Electronic Supplementary Information

Tailoring metal-support interaction over faceted TiO₂ and copper nanoparticles for electrocatalytic nitrate reduction to ammonia

Wahyu Prasetyo Utomo,^a Hao Wu,^{b,*} Liu Rui,^a Yun Hau Ng^{a,*}

^aLow-Carbon and Climate Impact Research Centre, School of Energy and Environment, City University of Hong Kong, Kowloon, Hong Kong SAR 999077, China

^bMacao Institute of Materials Science and Engineering (MIMSE), Faculty of Innovation Engineering, Macau University of Science and Technology, Taipa, Macau SAR 999078, China

*Corresponding authors: <u>wuhao@must.edu.mo</u> (H. Wu); <u>yunhau.ng@cityu.edu.hk</u> (Y.H. Ng)

1. Experimental

1.1 Materials

Titanium(IV) oxysulfate (TiOSO₄, ≥29 Ti (as TiO₂) basis), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O purity 99.99%), sodium sulfate (Na₂SO₄ purity \geq 99.9%), sodium hydroxide (NaOH purity >99.9%), sodium citrate dihydrate (HOC(COONa)(CH₂COONa)₂·2H₂O purity \geq 99%), salicylic acid (2-(HO)C₆H₄CO₂H purity \geq 99.0%), sodium hypochlorite (NaClO 10-15%), sodium nitroferricyanide (Na₂[Fe(CN)₅NO]·2H₂O purity ≥99%), sulfamic acid (H₃NO₃S purity 99.30%), N-(1-Naphthyl)ethylenediamine dihydrochloride (C10H7NHCH2CH2NH2·2HCl purity >98%), and sulfanilamide (H2NC6H4SO2NH2 purity \geq 99%), sodium nitrate (NaNO₃ purity \geq 99.9%), para-(dimethylamino)benzaldehyde ((CH₃)₂NC₆H₄CHO purity 99%) were purchased from Sigma Aldrich. Potassium nitrate (KNO₃ purity \geq 99.0%) was purchased from VWR chemicals. Sodium fluoride (NaF purity >99%) was purchased from Adamas. Hydrochloric acid (HCl 37%) was purchased from Fluka. All chemicals were directly used without further purification. Ultrapure water (18.2 megaohm·cm) was obtained by using Mili-Q Synthesis System.

1.2. Determination of ion concentration

The UV-vis spectrophotometer was used to detect the ion concentration of the catholyte before and after NO₃⁻RR. The catholyte was diluted to an appropriate concentration to match the range of the calibration curves. The details of the detection methods for each ion are as follows:

1.2.1. Determination of NO_3^- -N

A certain amount of electrolyte was taken from the cathode chamber and diluted to 5 mL. Then, 0.1 mL 1.0 M HCl and 0.01 mL 0.8 wt% sulfamic acid solution were added consecutively into the sample solution. The absorption spectrum was measured using a UV-vis spectrophotometer, and the absorption intensities at a wavelength of 220 nm and 275 nm were recorded. The final absorbance value was calculated by this equation: $A=A_{220nm}-2A_{275nm}$. The concentration-absorbance curve was calibrated using a series of standard potassium nitrate solutions. The potassium nitrate was dried at 105 °C for 2 h in advance before using it to prepare the standard solutions.

1.2.2 Determination of NO_2^- -N

The concentration of NO₂⁻-N was determined using the colorimetric method. A mixture of paminobenzenesulfonamide (4 g), N-(1-Naphthyl) ethylenediamine dihydrochloride (0.2 g), ultrapure water (50 mL), and phosphoric acid (10 mL, ρ =1.70 g/mL) was used as a coloring reagent. A certain amount of electrolyte was taken from the cathode chamber and diluted to 5 mL to meet the detection range. Then, 0.1 mL coloring reagent was mixed thoroughly to the sample solution. The solution was then aged for 20 min and finally measured using a UV-vis spectrophotometer. The absorption intensity at 540 nm was recorded. The concentrationabsorbance curve was calibrated using a series of standard sodium nitrite (NaNO₂) solutions. NaNO₂ was dried at 105 °C for 2 h in advance before using it to prepare the standard solutions. *1.2.3. Determination of NH₃-N*

