1	Supplementary Information
2	Spin polarized Fe ₁ -Ti pairs for highly efficient electroreduction nitrate to
3	ammonia
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23 Experimental details

Computational methods. Spin-polarized DFT calculations were performed by the 24 Vienna ab initio simulation package (VASP)^{2, 3}. The exchange–correlation interaction 25 was described by the PBE functional⁴. The Kohn-Sham equations were solved in a 26 plane wave basis set with a kinetic energy cutoff of 400 eV. The effect of van der Waals 27 interaction was described using the dispersion-corrected DFT-D3 functional⁵. Ab-28 initio molecular dynamics (AIMD) simulations were used to generate the amorphous 29 30 structure of TiO₂ through the melt-and-quench method, which has been successfully utilized to generate the atomistic models of amorphous oxides⁶⁻⁸. The rutile TiO₂ 31 containing 96 atoms underwent molecular dynamics for a duration of 10 ps at a 32 temperature of 2500 K (higher than the melting point 2116 K of TiO₂ crystal)⁹. We 33 further cooled the model to 300 K at the rate of 110 K/ps to obtain the amorphous 34 structure of TiO₂. To model SD-Fe₁-Ti, various possible sites of single Fe atom 35 deposited on surface were considered and the most stable structure was displayed in 36 Fig. 5b, where he Fe atom was stabilized by four Fe–O bonds, consistent well with our 37 38 EXAFS result (Supplementary Table 3). To model SP-Fe₁-Ti, we considered a single Fe atom anchored an OV on the surface according to the ESR result. It was found that 39 the signal intensity at g = 2.008, assigned to OVs, was decreased after the introduction 40 of Fe metal ions on TiO_x , indicating Fe atoms may be anchored on $OVs^{1, 10}$. Optimized 41 structure displayed that Fe atom coordinated with three O atoms forming three-42 coordinate configuration, in line well with the EXAFS result. A vacuum space along 43 the z direction was set to 12 Å to prevent the interaction between the repeating slabs. A 44 k-point mesh of $(3 \times 3 \times 1)$ was used to sample the slab Brillouin zone. Structure 45 relaxation was performed until the residual forces were less than 0.02 eV $Å^{-1}$. To correct 46 the strong electron-correlation properties of transition metal oxides, DFT+U 47 calculations¹¹ were performed with U_{eff} Vaules of 3.5 and 2 eV for Ti–3d and Fe–3d, 48 based on the literature¹². The crystal orbital Hamilton population (COHP) was analyzed 49 by the LOBSTER program^{13, 14}. 50

51 The adsorption energies (E_{ads}) of the adsorbed species were described by the 52 following equation: $E_{\mathrm{ads}} = E_{\mathrm{total}} - E_{\mathrm{adsorbate}} - E_{\mathrm{slab}}$

54 where E_{total} , $E_{\text{adsorbate}}$ and E_{surface} are the total energies of the adsorbate–slab complex, 55 the adsorbate and slab, respectively. The Gibbs free energy change (ΔG) of the 56 elementary step was estimated by

57
$$\Delta G = \Delta E_{\rm DFT} + \Delta E_{\rm ZPE} - T\Delta S$$

58 where ΔE_{DFT} is the change in the electronic energy difference calculated by DFT, ΔE_{ZPE} 59 is the change in the zero-point energy, *T* is the room temperature (300 K) and ΔS is the 60 entropy change. To avoid using the charged NO₃⁻ species as a reference, the neutral 61 HNO₃ was alternatively used to calculate the Gibbs free energy of NO₃ on the basis of 62 literature¹⁵⁻¹⁷, and the ΔG (*NO₃) can be calculated as

63
$$\Delta G_{*NO_3} = G_{*NO_3} - G_{*} - G_{HNO_3(g)} + 0.5G_{H_2(g)} + \Delta G_{correct}$$

64

53

where G_{*NO3} , G_* , $G_{HNO3(g)}$ and $G_{H2(g)}$ are the Gibbs free energies of adsorbed NO₃, clean substrate, HNO₃ and H₂ molecules in the gas phase, respectively. $\Delta G_{correct}$ denotes the correction of adsorption energy. ΔG_{S1} and ΔG_{S2} are the Gibbs free energy of formation of HNO₃(1) from NO₃⁻(aq) (0.317 eV) and the Gibbs free energy of vaporization of HNO₃(1) (0.075 eV). Both values can be obtained from the CRC handbook, and the same approach has been done in literature¹⁵⁻¹⁷.

