

Main-group indium single-atom catalysts for electrocatalytic NO reduction to NH₃†Cite this: *J. Mater. Chem. A*, 2023, 11, 6814

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Main-group metal elements show great potential for exploring high-performance catalysts for electrochemical reduction of NO to NH₃ (NORR) but remain largely unexplored. Herein, as a proof-of-concept, main-group In single atoms confined in an amorphous MoO₃ substrate (In₁/a-MoO₃) are explored as an efficient NORR catalyst, showing a maximum NH₃ yield of 242.6 μmol h⁻¹ cm⁻² and NH₃-faradaic efficiency of 92.8%. Further experiments and theoretical results identify single-site In atoms as the dominating active centers to simultaneously inhibit the hydrogen evolution and optimize the hydrogenation energetics of the NO-to-NH₃ pathway.

Ammonia is a critical industrial chemical which is widely used in modern economic development.^{1–3} Electrochemical N₂ fixation through N₂ electroreduction (NRR) enables sustainable NH₃ synthesis under ambient conditions with near-zero CO₂ emissions.^{4–8} Unfortunately, the NRR is still far from being practicable on account of the competitive hydrogen evolution reaction (HER) and ultrastrong N≡N bond.^{9–15}

Compared with the NRR, electrochemical NO-to-NH₃ conversion (NORR) is a more energy-efficient and practically feasible approach for sustainable NH₃ synthesis.^{16–21} Meanwhile, NO is one of the common atmospheric pollutants, arising from vehicle exhaust emissions and insufficient combustion of fossil fuels.¹⁸ Therefore, the NORR represents a fascinating method for realizing both detrimental NO treatment and effective NH₃ electrosynthesis.¹⁸ Nevertheless, the NORR is a multi-step process involving a complex five-electron process and hindered by the competing HER.^{22–25} Therefore, exploring high-performance catalysts to achieve both NORR promotion and HER inhibition is urgently demanded.

Diverse transition metal-based materials have been reported as active NORR catalysts,^{26–29} by virtue of their partially occupied

d-orbitals to enhance NO adsorption and dissociation. Nonetheless, d-orbitals also contribute to *H binding on the catalyst surface, which is beneficial for the competitive HER and unfavorable for FE_{NH₃}.³⁰ Alternatively, main-group metals, such as In, Sn, Sb and Bi, with partially occupied p-orbitals but an intrinsic characteristic of poor *H binding, have attracted growing attention for selective NH₃ electrosynthesis.^{31–36} On the other hand, single atom catalysts (SACs) with isolated metal sites have been extensively demonstrated to exhibit superior properties for various electrocatalytic reactions owing to their maximized atomic utilization and unique coordination configuration.^{37–42} Inspired by the above, main-group SACs may hold great promise toward the active and selective NORR.

In this study, as a proof-of-concept, we first explore main-group In single atoms confined in amorphous MoO₃ (In₁/a-MoO₃) as an effective NORR catalyst, which exhibits a maximum FE_{NH₃} of 92.8% and NH₃ yield rate of 242.6 μmol h⁻¹ cm⁻². Detailed experiments and computational studies are performed to elucidate the origin for the exceptional NORR properties of In₁/a-MoO₃.

In₁/a-MoO₃ was prepared by a facile supercritical CO₂ approach.^{43–45} The characteristic transmission electron microscopy (TEM, Fig. 1a) image of In₁/a-MoO₃ presents a nanosheet morphology, while the high-resolution TEM (HRTEM, Fig. 1b) image shows no obvious lattice fringes, similar to bare a-MoO₃ (Fig. S1†). The corresponding fast Fourier transform (FFT, Fig. 1c) pattern unravels a sun-like feature, consistent with the lunar halo displayed in the selected area electron diffraction (SAED, Fig. S2†) pattern. Additionally, no noticeable diffraction peaks can be seen in the X-ray diffraction (XRD, Fig. 1d) pattern. All these HRTEM/FFT/SAED/XRD results confirm the amorphous structure of In₁/a-MoO₃. In the aberration-corrected high angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) image (Fig. 1e), there are numerous bright points (marked by red circles) that are highly dispersed on the amorphous substrate, and this can be further unveiled by the 3D intensity profile (Fig. 1f), proving that In species are atomically dispersed on a-MoO₃. Elemental

