

Supporting Information

Boron-Doped TiO₂ for Efficient Electrocatalytic N₂ Fixation to NH₃ at Ambient Conditions

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Experimental section

Materials: Tetrabutyl titanate was purchased from Aladdin Ltd. (Shanghai, China). H_3BO_4 was purchased from Chendu Chemical Corporation. Sodium salicylate ($\text{C}_7\text{H}_5\text{O}_3\text{Na}$), p-dimethylaminobenzaldehyde ($\text{C}_9\text{H}_{11}\text{NO}$), sodium citrate dehydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), sodium hypochlorite solution (NaClO) were purchased from Beijing Chemical Corp. (China). Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Synthesis of TiO_2 : a mixture solution with 10 mL Tetrabutyl titanate and 60 mL alcohol was added drop-wise into 100 mL alcohol with 10 mL distilled water. The resultant mixture was stirred at room temperature for 1 h and then age 4 h to obtain the ivory sol. The sol was heated at 60 °C for 18 h to get the dry bulk which was ground to the powder. Finally, the powder was calcined at 400 °C for 3h to obtain pure TiO_2 .

Synthesis of B- TiO_2 : In a typical procedure, 1 g H_3BO_4 and 10 mL distilled water was firstly dissolved into 100 mL alcohol under continuous stirring. Then, a mixture solution with 10 mL Tetrabutyl titanate and 60 mL alcohol was added drop-wise into above solution under mechanical stirring. The resultant mixture was stirred at room temperature for 1 h and then age 4 h to obtain the ivory sol. The sol was heated at 60 °C for 18 h to get the dry bulk which was ground to the powder. Finally, the powder was calcined at 400 °C for 3h to obtain the boron-doped TiO_2 .

Characterization: XRD data were collected on X-ray diffractometer (Philip Company, Pw1730) equipped with a Cu $\text{K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). XPS data were collected on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. SEM measurements were performed on a Hitachi S-4800 filed emission scanning electron microscope at an accelerating voltage of 20kV. TEM measurements were carried out on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV.

Electrochemical measurement: N₂ reduction reaction tests were carried out in a two-compartment electrocatalytic cell separated by Nafion 211 membrane under ambient condition. The membrane was protonated by first boiling in ultrapure water for 1 h and treating in H₂O₂ (5%) aqueous solution at 80°C for 1 h. Then, the membrane was treaded in 0.1 M H₂SO₄ for 3 h at 80 °C and finally in water for 6 h. All the electrochemical measurements were tested using a CHI660E workstation (CH Instruments, China) in a typical three-electrode setup with an electrolyte solution of 0.1 M Na₂SO₄ (33 mL), a graphite rod as the counter electrode and Ag/AgCl as the reference electrode. The potentials reported in this work were converted to RHE scale via calibration with the following equation: $E \text{ (vs RHE)} = E \text{ (vs Ag/AgCl)} + 0.197 + 0.059 \times \text{pH}$. Before the measurement, the Na₂SO₄ electrolyte was bubbled with N₂ for 30 min.

Determination of NH₃: The produced NH₃ was spectrophotometrically determined by indophenol blue method. In detail, 4 mL of post-tested solution was got from the electrochemical reaction vessel. Then, 50 uL of oxidation (contains 0.4 M sodium salicylate and 0.32 M sodium hydroxide), 500 uL of the colouring solution (sodium hypochlorite and 0.75 M sodium hydroxide) and 50 uL pf catalyst solution (0.1g sodium nitroferricyanide(III) dehydrate diluted to 10ml with deionized water) were added respectively to the sample solution. Absorbance measurments were performed after 2 h. The concentration of indophenol blue was determined using the absorbance at awavelength of 660 nm. The concentration-absorbance curve was calibrated using standard ammonia chloride solution with a serious of concentrations. The fitting curve ($y = 0.709x + 0.017$, $R^2 = 0.999$) shows good linear relation of absorbance value with NH₃ concentration by three times independent calibrations. The NH₃ concentration was calculated form the calibration curve, and the rate of NH₃ yield was calculated using the following equation:

$$R_{NH3} = (c_{NH3} \times V) / (t \times m_{cat.})$$

where c_{NH3} is the measured NH₃ concentration, V is the volume of electrolyte, t is the reduction reaction time and $m_{cat.}$ is the loaded mass of catalyst.