 $\Delta G_{\text{correct}} = \Delta G_{\text{S1}} + \Delta G_{\text{S2}}$

71

73 Supplementary Figures



Supplementary Figure 1. The typical synthesis route of SP–Fe₁–Ti and SD–Fe₁–Ti
electrodes. The schematical illustration for the preparation of (a) SP–Fe₁–Ti and (b)
SD–Fe₁–Ti electrodes. Color code: Ti (blue), Fe (yellow) and O (red).

78



Supplementary Figure 2. NITRR activity of SP-Fe₁-Ti electrode annealing at 81 different temperatures. (a) LSV curves of SP-Fe₁-Ti electrode annealing at different 82 temperatures (200, 300, 400 °C) in 1 mol L^{-1} KOH with or without NaNO₃. (b) NH₃ 83 yield rate and FE_{NH3} of SP-Fe₁-Ti electrode annealing at different temperatures (200, 84 85 300, 400 °C) at -0.4 V vs. RHE. The error bars correspond to the standard deviation from three independent measurements. We also prepared the SP-Fe₁-Ti electrode at 86 500 °C, but it cannot keep the mechanical stability and cracked, which may result from 87 the hydrogen embrittlement. 88



91 Supplementary Figure 3. Investigation of the formation mechanism for oxygen
92 vacancies. Mass spectroscopy during the temperature programmed reaction
93 (TPR) measurement of pristine Ti foam in 5% H₂/Ar.



97 **Supplementary Figure 4.** HRTEM image of SP–Fe₁–Ti electrode. As visualized by the 98 HRTEM image of SP–Fe₁–Ti electrode, a distinct boundary was observed between the 99 interior crystalline Ti and surface amorphous TiO_x layer, consistent with our previous 100 work¹.



103Supplementary Figure 5. HRTEM image of SD-Fe1-Ti electrode. As visualized by104the HRTEM image of SD-Fe1-Ti electrode, a distinct boundary was observed between105the interior crystalline Ti and surface amorphous TiO_x layer, which was similar with106SP-Fe1-Ti.



Supplementary Figure 6. HAADF–STEM image of SD–Fe₁–Ti electrode. The
HAADF–STEM image demonstrated that single–atom Fe (marked by white circles)
was well dispersed on the oxide layer of Ti foam for SD–Fe₁–Ti electrode.





Supplementary Figure 7. XRD patterns of Ti foam, SD–Fe₁–Ti and SP–Fe₁–Ti 119 electrodes. The X–ray diffraction (XRD) patterns of SD–Fe₁–Ti and SP–Fe₁–Ti 120 electrodes excluded diffraction peaks of the metallic Fe crystalline.



Supplementary Figure 8. 3D surface intensity profile. Intensity profiles were taken along the yellow arrow in HAADF–STEM image. The 3D surface intensity profile along the yellow arrow and the corresponding showed the characteristics of single–site Fe on the Ti monolithic electrode.



132 Supplementary Figure 9. HADDF image and STEM elemental mapping of SD–Fe₁–

133 Ti electrode. The EDS elemental mapping images revealed the uniform dispersion of

134 Fe atoms on the surface of $SD-Fe_1-Ti$ electrode.



138 Supplementary Figure 10. k³-weighted WT-EXAFS spectra of Fe foil at the Fe K-

139 edge. The WT-EXAFS spectra of Fe foil showed the peak with a maximum intensity

140 at 9.6 $Å^{-1}$, which is assigned to Fe–Fe scattering path.



