Electronic Supplementary Information

Experimental section

Materials: Ti₃AlC₂ was purchased from Laizhou KaiKai Ceramic Materials Company Ltd. Nafion (5 wt%) was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Hydrochloric acid (HCl), and ethanol (C₂H₅OH) were purchased from Chengdu Kelong Chemical Reagent Factory. Potassium chlorate (KClO₃), sodium salicylate (C₇O₃H₅Na), sodium hypochlorite (NaClO), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O), para-(dimethylamino) benzaldehyde (p-C₉H₁₁NO), and hydrazine monohydrate (N₂H₄·H₂O) were purchased from Aladdin Ltd. (Shanghai, China). The water used throughout all experiments was purified through a Millipore system. All chemicals were used as received without further purification.

Preparation of Ti₃C₂T_x and Ti₃C₂T_x/CP: Ti₃C₂T_x was synthesized by etching Al from Ti₃AlC₂ using LiF and HCl according to the reported literature.¹ Typically, the delaminated Ti₃C₂T_x was prepared by dissolving LiF in 6 M HCl, followed by the slow addition of Ti₃AlC₂ powder and the reaction was last for 45 h at 40 °C. The resultant precipitates were repeatedly washed with deionized water and centrifuged at 3500 rpm for 20 min, until the supernatant reached a pH of approximate 6. After washing to remove the etching products, Ti₃C₂T_x powder was intercalated by dimethylsulfoxide (DMSO),² followed by sonicating the colloidal solution for 2 h under Ar gas atmosphere, and then stirred for 18 h at room temperature. The colloidal suspension was centrifuged to separate the intercalated powder from the liquid DMSO and washed with deionized water for several time. The final product was dried in vacuum oven at 60 °C for 24 h.

The working electrode (Ti₃C₂T_x/CP) was prepared as following: First, 10 mg of as-prepared Ti₃C₂T_x powder was dispersed in a mixture solution of deionized water (0.5 mL) and ethanol (0.48 mL) containing 20 μ L Nafion (5%) and sonicated for 1 h. Then 20 μ L catalyst ink was loaded on a 1 × 1 cm² carbon paper (CP) and dried under ambient condition for measurement.

Characterizations: XRD patterns were obtained from a Shimazu XRD-6100 diffractometer with Cu K α radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). SEM images were collected from the tungsten lamp-equipped SU3500 scanning electron microscope at an

accelerating voltage of 20 kV (HITACHI, Japan). TEM images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The UV-Vis absorbance spectra were measured on a SHIMADZU UV-1800 UV-Vis spectrophotometer.

Electrochemical measurements: Before NRR measures, the Nafion proton exchange film was pretreated by heating in 3% H₂O₂ solution, 0.5 M H₂SO₄ and ultrapure water at 80 °C for 1.5 h, respectively. Electrochemical measurements were carried out on a CHI 660E electrochemical analyzer (CHI Instruments, Inc., Shanghai) in a three-electrode system using $Ti_3C_2T_x$ /CP or CP as working electrode, Ag/AgCl as reference electrode, and graphite rod as counter electrode. All experiments were performed at ambient conditions. For N₂ reduction reaction experiments, the HCl electrolyte (0.1 M) was bubbled with high-purity N₂(99.999%) for 30 min before measurement. All potentials reported in this work were calibrated to RHE, using the following equation:

E (RHE) = E (Ag/AgCl) + (0.197 + 0.059 pH) V

Determination of NH₃: NH₃ concentration was determined by the indophenol blue method.³ The method contains the following details: 2 mL HCl post-NRR electrolyte was collected from the cathodic chamber. Then, 2 mL of 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into this solution. After mixing and standing at room temperature for 2 h, the UV-Vis absorption absorption spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH₄Cl solution (0.1 HCl solution as mother solution) with a serious of concentrations. The fitting curve (y = 0.475x + 0.066, R² = 0.999) shows good linear relation of absorbance value with NH₃ concentration by three times independent calibrations.

Determination of N₂H₄: Concentration of N₂H₄ in the electrolyte was estimated by the method of Watt and Chrisp.⁴ Typically, a mixture solution containing p-C₉H₁₁NO (5.99 g), concentrated HCl (30 mL) and ethanol (300 mL) was used as a color reagent. In detail, 2 mL electrolyte removed from the cathodic chamber was added into 2 mL above prepared color

reagent. After standing the mixture solution at room temperature for 20 min, UV-Vis absorption spectra were measured at a wavelength of 455 nm. The concentration-absorbance curves were calibrated using standard N₂H₄ solutions with a series of concentrations for three independent calibrations.

