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# Concave Fe<sub>2</sub>O<sub>3</sub> nanocubes with high-index facets for ammonia production from electrocatalytic nitrate reduction†

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**An iron oxide catalyst with high-index (13–44) and (12–38) facets achieves a high faradaic efficiency of 96.54% and a production rate of 1.13 mmol h<sup>-1</sup> cm<sup>-2</sup> towards electrocatalytic nitrate reduction to ammonia at 250 mA cm<sup>-2</sup>.**

Ammonia (NH<sub>3</sub>) is an essential chemical feedstock extensively utilized in the industrial production of fertilizers and other chemicals.<sup>1</sup> Additionally, it shows promise as a carbon-free energy carrier, potentially replacing fossil fuels. Currently, the predominant method for industrial ammonia production is the Haber–Bosch process (H<sub>2</sub> + N<sub>2</sub> → NH<sub>3</sub>), which operates at high temperatures (300–500 °C) and pressures (15–35 MPa), consuming significant energy.<sup>2,3</sup> An alternative solution is the electrocatalytic nitrogen reduction reaction, which utilizes electricity to drive the conversion of N<sub>2</sub> to NH<sub>3</sub> under ambient conditions.<sup>4,5</sup> Unfortunately, due to the challenge of breaking the extremely stable N≡N bond (941 kJ mol<sup>-1</sup>), NRR suffers from low ammonia faradaic efficiency and yield, significantly limiting its potential for large-scale industrial application.<sup>6</sup> In contrast, electrocatalytic nitrate reduction reaction (NtrRR) is thermodynamically more feasible because the breaking of the N–O bond requires a much lower energy input (204 kJ mol<sup>-1</sup>).<sup>6,7</sup> Meanwhile, soluble nitrate is widely present in industrial and agricultural effluents, causing significant environmental pollution.<sup>8</sup> Therefore, converting nitrate into high value-added ammonia is crucial for both environmental protection and energy utilization.

However, the kinetics of NtrRR remain slow due to the complexity of the multi-electron coupled multi-proton transfer process. Additionally, the various reaction pathways leading to

different products (*e.g.*, NH<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub> and NO<sub>x</sub>) reduce the selectivity for the desired ammonia products.<sup>9</sup> As a result, efforts have been focused on developing NtrRR electrocatalysts with high activity and selectivity. Currently, noble metal-based catalysts (such as Ru and Pd) demonstrate superior NtrRR performance,<sup>10–12</sup> but their high cost and limited availability restrict their use in large-scale applications. In this context, non-noble metals such as Cu, Co, and Fe are promising alternatives,<sup>13–15</sup> though their performance needs further improvement.

Since electrocatalytic reactions occur on or near the catalysts' surface, the surface atomic arrangement (*i.e.*, the crystal facets) plays a crucial role in determining catalytic activity. Specifically, nanocatalysts with high-index facets often exhibit superior catalytic performance compared to their low-index counterparts.<sup>16,17</sup> Indeed, numerous electrocatalysts with well-engineered high-index facets have been developed for both the oxygen evolution reaction (OER)<sup>18–20</sup> and hydrogen evolution reaction (HER).<sup>18,21</sup> However, the exploration of NtrRR electrocatalysts with high-index facets remains rare, with most examples primarily focusing on noble metal catalysts.<sup>22</sup>

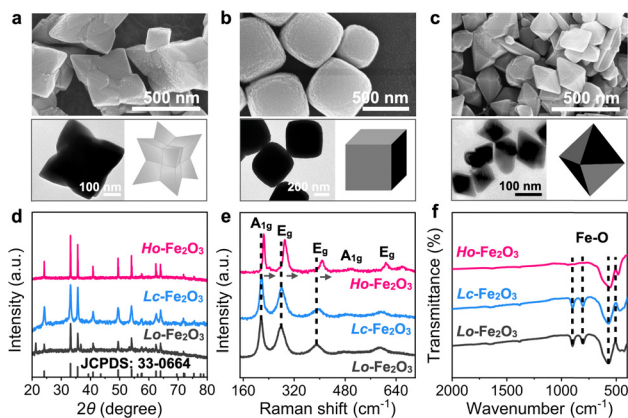
In this work, we systematically investigated the NtrRR performance of Fe<sub>2</sub>O<sub>3</sub> electrocatalysts with different crystal facets. We found that the octagonal Fe<sub>2</sub>O<sub>3</sub> with high-index (13–44) and (12–38) facets (H<sub>o</sub>-Fe<sub>2</sub>O<sub>3</sub>) exhibits outstanding NtrRR performance, achieving a high NH<sub>3</sub> faradaic efficiency of up to 96.54% and a production rate of 1.13 mmol h<sup>-1</sup> cm<sup>-2</sup> at 250 mA cm<sup>-2</sup>, outperforming most previously reported non-noble metal NtrRR catalysts. Furthermore, we assembled a “batterolyzer” by coupling the anodic N<sub>2</sub>H<sub>4</sub> oxidation reaction and cathodic NtrRR, following a concept previously developed by our group.<sup>23</sup> This batterolyzer combines the features of a traditional battery and electrolyzer, concurrently generating electricity (with a peak power density of 2.85 mW cm<sup>-2</sup>) and high-value ammonia.