Supplementary Figure 11. The determination of band edge positions of TiO_x/Ti and 143 SP-Fe₁-Ti electrodes. (a) Mott-Schottky plots of TiO_x/Ti and SP-Fe₁-Ti electrodes. 144 CB positions of TiO_x/Ti and SP-Fe₁-Ti were determined through converting the flat-145 band potentials (vs. SHE) obtained from Mott–Schottky plots to CB positions (E_{CB}) that 146 were usually ~ 0.1 eV higher than the flat-band potentials according to previous study¹⁸. 147 The Fermi level (E_F) of N-type semiconductors is located close to conduction band 148 minimum^{18, 19}. (b) UV–vis–NIR spectra of TiO_x/Ti and SP–Fe₁–Ti electrodes. Bandgaps 149 (E_g) of TiO_x/Ti and SP-Fe₁-Ti electrodes were calculated from the UV-vis-NIR 150 spectra based on the Tauc equation¹⁸. VB positions (vs. SHE) of TiO_x/Ti and SP-Fe₁-151 Ti electrodes were calculated according to $E_{VB} = E_{CB} - E_g$. Finally, the band edge 152 positions (vs. physical scale) of TiO_x/Ti and SP-Fe₁-Ti electrode were determined by 153 the SHE (V)–physical scale (eV) transformation via $E_{phys} = -(E_{SHE} + 4.44)^{18}$. 154 155





157 **Supplementary Figure 12.** Investigation of the interaction between oxygen vacancies 158 and the loaded Fe ions. Fe 2p XPS spectra of $FeCl_3/TiO_x$ without thermal treatment, 159 $SD-Fe_1-Ti$, and $SP-Fe_1-Ti$.



Supplementary Figure 13. The electrolysis curves at different applied potentials. The 163 electrolysis curves of (a) $SP-Fe_1-Ti$ and (b) $SD-Fe_1-Ti$ at different applied potentials.



166 Supplementary Figure 14. Standard calibration curves for UV-Vis detection of NH₃.

- 167 Standard calibration curves for UV-Vis detection of NH₃ from the Nessler's method (a)
- 168 the standard solutions (b) raw UV-Vis spectra (c) linear calibration.



173

174 **Supplementary Figure 15.** The calibration curve used for estimation of NH₃ by N¹⁵H⁴⁺ 175 ion of different concentrations. The maleic acid is selected as internal standard in 1H 176 NMR test. With the assistance of ¹H nuclear magnetic resonance, SP–Fe₁–Ti electrode 177 displayed an outstanding NH₃ yield rate of 15.3 mol_{NH3} g_{Fe}^{-1} h⁻¹ and 93% faradaic 178 efficiency at -0.4 V vs. RHE, which are in accordance with the results obtained from 179 UV–Vis spectrophotometry.



Supplementary Figure 16. LSV curves of SP $-Fe_1-Ti$ powders coated onto the carbon 183 fiber paper. LSV curves of SP $-Fe_1-Ti$ powders coated onto the carbon fiber paper with 184 and without addition of NO₃⁻.



Supplementary Figure 17. The detection of gas products. Representative GC of gas
products obtained on SP-Fe₁-Ti electrode at -0.4 V vs. RHE.



Supplementary Figure 18. Standard calibration curves for UV-Vis detection of NO₂⁻.

- 194 Standard calibration curves for UV-Vis detection of NO_2^- from the Griess's method (a)
- 195 the standard solutions (b) raw UV-Vis spectra (c) linear calibration.



Supplementary Figure 19. The product distribution during NITRR on SP-Fe₁-Ti 199 electrode. The FE of H_2 and NO_2^- and NH_3 during NITRR on on SP-Fe₁-Ti electrode 200 at -0.4 V vs. RHE.



203

Supplementary Figure 20. Cyclic voltammetry curves at the scan rates changed from 205 20 to 100 mV s⁻¹. Cyclic voltammetry curves of (a) TiO_x/Ti, (b) and SD–Fe₁–Ti (c) SP– 206 Fe₁–Ti electrodes. (d) Plots of half of the current density difference ($\Delta j/2$) at the 207 centered potential plotted against the scan rate. The slope of fitted straight line is the 208 C_{dl} value.



211 Supplementary Figure 21. The influence of nitrate concentration on electrode activity.

 NH_3 yield rate and FE_{NH3} of SP-Fe₁-Ti electrode at -0.4 V vs. RHE in 1 M KOH with

213 addition of 0.1, 0.5, 1 M NaNO₃.



Supplementary Figure 22. The electrode activity under alkaline and neutral conditions.

