## Electronic Supplementary Information

# Regulating active hydrogen adsorbed on grain boundary defects of nano-nickel for boosting ammonia electrosynthesis from nitrate

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#### **1** Experiment Details

**1.1 Synthesis of Ni-NPs-x:** The carbon cloth was cut into rectangle of area  $0.5 \times 0.7$  cm<sup>2</sup>, and then ultrasonicated in ethanol, ultra-pure water for 10 minutes, respectively. A certain amount of NiSO<sub>4</sub> · 6H<sub>2</sub>O was diluted in ultra-pure water to prepare  $0.33 \text{ mol L}^{-1}$ NiSO<sub>4</sub> solution (30 ml). Next, the treated carbon cloth, saturated calomel electrode (SCE), and platinum foil ( $1.5 \times 1.5$  cm<sup>2</sup>) were used as working electrode, reference electrode, and contour electrode, respectively.  $0.33 \text{ mol L}^{-1}$ NiSO<sub>4</sub> solution used as electrolyte. The Ni-NPs-x was synthesized by electrodeposition method under -x V (vs. SCE) for 1400s (x = 1.4, 1.6, 1.8). The loaded carbon cloth was rinsed by ultra-pure water for several times, and used for electrochemical experiment immediately. All ultra-pure water in experiment procedure was previously sparged with Ar for at least 15 min.

**Synthesis of control samples:** The chemical synthesized Ni materials of Ni-NaHB and Ni-H<sub>2</sub> were as following. Ni-NaHB: 30 mL  $0.3 \text{ mol L}^{-1} \text{ Ni}^{2+}$  was sparged with Ar for 10 min before adding 10 mL 2g/L NaHB. The obtained suspension was continuously sparged with Ar for 2 hours. The products were collected by centrifugation; Ni-H<sub>2</sub>: 2 g urea was added in 30 mL  $0.3 \text{ mol L}^{-1} \text{ Ni}^{2+}$ . The solution was transferred into 50mL teflon autoclave and maintained in 140 °C oven for 6 hours. Then the products was centrifuged and washed with ultra-pure water and ethanol for several times. After drying, it was heated in air at 400 °C for 10 h to obtain nickel oxide. Finally, the nickel oxide was reduced under a 5% H<sub>2</sub>(95% Ar) atmosphere at 400 °C for 6 h. Then the Ni-H<sub>2</sub> was obtained.

Working electrode prepare of the powder control samples: 4 mg powders and 40  $\mu$ L Nafion solution (5 wt %) were dispersed in 1 mL water and 1 mL ethanol to form a homogeneous ink. Then, 40  $\mu$ L ink was loaded on a carbon cloth (1 × 1 cm<sup>2</sup>).

**1.2 Characterization:** Scanning electron microscopy (SEM) images were obtained from Hitachi S-4800. Transmission electron microscopy (TEM) images were obtained from the JEM-2100EX. X-ray diffraction (XRD) was obtained from Bruker D8 advance using a Copper K $\alpha$  source ( $\lambda = 0.154$  nm). X-ray photoelectron spectrum (XPS) were obtained Thermo Scientific Nexsa with 10nm surface layer removed by Ar ion sputtering, the binding energies were adjusted refers to the C 1s peak at 284.8 eV. The ultraviolet-visible (UV-Vis) absorbance spectra were measured on Agilent 8453. The isotope tracing experiments and determination of NH<sub>3</sub> concentration were conducted on Bruker 1400-MHz system.

**1.3 Electrocatalytic activity test:** The electrochemical measurements were carried out in CHI 660E (equipped with CHI680C) electrochemical workstation (Chenhua, Shanghai) in an H-type cell (50 mL + 50 mL) separated by Nafion 117. The Ni-NPs-x loaded on carbon cloth, SCE and platinum foil was used as the working electrode, reference electrode and counter electrode, respectively. The area