Calculations of NH₃ yield and FE: NH₃ yield was calculated using the following equations:

 $R_{NH3} (\mu g h^{-1} m g_{cat.}^{-1}) = (c_{NH3} \times V) / (17 \times t \times m)$

Where c_{NH3} (µg mL⁻¹) is the measured NH₃ concentration; V (mL) is the volume of electrolyte (in our work 35 mL); t (s or h) is the reaction time; A (cm²) is the geometric area of the cathode; m (mg) is the mass loading of catalyst on CP.

FE was calculated according to following equation:

$$FE = 3 \times F \times c_{NH_3} \times V / (17 \times Q) \times 100\%$$

Where F is Faraday constant (96500 C mol^{-1}); Q (C) is the quantity of applied electricity.

Computational details: To gain more in-depth insights into the mechanism for nitrogen reduction reaction (NRR) on $Ti_3C_2T_x$ (X = F, OH) nanosheet, density functional theory (DFT) calculations are carried out using the Vienna ab initio simulation package (VASP).5,6 Exchange-correlation energy is described by Perdue-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA).⁷ The projector-augmented wave (PAW) method is used to represent the core-valence electron interaction.⁸ The calculations also adopt long-range dispersion interactions (DFT-D3 (BJ))^{9,10} A Hubbard U term is introduced to the PBE functional, with $U_{eff} = 4.2 \text{ eV}$ for Ti on its d orbital. An energy cutoff of 480 eV for basis-set expansion is used. A 2 \times 2 supercell and the corresponding 5 \times 5 \times 1 k-point mesh are modeled in the calculations. A vacuum region of about 20 Å is set to decouple the periodic replicas. Two F and OH groups attached to the hollow sites between the three neighboring carbon atoms are added on each side of Ti₃C₂T_x monolayer according to previous literatures.^{11,12} A OH group is removed to expose active sites for N₂ adsorption. The force tolerance and total energy for the relaxations are converged to 0.02 eV $Å^{-1}$ and 10⁻⁵ eV, respectively. The Gibbs free energy is calculated via the computational hydrogen electrode model proposed by Nørskov et al.¹³

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S$$

T and pH value are set to be 298.15K and 0 in this work, respectively. For adsorbates, ZPE and S are determined by vibrational frequencies calculations. For molecules, those are taken from the NIST database. [http://cccbdb.nist.gov/]



Fig. S1. SEM image of bulk Ti₃AlC₂.



Fig. S2. EDX spectrum of $Ti_3C_2T_x$.



Fig. S3. XPS survey spectrum of $Ti_3C_2T_x$.



Fig. S4. (a) UV-Vis absorption spectra of indophenol assays with different NH_3 concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH_3 concentrations.



Fig. S5. UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations.



Fig. S6. UV-Vis absorption spectra of the electrolytes stained with p-C₉H₁₁NO indicator after NRR electrolysis at a series of potentials.



Fig. S7. The NH₃ yields and FEs for $Ti_3C_2T_x/CP$ with different catalyst loadings.



Fig. S8. (a) Time-dependent current density curves for $Ti_3C_2T_x/CP$ at different potentials in 0.05 M H₂SO₄. (b) UV-Vis absorption spectra of the 0.05 M H₂SO₄ electrolytes stained with indophenol indicator after electrolysis at a series of potentials. (c) NH₃ yields and FEs at each given potential.



Fig. S9. (a) Time-dependent current density curves for $Ti_3C_2T_x/CP$ at different potentials in 0.1 M Na₂SO₄. (b) UV-Vis absorption spectra of the 0.1 M Na₂SO₄ electrolytes stained with indophenol indicator after electrolysis at a series of potentials. (c) NH₃ yields and FEs at each given potential.



Fig. S10. XRD patterns of bare CP, $Ti_3C_2T_x$ /CP and post-NRR $Ti_3C_2T_x$ /CP.



Fig. S11. XPS spectra of post-NRR $Ti_3C_2T_x$ in the (a) Ti 2p, (b) C 1s, (c) O 1s, and (d) F 1s regions.



Fig. S12. TEM image of $Ti_3C_2T_x$ NS after stability test.