- $\,$ NH_3 yield rate and FE_{\rm NH3} of SP–Fe₁–Ti electrode at -0.4 V vs. RHE in 1 M KOH and
- $218 \quad 0.5 \text{ M} \text{ Na}_2 \text{SO}_4 \text{ with addition of } 1 \text{ M} \text{ Na} \text{NO}_3.$



Supplementary Figure 23. Investigation of the electrode stability. The curves of
cycling stability tests.



Supplementary Figure 24. Investigation of the electrode structure change after NITRR
via XRD measurements. XRD patterns of pristine and post-reacted SP-Fe₁-Ti
electrode.





230 Supplementary Figure 25. Investigation of the electrode structure change after NITRR

via TEM measurements. (a) HRTEM image and (b) HADDF-STEM image and

corresponding elemental mapping of post-reacted SP–Fe₁–Ti electrode.



Supplementary Figure 26. Investigation of the electronic structure change of SP-Fe₁-Ti electrode after NITRR. (a) Fe 2p XPS spectra of pristine and post-reacted SP-Fe₁-Ti electrode. (b) Ti 2p XPS spectra of pristine and post-reacted SP-Fe₁-Ti electrode.





Supplementary Figure 27. Investigation of the Fe ions leaching during stability test.

242 Fe ions concentrations of the pristine electrolyte and the post-reacted electrolyte after

- 243 different cycles consecutive electrolysis.



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Supplementary Figure 28. The fitting results of EXAFS. R space fitting curves at Fe K-edge of (a) Fe_2O_3 , (b) $SP-Fe_1-Ti$ and (c) $SD-Fe_1-Ti$. Least square EXAFS fitting was performed to quantificational extract the local atomic structure parameters of SP- Fe_1-Ti and $SD-Fe_1-Ti$. It was found that the fitting curves matched quite well with the experiment spectra. The fitting structural parameters were displayed in Table S3.



Supplementary Figure 29. Potential energy diagrams for H₂O dissociation on SD–
Fe₁–Ti and SP–Fe₁–Ti. The insets are the optimized initial, transition and final states
for H₂O dissociation. Color code: Ti (grey), Fe (cyan), N (blue), O (red) and H (white).



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Supplementary Figure 30. Investigation of hydrogen radicals via ESR spectra. ESR spectra of pristine electrolyte, the electrolyte obtained after 10 min electrocatalysis on SP-Fe₁-Ti electrode in 1 M KOH without NO_3^- and the electrolyte obtained after 10 min electrocatalysis on SP-Fe₁-Ti electrode in 1 M KOH with NO_3^- under argon using DMPO as the \cdot H-trapping reagent.



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Supplementary Figure 31. Comparison of KIE values between SD–Fe₁–Ti and SP– Fe₁–Ti electrodes. LSV curves of SD–Fe₁–Ti and SP–Fe₁–Ti recorded in both H₂O and D₂O electrolytes with the addition of 1 mol L⁻¹ NaNO₃ 1 mol L⁻¹ KOH. Insert displays the KIE values obtained by calculating the current density ratios in H₂O and D₂O electrolytes of SD–Fe₁–Ti and SP–Fe₁–Ti electrodes at –0.4 V vs. RHE.





277 Supplementary Figure 32. The enlarged structures intermediates involving in NITRR.

278 Optimized most stable structures for intermediates involving in NITRR on (a) SD–Fe₁–

279 Ti and (b) SP–Fe₁–Ti. Color code: Ti (grey), Fe (cyan), N (blue), O (red) and H (white).

280

274



Supplementary Figure 33. The detection of key intermediates involving in NITRR via 283 the DEMS measurement. DEMS signals of NO and HNO during NITRR over SD $-Fe_1-$

- 284 Ti electrode.



Supplementary Figure 34. Calculated free energy diagrams for NHO adsorbed on Fe–
Ti1 and Fe–Ti2 pairs. Inset displayed the spin–polarized Ti1 and spin–depressed Ti2
atoms.



292

Supplementary Figure 35. HER vs. NITRR on SP–Fe₁–Ti pairs. The calculated free energies of *H on Fe and Ti sites of SP–Fe₁–Ti were 1.13 and 0.78 eV, respectively, much weaker than that of NO_3^- adsorbed on spin–polarized Fe–Ti pairs (–0.64 eV), suggesting its inhibiting effect on H₂ generation, and thus high FE can be obtained for NITRR on SP–Fe₁–Ti.