Calculation of Faradic efficiency (FE): Assuming three electrons were needed to produce one NH_3 molecule, the FE in 0.1 M Na_2SO_4 could be calculated as follows:

$$\text{FE} = 3F \times c_{\text{NH}_3} \times V / 17 \times Q$$

Where F is the Faraday constant, Q is the quantity of applied electricity.

Determination of N_2H_4 : The N_2H_4 presented in the electrolyte was estimated. A mixed solution of 5.99 g $\text{C}_9\text{H}_{11}\text{NO}$, 0.1 M Na_2SO_4 (30 mL) and 300 mL ethanol was used as a color reagent. Calibration curve was plotted as follow: First, preparing a series of reference solutions; second, adding 5 mL above prepared color reagent and stirring 20 min at room temperature; finally, the absorbance of the resulting solution was measured at 455 nm, and the yields of N_2H_4 were estimated from a standard curve using 5 mL residual electrolyte and 5 mL color reagent. Absolute calibration of this method was achieved using $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ solutions of known concentration as standards, and the fitting curve shows good linear relation of absorbance with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ concentration ($y = 1.149x + 0.035$, $R^2 = 0.999$) by three times independent calibrations.

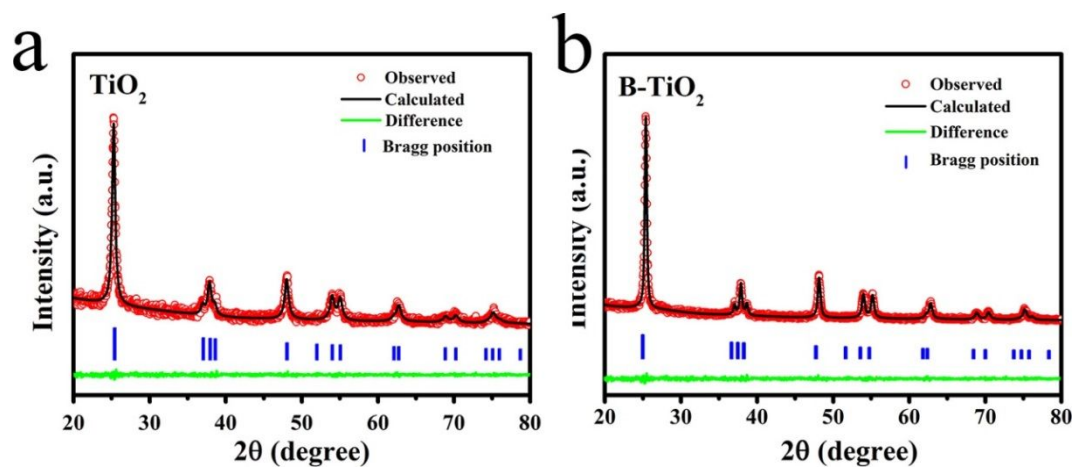


Figure S1. Powder XRD patterns as well as Rietveld refinements for (a) TiO_2 and (b) B-TiO_2 .

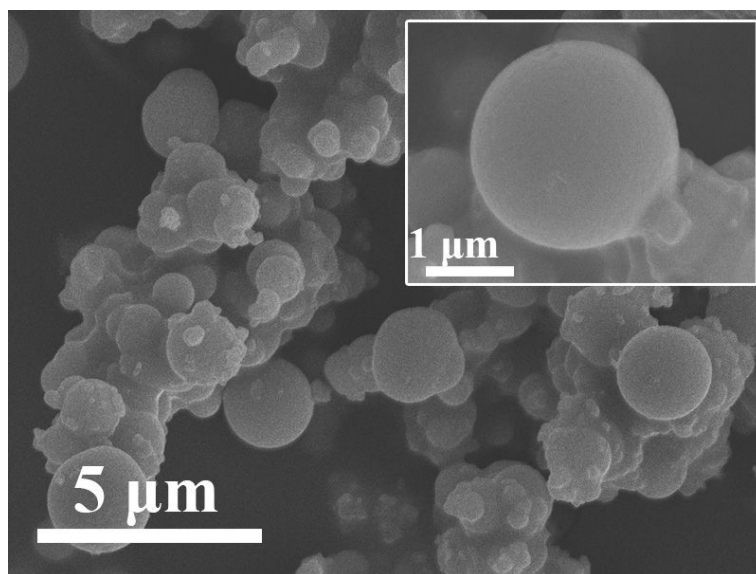


Figure S2. SEM images of pristine TiO₂ particles.