Fig. S13. Optimized geometric structures of intermediates along the reaction path proceeded on the $Ti_3C_2T_x$ NS. Colour code: light grey, Ti; dark grey, C; blue, N; red, O; light blue, F; white, H.



Fig. S14. DFT calculated energy profile for the electrocatalytic N_2 reduction reaction on the $Ti_3C_2T_x$ NS through alternating mechanism. See optimized stuctures in Fig. S13.

Catalyst	Electrolyte	NH ₃ yield rate	FE (%)	Ref.
Ti ₃ C ₂ T _x /CP	0.1 M HCl	20.4 µg h ⁻¹ mg _{cat.} ⁻¹	9.3	This work
γ-Fe ₂ O ₃	0.1 M KOH	$0.212 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	1.9	14
Fe ₂ O ₃ -CNT	KHCO ₃	$0.22 \ \mu g \ h^{-1} \ cm_{cat.}^{-2}$	0.15	15
Fe ₃ O ₄ /Ti	0.1 M Na ₂ SO ₄	$3.43 \ \mu g \ h^{-1} \ cm_{cat.}^{-2}$	2.60	16
Mo nanofilm	0.01 M H2SO4	$1.89 \ \mu g \ h^{-1} \ cm_{cat.}^{-2}$	0.72	17
MoO ₃	0.1 M HCl	29.43 $\mu g h^{-1} m g_{cat.}^{-1}$	1.9	18
MoS ₂ /CC	0.1 M Na ₂ SO ₄	$4.94 \ \mu g \ h^{-1} \ cm_{cat.}^{-2}$	1.17	19
Mo ₂ N	0.1 M HCl	78.4 $\mu g h^{-1} m g_{cat.}^{-1}$	4.5	20
MoN	0.1 M HCl	$18.42 \ \mu g \ h^{-1} \ cm_{cat.}^{-2}$	1.15	21
VN	0.1 M HCl	$5.14 \ \mu g \ h^{-1} \ cm_{cat.}^{-2}$	2.25	22
Au NRs	0.1 M KOH	$1.64 \ \mu g \ h^{-1} \ cm_{cat.}^{-2}$	3.88	23
a-Au/CeO _x -RGO	0.1 M HCl	8.3 $\mu g h^{-1} m g_{cat.}^{-1}$	10.1	24
TA-reduced Au/TiO ₂	0.1 M HCl	21.4 $\mu g h^{-1} m g_{cat.}^{-1}$	8.11	25
Pd/C	0.1 M PBS	$4.5 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	8.2	26
Pd0.2Cu0.8/rGO	0.1 M KOH	$2.80 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	4.5	27
carbon nitride	0.1 M HCl	$8.09 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	11.59	28
PCN	0.05 M H ₂ SO ₄	$27.2 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	1.42	29
N-doped porous carbon	0.1 M HCl	$15.7 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	1.45	30
hollow Cr ₂ O ₃ microspheres	0.1 M Na ₂ SO ₄	$25.3 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	6.78	31
TiO2-rGO	0.1 M Na ₂ SO ₄	$15.13 \ \mu g \ h^{-1} \ mg_{cat.}^{-1}$	3.3	32
Nb2O5 nanofiber	0.1 M HCl	43.6 $\mu g h^{-1} m g_{cat.}^{-1}$	9.26	33
Fe ₂ O ₃ nanorods	0.1 M Na ₂ SO ₄	$15.9 \ \mu g \ h^{-1} \ mg_{cat.}^{-1}$	0.94	34
defect-rich MoS ₂	0.1 M Na ₂ SO ₄	$29.28 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	8.34	35
B4C	0.1 M HCl	$26.57 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	15.95	36

Table S1. Comparison of the NH₃ electrosynthesis activity for $Ti_3C_2T_x/CP$ with other aqueous-based NRR electrocatalysts at ambient conditions.

MnO	0.1 M Na ₂ SO ₄	$1.11 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	8.02	37
SnO ₂	0.1 M Na ₂ SO ₄	$1.47 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	2.17	38
Ag nanosheet	0.1 M HCl	$4.62 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	4.8	39
TiO ₂	0.1 M Na ₂ SO ₄	$9.16 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	2.5	40
Mn ₃ O ₄ nanocube	0.1 M Na ₂ SO ₄	11.6 $\mu g h^{-1} m g^{-1} cat.$	3.0	41

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