301 Supplementary Figure 36. The interaction between Fe and NO. Schematic mechanism

302 of the interaction between Fe and NO.



Supplementary Figure 37. DOSs change of Fe atom on SP–Fe₁–Ti after NHO 306 adsorption. DOSs of Fe atom on SP–Fe₁–Ti before and after NHO adsorption.



Supplementary Figure 38. The integrated device composed of a flow-through NITRR 309 310 electrolyzer and a membrane-based ammonia recovery unit for simultaneous nitrate 311 electroreduction and ammonia recovery. (a) A schematic diagram of the integrated device composed of a flow-through NITRR electrolyzer and a membrane-based 312 ammonia recovery unit for simultaneous nitrate electroreduction and ammonia recovery. 313 (b) Photograph of the integrated device for simultaneous nitrate electroreduction and 314 ammonia recovery. The electrolyzer was an undivided cell of cathode and anode 315 chambers (internal dimensions: $7 \times 7 \times 5$ cm³) made of plexiglass (poly (methyl 316 methacrylate), PMMA). The SP-Fe₁-Ti cathode $(2 \times 2 \text{ cm}^2)$ and the DSA anode $(2 \times 2 \text{ cm}^2)$ 317 cm²) were fixed into the chambers in a more compact manner (2-cm spacing) and 318 separated by the nation film $(4.5 \times 4.5 \text{ cm}^2)$. The hollow polypropylene (PP) fibers were 319 assembled into the home-made fiber arrays, which were placed in acidic solution to act 320 321 as an NH₃ recovery reactor. The two open ends of the membrane arrays were fixed with epoxy resin and were connected with the electrolyzer by rubber tube. 322



Pristine membrane

Post-reacted membrane

- **Supplementary Figure 39.** The contact angle change after test. The contact angle of
- 326 (a) the pristine and (b) post-reacted membrane.

329 Supplementary Tables

	Electrode	Electrical conductivity (kS cm ⁻¹)
	SP–Fe ₁ –Ti	45
	SD-Fe ₁ -Ti	43
31		

Supplementary Table 1. The electrical conductivity of electrode at room temperature.

Component		Assignment	IS (mm s^{-1})	$QS (mm s^{-1})$	Area (%)
	D1	HS Fe ³⁺	0.29	0.94	23.7
CD F. T.	D2	LS Fe ³⁺	0.038	0.959	36.1
SP-rej-11	D3	HS Fe ²⁺	0.92	1.94	22.6
-	D4	HS Fe ²⁺	0.846	1.28	17.6
	D1	HS Fe ³⁺	0.467	0.73	24.0
SD–Fe ₁ –Ti	D2	LS Fe ³⁺	0.13	0.72	50.0
-	D3	HS Fe ²⁺	0.700	1.48	26.0

Supplementary Table 2. Summary of the Mossbauer spectra parameters and
 assignments to different iron species on SD–Fe₁–Ti and SP–Fe₁–Ti electrodes.

NH3 synthesis routes	Catalysts	Electrolyte	FE _{NH3}	NH ₃ yield rate (mmol gcat ⁻¹ h^{-1})	References
	SP–Fe ₁ –Ti	1 M KOH + 1 M NaNO ₃	95.2% at -0.4 V vs. RHE	16000mmol g _{cat} ⁻¹ h ⁻¹ at -0.4 V vs. RHE	This work
	Fe single atom	0.1 M K ₂ SO ₄ + 0.5 M KNO ₃	~ 75% at –0.66 V vs. RHE	308 mmol g_{cat}^{-1} h^{-1} at -0.66 V vs. RHE	Nat. Commun., 2021 , 12, 2870.
NITRR	Fe–PPy SACs	0.1 M KOH + 0.1 M KNO ₃	99.69% at –0.3 V vs. RHE	2507 mmol g_{cat}^{-1} h^{-1} -0.3 V vs. RHE	<i>Energy</i> <i>Environ. Sci.</i> , 2021 ,14, 3522
	FeB	1 M KOH + 0.1 M KNO3	96.8 % at -0.6 V vs. RHE	3150mmol g _{cat} ⁻¹ h ⁻¹ at -0.6 V vs. RHE	Angew. Chem. Int. Ed., 2023 , e202300054
	Fe ₂ TiO ₅	PBS + 0.1 M NaNO ₃	87.6 % at -0.9 V vs. RHE	730 mmol g_{cat}^{-1} h^{-1} at -1.0 V vs. RHE	Angew. Chem. Int. Ed., 2023 , 62, e202215782
	SA–Fe(II)	0.1 M PBS + 0.5	99.6 % at -1.0 V	$\begin{array}{c} 486 \text{ mmol} \\ g_{cat}{}^{-1} h^{-1} at - \end{array}$	Proc. Natl. Acad. Sci.,