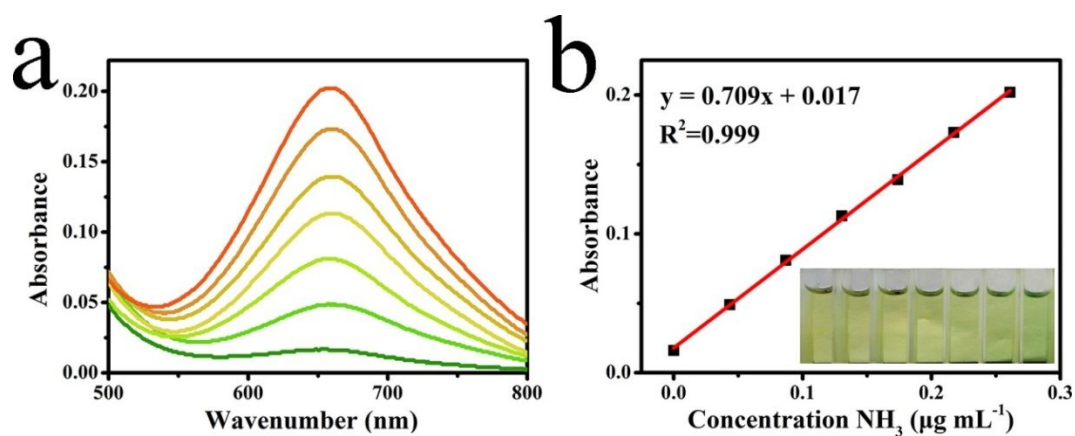


Figure S3. (a) UV-Vis absorption spectra of indophenol assays with NH_4^+ in 0.1 M Na_2SO_4 after incubated for 60 min at room temperature. (b) Calibration curve used for calculation of NH_3 concentration.

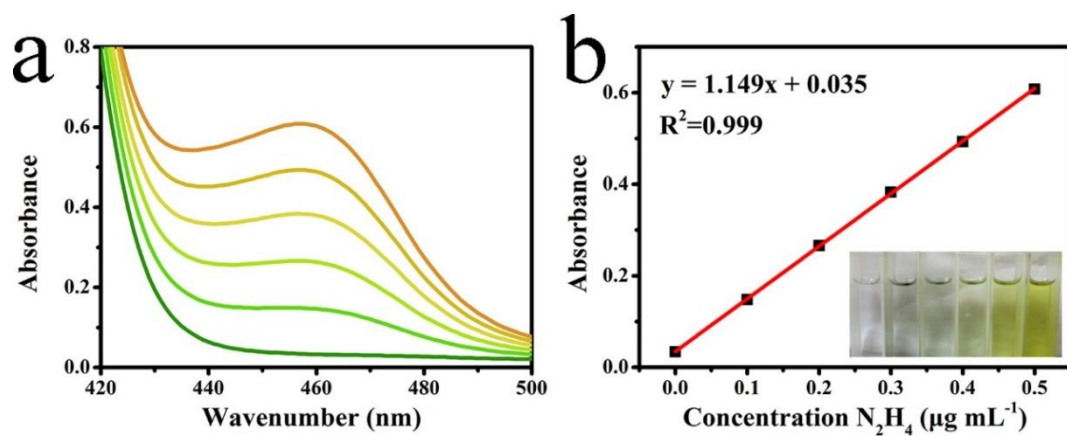


Figure S4. (a) UV-Vis absorption spectra of various N_2H_4 concentrations stained with $p\text{-C}_9\text{H}_{11}\text{NO}$ indicator after incubated for 20 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentration.