The concentration of NH₃ was determined by the indophenol-blue method using UV-vis spectrophotometry as in the previous report.^{1,2} In detail, 2 mL of standard solution or sample solutions obtained from the catholyte after the reaction were mixed with 2 mL of chromogenic reagent A, 1 mL of solution B, and 0.2 mL of catalyzing solution C (Solution A was made of 1.0 M NaOH containing 5 wt% salicylic acid and 5 wt% sodium citrate, solution B was 0.05 M sodium hypochlorite, and solution C was 1 wt% sodium nitro-ferricyanide). After shaking and standing for 1 h, the absorption spectrum of the solution was then measured using UV-vis spectrophotometer in the wavelength range of 550-800 nm. The formation of indophenol blue was determined from absorbance at 655 nm. The standard calibration curve was made using standard NH₄Cl solution with a series of concentrations. The ammonium chloride was dried at 105 °C for 4 h in advance before using it to prepare the standard solutions.

1.3 Performance calculation

The electrocatalytic performances are reflected by NH_3 yield, NH_3 Faradaic efficiency (FE_{NH3}), NO_3^- conversion, and NH_3 selectivity as well as NO_2^- selectivity.

The NH₃ yield was calculated based on Equation 1:

$$NH_3 yield = \frac{c \times v}{t \times m}$$
⁽¹⁾

, where *c* is the NH₃ concentration, *v* is the volume of the electrolyte in the cathode chamber, *t* is the reduction reaction time, and *m* is the mass of deposited catalyst. The FE_{NH3} was calculated by the Equation 2:

$$FE = \frac{8F \times c \times v}{17 \times Q} \tag{2}$$

, where *F* is the Faraday constant, *c* is a concentration of NH_3 , *v* is the volume of electrolyte in the cathode chamber, 17 is the molecular mass of NH_3 , and Q is the total charge used for the electrodes.

The conversion was calculated using Equation 3, while the selectivity of NH_3 and NO_2^- was obtained by Equation 4 as follow:

$$Conversion(\%) = \frac{\Delta c_{NO_3^-}}{c_0} \times 100\%$$
⁽³⁾

$$Selectivity (\%) = \frac{c}{\Delta c_{NO_3^-}} \times 100\%$$
⁽⁴⁾

, where $\Delta c_{NO_3^-}$ is the concentration difference of NO₃⁻ before and after the reaction, c_0 is the initial concentration of NO₃⁻, and *c* is the generated concentration of NH₃ or NO₂⁻.

1.4 Determination of hydrazine (N₂H₄)

The possible N₂H₄ product was estimated by the Watt and Chrisp method.¹ The chromogenic reagent was prepared by dissolving 2.0 g para-(dimethylamino)benzaldehyde in a mixture of 10 mL concentrated HCl and 100 mL methanol. For the measurement, 5 mL of samples was mixed with 5 mL of chromogenic reagent and stirred for 10 min. After stirring, the absorption spectrum solution was directly measured using the UV-vis spectrophotometer at a wavelength range of 410-500 nm. The hydrazine concentration was determined from the absorbance at 455

nm. The standard calibration curve was made using the standard N_2H_4 solution with a series of concentrations ranging from 0.1 to 0.5 μ g mL⁻¹ in 0.5 M Na₂SO₄.

1.5 Kinetic analyses

The apparent kinetics rate constant (k_{ap}) for NO₃⁻RR were calculated based on the pseudo-first order Langmuir-Hinshelwood model (Equation 5)

$$-\ln\frac{C}{C_0} = k_{ap} t \tag{5}$$

, where C_0 is the nitial concentration of NO₃⁻, C is the NO₃⁻ concentration at reaction time t, t is time (min) and kap is the apparent rate constant.³ The NO₃⁻RR was performed at -0.9 V vs. RHE.

The apparent activation energy (E_a) was determined according to the Arrhenius plot (Equation 6) by performing NO₃-RR experiment in various temperature (20, 40, and 60 °C) at -0.9 V vs. RHE.

$$k_{ap} = Ae^{\left(-\frac{E_a}{RT}\right)} \tag{6}$$

, where k_{ap} is the apparent rate constant, A is the pre-exponential factor, T is the reaction temperature, and R is the universal gas constant.^{3,4}

Tafel slopes were determined by Tafel plots (Equation 7).

$$E = a + b \log(J_{NH3}) \tag{7}$$

, where *E* is the applied potential (V vs. RHE), J_{NH3} is the partial current density of NH₃, *a* is a constant and *b* is the Tafel slope.³

2. Results



Figure S1 SEM images of a) (001)-dominant TiO_2 , b) (101)-dominant TiO_2 , and c) representative model of TiO_2 with (001) and (101) exposed facets used for the calculation.