Supplementary Table 3. Comparison of the NITRR performance of SP–Fe₁–Ti electrode with the other NH_3 synthesis routes including Haber–Bosch process and nitrogen reduction reaction (NRR).

	M Na ₂ SO ₄	vs. RHE	1.0 V vs.	2023 , 120,
	+ 200 ppm		RHE	e2209979120.
	NaNO ₃			
	0.1 M	05 20/	50 mmol	Proc. Natl.
	$Na_2SO_4 +$	85.2% at	${g_{cat}}^{-1} h^{-1} at -$	Acad. Sci.,
$Co-Fe@Fe_2O_3$	500 ppm	-0.75 V	0.75 V vs.	2022 , 119,
	NaNO ₃	VS. KHE	RHE	e2115504119.
		770/+	130 mmol	
	0.1 M PBS	/ /% at –	${g_{cat}}^{-1} h^{-1} at -$	Nat. Energy.,
Cu-PICDA	+ 500 ppm	0.4 V Vs.	0.4 V vs.	2020 , 5, 605.
	KNO3	KHE	RHE	
	1 \/	02.50/ at	6250 mmol	Nat.
CuDd		92.5% at	$g_{cat}^{-1} h^{-1} at -$	Commun.,
CuPa	KUH + I M	-0.0 V	0.6 V vs.	2022 , 13,
	KINO3	VS. KHE	RHE	2338.
	1 M N-OU	99 (0/ -+	3025 mmol	Nat.
CoP–CNS/ Cu		88.0% at	$\mathbf{g}_{cat}^{-1} \mathbf{h}^{-1} \mathbf{at}$	Commun.,
foam	+ 1 M	-1.03 V	-1.03 V vs.	2022 , 13,
	InalnO ₃	VS. KHE	RHE	7958.
	1 M N-OU	1000/	569 mmol	
		$\sim 100\%$	$\mathbf{g_{cat}}^{-1} \mathbf{h}^{-1} \mathbf{at}$	Energy
COP NAS/CFC	+1 M	at -0.3 V	-0.3 V vs.	Environ. Sci.,
	NaNO ₃	VS. KHE	RHE	2022 ,15, 760.
		97.20/ at	22210 mmol	Angew.
		0.2V	${g_{cat}}^{-1} h^{-1} at -$	Chem. Int.
Ku]=11O _X /11		-0.5 v	0.3V vs.	Ed. 2022, 61,
	INAINU3	VS. KHE	RHE	e202208215
Strained Ru	1 M KOH	~100%	5560 mmol	J. Am. Chem.
nanoclusters	+ 1 M	at -0.2 V	${\operatorname{g}_{\operatorname{cat}}}^{-1} \operatorname{h}^{-1} \operatorname{at} -$	Soc., 2020 ,

$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$			KNO ₃	vs. RHE	0.8 V vs.	142, 7036.
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					RHE	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Ru SACs on N doped carbon	0.05 M H ₂ SO ₄	29.6% at -0.2V vs. RHE	7.1 mmol $g_{cat}^{-1} h^{-1} at -$ 0.2 V vs. RHE	<i>Adv. Mater.</i> , 2018 , 30, 1803498.
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	NRR	Bi nanocrystals	0.5 M K ₂ SO ₄	66% at – 0.6 V vs. RHE	7.1 mmol $g_{cat}^{-1} h^{-1} at -$ 0.6 V vs. RHE	<i>Nat. Catal.</i> , 2019 , 2, 448
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		Bi ₄ V ₂ O ₁₁ /CeO ₂	0.1 M HCl	10.16% at –0.2V vs. RHE	1.4 mmol $g_{cat}^{-1} h^{-1} at -$ 0.6 V vs. RHE	Angew. Chem. Int. Ed., 2018 , 57, 6073
Co–LiH / / 4.7 mmol Nat. Chem.	Haber– Bosch	Ru/Ba– Ca(NH ₂) ₂	/	/	60.7 mmol ${\rm g_{cat}}^{-1} {\rm h}^{-1}$	Angew. Chem. Int. Ed., 2018 , 57, 2648.
$g_{cat}^{-1} h^{-1}$ 2017 , 9, 64	process	Co–LiH	/	/	4.7 mmol $g_{cat}^{-1} h^{-1}$	<i>Nat. Chem.</i> , 2017 , 9, 64