of the working electrode was controlled with  $0.4 \times 0.5 \text{ cm}^2$ . The catholyte was  $1 \text{ mol } L^{-1} \text{ NaNO}_3$  (if no special note) with  $1 \text{ mol } L^{-1} \text{ NaOH}$ , the anolyte was  $1 \text{ mol } L^{-1} \text{ NaOH}$ . Both anolyte and catholyte were sparged with Ar for at least 15 min before experiment. All electrochemical experiments were carried out under stirring. The catalyst was activated by cyclic voltammetry (CV) for 20 cycles from -0.6 to -0.8 V (vs. SCE) at  $0.1 \text{ V s}^{-1}$  before measurement. linear sweep voltammetry (LSV) was performed from -0.6 to -2.1 V (vs. SCE) at scan rate  $10 \text{ mV s}^{-1}$ . Then, the potentiostatic tests were conducted at different potentials for 5 hours under stirring. After electrocatalysis 2 mL of catholyte was taken out and diluted to 10 mL with  $0.2 \text{ MH}_2\text{SO}_4$  for next determination. The reference electrode was converted to RHE according to the following equation:

$$E_{RHE} = E_{SCE} + 0.0591 \,\text{pH} + 0.242$$

**1.3.1 Notations for nitrite reduction:** During the reduction of nitrite, an unstable substant  $NH_4NO_2$  will be generated, which is also highly toxic. It will spontaneously react with itself as following equation:

$$NH_4NO_2 \longrightarrow N_2(g) + 2H_2O$$

When current passes the cell, $Q=i^2 RT$ , the temperature of the cell rises, the reaction above will be also accelerated. Additionally, the decomposition rate of NH<sub>4</sub>NO<sub>2</sub> might be faster in a high concentration. In consideration of precise determination of NH<sub>4</sub><sup>+</sup>, here the reduction of nitrite under different reduce potential were conducted for 2 hours. The concentration of sodium nitrite was 1 molL<sup>-1</sup>. After electrocatalysis the catholyte was diluted with water for next determination.

**1.3.2 Electrochemical Active Surface Area (ECSA) determination:** The electrochemical doublelayer capacitance (Cdl) determination was measured in a potential window from -0.5 V to -0.6 V nearly without the Faradaic current at different scan rates of 40, 60, 80, 100, 120 mV s<sup>-1</sup>. The plot of current density at different potential against scan rate was fitted in linear and its slope is the Cdl. The specific capacitance of a flat surface was assumed as 60  $\mu$ F cm<sup>-2</sup>.

$$A_{ECSA} = \frac{Cdl}{60\mu F cm^{-2}}$$

**1.3.3 Reaction order calculation:** The order of the reaction was calculated by varying the concentration of nitrate and recording the reaction rate of nitrate. The calculation was based on the following equation.<sup>[1]</sup>

$$NO_3^- + 2H_2O \rightarrow NH_3 + OH^- c = k [NO_3^-]^{\alpha} [H_2O]^{\beta}$$

In the equation, *c* is the reaction rate of nitrate, *k* is the reaction constant,  $\alpha$ ,  $\beta$  is the reaction order for nitrate and water, respectively. Since  $[H_2O] \gg [NO_3^{-1}]$ ,  $[H_2O]^{\beta}$  can be treated as a constant. The reaction rate *c* is proportional to the current density *j*. So, the equation can be rewritten as:

$$\ln j = \mathbf{K} + \alpha \ln \left[ \mathbf{NO}_3^{-} \right]$$

The reaction order  $\alpha$  can be obtained by linearly fit  $\ln j$  with  $\ln [\text{NO}_3^-]$ .

**1.3.4 H\* detection using DMPO:** For the H\* trapping experiment, the electrolyte was set as 20mL, and the cathode area was set as  $2 \times 2 \text{ cm}^2$  to ensure enough H\* were generated. The reduce potential was set as -1.8V vs. SCE, after 10min 20 µL electrolyte was extracted and mixed with 20 µL DMPO. The mixture was transferred to capillary for detection. The data was obtained after removing the peaks of impurity.