We synthesized H<sub>o</sub>-Fe<sub>2</sub>O<sub>3</sub> catalysts with high-index (13–44) and (12–38) facets using a recipe we previously developed.<sup>24</sup> For comparison, we also synthesized Fe<sub>2</sub>O<sub>3</sub> cubes with low-index (10–12) facets (L<sub>c</sub>-Fe<sub>2</sub>O<sub>3</sub>)<sup>25</sup> and octahedra with low-index (10–14)

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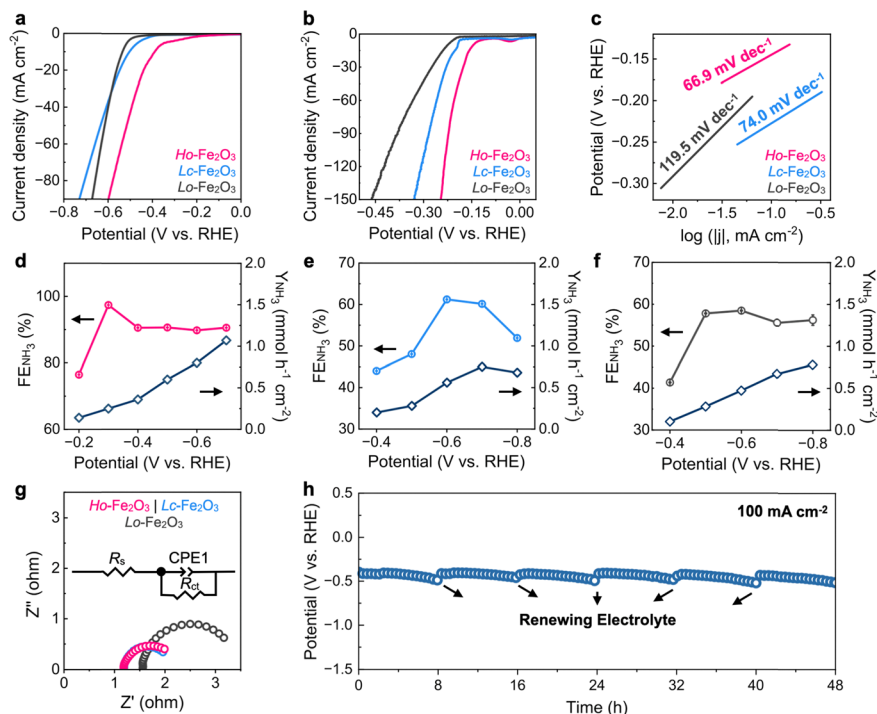
**Fig. 1** Physical characterizations of the  $\text{Fe}_2\text{O}_3$  catalysts. SEM, TEM images and structure illustrations of (a)  $\text{H}_\text{o}$ - $\text{Fe}_2\text{O}_3$ , (b)  $\text{L}_\text{c}$ - $\text{Fe}_2\text{O}_3$ , and (c)  $\text{L}_\text{o}$ - $\text{Fe}_2\text{O}_3$ . (d) XRD patterns, (e) Raman spectra and (f) FTIR spectra of the three catalysts.

facets ( $\text{L}_\text{o}$ - $\text{Fe}_2\text{O}_3$ )<sup>26</sup> using a reported wet chemical method (see details in ESI†). Scanning electron microscopy (SEM) images show the three catalysts have well-defined morphologies (Fig. 1a–c). Transmission electron microscopy (TEM) images reveal that the average particle sizes of  $\text{H}_\text{o}$ - $\text{Fe}_2\text{O}_3$ ,  $\text{L}_\text{c}$ - $\text{Fe}_2\text{O}_3$ , and  $\text{L}_\text{o}$ - $\text{Fe}_2\text{O}_3$  are about 200, 300, and 100 nm, respectively. X-ray diffraction (XRD) analysis suggests that the diffraction peaks of the synthesized  $\text{Fe}_2\text{O}_3$  with different exposed facets align with those of hematite (JCPDS no. 33-0664). Raman

spectra further confirm the successful synthesis of the three  $\text{Fe}_2\text{O}_3$  catalysts (Fig. 1e). In addition, the Raman peaks of  $\text{H}_\text{o}$ - $\text{Fe}_2\text{O}_3$  shift to higher wavenumber, indicating the presence of strain and stress due to the high-index facets.<sup>27</sup> Fourier transform infrared spectroscopy (FTIR) spectra also reveal that all the characteristic peaks can be attributed to  $\text{Fe}_2\text{O}_3$  (Fig. 1f).

