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Supporting Information

Selective electrocatalytic reduction of nitrate-to-ammonia using Co(II)-decorated TiO₂ nanosheets[†]

Yan-Tong Xu,^a Ying Han^a Daniel Kobina Sam^{a,c} and Yan Cao^{*a,b}

^a Guangdong Provincial Key Laboratory of New and Renewable Energy Research and

Development, Guangzhou Institute of Energy Conversion, Chinese Academy of

Sciences, Guangzhou 510640, China.

^b College of Chemistry and Chemical Engineering, Anhui University, Hefei 230601,

China.

* Correspondence: caoyan@ms.giec.ac.cn (Y. C.)

Chemicals and Materials. KNO₃ (99%), Titanium butoxide (Ti(OBu)₄·(TBOT), 99%), hydrofluoric acid (HF, 40%), glycol (99%), potassium phosphate dibasic(K₂HPO₄·3H₂O, 99.0%), potassium phosphate monobasic(KH₂PO₄, 99.5%), cobalt(II) acetate tetrahydrate (Co(OAc)₂·4H₂O, 99.5%), copper(II) acetate monohydrate (Cu(OAc)₂·H₂O, 99.0%) and iron chloride hexahydrate (FeCl₃·6H₂O, 99.0%) were purchased

from Aladdin. Carbon cloth (CC) was purchased from CE Tech Co., Ltd. Ar gas (99.999%) was purchased from Sheng Ying gas Co., Ltd.

Characterization. Scanning electron microscopy (SEM) images were collected with the adaption of the Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping images were performed with the Japan Electron Optics Laboratory JEM-2100F transmission electron microscope, equipped with JEM-2010HR-Vantage typed energy spectrometer. X-ray diffraction (XRD) patterns were recorded with the PANalytical X'Pert Pro MPD using a Cu K α source (λ = 0.154184 nm), whose working voltage and current of 40 kV and 40 mA, respectively. X-ray photoelectron spectrum (XPS) analysis was performed on the Thermo Fisher Scientific ESCALAB 250Xi with monochromatic Al K α radiation, and the obtained binding energies were further calibrated by the reference of the C1s peak at 284.8 eV. Fourier transformed-infrared (FI-IR) spectroscopy was tested on Shimadzu IRPrestige-21 spectrometer. Inductively-coupled plasma optical emission spectroscopy (ICP-OES,) was performed on the PerkinElmer OPTIMA 8000DV spectrometer. Quantachrome Autosorb-iQ-2 system was adapted for the 77 K N₂ adsorption isotherm test.

ICP-OES test. A certain amount of sample was mixed with 1.0 mL HF (40%) and heated at 150 °C for 24 h. After cooling down to room temperature, the clear solution was diluted into 10.0 mL with distilled water in a volumetric flask for the ICP-OES test. Finally, the content (M%) was calculated by the following equation:

$$M\% = c_{\rm M} \times V/m_{\rm M/TiO2 NS} \times 100\%$$

where $c_{\rm M}$ represents the detected concentration of Co, Cu and Fe; V is the volume of the detected solution, which is 10.0 mL; $m_{\rm M/TiO2\,NS}$ is the weight of corresponding the sample.

Samples	<i>c</i> _M / mg L ⁻¹	m _{M/TiO2 NS} / mg	V / mL	M%
Co/TiO ₂ NS	2.840	2.1	10.0	1.35%
Cu/TiO ₂ NS	5.806	2.0	10.0	2.90%
Fe/TiO ₂ NS	9.067	2.0	10.0	4.53%

Table S1 ICP-OES results

XAFS Measurement and Analysis. The Co *K*-edge XAFS data of Co/TiO₂ NS was collected at 1W1B-XAFS beamline at the Beijing Synchrotron Radiation Facility (BSRF), operating at 2.5 GeV with an average current of 250 mA. Using Si(111) double-crystal monochromator, the data was collected in the fluorescence mode using ionization chamber at ambient conditions. The obtained XAFS data were analyzed by Athena and Artemis software, according to the standard procedures. The k^2 -weighted EXAFS spectra were obtained by

subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k^2 -weighted $\chi(k)$ data of Co *K*-edge in the *k*-space from 3-10.86 Å⁻¹ were Fourier transformed to *R* space using a hanning windows (dk=1.0 Å⁻¹) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around Co atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of IFEFFIT software packages.

Table S2 Fitting results for Co K-edge EXAFS of Co/TiO₂ NSs.