**1.3.5 Electron transfer number calculation:** The electron transfer number was estimated according to Koutecky-Levich equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.62nFAD_0^{2/3}\omega^{1/2}v^{-1/6}C_0}$$

where *i* refers to the current,  $i_k$  is the limiting current, *n* is the electron number transferred during reaction, *F* is the Faraday constant (96485 C/mol), *A* is the area of RDE (0.19625 cm<sup>2</sup>),  $D_0$  is the diffusion coefficient of the nitrate  $(1.80 \times 10^{-5} \text{ cm}^{-1} \text{ s}^{-1})$ ,  $\omega$  is the rotation rate, is the kinematic viscosity (0.0118 cm<sup>2</sup> s<sup>-1</sup>), and  $C_0$  is the bulk concentration of nitrate  $(0.033 \times 10^{-3} \text{ mol cm}^{-3})$ . The inverse of current is proportional to the inverse of square root of the rotation rate  $(1/\omega^{1/2})$ .

In the experiment, Ni nanoparticles was deposited on RDE under -1.6 V vs. SCE. The experiment was conducted in 180 mL containing 0.5 g NaNO<sub>3</sub> + 7.2 g NaOH electrolyte. The LSV curve was measured under 400, 800, 1200, 1400 rpm.

**1.3.6 Solvent kinetic isotope effect:** The solvent kinetic isotope effect (SKIE) was conducted under mixed  $D_2O + H_2O$  solution. The SKIE was the ration of the reaction rate under pure deuterium and pure protic medium.

$$SKIE = \frac{k_n}{k_0}$$

*n* is the deuterium proportion  $[D_2O]/([D_2O] + [H_2O])$ , *k* is the reaction rate, here can be roughly replaced by current density *j*. The SKIE experiment was conducted under different electrolyte with

a different *n*, the concentration of NaNO<sub>3</sub> was 0.5 M. In pure deuterium medium, the electrolyte was NaNO<sub>3</sub> + NaOD + D<sub>2</sub>O. In pure protic medium, the electrolyte was NaNO<sub>3</sub> + NaOH + H<sub>2</sub>O.

**1.3.7** Assemble of Zn-nitrate battery: The metal-nitrate battery was constructed by using the deposited carbon cloth  $(1 \times 1 \text{ cm}^2)$  and commercial Zn foil  $(2 \times 2 \text{ cm}^2)$  as electrode. The catholyte of the battery is 1M NaOH and anolyte was 1MNaNO<sub>3</sub>, and separated by bipolar membrane. The electronic timer was originally powered by a triple-A battery, its battery was removed before experiment. The assembled battery can power an electronic timer. It can still power the timer after 2 days, but we end it.

**1.3.8 Determination of NO<sub>2</sub><sup>-</sup> – N:** The concentration of NO<sub>2</sub><sup>-</sup> – N was measured by Griess method.<sup>[2]</sup> The color reagent was prepared as follows: 4 g Sulfanilamide and 0.2 g N-(1-naphthyl) ethylenediamine dihydrochloride were dissolved in 50 mL ultrapure water, then 10 mL phosphoric acid (85 wt%) was added to the aforementioned solution.

A certain amount of catholyte was diluted to 10 mL to detection range. then, 200  $\mu$ L color reagent was added. After 15 min the absorption intensity at a wavelength of 540 nm was recorded. The concentration-absorbance curve was got using a series of standard NaNO<sub>2</sub> solutions. The concentration and amount of produced NO<sub>2</sub><sup>-</sup> can be calculated.

**1.3.9 Determination of NH<sub>4</sub><sup>+</sup>–N:** <sup>1</sup>H NMR method: A certain amount of catholyte was taken out and diluted with ultrapure water to 10 mmol L<sup>-1</sup>, 10 µL aforementioned solution, 10 µL 10.23 mmol L-1 maleic acid, 510 µL D6-DMSO (with 0.03% TMS), 20 µL 4 M H<sub>2</sub>SO<sub>4</sub> were mixed and sealed into NMR tube. The concentration of ammonia (C<sub>a</sub>) in NMR tube can be measured by comparing the integral area of the vinylic singlets for maleic acid (I<sub>m</sub>) and the typical triplet for ammonium as follows<sup>[3]</sup>:

$$C_a = \frac{I_a/H_a}{I_m/H_m} \cdot C_m$$

in the equation,  $C_m$  is the concentration of maleic acid ( $C_m = 0.186 \text{ mmol L}^{-1}$ ) in NMR tube,  $I_a, I_m$  refer to the integrals of <sup>1</sup>H NMR peaks for ammonium and maleic acid.  $H_a, H_m$  refer to the number of protons for ammonium and maleic acid. With the  $C_a$  in NMR tube in hand, the concentration and amount of produced ammonia can be calculated.