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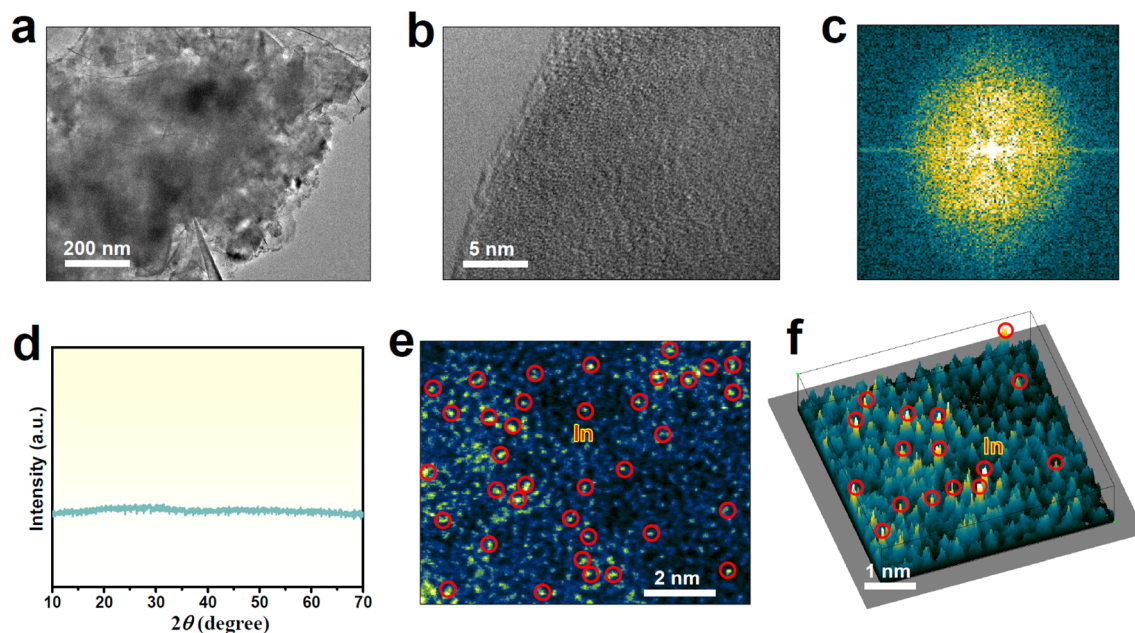


Fig. 1 Characterization of $\text{In}_1/\text{a-MoO}_3$: (a) TEM image, (b) HRTEM image and corresponding FFT pattern (c), (d) XRD pattern, (e) AC-HAADF-STEM image and corresponding (f) 3D intensity profile.

mapping images (Fig. S3†) display an even distribution of In single atoms over the a- MoO_3 support. The In content in $\text{In}_1/\text{a-MoO}_3$ is measured to be as high as 8.2 wt%, much higher than that of reported In single atoms on carbon substrates.^{40,46,47}

The valence states and local atomic coordination structure of $\text{In}_1/\text{a-MoO}_3$ are studied by X-ray absorption fine structure (XAFS) analyses. The In K-edge X-ray absorption near-edge structure (XANES) spectra show that the absorption edge of $\text{In}_1/\text{a-MoO}_3$ (Fig. 2a) lies between In foil and In_2O_3 references, indicating

that In single atoms are in a positive valence state.⁴⁸ In the In K-edge extended X-ray adsorption fine structure (EXAFS) spectra (Fig. 2b), $\text{In}_1/\text{a-MoO}_3$ shows a distinct peak located at 1.61 Å, which is ascribed to the In–O coordination bond. The absence of the In–In coordination bond (2.97 Å) indicates that In presents as an isolated atomic state,^{49–52} consistent with the AC-HAADF-STEM observation (Fig. 1e). Meanwhile, unlike the In_2O_3 reference, no second-shell In–O–In bond (3.09 Å) shows up in $\text{In}_1/\text{a-MoO}_3$, excluding the existence of In_2O_3 species on