343 Supplementary Table 4. Comparison of the applied potentials for maximizing FE_{NH3},

Ca	talysts	The applied potentials for maximizing FE _{NH3} (V vs. RHE)	The onset potential (V vs. RHE)	Current densit 0.4 V vs. RHI cm ⁻²)	ry @ - E (mA References	
				~75		
				(monolithic		
SP-	-Fe ₁ -Ti	-0.4	~0.1	electrode)	This work	
				~190		
				(powder)		
Fe	single	-0.66	~0.3	~5	Nat. Commun.,	
:	atom				2021, 12, 2870.	
Fe	-PPv				Energy Environ.	
	SACs	-0.3	~0.3	~12	Sci., 2021,14,	
L					3522.	
					Angew. Chem. Int.	
	FeB	-0.6	~0.2	~150	Ed., 2023,	
					e202300054.	
					Angew. Chem. Int.	
Fe	e ₂ TiO ₅	-0.9	~0.1	~18	Ed., 2023, 62,	
					e202215782	
					Proc. Natl. Acad.	
SA	–Fe(II)	-1.0	~0.3	~10	Sci., 2023, 120,	
					e2209979120.	
					Angew. Chem. Int.	
Cu	Cl/TiO ₂	-0.8	~0.3	~8	Ed. 2021, 60,	
					22933.	

onset potentials and current density of top-level NITRR electrocatalysts.

				Angew. Chem. Int.
NWAs	-0.85	~0.2	~35	Ed.2020,59, 5350 –
1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1				5354
	0.4	0.27	. 15	Nat. Energy., 2020,
Cu-I ICDA	-0.4	0.27	~15	5, 605.
Co				Proc. Natl. Acad.
Co-	-0.75	~0.2	~5	Sci., 2022, 119,
$re(wre_2O_3)$				e2115504119.
CoD CNS	-1.02	0	200	Nat. Commun.,
COP-CINS	-1.05	~0	~200	2022, 13, 7958.
	0.2	0.1	200	Energy Environ.
COP NAS	-0.5	~0.1	~300	Sci., 2022,15, 760.
				Angew. Chem. Int.
Ru ₁ -TiO _x /Ti	-0.3	~0.1	~100	Ed. 2022, 61,
				e202208215
Stuain ad Day	0.2	0.2	110	J. Am. Chem. Soc.,
Strained Ku	-0.2	~0.2	~110	2020, 142, 7036.
Ru15C085	0	0.4	1	Nat Catal 2023, 6,
HNDs	0	~0.4	/	402.
CuCo	0.2 M	0.1	1	Nat Commun
nanosheet	-0.2 V	~0.1	/	2022, 13, 7899
Du CuNW	0.04	0.2	1	Nat. Nanotechnol.
Ku-Culn w	0.04	~0.2	/	2022, 17, 759.
Der Cra /rCO	0.05	0.4	1	Adv. Mater. 2023,
Ru ₁ Cu ₁₀ /rGO	-0.05	~0.4	/	35, 2202952.
CD 1	0.6	0	100	Nat. Commun.,
Cura	-0.0	~0	~180	2022, 13, 2338.