Path	CN ^[a]	R (Å) ^[b]	σ² (Ų) ^[c]	ΔE_0 (eV) ^[d]	<i>R</i> -factor ^[e]
Co-O	3.3 ± 0.6	2.08 ± 0.01	0.001 ± 0.002	-4.69 ± 2.66	1 22%
Co-Ti	1.2 ± 0.9	2.50 ± 0.06	0.011 ± 0.008	7.33 ± 8.91	1.22%

^[a]CN: coordination numbers; ^[b]*R*: bond length; ^[c] σ^2 : Debye-Waller factor; ^[d] ΔE_0 : the inner potential correction; ^[e]*R*-factor: goodness of fit. In addition, S_0^2 was fixed as 0.73, which was obtained through fitting reference Co sample.

DFT calculation. The DFT calculation with spin-polarization was performed on National Supercomputing Center in Shenzhen (NSCS) with the adoption of CASTEP procedure. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional was used, and the energy cutoff was set as 340.0 eV. All atomic positions were fully relaxed until energy and force reached the tolerance of 1×10^{-6} eV and 0.03 eV Å⁻¹, respectively. Moreover, the proton transfer energy (E) was calculated according to the following equation:

E = E(final) - E(initial)

where E(final) and E(initial) represent the energies of final and initial state, respectively.

Synthesis of TiO₂ nanosheet (TiO₂ NS). The preparation of TiO₂ NS was according to the previous report [*Adv. Mater.* **2018**, *30* (11), 1705369] with a tiny modification. 5 mL 40% HF solution was added slowly into 50 mL Ti(OBu)₄·(TBOT) under vigorous stirring for 2 h. Then the mixtures were transferred into the Teflon-lined autoclave and then heated at 180 °C for 36 h. After cooling down to room temperature, the white product was collected by centrifugation and washed with anhydrous ethanol and distilled water several times. Subsequently, the product was dispersed in 0.1 M NaOH aqueous and stirred for 8 h at room temperature. Finally, the product was washed with distilled water several times and then dried at 70 °C overnight prior to

the following decoration.

Synthesis of M/TiO_2 NS (M = Co, Fe and Cu). Take Co/TiO_2 NS as an example, 100 mg TiO_2 NS was dispersed in 50 mL 0.2 g/L Co(OAc)₂ aqueous solution with stirring for 1 hour. The obtained powders were collected by centrifugation and washed with distilled water, and finally dried at 70 °C overnight. Fe/TiO₂ NS and Cu/TiO₂ NS were synthesized by the similar routes, only replacing Co(OAc)₂ by Cu(OAc)₂ and FeCl₃, respectively.

Preparation of M/TiO₂ NS (M = Co, Fe and Cu) coated carbon cloth (CC) electrode. To prepare the catalystcoated CC electrode, 5 mg of M/TiO₂ NS powders were dispersed in 1 mL ethanol solution with 20 μ L 5 wt% Nafion by ultrasonic treatment for 1 hour, giving a catalyst suspension. And then the catalyst ink was dropped onto a 1 × 1 cm² carbon cloth (CC) to afford the target mass loading. Notably, the mass loading of M/TiO₂ NS used for NARR test is 5 mg/cm².

Electrochemical Measurements. Electrochemical measurements were performed on the CHI 760E electrochemical workstation (Chenhua Co., Shanghai) in an H-type electrolytic cell separated by a proton exchange membrane (Nafion 211). Notably, the volume of cathodic electrolyte solution is fixed at 15.0 mL in all electrocatalytic tests. A graphite rod and an Ag/AgCl electrode with saturated KCl solution were employed as the counter, and reference electrodes, respectively. Electrolyte solution were bubbled by Ar flow for at least 30 mins prior to all electrochemical tests.

1.0 M phosphate buffer solution (PBS, pH = 6.53) was prepared by equivalently mixing 1.0 M K₂HPO₄ solution and 1.0 M KH₂PO₄ solution. For KNO₃-PBS solution, 1.0, 2.0, 4.0, 6.0 and 8.0 g of KNO₃ were dissolved in100 mL of the as-prepared PBS, forming the KNO₃ concentration of 0.1, 0.2, 0.4, 0.6 and 0.8 M, respectively. All potentials were calculated in the reference of reversible hydrogen electrode (RHE) according to Nernst equation:

$$E(RHE) = E(experiment) + E(Ag/AgCl, sat. KCl) + 0.059pH$$

The linear sweep voltammetry (LSV) was performed with a scan rate of 10 mV·s⁻¹. The *i-t* curve was measured through chronoamperometry (CA) test at -0.72 V potential. All static potential test were conducted with magnetic stirring of 900 rpm. 15 mL of cathodic electrolyte was collected after each testing for products quantification.