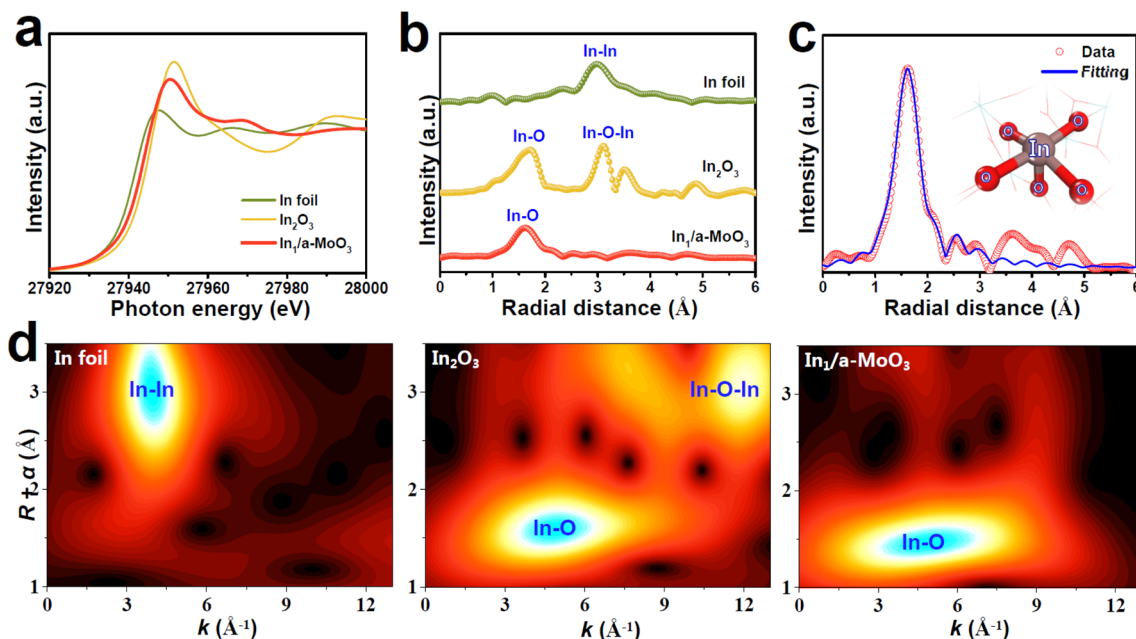


Fig. 2 (a) In K-edge XANES, (b) EXAFS spectra and (d) WT pattern of $\text{In}_1/\text{a-MoO}_3$ and reference samples. (c) EXAFS fitting curve of $\text{In}_1/\text{a-MoO}_3$ (inset: fitting model).

In₁/a-MoO₃. These EXAFS findings can be further corroborated by wavelet transform (WT) analysis (Fig. 2d), revealing that In₁/a-MoO₃ exhibits the solo In–O maximum intensity with no presence of In–In/In–O–In WT signals. Quantitative EXAFS fitting of In₁/a-MoO₃ (Fig. 2c and S4†) uncovers that single-site In is coordinated with five O atoms to form an In₁–O₅ motif. Moreover, *ab initio* molecular dynamic (AIMD, Fig. S5†) simulations reveal that the In₁–O₅ motif can well maintain the equilibrium temperature/energy states at temperature as high as 500 K, confirming the high thermodynamic stability of the In₁–O₅ motif, which is attributed to the strong In₁–O₅ electronic coupling to well stabilize In single atoms on the a-MoO₃ substrate (Fig. S6†).

The electrocatalytic NORR properties of In₁/a-MoO₃ are assessed in a gas-tight H-type cell with 0.5 M Na₂SO₄.²⁹ Colorimetric methods are used to detect the liquid reduction products (Fig. S7 and S8†), while gas products are detected by gas chromatography. To initially assess the NORR activity of In₁/a-MoO₃, we perform linear sweep voltammetry (LSV) measurements (Fig. 3a). A remarkable current density (*j*) enhancement can be observed in NO-solution relative to Ar-solution, verifying a good electrocatalytic NORR ability of In₁/a-MoO₃. We then quantify the NORR performance of In₁/a-MoO₃ at various potentials through combined chronoamperometry (Fig. 3b) and colorimetric methods. As shown in Fig. 3c, with increasing the potentials, In₁/a-MoO₃ shows a volcano-type variation in both the NH₃ yield rate and FE_{NH₃}, attaining their highest values of 242.6 μmol h⁻¹ cm⁻² and 92.8% at -0.6 V, respectively, which are higher than those of nearly all previously reported catalysts (Fig. 3d, Table S2†). Strikingly, In₁/a-MoO₃ drastically outperforms bare a-MoO₃ in both the NH₃ yield rate and FE_{NH₃} (Fig. S9 and S10†), suggesting that single-atomic In introduction plays a pivotal role in greatly boosting the NORR performance. The significant reduction of the NH₃ yield rate and FE_{NH₃} at -0.7 V is