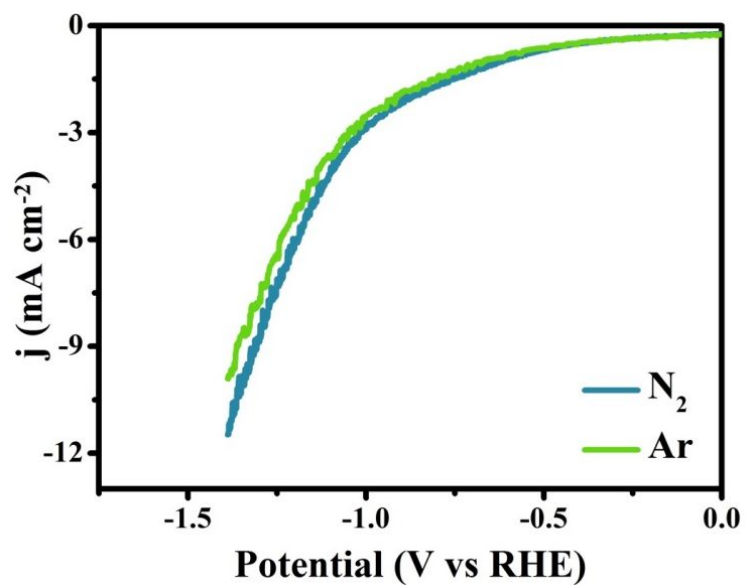


Figure S5. LSV curves of B-TiO₂/CPE in N₂ and Ar saturated 0.1 M Na₂SO₄ with a scan rate of 20 mV s⁻¹.

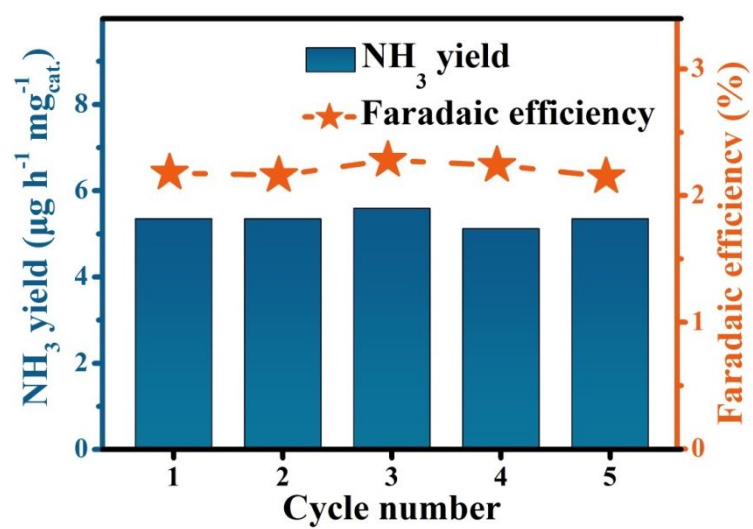


Figure S6. Recycling tests at potential of -0.80 V for TiO_2 .

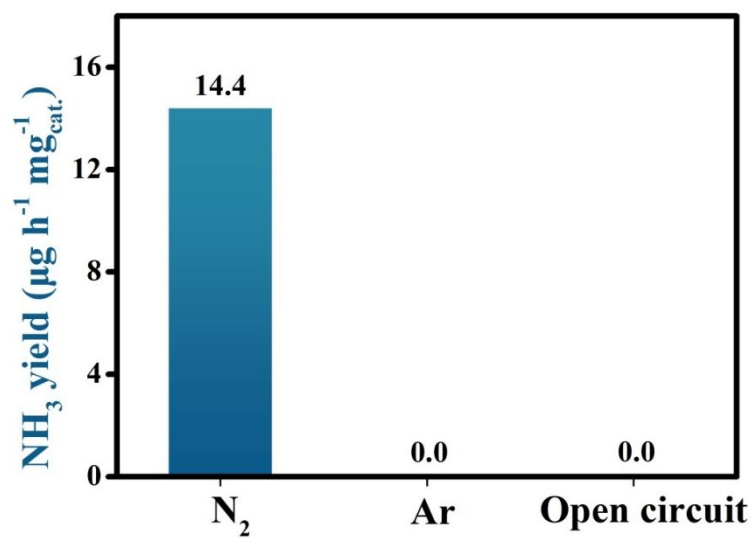


Figure S7. NH_3 yields at -0.80 V in N_2 -saturated solution, and -0.80 V in Ar-saturated solution, and open circuit potential in N_2 -saturated solution.

