## **Electronic Supplementary Information**

## **Experimental section**

Materials: Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98.0%), hydrochloric (HCl, 99.0%), ethanol  $(C_2H_6O_1)$ 99.0%), acid **p**dimethylaminobenzaldehyde  $(C_9H_{11}NO),$ sodium nitroferricyanide dihydrate  $(C_5FeN_6Na_2O \cdot 2H_2O)$ , sodium salicylate  $(C_7H_5O_3Na)$ , sodium hypochlorite solution (NaClO), Sodium hydroxide (NaOH) were purchased from Aladdin Ltd. (Shanghai, China). Nafion (5 wt%) solution was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Hydrochloric acid, sulfuric acid, hydrogen peroxide, hydrazine monohydrate ( $N_2H_4$ · $H_2O$ ) and ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH) were purchased from Beijing Chemical Corp. (China). chemical Ltd. in Chengdu. Ti mesh (TM) purchased from Hongshan District, Wuhan Instrument Surgical Instruments business. The water used throughout all experiments was purified through a Millipore system. All chemicals were used as received without further purification.

*Preparation of Ti*<sup>3+</sup>-*TiO*<sub>2-x</sub> *NW/TM:* In a typical synthesis process, preparing H<sub>2</sub>O<sub>2</sub> (10%) then Ti mesh was put into 10% H<sub>2</sub>O<sub>2</sub> aqueous solution in a 50 ml beaker. The beaker was kept at 70°C for 24 h in oil bath. After the beaker was cooled down naturally to room temperature, the samples were removed, wash with DI water several times and dried under ambient condition. Finally, we obtained TM with black surface. Subsequently, the product was annealed at 300 °C for 3 h with a heating rate of 2 °C min<sup>-1</sup> in an electronic furnace to form TiO<sub>2</sub>/TM. During the process of wet-chemical oxidation, Ti and H<sub>2</sub>O<sub>2</sub> can react through a "surface oxide–interface diffusion–redox" reaction mechanism. The surface of Ti mesh was gradually converted to a cross-linked [–O–Ti–O–]<sub>n</sub>–Ti–(OH)<sub>x</sub>·mH<sub>2</sub>O matrix. Finally, Ti<sup>3+</sup>-TiO<sub>2-x</sub> NW/TM was obtained by the dehydration.<sup>1,2</sup>

*Characterizations:* XRD patterns were obtained from a Shimazu XRD-6100 diffractometer with Cu K $\alpha$  radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). SEM images were collected from the field-emission Apreo S scanning electron microscope at an accelerating voltage of 20 kV (FEI, America). The samples were sprayed with Au before SEM and EDX characterization to enhance conductivity. 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.

*Electrochemical measurements:* Electrochemical measurements were performed with a CS 350H electrochemical analyzer (CS Instruments, Inc., Wuhan) using a standard threeelectrode system using  $Ti^{3+}$ – $TiO_{2-x}$  NW/TM as the working electrode (the  $Ti^{3+}$ – $TiO_{2-x}$ /TM,  $TiO_2$ /TM and TM were cutted into an area of 1 x 1 cm<sup>2</sup> as the working electrode), graphite rod as the counter electrode, and saturated Ag/AgCl electrode as the reference electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub>. In all measurements, saturated Ag/AgCl electrode was calibrated with respect to reversible hydrogen electrode as following: in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution,  $E(RHE) = E(Ag/AgCl) + 0.059 \times pH + 0.197$  V. All experiments were carried out at room temperature. Prior to entering the cell, gases were passed through a saturator filled with 0.05 M H<sub>2</sub>SO<sub>4</sub>(aq.) to remove any possible ammonia and nitrogen oxides contaminants. Then N<sub>2</sub> reduction experiments, the 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte was purged with N<sub>2</sub> for 30 min before the measurement. Potentiostatic test was conducted in N<sub>2</sub>-saturated 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution in a two-compartment cell, which was separated by Nafion 117 membrane.

Determination of  $NH_3$ : Concentration of produced NH<sub>3</sub> was determined by spectrophotometry measurement with indophenol blue method<sup>3</sup>. In detail, 4 mL electrolyte was obatined from the cathodic chamber and mixed with 50 µL oxidizing solution containing NaClO (4.5%) and NaOH (0.75 M), 500 µL coloring solution containing C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>Na (0.4 M) and NaOH (0.32 M), and 50 µL catalyst solution Na<sub>2</sub>Fe(CN)<sub>5</sub>NO·2H<sub>2</sub>O (1 wt%) for 1 h. The concentrationabsorbance curve was calibrated using the standard NH<sub>4</sub>Cl solution with NH<sub>3</sub> concentrations of 0.0, 0.05, 0.10, 0.15, 0.20 and 0.25 µg mL<sup>-1</sup> in 0.1 M Na<sub>2</sub>SO<sub>4</sub>. These solutions were identified via UV-Vis spectroscopy at the wavelength of 655 nm. The concentrationabsorbance curve was calibrated using standard NH<sub>4</sub><sup>+</sup> solution with a serious of concentrations. The fitting curve (y = 0.466x + 0.026, R<sup>2</sup> = 0.999) shows good linear relation of absorbance value with NH<sub>4</sub><sup>+</sup> concentration.