due to the enhancement in the competing HER process (Fig. 3e). Meanwhile, Fig. 3e shows that the FE_{NH₃} of In₁/a-MoO₃ is much higher than the FEs of other nitrogen-containing N₂ and N₂H₄ by-products, in accordance with the partial current density data (Fig. S11†), indicating that In₁/a-MoO₃ has an exceptional NORR selectivity for NO-to-NH₃ conversion. The NORR stability of In₁/a-MoO₃ is assessed by 15 h of continuous electrolysis (Fig. S12†), which shows that the current density is rather steady and the corresponding FE_{NH₃} does not show remarkable changes, suggesting that In₁/a-MoO₃ has good long-term stability. Besides, during seven electrolysis cycles (Fig. 3f), the resulting NH₃ yield rates and FE_{NH₃} only slightly fluctuate, proving the excellent cycling stability of In₁/a-MoO₃.⁵³ After the stability test, In₁/a-MoO₃ well retains its nanosheet morphology, amorphous structure and atomic Ir dispersion state (Fig. S13†), demonstrating that the surface reconstruction of In₁/a-MoO₃ barely occurs and thus In₁/a-MoO₃ possesses high structural stability. Furthermore, the control colorimetric test (Fig. S14†), Ar–NO alternating cycle test (Fig. S15†), and ¹H nuclear magnetic resonance test (NMR, Fig. S16†) prove that the generated NH₃ comes from the NORR process.

Theoretical computations are carried out to shed light on the NORR mechanism of In₁/a-MoO₃. Based on the EXAFS fitting result (Fig. 2c), an isolated In₁–O₅ motif constructed on a-MoO₃ is employed to simulate In₁/a-MoO₃. Upon the adsorption of NO on the In site, the charge density difference map (Fig. 4a) depicts a considerable *NO/In electronic interaction. Notably, *NO shows pronounced positive charge accumulation, implying that the In site can effectively activate the NO molecule through a “σ-donation” mechanism. Prior to assessing the hydrogenation energetics of the NORR pathway, we conduct online differential electrochemical mass spectrometry (DEMS) to monitor the key intermediates and determine the optimal reaction path on In₁/a-MoO₃. Fig. 4b displays the absence of the