We investigated the NtrRR performance of the three electrocatalysts. Given that NtrRR generates additional hydroxyl groups, thereby alkalinizing the electrolyte, we selected 1 M KOH as the supporting electrolyte. We first assessed the NtrRR activity of  $\text{H}_\text{o}$ - $\text{Fe}_2\text{O}_3$  along with  $\text{L}_\text{c}$ - $\text{Fe}_2\text{O}_3$  and  $\text{L}_\text{o}$ - $\text{Fe}_2\text{O}_3$  controls, using stabilized polarization curves in 1 M KOH electrolyte with and without 0.1 M  $\text{KNO}_3$ . No significant HER is observed for  $\text{H}_\text{o}$ - $\text{Fe}_2\text{O}_3$ ,  $\text{L}_\text{c}$ - $\text{Fe}_2\text{O}_3$  and  $\text{L}_\text{o}$ - $\text{Fe}_2\text{O}_3$  (Fig. 2a). Notably,  $\text{H}_\text{o}$ - $\text{Fe}_2\text{O}_3$  catalysts require only  $-0.145$  V vs. RHE to initiate NtrRR, which is much lower than that of  $\text{L}_\text{c}$ - $\text{Fe}_2\text{O}_3$  and  $\text{L}_\text{o}$ - $\text{Fe}_2\text{O}_3$  catalysts ( $-0.225$  and  $-0.194$  V vs. RHE, respectively, Fig. 2b). Tafel plots further reveal the fastest NtrRR kinetics on  $\text{H}_\text{o}$ - $\text{Fe}_2\text{O}_3$ , indicated by the smallest slope ( $66.93$  mV  $\text{dec}^{-1}$ , Fig. 2c). To exclude the impact of surface area, we performed cyclic voltammetry (CV) tests within non-faradaic regions and calculated the double layer capacitances ( $C_{\text{dl}}$ , Fig. S2, ESI†). The results reveal that the three catalysts have very similar  $C_{\text{dl}}$  values, and thus similar electrochemically active surface areas (ECSA). This indicates that the different exposure of crystal facets, rather than the surface area, primarily accounts for the varying NtrRR activities.

We then conducted a 7200 s chronopotentiometry test at  $250$   $\text{mA cm}^{-2}$  (Fig. S3, ESI†) and subsequently evaluated the



**Fig. 2** Electrocatalytic NtrRR performance. (a) Polarization curves in 1 M KOH (with  $iR$  correction). (b) Polarization curves in 1 M KOH/0.1 M  $\text{KNO}_3$  (with  $iR$  correction) and (c) the derived Tafel plots of the three catalysts. (d)–(f) Ammonia faradaic efficiencies of (d)  $\text{H}_\text{o}$ - $\text{Fe}_2\text{O}_3$ , (e)  $\text{L}_\text{c}$ - $\text{Fe}_2\text{O}_3$  and (f)  $\text{L}_\text{o}$ - $\text{Fe}_2\text{O}_3$  in 1 M KOH/0.1 M  $\text{KNO}_3$  mixed electrolyte. (g) EIS spectra of the three catalysts. (h) Chronopotentiometry curves of the  $\text{H}_\text{o}$ - $\text{Fe}_2\text{O}_3$  catalyst at  $100$   $\text{mA cm}^{-2}$  in 1 M KOH/0.1 M  $\text{KNO}_3$  mixed electrolyte.

ammonia production efficiency using ion chromatography (IC) (see ammonia and nitrate standard curves in Fig. S4, ESI†). The  $H_o$ - $Fe_2O_3$  catalysts exhibit superb faradaic efficiency (96.54%, Fig. S5a, ESI†) and ammonia yield ( $1.13 \text{ mmol h}^{-1} \text{ cm}^{-2}$ , Fig. S5b, ESI†), whereas  $L_c$ - $Fe_2O_3$  and  $L_o$ - $Fe_2O_3$  show lower faradaic efficiencies (75.98% and 72.11%) and ammonia yields ( $0.89$  and  $0.84 \text{ mmol h}^{-1} \text{ cm}^{-2}$ ). This evidence suggests that  $H_o$ - $Fe_2O_3$  exposing high-index facets not only enhances  $NO_3^-$  adsorption and activation but also effectively improves ammonia faradaic efficiency and yield rate. Notably, the three catalysts produced negligible nitrite byproducts during the chronopotentiometry tests. Specifically, the nitrite faradaic efficiencies of the  $H_o$ - $Fe_2O_3$ ,  $L_c$ - $Fe_2O_3$  and  $L_o$ - $Fe_2O_3$  catalysts were only 3.01%, 3.66% and 4.61%, respectively (Fig. S5a, ESI†). Overall, the NtrRR performance of  $H_o$ - $Fe_2O_3$  catalysts significantly outperforms the vast majority of recently reported NtrRR catalysts (Table S1, ESI†).

