Q. Liu, M. Hamdy, B. Tang and X. Sun, *Chem*, 2023, **9**, 1768.
- 4 Y. Xiong, Y. Wang, J. Zhou, F. Liu, F. Hao and Z. Fan, *Adv. Mater.*, 2023, **36**, 2304021.
- 5 H. Zhang, H. Wang, X. Cao, M. Chen, Y. Liu, Y. Zhou, M. Huang, L. Xia, Y. Wang, T. Li, D. Zheng, Y. Luo, S. Sun, X. Zhao and X. Sun, *Adv. Mater.*, 2024, **36**, 2312746.
- 6 L. Ouyang, J. Liang, Y. Luo, D. Zheng, S. Sun, Q. Liu, M. Hamdy, X. Sun and B. Ying, *Chin. J. Catal.*, 2023, **50**, 6.
- 7 T. Xie, X. He, L. He, K. Dong, Y. Yao, Z. Cai, X. Liu, X. Fan, T. Li, D. Zheng, S. Sun, L. Li, W. Chu, A. Farouk, M. Hamdy, C. Xu, Q. Kong and X. Sun, *Chin. Chem. Lett.*, 2024, **35**, 110005.
- 8 J. Miao, Q. Hong, L. Liang, G. Li, Z. Liu, S. Yin and Y. Chen, *Chin. Chem. Lett.*, 2024, **35**, 108935.
- 9 C. Cang and H. Zheng, *Chin. J. Struct. Chem.*, 2023, **42**, 100143.
- 10 Y. Kim, J. Ko, M. Shim, J. Park, H. Shin, Z. Kim, Y. Jung and H. Byon, *Chem. Sci.*, 2024, **15**, 2578.
- 11 Q. Hong, B. Miao, T. Wang, F. Li and Y. Chen, *Energy Lab.*, 2023, **1**, 220022.
- 12 K. Dong, Y. Yao, H. Li, H. Li, S. Sun, X. He, Y. Wang, Y. Luo, D. Zheng, Q. Liu, Q. Liu, D. Ma, X. Sun and B. Tang, *Nat. Synth.*, 2024, **3**, 763.
- 13 Y. Wang, C. Wang, M. Li, Y. Yu and B. Zhang, *Chem. Soc. Rev.*, 2021, **50**, 6720.
- 14 J. Zhou, M. Wen, R. Huang, Q. Wu, Y. Luo, Y. Tian, G. Wei and Y. Fu, *Energy Environ. Sci.*, 2023, **16**, 2611.
- 15 Z. Y. Wu, M. Karamad, X. Yong, Q. Huang, D. A. Cullen, P. Zhu, C. Xia, Q. Xiao, M. Shakouri, F. Y. Chen, J. Kim, Y. Xia, K. Heck, Y. Hu, M. Wong, Q. Li, L. Gates, S. Siahrostami and H. Wang, *Nat. Commun.*, 2021, **12**, 2870.
- 16 F. Y. Chen, Z. Y. Wu, S. Gupta, D. J. Rivera, S. V. Lambeets, S. Pecaut, J. Y. T. Kim, P. Zhu, Y. Z. Finfrook, D. M. Meira, G. King, G. Gao, W. Xu, D. Cullen, H. Zhou, Y. Han, D. Perea, C. Muhich and H. Wang, *Nat. Nanotechnol.*, 2022, **17**, 759.
- 17 Y. Wang, M. Sun, J. Zhou, Y. Xiong, Q. Zhang, C. Ye, X. Wang, P. Lu, T. Feng, F. Hao, F. Liu, J. Wang, Y. Ma, J. Yin, S. Chu, L. Gu, B. Huang and Z. Fan, *Proc. Natl. Acad. Sci. U. S. A.*, 2023, **120**, e2306461120.
- 18 Z. Zhang, A. Niu, Y. Lv, H. Guo, J. S. Chen, Q. Liu, K. Dong, X. Sun and T. Li, *Angew. Chem., Int. Ed.*, 2024, **63**, e202406441.