**Nessler's reagent method:** A certain amount of catholyte was taken out and diluted with ultrapure water to detection range, 200  $\mu$ L Nessler's reagent was added into 10 mL aforementioned solution, after 15 mins the absorption intensity at a wavelength of 420 nm was recorded. The concentration-absorbance curve was got using a series of standard NH<sub>4</sub>Cl solutions.<sup>[4]</sup>

1.3.10 <sup>15</sup>N labeling experiment: The isotope tracing experiments were all conducted at reduce po-

tential -0.33 V (vs. RHE) for 3h. The catholyte was 15mM Na<sup>15</sup>NO<sub>3</sub> (<sup>15</sup>N  $\ge$  99% atom) + 1M NaOH. After electrocatalysis, a certain amount catholyte was taken out and diluted to detection range with water (see <sup>1</sup>H NMR method for the determination of ammonia). The <sup>1</sup>H NMR spectrum of the products was compared with that reduced from Na<sup>14</sup>NO<sub>3</sub> as N source, spectrum of <sup>15</sup>NH<sub>4</sub>Cl solution and spectrum of <sup>14</sup>NH<sub>4</sub>Cl solution. In <sup>1</sup>H NMR, <sup>15</sup>NH<sub>4</sub><sup>+</sup> shows a typical two peaks and <sup>14</sup>NH<sub>4</sub><sup>+</sup> shows a typical three peaks.<sup>[5]</sup>

**1.3.11 Faradaic efficiency for ammonia:** The Faradaic efficiency for ammonia is calculated as follows:

$$FE_{NH_3} = \frac{n \times c_{NH_3} \times V_{catholyte} \times F}{Q_{cell}}$$

n is the electrons number that transfers during  $NO_3^- \longrightarrow NH_3$ , n=8.  $c_{NH_3}$  is the concentration in catholyte cell after electrocatalysis, which is calculated through Nessler's reagent and HMR method.  $V_{catholyte}$  is the volume of the catholyte after experiment. F is the Faraday constant, F=96485 C mol<sup>-1</sup>.  $Q_{cell}$  refers to the total charge transferred in experiment, which is calculated from the integral of i-t curves.

Faradaic efficiency for nitrite: The Faradaic efficiency for nitrite is calculated as follows:

$$FE_{NO_2^-} = \frac{n \times c_{NO_2^-} \times V_{catholyte} \times F}{Q_{cell}}$$

n is the electrons number that transfers during NO<sub>3</sub><sup>-</sup>  $\longrightarrow$  NO<sub>2</sub><sup>-</sup>, n=2.  $c_{NO_2^-}$  is concentration in catholyte cell after electrocatalysis, which is calculated by Griess method.

**Faradaic efficiency for gas:** The gas including hydrogen, dinitrogen, etc. is not detected in the experiment, the FE for gas is calculated by the following equation:

$$FE_{gas} = 1 - FE_{NH_3} - FE_{NO_2}$$

1.3.12 NH<sub>3</sub> rate: NH<sub>3</sub> rate is calculated as follows:

*NH*<sub>3</sub> *rate*(*mmol* 
$$h^{-1}$$
 *cm*<sup>-2</sup>) =  $\frac{c_{NH_3 \times V_{catholyte}}}{S \times T}$ 

S refers to the surface area of the carbon cloth  $(cm^2)$ , T is the electrocatalysis time (h).