In addition to the chronopotentiometry tests, we also performed chronoamperometry tests (Fig. S6a–c, ESI†) to further investigate the effect of reaction potential on NtrRR faradaic efficiency and ammonia yield rate (Fig. 2d–f). The ammonia faradaic efficiency of the  $H_o$ - $Fe_2O_3$  catalyst remains consistently above 90% from  $-0.3$  to  $-0.7 \text{ V vs. RHE}$  (Fig. 2d). More importantly, at  $-0.7 \text{ V vs. RHE}$ , the  $H_o$ - $Fe_2O_3$  catalyst achieves a high ammonia yield rate of  $1.07 \text{ mmol h}^{-1} \text{ cm}^{-2}$ . In contrast, the faradaic efficiencies of the  $L_o$ - $Fe_2O_3$  and  $L_c$ - $Fe_2O_3$  catalysts for ammonia production are below 60%, and their ammonia yield rates are less than  $1 \text{ mmol h}^{-1} \text{ cm}^{-2}$  (Fig. 2e and f). These results indicate that the  $H_o$ - $Fe_2O_3$  catalyst maintains the highest intrinsic NtrRR activity for ammonia production among the three catalysts, suggesting that the high-index facets of  $H_o$ - $Fe_2O_3$  optimize the adsorption and reaction of intermediates for NtrRR. In addition, we measured the electrochemical impedance spectra (EIS), which show that both  $H_o$ - $Fe_2O_3$  and  $L_o$ - $Fe_2O_3$  exhibit lower impedance (Fig. 2g and Table S2, ESI†), indicating faster electron transfer, consistent with the Tafel results. The  $H_o$ - $Fe_2O_3$  catalysts could stably produce ammonia at  $100 \text{ mA cm}^{-2}$  for at least 48 h (Fig. 2h). Notably, no hydrogen production was observed during this process, and the decreased potential could be restored by renewing the electrolyte.

All three catalysts exhibit decent stability over long-term tests (Fig. 2h and Fig. S7, ESI†). We further conducted a series of physical characterization studies to examine their structural stability. SEM images reveal no significant changes in bulk morphology, although the surfaces of the catalysts appear smoother after NtrRR, suggesting slight surface reconstruction (Fig. S8, ESI†). However, XRD analysis (Fig. 3a and Fig. S9, ESI†) indicates that the phase composition remains unchanged for all three catalysts, explaining their outstanding stability. Additionally, the Fe 2p X-ray photoelectron spectroscopy (XPS) spectra of the catalysts after long-term stability tests are nearly identical to those of pristine samples (Fig. 3b and Fig. S10, ESI†). We further collected the LSV curve of  $H_o$ - $Fe_2O_3$  after stability test, which shows that the activity of  $H_o$ - $Fe_2O_3$  barely changes (Fig. S11, ESI†). These results again demonstrate that

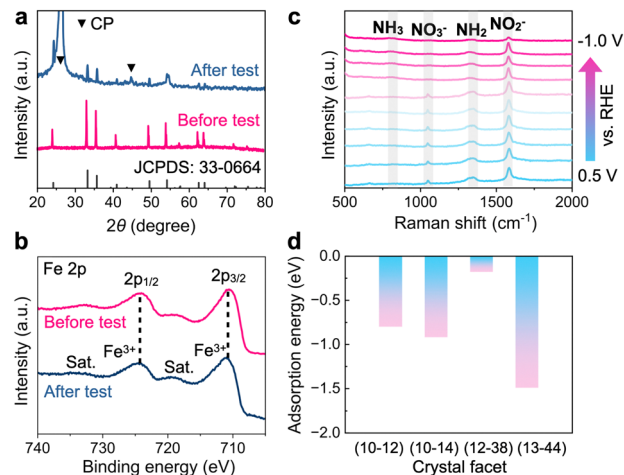


Fig. 3 (a) XRD pattern, and (b) Fe 2p XPS spectrum of  $H_o$ - $Fe_2O_3$  after long-term stability tests. (c) *In situ* Raman spectra of  $H_o$ - $Fe_2O_3$  at various potentials. (d) Adsorption energy of different crystal facets for  $NO_3^-$ .

the exposure of  $Fe_2O_3$  to different crystal facets is the primary factor affecting its NtrRR performance.