The (001) facet exposure is calculated based on Equation 5^5

$$S_{(001)}\% = \frac{a^2}{a^2 + (a+b)(b-a)\tan 68.3^\circ} \times 100\%$$
(5)

with θ is the theoretical angle value (68.3°) between (101) and (001) direction of anatase TiO₂.⁵ Based on the calculation over 30 representative measured particles, the facet exposure can be determined as follows:

- a) Facets exposure on (001)-dominant TiO₂: ~70.2% of (001) facets and ~29.8% of (101) facets.
- b) Facets exposure on (101)-dominant TiO₂: ~33.2% of (001) facets and ~66.8% of (101) facets.



Figure S2 a) TEM image of (001)-dominant Cu-TiO₂ with corresponding elemental mapping of b) Ti, c) O, and d) Cu elements.



Figure S3 a) TEM image of (101)-dominant Cu-TiO₂ with corresponding elemental mapping of b) Ti, c) O, and d) Cu elements.



Figure S4 a-c) HRTEM images of (001)-dominant $Cu-TiO_2$ used to calculate the average size of Cu nanoparticles loaded on (001)-dominant TiO₂. The calculation was performed over 100 representative Cu nanoparticles.



Figure S5 a-c) HRTEM images of (101)-dominant Cu-TiO₂ used to calculate the average size of Cu nanoparticles loaded on (101)-dominant TiO₂. The calculation was performed over 100 representative Cu nanoparticles.



Figure S6 CV curves of (001)-dominant Cu-TiO₂, (101)-dominant Cu-TiO₂, and Cu₂O in 0.5 M Na₂SO₄. Cu₂O is used as a reference material.



Figure S7 LSV curves of pristine (001)-dominant TiO_2 and (101)-dominant TiO_2 . The LSV measurements were performed in 0.5 M Na₂SO₄ without and with the addition of 50 ppm NO₃⁻-N.



Figure S8 The calibration curves of a) NO_3^--N , b) NH_3-N , and c) NO_2^--N .



Figure S9 NO_3^- conversion over faceted-TiO₂-based electrocatalysts. All catalytic activity experiments were performed in 0.5 M Na₂SO₄ containing 50 ppm NO₃⁻-N.



Figure 10 FE_{NH3} over faceted-TiO₂-based electrocatalysts. All catalytic activity experiments were performed in 0.5 M Na₂SO₄ containing 50 ppm NO₃⁻-N.



Figure S11 FE_{H2} over faceted-TiO₂-based electrocatalysts. All catalytic activity experiments were performed in 0.5 M Na₂SO₄ containing 50 ppm NO₃⁻-N.



Figure S12 NO_2^- selectivity over faceted-TiO₂-based electrocatalysts. All catalytic activity experiments were performed in 0.5 M Na₂SO₄ containing 50 ppm NO₃⁻-N.



Figure S13 FE_{NO2} over faceted-TiO₂-based electrocatalysts. All catalytic activity experiments were performed in 0.5 M Na₂SO₄ containing 50 ppm NO₃⁻-N.



Figure S14 a) UV-Vis absorption spectra of N_2H_4 standard solution and b) corresponding calibration curve of the N_2H_4 . The absorbance is taken from the wavelength of 455 nm. c) The UV-Vis absorption spectra of electrolyte before and after reaction. The electrolyte was taken from the reaction using (101)-dominant Cu-TiO₂ performed at -0.9 V vs. RHE in 0.5 M Na₂SO₄ containing 50 ppm NO₃⁻-N.



Figure S15 Control experiment using (101)-dominant Cu-TiO₂ without the addition of NO₃, and in open circuit potential (OCP). Note that the absorbance curve of (101)-dominant Cu-TiO₂ is obtained after 20 times of dilution from the catholyte, while no dilution was performed for the control experiment without NO₃⁻ and in OCP.



Figure S16 UV absorbance spectra of the electrolyte (0.5 M Na₂SO₄) containing 50 ppm NO_3^- –N after exposure to air for 8 h. No accumulation of NH₃ during 8 hours of exposure excluding the possible contamination from the environment (atmosphere).



Figure S17 EPR spectra of pristine (101)-dominant TiO₂ (black) and NaBH₄-reduced (101)-dominant TiO₂. (101)-dominant TiO₂ is used as the representative samples to verify the formation of OVs upon NaBH₄ treatment. Both pristine (101)-dominant TiO₂ and reduced (101)-dominant TiO₂ show a pair of steep peaks at g = 2.003, which can be correlated with the electron trapping at OVs.⁶ The slightly higher peak intensity of reduced (101)-dominant TiO₂ compared to the pristine counterpart suggests the formation of OVs at certain degree upon NaBH₄ reduction process.