**1.3.13 DFT calculation:** The reaction pathway of  $NO_3^-+6H_2O+8e^- \longrightarrow NH_3+9OH^-$  was subdivided into two parts, namely continuous deoxidation process, followed by a continuous hydrogenation process, which was as follows. In the equations, \* represents the absorption site.

$$NO_3^* \rightarrow HNO_3^* \rightarrow NO_2^* \rightarrow NO^* \rightarrow N^* \rightarrow *NH \rightarrow *NH_2 \rightarrow *NH_3$$

The all spin-polarized Density Function Theory simulations were performed with the Vienna Ab initio Package (VASP) <sup>[6]</sup> within the generalized gradient approximation (GGA). The Perdew-Burke-Ernzerhof (PBE) <sup>[7]</sup> formulation was used in the simulation. The projected augmented wave (PAW) potentials <sup>[8]</sup> was used to describe the ionic cores. The valence electrons was taken into account using a plane wave basis with 450eV kinetic energy cutoff. Partial occupancy of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.2 eV. If the energy change was smaller than 10<sup>-5</sup> eV, the electronic energy was considered as self-consistent. When the energy change was smaller than 0.04 eV Å<sup>-1</sup>, A geometry optimization was considered convergent. The vacuum spacing in a direction perpendicular to the plane of the structure was set as 18 Å. The Gibbs free energy for each elementary step was calculated as:

#### $G = E_{elec} + E_{ZPE} - TS$

in which  $E_{elec}$  is the electronic energy at 0 K calculated by DFT,  $E_{ZPE}$  is the zero-point energy term, and T is the absolute temperature (here 298.15 K), S is the entropy.

#### 2 Results and Discussion



**Fig. S1** The Ni<sup>2+</sup> is  $0.33 \text{ mol L}^{-1}$ , 30mL; The area of carbon cloth is  $0.5 \times 0.4 \text{ cm}^2$ ; The scan rate is  $10 \text{ mV s}^{-1}$ . The red solid line is the LSV curve of fresh carbon cloth. The blue solid line is the LSV curve of carbon cloth that has already been deposited with Ni NPs for 400 s. The dashed lines are the first derivative of the two LSV curves above.



(b)



**Fig. S2** Ni-NPs-1.6 characterization: SEM images observed from bottom (a) and side (b) views (the thickness is about  $5.6 \mu m$ ), and appearance of the material (c).



Fig. S3 SEM images of Ni-NPs-1.4 in different magnification.



Fig. S4 SEM images of Ni-NPs-1.8 in different magnification.



Fig. S5 XRD of Ni-NPs-1.4 (a) and Ni-NPs-1.8 (b) before and after electrocatalysis.



Fig. S6 XPS survey spectra of fresh Ni-NPs-1.6.



**Fig. S7** HRTEM images of Ni-NPs-1.4 (a) 1.6 (b) and 1.8 (c). The edge of nanograins are marked with dashed line, yellow for Ni(111) and green for Ni(200).



**Fig. S8** (a)XRD spectra obtained in powder of Ni-NPs-1.4, 1.6 and 1.8. The grain size fitted curves (b-d) of using Scherrer formula and the strain fitted curves (e-g) using Williamson-Hall method of Ni-NPs-1.4, 1.6 and 1.8. (h) is the geometric phase analysis (GPA) of one specific GB region.



**Fig. S9** HRTEM images about Ni-NPs-1.6. The GBs are marked with dashed line, the orientation of different lattice planes was marked with solid line, orange for Ni(111), yellow for Ni(200) and green for Ni(220).



**Fig. S10** STEM-HAADF images of different types of GB ragions with different angle. The dashed line represents the GB; The solid line represents the lattice planes and orientations of different fringes, orange for Ni (111) and yellow for Ni (200).



Fig. S11 UV-Vis absorption spectra (a) and concentration-absorbance calibration curve(b) of nitrite.



Fig. S12 UV-Vis absorption spectra (a) and concentration-absorbance calibration curve(b) of ammonia.



Fig. S13 Comparison of NH<sub>3</sub> rate determined by Nessler's reagent and NMR method.



**Fig. S14** Active number calculation using redox peak method. (a) is the LSV curve of Ni-NPs-1.4, 1.6 and 1.8 recorded in 1 M KOH, with scan rate of  $5 \text{ mV s}^{-1}$ . (b) is the TOF value of Ni-NPs-1.4, 1.6 and 1.8 under different applied potential. (The massive GB defects could lead to a high TOF, which stays consistent with the DFT simulation results.)