Metal	Symbol	Unit of Measure	U.S.
Palladium	Pd	g	86.72 \$
Ruthenium	Ru	g	24.11 \$
Cobalt	Co	g	0.033 \$
Copper	Cu	g	0.0082 \$
Titanium	Ti	g	0.0063 \$
Iron	Fe	g	0.00010 \$

347 Supplementary Table 5. Price of different metals^[a]

348 [a] The prices for various metals are from the metalary & tradingeconomics website on

July 13, 2023. (https://www.metalary.com; https://tradingeconomics.com)

Catalysts	FE _{NH3}	NH ₃ yield rate	References
	<u> </u>	$(\text{mmol cm}^2 \text{ h}^1)$	-
SP_Fe ₁ _Ti	98.51% at -0.4	0.99	This work
	V vs. RHE	0.55	
	$\sim 75\%$ at		Nat Commun 2021 12
Fe single atom	–0.66 V vs.	0.12	2870
	RHE		2670.
	99.69% at -0.3	0.16	Energy Environ. Sci.,
re-rry sacs	V vs. RHE	0.10	2021,14, 3522
	96.8 % at		Angerry Change Int
FeB	–0.6 V vs.	1.5	Angew. Chem. Int.
	RHE		Ed., 2023, e202300054
	87.6 % at -0.9	0.072	Angew. Chem. Int.
Fe ₂ 1105	V vs. RHE	0.073	Ed., 2023, 62, e202215782
SA E ₂ (II)	99.6 % at -1.0	0.20	Proc. Natl. Acad. Sci.,
5A-re(11)	V vs. RHE	0.29	2023, 120, e2209979120.
CuCl/TiO	85~% at –0.8 V	0.12	Angew. Chem. Int. Ed.
	vs. RHE	0.15	2021, 60, 22933.
Cu/Cu ₂ O	95.8 % at -0.85	0.24	Angew. Chem. Int.
NWAs	V vs. RHE	0.24	Ed.2020,59, 5350 –5354
	77 % at –0.4 V	0.026	Nat Energy 2020 5 605
Cu-PICDA	vs. RHE	0.020	That. Energy., 2020, 3, 003.
Co	85.2 % at -		Proc Natl Acad Sci
Ee@EacOa	0.75 V vs.	0.089	2022 110 a211550/110
Fe@Fe2O3	RHE		2022, 117, 02113304119.

351 Supplementary Table 6. Comparison of the NH₃ yield rate defined by the electrode

352 area among various electrode.

	88.6 % at		NL 4 C 2022 12
CoP-CNS	-1.03 V vs.	8.47	Nat. Commun., 2022, 13,
	RHE		7958.
	~ 100 % at		Ensure Environ Soi
CoP NAs	-0.3 V vs.	3.09	2022 15 7(0
	RHE		2022,15, 760.
	87.3 % at –	1	Angew. Chem. Int.
Ku _l -11O _x /11	0.3V vs. RHE	1	Ed. 2022, 61, e202208215
Studie of Dec	${\sim}100$ % at –0.2	1.02	J. Am. Chem. Soc., 2020,
Strained Ku	V vs. RHE	1.05	142, 7036.
Ru15Co85	97 % at 0 V vs.	1.02	Nat Catal 6, 402–414
HNDs	RHE	1.92	(2023).
CuCo	100 % at -0.2	1 0	Nat Commun 13, 7899
nanosheet	V vs. RHE	4.8	(2022)
Du CuNUU	96 % at 0.04 V	15	Nat. Nanotechnol. 17, 759–
Ku-Cuin w	vs. RHE	4.3	767 (2022).
	98 % at -0.05	0.20	Adv. Mater. 2023, 35,
Ku1Cu10/rGO	V vs. RHE	0.38	2202952.
	92.5 % at -0.6	1.05	Nat. Commun., 2022, 13,
CuPd	V vs. RHE	1.20	2338.

Samples	Scattering path	CN	R (Å)	$\sigma^{2}(10^{-3}\text{\AA}^{2})$	$\Delta E_0 (eV)$	R factor
Fe ₂ O ₃	Fe–O	6	1.95	9.8	-9.2	0.016
SP–Fe ₁ –Ti	Fe–O	3.3	1.95	3.1	-8.5	0.027
SD–Fe ₁ –Ti	Fe–O	4.1	1.93	5.1	-10.0	0.023

Supplementary Table 7. Structural parameters extracted from the EXAFS fitting. ($S_0^2=0.78$ for Fe K-edge).

Notes: CN is the coordination number; R is interatomic distance; σ^2 is Debye–Waller factor (a measure of thermal and static disorder in absorber–scatterer distances); ΔE_0 is

359 edge–energy shift (the difference between the zero kinetic energy value of the sample

and that of the theoretical model); R factor is used to value the goodness of fitting.

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