The Faradic efficiencies toward NH₃ (FE_{NH3}), partial current density toward NH₃ (J_{NH3}), NH₃ formation rate (r_{NH3}) and Faradic efficiency toward NO₂⁻ (FE_{NO2}-) can be calculated by following equations:

$$FE_{NH3}$$
 (%) = 8 $c(NH_3) \times V \times F / Q \times 100\%$

$$J_{\rm NH3} = Q \times {\rm FE}_{\rm NH3} / (A \times t)$$
$$r_{\rm NH3} = c({\rm NH}_3) \times V / (A \times t)$$
$${\rm FE}_{\rm NO2} - (\%) = 2c({\rm NO}_2^-) \times V \times {\rm F} / Q \times 100\%$$

where Q is the total charge during the NARR test; $c(NH_3)$ and $c(NO_2^-)$ are the concentration of NH_3 and NO_2^- , respectively; V is the volume of cathodic electrolyte, which is 15 mL; F is 96485 C mol⁻¹; A is 1 cm² and t is the electrolysis time.

Ammonia detection and quantification. The concentration of NH_3 was determined according to colorimetric methods by an ammonia nitrogen analyzer (HACH AMTAX compact II type). The calibration curve between concentration of NH_3/NH_4^+ and absorbance was shown as follow:



Fig. S1 The standard curve for NH₃ quantification.

Nitrate detection and quantification. The concentration of NO_3^- was confirmed by a home-built ultraviolet spectrophotometry (equipped with Deuterium lamp light source and photomultiplier detector) at the wavelength of 220 nm. The calibration curve between concentration of NO_3^- and absorbance was shown as follow:



Fig. S2 The standard curve for NO_3^- quantification.

Nitrite detection and quantification. 0.4 mL sulfanilic acid solution (4 g/L sulfanilic acid in 20% HCl) was mixed with 10 mL nitrite-containing sample. After standing for 5 mins, 0.2 mL *N*-(1-naphthyl)- ethylenediamine dihydrochloride solution (2 g/L) was added and the mixture was further stand for 15 mins. Finally, the solution was detected at 550 nm. The calibration curve between concentration of NO_2^- and absorbance was shown as follow:



Fig. S3 The standard curve for NO_2^- quantification.



Fig. S4 TEM image of pristine TiO₂ NSs.



Fig. S5 AFM image of Co/TiO2 NSs with thickness profiles for the corresponding dotted lines.



Fig. S6 The survey of XPS profiles for Co/TiO₂ NSs, Fe/TiO₂ NSs and Cu/TiO₂ NSs.



Fig. S7 EXAFS fitting result of Co K-edge for Co/TiO_2 NSs at *R* space.



Fig. S8 Schematic illustration of electrocatalytic NARR test.



Fig. S9 Time-dependent J_{NH3} and r_{NH3} over the Co/TiO₂ NSs in 0.4 M KNO₃ at -0.72 V (vs. RHE).



Fig. S10 Three 30-min consecutive recycling NARR processes at -0.72 V (*vs.* RHE) by Co/TiO₂ NSs: (a) *i-t* curves and (b) the corresponding FE_{NH3} and FE_{NO2}⁻ per cycle.



Fig. S11 The voltage effect of $J_{\rm NH3}$ and $r_{\rm NH3}$ of the Co/TiO₂ NSs in 0.4 M KNO₃ for 30 mins.



Fig. S12 Comparison of $J_{\rm NH3}$ and $r_{\rm NH3}$ over the Co/TiO₂ NSs in different nitrate concentrations at -0.72 V (vs.

RHE) for 30 mins.



Fig. S13 TEM image of the Co/TiO_2 NSs after long-term electrolysis and collected from the electrode by ultrasonic treatment.



Fig. S14 XRD pattern of the Co/TiO₂ NSs after long-term electrolysis and collected from the electrode by ultrasonic treatment.



Fig. S15 XRD patterns of Co/TiO_2 NSs samples with different Co contents.



Fig. S16 Comparison of FE_{NH3} of Co/TiO₂ NSs samples with different Co contents at -0.72 V (*vs.* RHE) for 30 mins. The decline of FE_{NH3} with high Co content probably caused by aggregation of Co atoms.