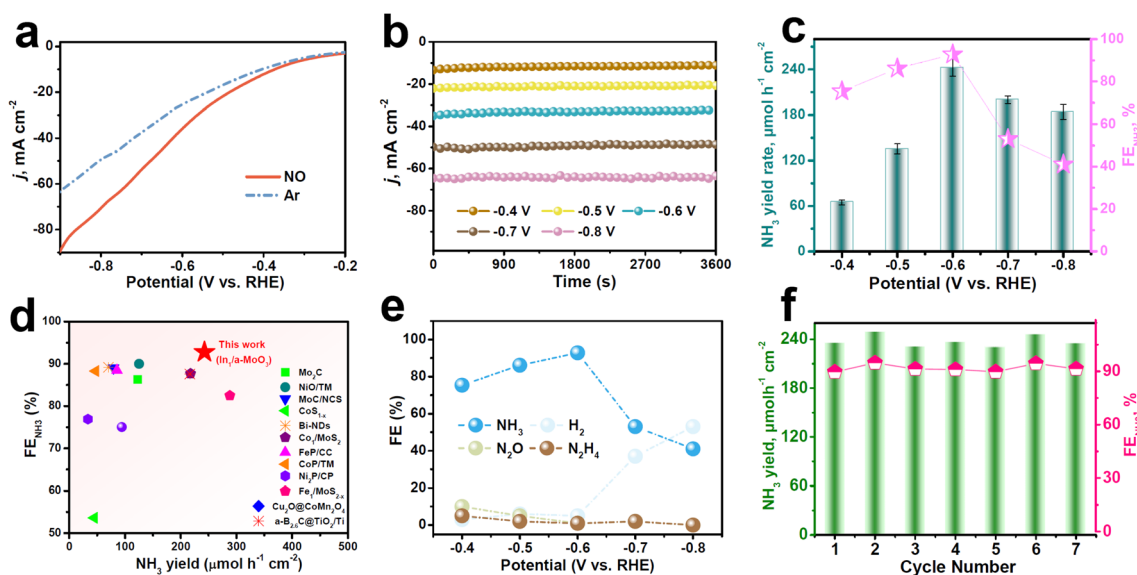


Fig. 3 (a) LSV curves of In₁/a-MoO₃ in Ar/NO-saturated 0.5 M Na₂SO₄ at a rate of 10 mV s⁻¹. (b) Chronoamperometry test of In₁/a-MoO₃ at various potentials, and resulting (c) NH₃ yield rates and FE_{NH₃}. (d) Comparison of NH₃ yields and FE_{NH₃} between In₁/a-MoO₃ and reported NORR catalysts. (e) FEs of different products on In₁/a-MoO₃ after NORR electrolysis at various potentials. (f) Cycling test of In₁/a-MoO₃ at -0.6 V.