Sample	Area of redox peak V·A cm <sup>-2</sup>	Charge transfer C cm <sup>-2</sup>	Active site number $\times 10^{18} \text{ cm}^{-2}$
Ni-NPs-1.4	0.01009	2.018	6.30
Ni-NPs-1.6	0.01026	2.052	6.40
Ni-NPs-1.8	0.00952	1.850	5.77

 Table S1. Active number calculation using Redox Peak method.

Sample	Applied potential V vs. RHE	$ m NH_3$ number per cm <sup>2</sup> per s $ m  imes 10^{20}~cm^{-2}~s^{-1}$	TOF s <sup>-1</sup>
	-0.13	2.89	45.90
	-0.33	4.67	74.11
Ni-NPs-1.4	-0.53	9.77	155.19
	-0.73	14.6	231.11
	-0.93	21.6	343.05
	-0.13	3.60	56.28
	-0.33	7.27	113.52
Ni-NPs-1.6	-0.53	14.3	222.85
	-0.73	21.2	330.70
	-0.93	25.9	404.59
	-0.13	1.95	33.71
	-0.33	4.33	74.92
Ni-NPs-1.8	-0.53	6.31	109.31
	-0.73	8.58	148.65
	-0.93	10.6	183.93

Table S2. TOF calculation.



Fig. S15 CV curves of Ni-NPs-1.4(a), Ni-NPs-1.6(b), Ni-NPs-1.8(c); and Cdl of the samples(d); LSV curves normalized by ECSA(e).

Table S3.	ECSA	of different	sampl	les.

Sample	$Cdl (mF cm^{-2})$	ECSA(cm <sup>2</sup> )
Ni-NPs-1.4	39.1	652
Ni-NPs-1.6	33.9	565
Ni-NPs-1.8	32.6	543



Fig. S16 LSV curves of Ni-NPs-1.6 at different electrodeposition time. (The current density rises when the deposition time increases from 600s to 1400s, but remains almost no change with further increase.)



Fig. S17 LSV curves of Ni-NPs-1.6 in different NaNO<sub>3</sub> concentration, bubbles generated at cathode in circled area.



Fig. S18 i-t curves of Ni-NPs-1.4 in different reduce potential.



Fig. S19 i-t curves of Ni-NPs-1.6 in different reduce potential.



Fig. S20 i-t curves of Ni-NPs-1.8 in different reduce potential.



**Fig. S21** NH<sub>3</sub> rate of Ni-NPs-1.6 without NaNO<sub>3</sub>. (Carbon cloth with  $1 \text{ mol } L^{-1} \text{ NaNO}_3 + 1 \text{ mol } L^{-1} \text{ NaOH}$ , Ni-NPs-1.6 with  $1 \text{ mol } L^{-1} \text{ NaNO}_3 + 1 \text{ mol } L^{-1} \text{ NaOH}$  at -0.33 V (vs. RHE) reduce potential. Time = 5 h.)



**Fig. S22** Reductive products composition of carbon cloth. Electrolyte:  $1 \mod L^{-1} \operatorname{NaNO}_3 + 1 \mod L^{-1} \operatorname{NaOH}$ . Time = 5 h. Reduce potential = -0.33 V (vs. RHE).



Fig. S23 XPS survey spectra (a) and XPS spectra of Ni 2p (b) of Ni-NPs-1.6 after experiment.



Fig. S24 XRD pattern comparison of Ni-NPs-1.6 before and after electrocatalysis.



Fig. S25 SEM images in different magnification of Ni-NPs-1.6 after electrocatalysis. (The structure of the material is maintained, indicating a good stability.)



Fig. S26 TEM and HRTEM images of Ni-NPs-1.6 after electrocatalysis.



Fig. S27 Composition of the products at different reduce potential (Ni-NPs-1.4).



Fig. S28 Composition of the products at different reduce potential (Ni-NPs-1.8).



**Fig. S29** Catalytic activity of bulk Ni materials (Ni plate and Ni foam) and chemical synthesized Ni material (Ni  $H_2$  and Ni NaHB). (a) is the LSV curve, (b) is the i-t curve, (c) is the NH<sub>3</sub> rate, (d) is the products distribution.