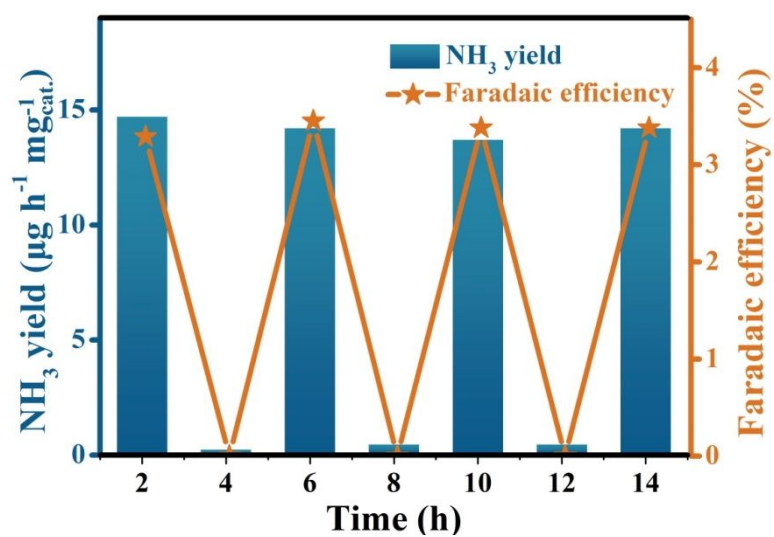


Figure S8. NH₃ production rates and FEs of B-TiO₂/CPE.

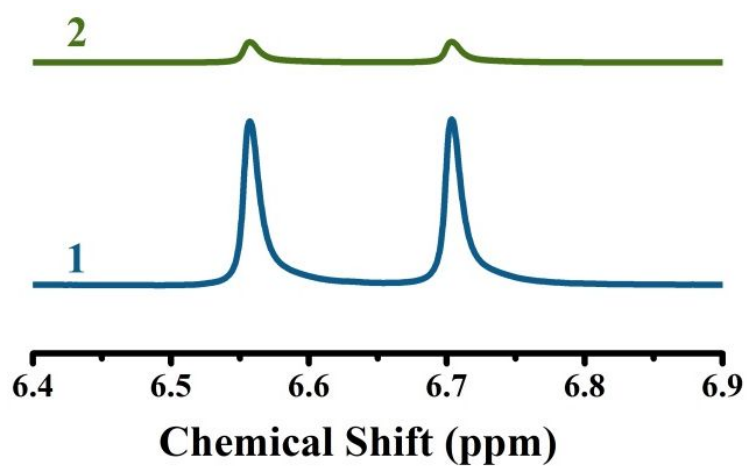


Figure S9. ^1H NMR spectra for $^{15}\text{NH}_4^+$ standard sample (curve 1) and the electrolysis product using $^{15}\text{N}_2$ as the feeding gas (curve 2).

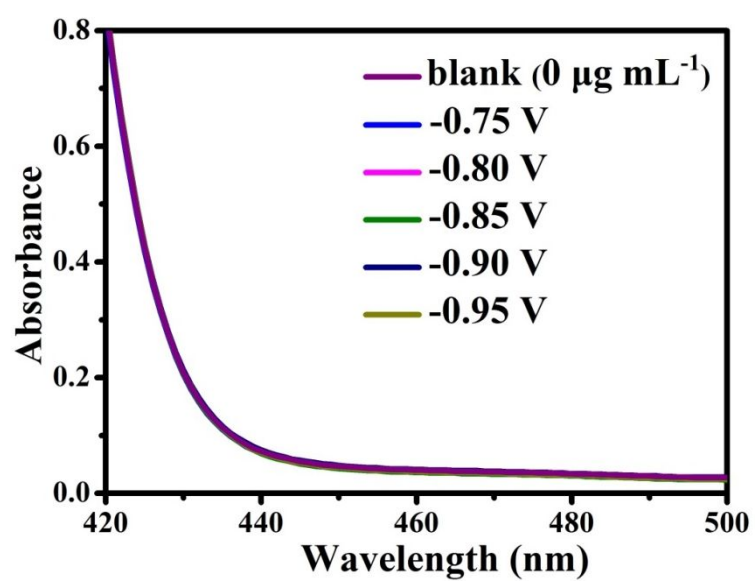


Figure S10. UV-Vis absorption spectra of the electrolytes stained with p-C₉H₁₁NO indicator after NRR electrolysis at a series of potentials.