Figure S18 Comparison of a) NH₃ yield and b) NH₃ selectivity over pristine (001)dominant TiO₂, reduced-(001)-dominant-TiO₂, and (001)-dominant Cu-TiO₂. Comparison of c) NH₃ yield and d) NH₃ selectivity over pristine (101)-dominant TiO₂, reduced-(101)-dominant-TiO₂, and (101)-dominant Cu-TiO₂. All experiments were performed in 0.5 M Na₂SO₄ containing 50 ppm NO₃⁻-N.



Figure S19 Comparison of a) NH₃ yield and b) NH₃ selectivity over pristine (001)dominant TiO₂, Cu nanoparticles, and (001)-dominant Cu-TiO₂. Comparison of c) NH₃ yield and d) NH₃ selectivity over pristine (101)-dominant TiO₂, Cu nanoparticles, and (101)-dominant Cu-TiO₂. Note that the sum of the NH₃ yield of pristine faceted TiO₂ (in both (001)-dominant TiO₂ and (101)-dominant TiO₂) with the Cu nanoparticles in each potential are still lower compared to the NH₃ yield exhibited by (001)-dominant Cu-TiO₂ and (101)-dominant Cu-TiO₂. This result indicates that the enhancement of NH₃ yield in Cu-loaded faceted TiO₂ is mainly determined by the interaction between Cu nanoparticles and the faceted TiO₂ instead of the individual/independent contribution between the two components. All experiments were performed in 0.5 M Na₂SO₄ containing 50 ppm NO₃⁻-N.



Figure S20 Langmuir-Hinshelwood plots on NO_3^- concentration decrease over faceted-TiO₂-based catalysts. All experiments were performed at -0.9 V vs. RHE in 0.5 M Na₂SO₄ containing 50 ppm NO_3^- –N under ambient conditions.



Figure S21 Arrhenius plots on NO_3^- concentration decrease over faceted-TiO₂-based catalysts. All experiments were performed at -0.9 V vs. RHE in 0.5 M Na₂SO₄ containing 50 ppm NO_3^- –N. The temperatures varied at 20, 40, and 60 °C.



Figure S22 Tafel plots over (001)-dominant Cu-TiO₂ and (101)-dominant Cu-TiO₂.



Figure S23 NO₃⁻, NH₃, and NO₂⁻ concentration changes over a) (101)-dominant TiO₂ and b) (101)-dominant Cu-TiO₂ during 4 h of reaction. All experiments were performed at -0.9 V vs. RHE in 0.5 M Na₂SO₄ containing 50 ppm NO₃⁻–N.



Figure S24 Comparison of NO_2^- concentration changes over (001)-dominant Cu-TiO₂ and (101)-dominant Cu-TiO₂. The experiments were performed at -0.9 V vs. RHE in 0.5 M Na₂SO₄ containing 50 ppm NO_3^- –N.



Figure S25 CV plots over faceted-TiO₂-based catalysts in non-Faradaic regions with various scan rates.



Figure S26 Mott-Schottky plots of a) (001)-dominant TiO_2 and (001)-dominant Cu-TiO₂ and b) (101)-dominant TiO₂ and (101)-dominant Cu-TiO₂.

No	Electrocatalyst	Electrolyte	NH ₃ yield rate (μg mg _{cat} ⁻¹ h ⁻)	FE _{NH3} (%)	NH ₃ selectivity (%)	Potential (V vs. RHE)	Ref
1	(101)-dominant Cu-TiO ₂	0.5 M Na ₂ SO ₄ + 50 ppm NO ₃ ⁻ -N	447.5	67.1 (-0.8 V)	66.7	-0.9	This work
2	TiO _{2-x}	0.5 M Na ₂ SO ₄ + 50 ppm NO ₃ ⁻ -N	~765	85.0	87.1	-1.6 ^{a)}	7
3	Defected-TiO ₂ nanotube	0.5 M Na ₂ SO ₄ + 15 mM NO ₃ ⁻ (210 ppm NO ₃ ⁻ -N)	~1190	43	91	-1.6	8
4	Co@TiO2/titanium plate	0.1 M PBS + 0.1 M NO ₃ ⁻ (~1400 ppm NO ₃ ⁻ -N)	~13600 ^{b)}	96.7	-	-1.0	9
5	Nb-doped TiO ₂	0.1 M PBS + 0.1 M NO ₃ ⁻ (~1400 ppm NO ₃ ⁻ -N)	27940	70.64	-	-1.35	10
6	Ti foil	0.4 M [NO ₃ ⁻] at pH ~0.77	-	82	-	-1	11
7	Co ₃ O ₄ /Ti	0.05 M Na ₂ SO ₄ + 100 ppm NO ₃ ⁻ -N	-	-	32		12
8	Cu nanobelts (100)	50.1 M PBS + 500 ppm KNO ₃	~2227	~50	72.88	-0.6	13
9	Cu-molecular	$0.1 \text{ M PBS} + 500 \text{ ppm NO}_3^-$	~442	85.9	-	-0.4	14