Fig. S17 High resolution XPS profile of Cu2*p* for Cu/TiO₂ NSs. It can be observed that there should be two kinds of Cu species in the sample, most of which could be indexed at Cu²⁺ at around 935 eV and a small amount of Cu⁰. The formation of a small amount of metallic Cu is likely related to the photo-induced reduction of copper (*J. Water Process Eng.* **2019**, *32*, 100958).



Fig. S18 High resolution XPS profile of Fe2p for Fe/TiO₂ NSs. It can be found that there is almost Fe³⁺ located at around 710.5 eV in the sample.



Fig. S19 TEM image of Cu/TiO₂ NSs.



Fig. S20 TEM image of Fe/TiO₂ NSs.



Fig. S21 EDS elemental mapping images of Cu/TiO₂ NSs.



Fig. S22 EDS elemental mapping images of Fe/TiO₂ NSs.



Fig. S23 High resolution O1s XPS profiles for (a) Co/TiO₂ NSs (O1: 350.4 eV; O2: 531.3 eV; O3: 532.7 eV) and (b) TiO₂ NSs (O1: 530.0 eV; O2: 531.3 eV; O3: 532.8 eV). Notably, peaks of O1, O2 and O3 can be attributed to the lattice oxygen, oxygen defects, and surface-adsorbed oxygen species, respectively (Nat. Commun. 2018, 9, 1302). Oxygen vacancy is one kind of potential catalytic site toward NARR. The peak area fraction of O2 in Co/TiO₂ NSs is slightly lower than that in TiO₂ NSs, demonstrating the less oxygen vacancies exist in Co/TiO₂ NSs. Meanwhile, considering the higher performance compared to TiO₂, it can be concluded that the activity origin of Co/TiO₂ NSs should be mainly contributed by the decorating Co(II) rather than oxygen vacancy.



Reaction coordinates

Fig. S24 Gibbs free energy diagram based on the DFT calculation for Co/TiO₂ and TiO₂. Reaction pathway: * \rightarrow *NO₃ \rightarrow *NO₂ \rightarrow *NO \rightarrow *ONH \rightarrow *ONH₂ \rightarrow *ONH₃ \rightarrow *O \rightarrow *OH \rightarrow *. It can be found that the last step, the *OH desorption step, undergoes the greatest change in Gibbs free energy with comparison to that of Co/TiO₂ (+1.506 eV) is lower than TiO₂ (+1.794 eV), revealing that the Co(II) decoration can insightful drop the reaction barrier and thus enhance the NARR performance toward the increase of the NH₃ selectivity. The overall electrocatalytic NARR process "NO₃⁻ + 9H⁺ + 8e⁻ \rightarrow NH₃ +3H₂O" can be described as nine elementary steps:

Step 1:
$$* + NO_3^- \rightarrow *NO_3 + e^-$$
Step 2: $*NO_3 + 2H^+ + 2e^- \rightarrow *NO_2 + H_2O$ Step 3: $*NO_2 + 2H^+ + 2e^- \rightarrow *ON + H_2O$ Step 4: $*ON + H^+ + e^- \rightarrow *ONH$ Step 5: $*ONH + H^+ + e^- \rightarrow *ONH_2$ Step 6: $*ONH_2 + H^+ + e^- \rightarrow *ONH_3$ Step 7: $*ONH_3 \rightarrow *O + NH_3$ Step 8: $*O + H^+ + e^- \rightarrow *OH$ Step 9: $*OH \rightarrow * + H_2O$

To avoid calculating the energy of charged NO₃⁻ directly, gaseous HNO₃ is chosen as a reference (*ACS Catal.* **2022**, *12*, 8698–8706). As a result, the NO₃⁻ adsorption can be described as * + HNO₃(g) \rightarrow *NO₃ + H⁺ +e⁻. Correspondingly, the adsorption energy of NO₃⁻, which is defined as ΔG (*NO₃), can be approximated by

$$\Delta G(*NO_3) = G(*NO_3) - G(*) - G(HNO_3, g) + 1/2 G(H_2) + 0.3917 eV$$

where $G(*NO_3)$ is the Gibbs free energy of NO_3^- adsorbed on catalysts; G(*) is the free energy of catalysts, and $G(HNO_3, g)$; $G(H_2, g)$ are the free energy of HNO_3 and H_2 molecules in the gas phase, respectively. In the view of computational hydrogen electrode (CHE) model, the ΔG of each elementary step is defined as

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S + \Delta G_{\text{pH}}$$

where ΔE denotes the energy change obtained from DFT calculations; ΔZPE and ΔS are the correction of zeropoint energy and entropy, respectively; T is equal to 298.15 K. The pH effect can be corrected by $\Delta G_{pH} = pH \times k_{B}T \ln 10$.