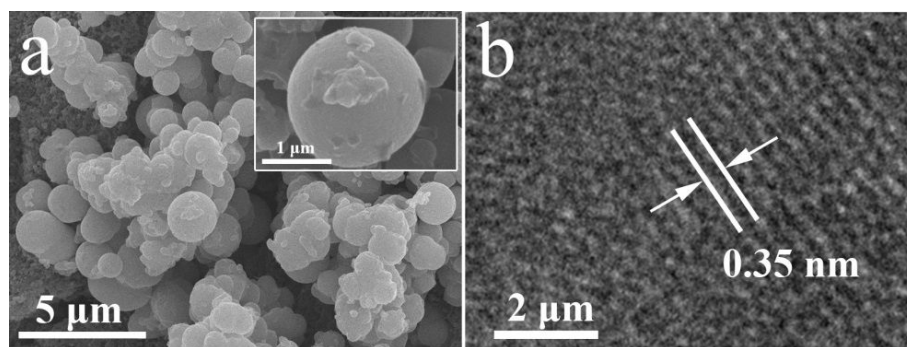


Figure S11. (a) SEM and (b) HRTEM images for B-TiO₂ after long-term NRR test.

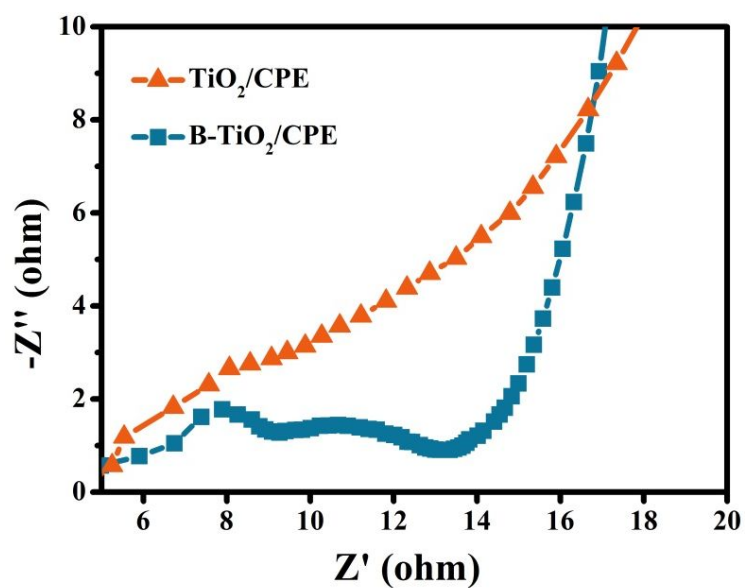


Figure S12. Nyquist plots of B-TiO₂/CPE and TiO₂/CPE in the frequency range from 1000 kHz to 1Hz with a voltage amplitude of 5 mV, and all the three electrodes are in one compartment cell being full of 0.1 M Na₂SO₄ solution at room temperature (25 °C).