*Determination of*  $N_2H_4$ : The N<sub>2</sub>H<sub>4</sub> presented in the electrolyte was estimated by the method of Watt and Chrisp<sup>4</sup>. Typically, 2 mg mL<sup>-1</sup> N<sub>2</sub>H<sub>4</sub> solution was prepared and diluted to 2 µg mL<sup>-1</sup>.

Then, 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 5 mL N<sub>2</sub>H<sub>4</sub> solution (2  $\mu$ g mL<sup>-1</sup>) were poured into 10 mL plastic tubes and separately diluted to 5 mL with 0.1 M Na<sub>2</sub>SO<sub>4</sub> and the resulting concentrations of N<sub>2</sub>H<sub>4</sub> in the solutions are 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0  $\mu$ g mL<sup>-1</sup>. A mixed solution of C<sub>9</sub>H<sub>11</sub>NO (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. In detail, 2 mL electrolyte was removed from the electrrochemical reaction vessel, and added into 2 mL above prepared color reagent and stirring 15 min at room temperature. Moreover, the absorbance of the resulting solution was measured at a wavelength of 455 nm. The concentration absorbance curves were calibrated using standard N<sub>2</sub>H<sub>4</sub> solution with a series of concentrations. The fitting curve (y = 0.696x + 0.062, R<sup>2</sup> = 0.999) shows good linear relation of absorbance value with N<sub>2</sub>H<sub>4</sub> concentration.

*Determination of FE and NH*<sub>3</sub> *yield:* The FE for N<sub>2</sub> reduction was defined as the amount of electric charge used for synthesizing NH<sub>3</sub> divided the total charge passed through the electrodes during the electrolysis. Assuming three electrons were needed to produce one NH<sub>3</sub> molecule, the FE could be calculated as follows:

FE (NH<sub>3</sub>) = 
$$3 \times F \times [NH_3] \times V / (17 \times Q) \times 100\%$$

The total amount of NH<sub>3</sub> produced was measured using colorimetric methods. The rate of NH<sub>3</sub> formation was calculated using the following equation:

NH<sub>3</sub> yield = [NH<sub>3</sub>] 
$$\times$$
 V / (17  $\times$  t  $\times$  A)

The amount of NH<sub>3</sub> was calculated as follows:

$$m_{NH3} = [NH3] \times V$$

Where  $[NH_3]$  is the measured  $NH_3$  concentration; V is the volume of the cathodic reaction electrolyte; t is the potential applied time; A is the loaded area of catalyst; F is the Faraday constant; and Q is the quantity of applied electricity.

## **Theoretical section**

*Computational details:* During the density functional theory (DFT) calculations, the projector augmented wave and generalized gradient approximation in the form of the Perdew-Burke-Ernzerh of exchange-correlation functional<sup>5,6</sup>, is adopted through Vienna Ab Initio Simulation Package (VASP)<sup>7-9</sup>. The empirical correction scheme of Grimme is used to describe the van der Waals interaction is described. The energy cutoffs of plane wave for carbon, hydrogen, oxygen, and nitrogen are selected as 520 eV. A vacuum layer of 18 Å is added to avoid the

interaction between nearby supercells. The convergence criterions of structures' optimizations are set to  $10^{-4}$  eV for atomic energy and -0.02 eV Å<sup>-1</sup> for atomic force. The anode reaction i.e.  $H^2 \leftrightarrow 2(H^+ + e^-)$  of NRR processes is taken as a convenient reference, which works as the source of proton and electrons. Six net proton coupled electron transfer steps (N<sub>2</sub> + 6H<sup>+</sup> + 6e<sup>-</sup>  $\rightarrow$  NH<sub>3</sub>) are involved. There are several steps in dissociate and associative mechanisms where the nitrogen molecular are hydrogenated by protons.



Fig. S1. EDX spectrum for  $Ti^{3+}$ - $TiO_{2-x}/TM$ .



Fig. S2. SEM image and the EDX elemental mapping images of Ti and O.



Fig. S3. XPS survey spectrum for  $Ti^{3+}-TiO_{2-x}/TM$ .



Fig. S4. (a) UV-Vis absorption spectra of indophenol assays with  $NH_3$  after incubation for 2 h at room temperature in 0.1 M  $Na_2SO_4$  (b) Calibration curve used for calculation of  $NH_3$  concentrations.



**Fig. S5.** (a) UV-Vis absorption spectra of N<sub>2</sub>H<sub>4</sub> concentrations after incubated for 15 min at room temperature. (b) Calibration curve used for calculation of N<sub>2</sub>H<sub>4</sub>.