Fig. S30 i-t curve under different reduce potential for the reduction of nitrite. (The nitrite generated during nitrate reduction can also be regarded as intermediate product, not final product.)



Fig. S31 Equipment schematic for stability test and industrial simulation, the electrolyte flow rate was set as  $\sim 1 \, \text{mL min}^{-1}$ .



Fig. S32 V-t curves (a) of the 2-hour experiments to calculate the FE and NH<sub>3</sub> rate and (b) the NH<sub>3</sub> rate comparison before and after stability test.

Current density (A cm <sup>-2</sup> )	Stability test duration (h)	FE change for NH <sub>3</sub> (%)	Reference
2	30	92.4 → 85.8	This work
~0.3	12	$92.5 \rightarrow 85.1$	Nat. Commun. 2022, 13, 2338
~0.24	20	$\sim 94 \rightarrow \sim 92$	CCS Chem. 2022, 4, 2053-2064
~0.08	10	$\sim 97 \rightarrow \sim 80$	Small 2022, 18, 2107136

Table S4. Stability comparison with some published articles



Fig. S33 The data fitting of electrons transfer number estimation.

T-11. CE	E'44 1	1	1 1 4	· · · ·	1 1	1.00	1
Lable S5.	Fiffed	sione ar	id electron	transfer num	ber linder	different	potential
14010 000	1 10000	biope an		transfer mann	oor ander	annerene	potentian

Potential (V vs. RHE)	Slope $(A^{-1} s^{-1/2})$	Number of electron transfer
-0.20	-703	2.6
-0.25	-435	4.1
-0.30	-354	5.1
-0.35	-339	5.3



**Fig. S34** Linear fit of  $\ln[j]$  against  $\ln[c](a)$  to obtain the reaction rate order (b).



Fig. S35 LSV curves of Ni-NPs-1.6 in different proportion of mixed  $D_2O$  and  $H_2O$  solution,  $n = D_2O/[D_2O + H_2O]$ .



Fig. S36 Side view of the built structure for grainboundary Ni (a) and pristine Ni (b).



Fig. S37 Adsorption configuration of different intermediates on grainboundary and pristine Ni, top view and side view.



Fig. S38 Schematic for one catalytic cycle.



Fig. S39 The adsorption configuration of the intermediates in HER.

Catalyst	Electrolyte	FE	Reduce potential (V vs. RHE)	NH₃ rate (mmol h <sup>-1</sup> cm <sup>-2</sup> )	Ref.
Ni-NPs-1.6	1 M NaNO₃ + 1M NaOH	92.6%	-0.73	12.66	This work
Ni-NPs-1.6	1 M NaNO₃ + 1M NaOH	93.0%	-0.93	15.49	This work
Strained Ru nanoclusters	1 M KNO <sub>3</sub> + 1M KOH	~100%	-0.2	1.17	J. Am. Chem. Soc. 2020, 142, 7036–7046.
Fe SAC	0.1 M KNO₃ + 1M KOH	86%	-0.21	0.28	Nat. Commun. 2021, 12, 2870.
HSCu-AGB@C	0.1 M KNO₃ +1 M KOH	94%	-0.2	0.98	CCS Chem. 2021, 4, 2053- 2064.
CoP/CFC	1 M NaNO₃ + 1M NaOH	~100%	-0.3	0.96	Energy Environ. Sci. 2022, 15, 760–770.
Fe SAC	0.1 M KNO₃ + 0.1 M KOH	98%	-0.7	0.16	Energy Environ. Sci. 2021, 14, 3522–3531.
Cu-NBs-100	0.1 M KNO <sub>3</sub> +1 M KOH	95%	-0.15	1.30	Energy Environ. Sci. 2021, 14, 4989–4997.
Fe-cyano-R NSs	0.1 M KNO₃ + 1M KOH	86%	-0.6	1.57	ACS Nano 2022, 16, 1072– 1081.
Ru-CuNW	0.1 M KNO3 + 1M KOH	95.6%	-0.135	4.5	Nat. Nanotechnol. 2022, 17, 759–767.
CuCo SP	0.1 M KNO <sub>3</sub> + 0.1M KOH	90.6%	-0.175	1.17	Nat. Commun. 2022, 13, 1129.
$Cu_{50}Ni_{50}$ alloy	0.1 M KNO <sub>3</sub> + 1M KOH	99%	-0.15	0.25	J. Am. Chem. Soc. 2020, 142, 5702–5708