To further investigate the NtrRR reaction pathway on  $H_o$ - $Fe_2O_3$ , we performed *in situ* Raman tests. The evolution of Raman peaks indicates the disappearance of the characteristic peaks of  $NO_3^-$ , along with the appearance of the characteristic peaks of  $NO_2^-$ ,  $NH_2$ , and  $NH_3$  as the applied potential gradually decreases from  $0.5$  to  $-1.0 \text{ V vs. RHE}$  (Fig. 3c). Thus, the reaction pathway likely follows  $NO_3^- \rightarrow NO_2^- \rightarrow NH_2 \rightarrow NH_3$ , which has been observed in NtrRR on various catalysts.<sup>28–30</sup> *In situ* EIS analysis reveals that  $H_o$ - $Fe_2O_3$  exhibits a smaller phase angle than  $L_o$ - $Fe_2O_3$  and  $L_c$ - $Fe_2O_3$  under the same bias, indicating that more charges participated in the redox reaction (Fig. S12, ESI†). To better understand the role of crystal facets, we conducted theoretical simulations. Previous studies suggest that the adsorption of  $NO_3^-$  is a crucial step that directly determines the NtrRR performance.<sup>22,31</sup> We calculated the adsorption energies of  $NO_3^-$  on different crystal facets of  $Fe_2O_3$  (Fig. 3d). The result shows that the (13–44) has the most negative value of  $-1.488 \text{ eV}$ , followed by (10–14) and (10–12). Such favourable adsorption would promote the reaction kinetics, leading to enhanced NtrRR activity of  $H_o$ - $Fe_2O_3$ .

We further assembled a batteryolyzer by coupling the cathodic NtrRR and anodic hydrazine oxidation reaction (Fig. S13, ESI†).<sup>23</sup> Hydrazine ( $N_2H_4$ ) is widely distributed in industrial wastewaters such as pharmaceuticals, dyes, and rubber, *etc.* We used  $RuO_x$  as the anode catalyst and  $H_o$ - $Fe_2O_3$  as the cathode catalyst. The batteryolyzer shows a maximum discharge power density of up to  $2.85 \text{ mW cm}^{-2}$  at the current density of  $18 \text{ mA cm}^{-2}$  (without IR correction, Fig. 4a). This device can generate power continuously for at least 25 000 s at  $10 \text{ mA cm}^{-2}$  (Fig. 4b). In short, the batteryolyzer proposed in this study provide an alternative and promising green approach for practical ammonia production and sustained power output.

In conclusion, we demonstrated the crystal facet-dependent NtrRR performance of non-noble metal  $Fe_2O_3$  catalysts.

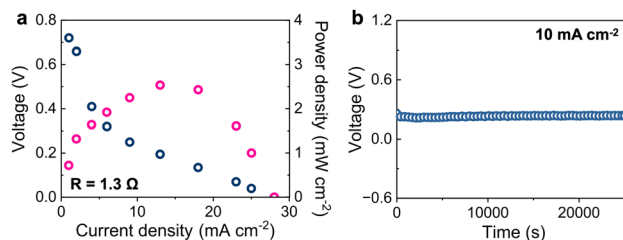


Fig. 4 (a) Polarization and power density curves, and (b) long-term chronopotentiometry curve under  $10 \text{ mA cm}^{-2}$  output of a  $\text{N}_2\text{H}_4$ -nitrate battery.

Specifically, we showed that the  $\text{H}_0\text{-Fe}_2\text{O}_3$  catalyst with high-index (13–44) and (12–38) facets exhibits optimal NtrRR activity and selectivity, achieving a high faradaic efficiency of up to 96.54% and an ammonia production rate of up to  $1.13 \text{ mmol h}^{-1} \text{ cm}^{-2}$  at  $250 \text{ mA cm}^{-2}$ . In addition, the developed catalysts enabled the  $\text{N}_2\text{H}_4$ -nitrate battery to generate electricity at a high power density of  $2.85 \text{ mW cm}^{-2}$ , with sustained nitrate-to-ammonia conversion. Our work not only establishes  $\text{H}_0\text{-Fe}_2\text{O}_3$  as a highly active non-noble metal NtrRR electrocatalyst, but also highlights the important role of high-index facets in improving electrocatalytic performance.

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## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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