**Fig. S6.** (a) Ion chromatogram for the NH<sub>3</sub> ions. (b) Calibration curve used for estimation of NH<sub>3</sub>. (c) Ion chromatogram for the electrolytes at a series of potentials after electrolysis for 2 h. (d) Amount of NH<sub>3</sub> generated with  $Ti^{3+}$ - $TiO_{2-x}/TM$  at corresponding potentials.



Fig. S7. UV–Vis spectra of the electrolyte estimated by the method of Watt and Chrisp before and after 2 h electrolysis in  $N_2$  atmosphere at the best potential under ambient conditions.



Fig. S8. The UV-Vis absorption spectra of indophenol assays with electrolyte of  $Ti^{3+}-TiO_{2-x}/TM$ ,  $TiO_2/TM$  and TM after 2-h electrolysis.



Fig. S9. Amount of NH<sub>3</sub> generated with  $Ti^{3+}$ - $TiO_{2-x}/TM$  under different conditions.



Fig. S10. Time-dependent current density curve of  $Ti^{3+}$ - $TiO_{2-x}/TM$  at a potential of -0.55 V.



Fig. S11. The photographs of pH test papers of the Na2SO4 aqueous solution before and afterelectrolysisfor $Ti^{3+}$ -TiO2-x/TM.



Fig. S12. SEM image of  $Ti^{3+}$ - $TiO_{2-x}/TM$  after stability test.



Fig. S13. Topview (a) and sideview (c) of  $TiO_2$  (101) surface structures without oxygen vacancies; and topview (b) and sideview (d) of  $TiO_2$  (101) surface structures with oxygen vacancies at  $O_2c$  sites.



**Fig. S14.** Gibbs free energy changes for associative alternating (a) and associative distal (b) mechanisms of N2-to-NH3 occurring at Ti5c site on TiO2 (101) surface without oxygen vacancy. Asterisk (\*) denotes the adsorbed sites. The intermediated configurations during reaction paths are also demonstrated as insert figures. The cases of applied a potential at different values, U=0V and U=-0.55V, are labelled by blue and red, respectively.



**Fig. S15.** Gibbs free energy changes for dissociate (a) and associate mechanisms of  $N_2$ -to-NH<sub>3</sub> occurring at Ti<sub>5c</sub> site on TiO<sub>2</sub> (101) surface with oxygen vacancy. Asterisk (\*) denotes the adsorbed sites. The intermediated configurations during reaction paths are also demonstrated as insert figures. The cases of applied a potential at different values, U=0V and U=-0.55V, are labelled by blue and red, respectively.

Catalyst	Electrolyte	NH <sub>3</sub> yield	FE%	Ref.
Ti <sup>3+</sup> -TiO <sub>2-x</sub> /TM	0.1 M Na <sub>2</sub> SO <sub>4</sub>	3.51 x 10 <sup>-11</sup> mol s <sup>-1</sup> cm <sup>-2</sup>	14.62	This work
TiO <sub>2</sub> /Ti	0.1 M Na <sub>2</sub> SO <sub>4</sub>	9.16 x 10 <sup>-11</sup> mol s <sup>-1</sup> cm <sup>-2</sup>	2.5	10
TiC/C	0.1 M HCl	14.1 $\mu g h^{-1} m g^{-1}{}_{cat.}$	5.8	11
C-doped TiO <sub>2</sub>	0.1 M Na <sub>2</sub> SO <sub>4</sub>	$16.22 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	1.84	12
d-TiO <sub>2</sub> /TM	0.1 M HCl	$1.24 \text{ x } 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	9.17	13
Zr- TiO <sub>2</sub>	0.1 M KOH	$8.90 \ \mu g \ h^{-1} \ cm^{-2}$	17.3	14
C-doped TiO <sub>2</sub> /C	0.1 M LiClO <sub>4</sub>	14.8 $\mu g h^{-1} m g^{-1}{}_{cat.}$	17.8	15
Fe-doped TiO <sub>2</sub>	0.5 M LiClO <sub>4</sub>	$25.47 \ \mu g \ h^{-1} \ mg^{-1}{}_{cat.}$	25.6	16
MXene $(Ti_3C_2T_x)$	1 M HCl and 0.5 M Li <sub>2</sub> SO <sub>4</sub> (PH=2)	$4.72 \ \mu g \ h^{-1} \ cm^{-2}$	5.78	17
TiO <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	0.1 M HCl	$26.32 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	8.42	18
$Ti_3C_2T_x(T = F, OH)$ MXene	0.1 M HCl	$20 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	9.3	19
MnO <sub>2</sub> -Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	0.1 M HCl	34.12 $\mu$ g h <sup>-1</sup> cm <sup>-2</sup>	11.39	20
$TiO_2/Ti_3C_2T_x$	0.1 M HCl	$32.17 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	16.07	21

Table S1. Comparison of electrocatalytic  $N_2$  reduction performance for  $Ti^{3+}-TiO_{2-x}/TM$  with other Ti-based electrocatalysts at ambient conditions.

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