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Electronic Supplementary Information

Experimental section

Materials:, Tetrabutyl titanate (Ti(OC₄H₉)₄), poly-(vinyl pyrrolidone) (PVP, Mw = 1300000), ammonium chloride (NH₄Cl), salicylic acid (C₇H₆O₃), sodium citrate dehydrate (C₆H₅Na₃O₇·2H₂O), absolute ethanol (C₂H₅OH), hydrochloric acid (HCl), sodium hydroxide (NaOH), acetic acid, *p*-dimethylaminobenzaldehyde (C₉H₁₁NO), sodium hypochlorite solution (NaClO), titanium carbide powder, potassium chloride (KCl), salicylic acid (C₇H₆O₃), sodium salicylate (C₇H₅NaO₃), potassium sulphate (K₂SO₄) and sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O), were purchased from Aladdin Ltd. (Shanghai, China). hydrazine monohydrate (N₂H₄·H₂O) and ethanol were purchased from Kelong chemical Ltd. (Chengdu, China). Nafion solution (5 wt%) was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All reagents were analytical reagent grade without further purification.

Preparation of $Cr_3C_2@C$ *NF and CNF:* In a typical synthesis process of TiC/C NF, 12 wt% of PVP, 1 mL acetic acid and 1.5 mL Ti(OC₄H₉)₄ were dissolved in 10 mL absolute ethanol and stirred to form the transparent precursor solution for electrospinning. Then such solution was transferred into a 5 mL syringe. A high voltage of 15 kV was applied with a flow rate of 15 µL min⁻¹ for electrospinning. Then, the collected fibers were sintered at 1350 °C for 2 hours under Ar atmosphere to obtain the TiC/C NF. The CNF was fabricated in a similar process without Ti(OC₄H₉)₄.

Characterizations: X-ray diffraction (XRD) analysis was conducted by a LabX XRD-6100 X-ray diffractometer at 40 kV, the radiation is Cu K α (λ = 1.5418 Å). The microstructure of the as-spun and sintered fibers was examined by SEM (XL30 ESEM FEG) and TEM (HITACHI H-8100) system with the accelerating voltage of 20 kV and 200 kV respectively. XPS tests were measured using an Escalab 250Xi (Thermo Fisher) X-ray photoelectron spectrometer with Al as the exciting source.

Working electrode preparation: 5 mg catalyst was grinded into powder and mixed with 1 mL of ethonal containing Nafion solution (5%) followed by 30 min ultrasonic dispersion to form a homogeneous suspension. 20 μ L of such suspension was then dropped on a 1 cm² carbon paper and dried ambiently. The loading mass of electrocatalysts is 0.1 mg.

Electrochemical Measurements: A H-type electrolytic cell separated by a Nafion membrane is used to conduct the electrolysis process which is controlled by a CHI 659E electrochemistry workstation in 0.1 M HCl. A three-electrode configuration is used for electrochemical experiments wherein the Ag/AgCl/saturated KCl is the reference electrode, graphite plate as the counter electrode and the catalyst coated carbon paper as the working electrode. The potential used in this work is converted into a RHE scale via the equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.256 V, and the collected current density is normalized to the geometric surface area (1 cm²). The double layer capacitance is measured by a CV method. A potential-range from -0.07 V to -0.17 V vs. Ag/AgCl is selected for the CV test in different scan rates of 20 mV s⁻¹, 40 mV s⁻¹, 60 mV s⁻¹, 80 mV s⁻¹, 100 mV s⁻¹ without faradic current. The halves of differences between positive and negative current density at the potential-range center were plotted vs. scan rates and the slopes of curves were a double-layer capacitance. LSV was carried out with a scan rate of 5 mV s⁻¹.

Determination of NH_3 : The Indophenol blue method was used to quantify the concentration of the produced NH₃ in electrolyte.¹ In 0.1M HCl and 0.1 M KOH, firstly, 2 mL of the electrolyte taken from cathode was mixed with 2 mL 1 M NaOH containing 5% sodium citrate and 5% salicylic acid. Then, 1 mL 0.05 M NaClO was

added into such mixed solution. Finally, 0.2 mL 1% C₅FeN₆Na₂O was added. After standing for 2h without exposure, such solution was identified via UV-Vis spectroscopy at the wavelength of 655 nm. In 0.1 M K₂SO₄, 4 mL electrolyte was obatined from the cathodic chamber and mixed with 50 μ L oxidizing solution containing NaClO (ρ Cl = 4 ~ 4.9) and NaOH (0.75 M), 500 μ L coloring solution containing 0.4 M C₇H₅NaO₃ and 0.32 M NaOH, and 50 μ L catalyst solution (1 wt% Na₂[Fe(CN)₅NO]) for 1 h. The NH₃ yields were quantified by the well-fitted calibration curve of NH₄Cl.