Fig. S25 NARR performance of Fe/TiO₂ NSs under different potentials: (a) FE_{NH3} and (b) J_{NH3} and r_{NH3} .









Fig. S27 NARR performance of TiO₂ NSs under different potentials: (a) FE_{NH3} and (b) J_{NH3} and r_{NH3} .



Fig. S28 LSV curves of Co/TiO₂ NSs with different mass loadings for electrocatalytic HER.



Fig. S29 Tafel curves of Co/TiO₂ NSs with different mass loadings for electrocatalytic HER, which was calculated by $\eta = a \lg(|j|) + b$.



Fig. S30 Photograph of bubbles generated on electrode surface after 5 min electrolysis in 1 M PBS.



Fig. S31 Photograph of bubbles generated on electrode surface after 5 min electrolysis during 1 M PBS and

0.4 M KNO₃.



Fig. S32 Collecting gas products during electrolysis.



Fig. S33 GC profiles for produced H_2 in the PBS with and without nitrate for 30 min at -0.73 V vs. RHE.



Fig. S34 Comparison of FE_{H2} in the PBS with and without nitrate through static-voltage electrolysis under different potentials for 30 min.



Fig. S35 Comparison of proton transportation energy during HER and NARR based on DFT calculation.



Fig. S36 The structure models of proton transportation energy calculation for HER process: (a) initial state and (b) final state.



Fig. S37 The structure models of proton transportation energy calculation for NARR process: (a) initial state and (b) final state.



Fig. S38 The delocalized electronic structure of nitrate: (a) the Highest Occupied Molecular Orbital (HOMO) and (b) the Lowest Unoccupied Molecular Orbital (LUMO).

Materials	Condition	FE _{NH3}	<i>r</i> _{NH3} / mmol cm ⁻² h ⁻¹	Reference	
Co/TiO₂ NS	0.4 M KNO ₃ + 1.0 M PBS, pH =	97.4%	0.223		
	6.5, −0.72 V vs.			This work.	
	RHE				
	0.4 M KNO ₃ +	55.3%	0.143	This work.	
	1.0 M PBS, pH =				
	6.5, -0.72 V vs.				
	RHE				
Fe/TiO₂ NS	0.4 M KNO ₃ +	80.1%	0.151	This work.	
	1.0 M PBS, pH =				
	6.5, -0.72 V vs.				
	RHE				
	0.4 M KNO ₃ +	62.7%	0.075	This work.	
TiO ₂ NS	1.0 M PBS, pH =				
	6.5, -0.72 V vs.				
	RHE				
	0.4 M KNO ₃ +	90.5%	0.160	ChemSusChem 2022 , e202102450	
TiO ₂ microspheres	1.0 M PBS, pH =				
	6.6, -1.0 V vs.				
	RHE				
TiO _{2-x} nanotube	50 ppm NaNO ₃	85.0%	0.0162	ACS Catal. 2020 , 10, 3533	
	+ 0.5 M Na ₂ SO ₄ ,				
	-1.6 V vs SCE				
Pd-doped TiO ₂	1 M LiCl + 0.25	02.1%	1% 0.066	Energy Environ. Sci. 2021 ,14, 3938	
nanoaarray	M LiNO ₃ , -0.7 V	JZ.1/0			

 Table S3 Comparison of NARR performance by reported TiO₂-based catalysts.

	vs. RHE			
10Cu/TiO2-x	0.5 M Na ₂ SO ₄ +	91 240/	N/A	J. Mater. Chem. A 2022 , 10, 6448
	200 ppm NaNO ₃	01.34%		
TiO _{2-x} (P25-600)	0.5 M Na ₂ SO ₄ +	78.0%	0.104	Appl. Catal. A Gen. 2022 , 636, 118596
	100 ppm			
	NaNO₃, −1.0 V			
	vs. RHE			
CuCl/TiO ₂ /MXene	0.5 M Na ₂ SO ₄ +	44.7 %	N/A	Angew. Chem. Int. Ed. 2021 , 60, 22933.
	100 mg L ⁻¹ NO ₃ -,			
	–1.0 V vs. RHE			