Table S1 Comparison of the activity of Ti-based electrocatalysts and Cu catalysts toward electrocatalytic NO3⁻RR in neutral media.

 $^{a)}V$ vs. SCE $^{b)}\mu g~cm^{\text{-}2}~h^{\text{-}1}$

Sample	R _s (Ohm)	<i>R</i> ст (Ohm)
(001)-dominant TiO ₂	6.06	74.38
(001)-dominant Cu-TiO ₂	5.51	27.20
(101)-dominant TiO ₂	5.52	152.50
(101)-dominant Cu-TiO ₂	5.78	40.28

Table S2 R_S and R_{CT} values over faceted-TiO₂-based catalysts.

References:

- 1 L. Li, C. Tang, B. Xia, H. Jin, Y. Zheng and S.-Z. Qiao, ACS Catal., 2019, 9, 2902–2908.
- 2 Y. Zhang, J. Hu, C. Zhang, Y. Liu, M. Xu, Y. Xue, L. Liu and M. K. H. Leung, *J. Mater. Chem. A*, 2020, **8**, 9091–9098.
- 3 Y. Wang, L. Zhang, Y. Niu, D. Fang, J. Wang, Q. Su and C. Wang, *Green Chem.*, 2021, 23, 7594–7608.
- 4 P. Wang, L. Yang, Y. Q. Gao and X. S. Zhao, Nucleic Acids Research, 2015, 43, 7207–7216.
- 5 N. Sutradhar, A. K. Biswas, S. K. Pahari, B. Ganguly and A. B. Panda, *Chem. Commun.*, 2014, **50**, 11529–11532.
- 6Z. Han, C. Choi, S. Hong, T.-S. Wu, Y.-L. Soo, Y. Jung, J. Qiu and Z. Sun, *Appl. Catal. B*, 2019, **257**, 117896.
- 7 R. Jia, Y. Wang, C. Wang, Y. Ling, Y. Yu and B. Zhang, ACS Catal., 2020, 10, 3533–3540.
- 8 Q. Zhang, Y. Li, M. Geng, J. Zhu, H. Sun and B. Jiang, *Applied Catalysis B: Environmental*, 2023, **330**, 122658.
- 9 X. Fan, D. Zhao, Z. Deng, L. Zhang, J. Li, Z. Li, S. Sun, Y. Luo, D. Zheng, Y. Wang, B. Ying, J. Zhang, A. A. Alshehri, Y. Lin, C. Tang, X. Sun and Y. Zheng, *Small*, 2023, **19**, 2208036.
- 10 X. Du, K. Wang, T. Wang, H. Guo, J. S. Chen, J. Wang and T. Li, *International Journal of Hydrogen Energy*, DOI:10.1016/j.ijhydene.2023.06.127.
- 11 J. M. McEnaney, S. J. Blair, A. C. Nielander, J. A. Schwalbe, D. M. Koshy, M. Cargnello and T. F. Jaramillo, *ACS Sustainable Chem. Eng.*, 2020, **8**, 2672–2681.
- 12 L. Su, K. Li, H. Zhang, M. Fan, D. Ying, T. Sun, Y. Wang and J. Jia, *Water Res.*, 2017, **120**, 1–11.
- 13 Q. Hu, Y. Qin, X. Wang, Z. Wang, X. Huang, H. Zheng, K. Gao, H. Yang, P. Zhang, M. Shao and C. He, *Energy Environ. Sci.*, 2021, **14**, 4989–4997.
- 14 G.-F. Chen, Y. Yuan, H. Jiang, S.-Y. Ren, L.-X. Ding, L. Ma, T. Wu, J. Lu and H. Wang, *Nat. Energy*, 2020, **5**, 605–613.