Determination of hydrazine (N_2H_4): the hydrazine was identified by the Watt and Chrisp method.² Typically, 5 mL electrolyte solution was added with 5 mL of the reagent prepared by 5.99 g C₉H₁₁NO, 30 mL HCl and 300 mL ethanol. Followed by 20 min complete stir, the absorbance of such solution at the absorbance of 455 nm was measured to quantify the hydrazine yields with a standard curve of hydrazine (y = 0.34x + 0.034, R² = 0.999).

Faradic efficiency (FE) determination: The FE was calculated by equation (1):

$$FE = 3 \times F \times [NH_4Cl] \times V / (53.5 \times Q)$$
(1)

The yield of NH₃ was calculated by equation (2):

$$NH_3 \text{ yield} = [NH_4Cl] \times V \times 17 / (53.5 \times m_{cat.} \times t)$$
 (2)

Where 3 is the number of the electrons transferred for one NH_3 molecule production, 17 and 53.5 are the molar masses of NH_3 and NH_4Cl , $[NH_4Cl]$ is the measured NH_4Cl concentration, V is the volume of cathodic electrolyte, t is the testing time, $m_{cat.}$ is the loading mass of catalyst.

Computation method: First-principles calculations were performed by using the Vienna Ab initio Simulation Package (VASP) to investigate the N_2 reduction reaction (NRR) on the TiC (111) surface.^{3–6} The valence-core electrons interactions were

treated by Projector Augmented Wave (PAW) potentials⁷ and the electron exchange correlation interactions were described by the generalized gradient approximation (GGA) with the Perdew-Burke-Emzerhof (PBE) functional.⁸ Considering long-range interaction between molecules/intermediates and surface, Van der Waals interactions were considered using DFT-D3 correlation.⁹ A $3\times3\times1$ supercell slab model was built to simulate the surface of TiC (111), and to avoid effects from other slab, a vacuum of 20 Å was added along z direction. The convergence criterion of geometry relaxation was set to 0.01 eV•Å⁻¹ in force on each atom. The energy cutoff for plane wave-basis was set to 450 eV. The K points were sampled with $2\times2\times1$ by the Monkhorst-Pack method.¹⁰ Free energies of each reaction steps were calculated as $G=E_{DFT}+E_{ZPE}-T\Delta S$, where E_{DFT} is the DFT calculated energy, E_{ZPE} and $T\Delta S$ calculated by DFT vibration frequency calculations and presented in Table S1. In order to consider the effect of an applied electric potential on the electrode reaction, a value of –neU was added to calculate the free energy of each step, where n was the number of electrons involved in the reaction and U the applied bias.



Fig. S1. HRTEM image of TiC/C NF. All of observed nanoparticles in HRTEM image show well-resolved lattice fringes with an interplanar distance of 0.248 nm corresponding to the (111) plane of TiC, implying nanoparticles in TiC/NF include only



Fig. S2. The XPS spectra of TiC/C in C 1s (a) and Ti 2p (b) region.



Fig. S3. LSV curves of TiC/C NF in Ar- and N_2 -saturated 0.1 M HCl with the scan rate of 5 mV/s.



Fig. S4. (a) UV-Vis absorption spectra of indophenol assays with NH_4Cl after incubation for 2 h at room temperature in 0.1 M HCl (b) Calibration curve used for estimation of NH_3 by NH_4Cl concentration.



Fig. S5. (a) UV-Vis curves of various N_2H_4 concentrations after adding into chemical indicator by the method of Watt and Chrisp. (b) Calibration curve used for calculation of N_2H_4 concentrations.



Fig. S6. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp after electrolysis in N_2 -saturated 0.1 M HCl at a series of potentials for TiC/C NF.



Fig. S7. The SEM pattern of CNF (a) and commercial TiC powder (b).



Fig. S8. The UV-Vis absorption spectra of indophenol assays with electrolyte of TiC/C NF, commercial TiC and CNF after 2-h electrolysis.



Fig. S9. (a) UV-Vis absorption spectra of indophenol assays with NH₄Cl after incubation for 1 h at room temperature in 0.1 M K₂SO₄. (b) Calibration curve used for estimation of NH₃ by NH₄Cl concentration in 0.1 M K₂SO₄. (c) UV-Vis absorption spectra of the electrolytes (0.1 M K₂SO₄) stained with indicator at a series of potentials after electrolysis for 2 h. (d) NH₃ yields and FEs for TiC/C NF at corresponding potentials when tested in 0.1 M K₂SO₄.