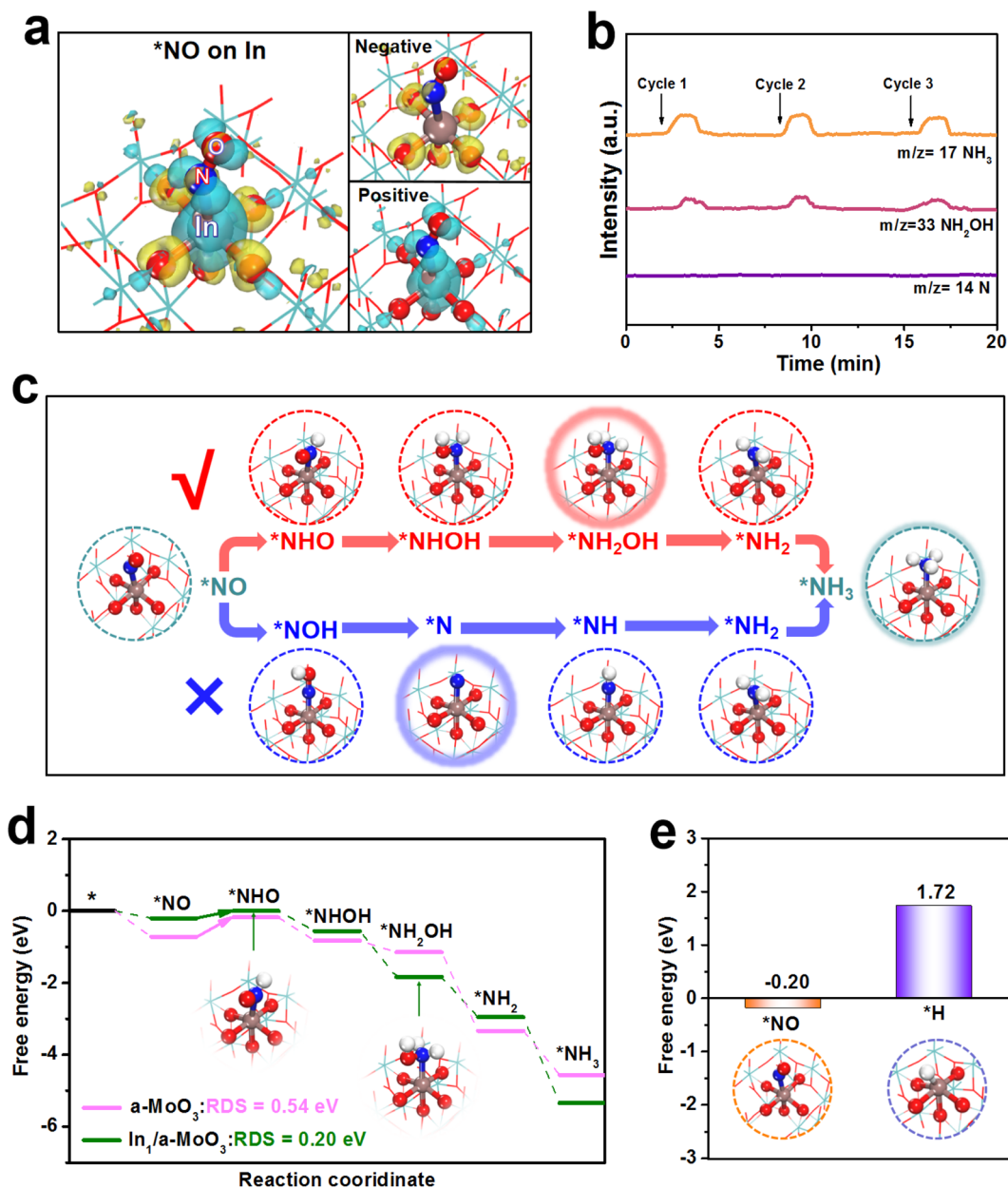


Fig. 4 (a) Charge density difference of absorbed NO ($*NO$) on $In_1/a-MoO_3$. Yellow and cyan regions represent electron depletion and accumulation, respectively. (b) Online DEMS spectra of $In_1/a-MoO_3$ during the electrolysis at -0.6 V. (c) Schematic of typical NOH and NHO pathways on $In_1/a-MoO_3$. (d) Free energy profiles of the NORR process (NHO pathway) on the Mo site ($a-MoO_3$) and In site ($In_1/a-MoO_3$). (e) Binding free energies of $*NO$ and $*H$ on the In site of $In_1/a-MoO_3$.

N intermediate but the presence of the NH_2OH intermediate, implying that $In_1/a-MoO_3$ prefers to adopt a NHO pathway ($*NO \rightarrow *NHO \rightarrow *NHOH \rightarrow *NH_2OH \rightarrow *NH_2 \rightarrow *NH_3$) rather than a NOH pathway ($*NO \rightarrow *NOH \rightarrow *N \rightarrow *NH \rightarrow *NH_2 \rightarrow *NH_3$) to drive the NORR process (Fig. S17[†]),^{54,55} as illustrated in Fig. 4c. As shown in the free energy diagrams along the NHO pathway (Fig. 4d), the In site presents the initial $*NO$ protonation ($*NO \rightarrow *NHO$) as the rate-determining step (RDS) with a low energy barrier of 0.20 eV. As a sharp comparison, the Mo site of bare $a-MoO_3$ shows the same $*NO \rightarrow *NHO$ as the RDS, but exhibits a largely increased RDS barrier of 0.54 eV due to too strong $*NO$ binding on the Mo site. Thus, single-site In can

effectively optimize the binding energy of $*NO$ to reduce the RDS barrier, thereby significantly promoting the hydrogenation energetics of the NO-to- NH_3 pathway.

As the HER is regarded as the major competitive reaction against the NORR,^{56–62} we further evaluate the HER activity of $In_1/a-MoO_3$. Fig. 4e shows that the binding free energy of $*H$ (1.72 eV) on the In site is much more positive than that of $*NO$ (-0.20 eV), proving that the In site can favorably absorb NO while restricting H binding. In the molecular dynamics (MD) simulations (Fig. S18[†]), $*NO/In$ interaction is found to be much stronger than $*NO/In$ interaction after simulations, as evidenced by the radial distribution function (RDF, Fig. S19[†])

curves and integrated RDF curves (Fig. S20†), verifying the priority of In₁/a-MoO₃ for the absorption and coverage of NO over H.^{63–66} Therefore, in addition to promoting the NO hydrogenation energetics, single-site In can facilitate HER suppression to enable the achievement of a high NORR selectivity.

In summary, In₁/a-MoO₃ is validated as an effective NORR catalyst. As unraveled by the experimental measurements and theoretical calculations, the prominent NORR properties of In₁/a-MoO₃ are attributed to the ability of single-site In to inhibit the HER and boost the hydrogenation energetics of the NO-to-NH₃ pathway. This work would open a new avenue for the development of efficient main-group SACs for high-performance NORR electrocatalysis.

Conflicts of interest

There are no conflicts of interest to declare.

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