- 19 J. Liang, P. Liu, Q. Li, T. Li, L. Yue, Y. Luo, Q. Liu, N. Li, B. Tang, A. A. Alshehri, I. Shakir, P. Agboola, C. Sun and X. Sun, *Angew. Chem., Int. Ed.*, 2022, **61**, e202202087.



- 20 R. Zhang, Y. Zhang, B. Xiao, S. Zhang, Y. Wang, H. Cui, C. Li, Y. Hou, Y. Guo, T. Yang, J. Fan and C. Zhi, *Angew. Chem., Int. Ed.*, 2024, **63**, e202407589.
- 21 B. Li, F. Xia, Y. Liu, H. Tan, S. Gao, J. Kaelin, Y. Liu, K. Lu, T. J. Marks and Y. Cheng, *Nano Lett.*, 2023, **23**, 1459.
- 22 S. Han, H. Li, T. Li, F. Chen, R. Yang, Y. Yu and B. Zhang, *Nat. Catal.*, 2023, **6**, 402.
- 23 Z. Huang, J. Song, Y. Du, S. Xi, S. Dou, J. M. V. Nsanzimana, C. Wang, Z. J. Xu and X. Wang, *Nat. Energy*, 2019, **4**, 329.
- 24 R. Qi, L. Zhang, S. Ren, B. Shi, M. Zhong, Z. Chen and X. Lu, *Nano Lett.*, 2024, **24**, 8964.
- 25 Z. Sun, Y. Wang, L. Zhang, H. Wu, Y. Jin, Y. Li, Y. Shi, T. Zhu, H. Mao, J. Liu, C. Xiao and S. Ding, *Adv. Funct. Mater.*, 2020, **30**, 1910482.
- 26 X. Li, Y. Pan, H. Yi, J. Hu, D. Yang, F. Lv, W. Li, J. Zhou, X. Wu, A. Lei and L. Zhang, *ACS Catal.*, 2019, **9**, 4632.
- 27 Y. Li, W. Wang, B. Zhang, L. Fu, M. Wan, G. Li, Z. Cai, S. Tu, X. Duan, Z. W. Seh, J. Jiang and Y. Sun, *Nano Lett.*, 2021, **21**, 6656.
- 28 Y. Zhang, Z. Li, C. Qiang, K. Chen, Y. Guo and K. Chu, *ACS Nano*, 2024, **18**, 25316.
- 29 H. Sun, S. Lee, R. Tang, L. Wang, C. Yang, W. Liang, S. Zhao, C. Dong, A. Soon and J. Huang, *Adv. Funct. Mater.*, 2024, 2415859.
- 30 D. Deng, Y. Wang, J. Jiang, Y. Bai, Y. Chen, H. Zheng, H. Ou and Y. Lei, *Chem. Commun.*, 2024, **60**, 9364.
- 31 Q. Liang, S. Zhao, Z. Li, Z. Wu, H. Shi, H. Huang and Z. Kang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 40754.
- 32 C. Liu, Y. Li, T. Peng, S. Luo, Y. Feng, W. Xie, D. Lu and W. Sun, *J. Power Sources*, 2020, **468**, 228393.
- 33 W. Li, S. Chen, M. Zhong, C. Wang and X. Lu, *Chem. Eng. J.*, 2021, **415**, 128879.
- 34 X. Zhou, J. Wu, Q. F. Li, T. Zeng, Z. Ji, P. He, W. G. Pan, X. M. Qi, C. Y. Wang and P. K. Liang, *J. Catal.*, 2017, **355**, 26.
- 35 Q. Wang, Y. J. Chen, X. Liu, L. G. Li, L. Z. Du and G. H. Tian, *Chem. Eng. J.*, 2021, **421**, 129968.
- 36 J. Ding, Z. Geng, L. Li, Y. Wang, Y. Zuo, H. Li, M. Yang and G. Li, *J. Mater. Chem. A*, 2021, **9**, 12623.
- 37 L. Lv, Y. Shen, J. Liu, X. Meng, X. Gao, M. Zhou, Y. Zhang, D. Gong, Y. Zheng and Z. Zhou, *J. Phys. Chem. Lett.*, 2021, **12**, 11143.