Fig. S10. (a) UV-Vis absorption spectra of indophenol assays with NH_4Cl after incubation for 2 h at room temperature in 0.1 M KOH. (b) Calibration curve used for estimation of NH_3 by NH_4Cl concentration in 0.1 M KOH. (c) UV-Vis absorption spectra of the electrolytes (0.1 M KOH) stained with indicator at a series of potentials after electrolysis for 2 h. (d) NH_3 yields and FEs for TiC/C NF at corresponding potentials when tested in 0.1 M KOH.



Fig. S11. The EIS of the TiC/C NF and commercial TiC at -0.5V in N₂ saturated electrolyte. For comparison, the R_{Ω} was omitted in the Nyquist plots



Fig. S12. CVs of (a) commercial TiC and (b) TiC/C NF with various scan rates $(20-100 \text{ mV s}^{-1})$ in the -0.07 V to -0.17 V vs. Ag/AgCl. Capacitive current densities at -0.12 V vs. Ag/AgCl as a function of scan rates for (c) Commercial TiC and (d) TiC/C NF.



Fig. S13. UV-Vis absorption spectra of indophenol assays with the electrolytes under different condition.



Fig. S14. (a) Time-dependent current density curves of TiC/C NF at -0.5 V for 5 cycles. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after NRR electrolysis under different conditions for 5 cycles.



Fig. S15. The XPS Ti 2p spectrum of initial TiC/C NF and the sample after electrolysis.



Fig. S16. The HAADF-STEM image of TiC/C NF after NRR tests.

Adsorption Species	E _{ZPE} (eV)	<i>T∆S</i> (eV)
*N ₂	0.20	0.23
*NNH	0.43	0.21
*NNH ₂	0.79	0.16
*NNH ₃	1.19	0.12
*NHNH	0.81	0.15
*NHNH ₂	1.13	0.13
*NH ₂ NH ₂	1.26	0.18
*NH ₂ NH ₃	1.71	0.24
*N	0.08	0.06
*NH	0.25	0.07
*NH ₂	0.63	0.15
*NH ₃	0.93	0.08
*HNNH	0.79	0.13
*HNNH ₂	1.16	0.22
*H ₂ NNH ₂	1.53	0.21
*H ₂ NNH ₃	1.75	0.21

Table S1. Calculated zero point energies and entropy of different adsorptionspecies, where the * denotes the adsorption site. T was set as 300K.

Catalyst	Electrolyte	NH ₃ yield	FE (%)	Ref.	
TiC/C NF	0.1 M HCl	14.1 μg h ⁻¹ mg ⁻¹ _{cat.}	5.8	This work	
PEBCD/C	0.1 M Li ₂ SO ₄	$1.58 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	2.85	11	
Mn ₃ O ₄ NC	0.1 M Na ₂ SO ₄	11.6 μg h ⁻¹ mg ⁻¹ _{cat.}	3.0	12	
FL-BP NSs	0.01 M HCl	31.37 μ g h ⁻¹ mg ⁻¹ _{cat.}	5.07	13	
Bi NS	0.1 M Na ₂ SO ₄	13.23 μ g h ⁻¹ mg ⁻¹ _{cat.}	10.46	14	
TiO ₂ /rGO	0.1 M Na ₂ SO4	15.13 μ g h ⁻¹ mg ⁻¹ _{cat.}	3.3	15	
Rh	0.1 M KOH	23.88 μ g h ⁻¹ mg ⁻¹ _{cat.}	0.217	16	
Pd/C	0.1 M PBS	$4.5 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	8.2	17	
Bi ₄ V ₂ O ₁₁ /CeO ₂	0.1 M HCl	23.21 μ g h ⁻¹ mg ⁻¹ _{cat.}	10.16	18	
γ-Fe ₂ O ₃	0.1 M KOH	$0.212 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	1.9	19	
CoP HNC	1 M KOH	10.78 µg h ⁻¹ mg ⁻¹ _{cat.}	7.36	20	
BNS	0.1 M Na ₂ SO ₄	13.22 μ g h ⁻¹ mg ⁻¹ _{cat.}	4.04	21	
Pd-Co/CuO	0.1 M KOH	$10.04 \ h^{-1} \ mg^{-1}_{cat.}$	2.16	22	
N-doped porous carbon	0.05 M H ₂ SO ₄	23.8 μ g h ⁻¹ mg ⁻¹ _{cat.}	1.42	23	
MoO ₃	0.1 M HCl	29.43 $\mu g h^{-1} m g^{-1}_{cat.}$	1.9	24	
Defect-Rich Bi	0.2 M Na ₂ SO ₄	5.453 μ g h ⁻¹ mg ⁻¹ _{cat.}	11.68	25	
NPC	0.1 M HCl	$0.97 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	4.2	26	
PdRu TPs	0.1 M KCl	$37.23 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	1.85	27	

Table S2. Comparison of electrocatalytic N_2 reduction performance for TiC/C NF with other electrocatalysts under ambient conditions.

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