**Table S6.** Summary of the electrocatalytic activity in reported literature (Nitrate to ammonia).

Catalyst	Electrolyte	FE	Reduce potential (V vs. RHE)	NH₃ rate (mmol h <sup>-1</sup> cm <sup>-2</sup> )	Ref.
Ni-NPs-1.6	1 M NaNO <sub>2</sub> + 1M NaOH	98%	-0.73	13.71	This work
Ni-NPs-1.6	1 M NaNO <sub>2</sub> + 1M NaOH	85%	-0.93	11.44	This work
Co@JDC/GF	0.1 M KNO <sub>3</sub> + 0.1M KOH	96%	-0.9 vs. Ag/AgCl	2.35	J. Mater. Chem. A 2022, 10, 2842–2848.
CoP NA/TM	500 ppm NaNO <sub>2</sub> + 0.1 M PBS	90%	-0.2	0.13	Nano Res. 2022, 15, 972–977.
Ni <sub>35</sub> /NC-sd	0.3 M NaNO <sub>2</sub> +0.5 M Na <sub>2</sub> SO <sub>4</sub>	80%	-1.4	1.47	Angew. Chem. Int. Ed. 2021, 60, 20711–20716.
Cu₃P NA/CF	0.1 M NaNO2 0.1 M PBS	91%	-0.5	0.09	Green Chem. 2021, 23, 5487–5493.
Ni-NSA-V <sub>Ni</sub>	200 ppm NaNO <sub>2</sub> + 0.2 M Na <sub>2</sub> SO <sub>4</sub>	89%	-1.2 vs. SCE	0.24	J. Mater. Chem. A 2021, 9, 239–243.

**Table S7.** Summary of the electrocatalytic activity in reported literature (nitrite to ammonia).

#### **3** References

Carvalho, O. Q.; Marks, R.; Nguyen, H. K. K.; Vitale-Sullivan, M. E.; Martinez, S. C.; Árnadóttir,
 L.; Stoerzinger, K. A., Role of Electronic Structure on Nitrate Reduction to Ammonium: A Periodic
 Journey. J. Am. Chem. Soc. 2022, 144 (32), 14809–14818.

2. Wang, Y.; Zhou, W.; Jia, R.; Yu, Y.; Zhang, B., Unveiling the Activity Origin of a Copper-based Electrocatalyst for Selective Nitrate Reduction to Ammonia. Angew. Chem. Int. Ed. 2020, 59 (13), 5350-5354.

3. Li, P.; Jin, Z.; Fang, Z.; Yu, G., A single-site iron catalyst with preoccupied active centers that achieves selective ammonia electrosynthesis from nitrate. Energy Environ. Sci. 2021, 14 (6), 3522-3531.

4. Gao, Q.; Pillai, H. S.; Huang, Y.; Liu, S.; Mu, Q.; Han, X.; Yan, Z.; Zhou, H.; He, Q.; Xin, H.; Zhu, H., Breaking adsorption-energy scaling limitations of electrocatalytic nitrate reduction on intermetallic CuPd nanocubes by machine-learned insights. Nat. Commun. 2022, 13 (1), 2338.

5. Wang, Y.; Li, H.; Zhou, W.; Zhang, X.; Zhang, B.; Yu, Y., Structurally disordered RuO2 nanosheets with rich oxygen vacancies for enhanced nitrate electroreduction to ammonia. Angew. Chem. Int. Ed. 2022, 61 (19), e202202604.

6. (a) Kresse, G.; Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. J. Comput. Mater. Sci. 1996, 6, 15–50. (b) Kresse, G.; Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. J. Phys. Rev. B 1996, 54, 11169–11186.

7. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.

8. (a) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Phys. Rev. B 1999, 59, 1758-1775. (b) Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B 1994, 50, 17953-17979.