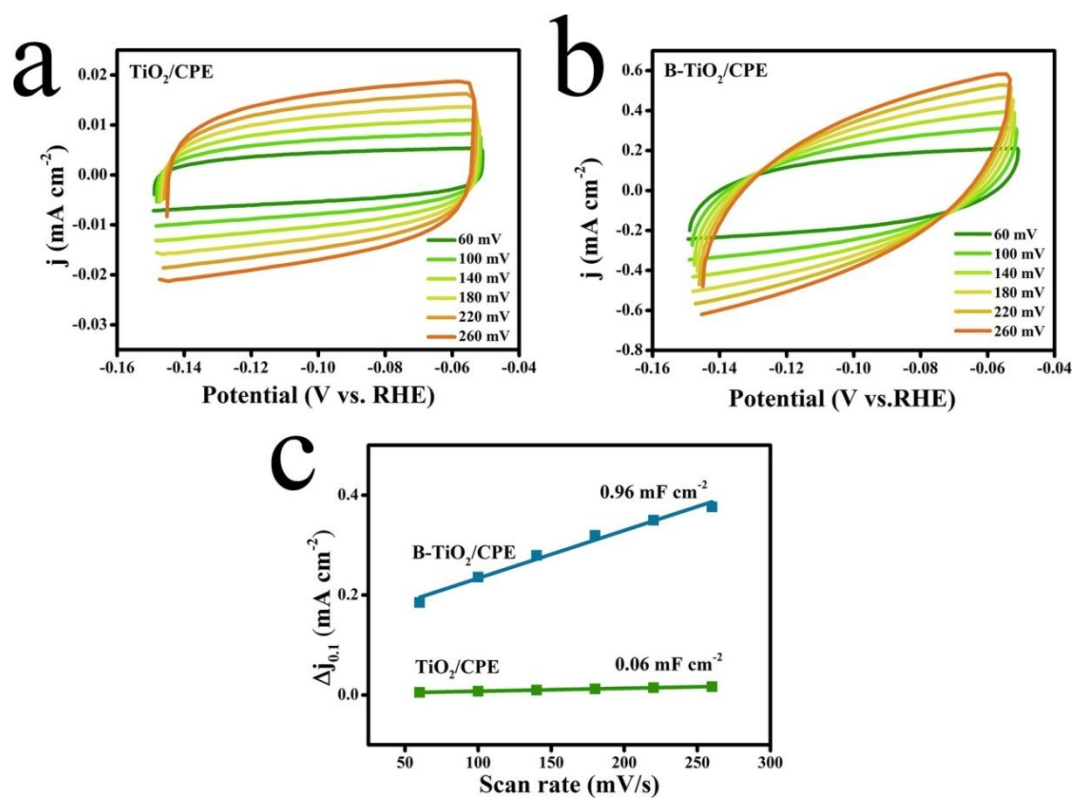


Figure S13. CV curves (a) TiO_2/CPE and (b) $\text{B-TiO}_2/\text{CPE}$. (c) The capacitive currents at -0.10 V as a function of scan rates for $\text{B-TiO}_2/\text{CPE}$ and TiO_2/CPE .

Table S1. Rietveld refinement of XRD data for TiO₂ and B-TiO₂.

Sample	Lattice parameter			Unit cell volume (Å ³)	R _{wp}	R _p	X ²
	a-Axis	b-Axis	c-Axis				
TiO ₂	3.7870	3.7870	9.492	136.14	12.74	9.11	0.9337
B-TiO ₂	3.7844	3.7844	9.516	136.29	10.92	7.91	1.4314

Table S2. Comparison of the NRR performances for B-TiO₂ with other

Catalyst	Electrolyte	NH ₃ yield	FE(%)	Ref.
B-TiO ₂	0.1 M Na ₂ SO ₄	14.4 μg h ⁻¹ mg ⁻¹ _{cat.}	3.4	This work
TiO ₂ nanosheets array	0.1 M Na ₂ SO ₄	5.6 μg h ⁻¹ cm ⁻²	2.5	(1)
TiO ₂ -rGO	0.1 M Na ₂ SO ₄	15.13 μg h ⁻¹ mg ⁻¹ _{cat.}	3.3	(2)
γ-Fe ₂ O ₃	0.1 M KOH	0.212 μg h ⁻¹ mg ⁻¹ _{cat.}	1.9	(3)
Fe ₃ O ₄ /Ti	0.1 M Na ₂ SO ₄	3.42 μg h ⁻¹ cm ⁻²	2.6	(4)
Fe ₂ O ₃ nanorods	0.1 M Na ₂ SO ₄	15.9 μg h ⁻¹ mg ⁻¹ _{cat.}	0.94	(5)
MoS ₂ /CC	0.1 M Na ₂ SO ₄	4.94 μg h ⁻¹ cm ⁻²	1.17	(6)
Pd _{0.2} Cu _{0.8} /rGO	0.1 M KOH	2.8 μg h ⁻¹ mg ⁻¹ _{cat.}	4.5	(7)
PEBCD/C	0.5 M Li ₂ SO ₄	1.58 μg h ⁻¹ cm ⁻²	2.85	(8)
Au nanorods	0.1 M KOH	1.6 μg h ⁻¹ cm ⁻²	3.88	(9)
Mn ₃ O ₄ nanocube	0.1 M Na ₂ SO ₄	11.6 μg h ⁻¹ mg ⁻¹ _{cat.}	3.0	(10)
TiO ₂ -rGO	0.1 M Na ₂ SO ₄	15.13 μg h ⁻¹ mg ⁻¹ _{cat.}	3.3	(11)
hollow Cr ₂ O ₃ microspheres	0.1 M Na ₂ SO ₄	25.3 μg h ⁻¹ mg ⁻¹ _{cat.}	6.78	(12)
β-FeOOH nanorod	0.5 M LiClO ₄	23.32 μg h ⁻¹ mg ⁻¹ _{cat.}	6.7	(13)
SnO ₂	0.1 M Na ₂ SO ₄	1.47 × 10 ⁻¹⁰ mol s ⁻¹ cm ⁻²	2.17	(14)

electrocatalysts in neutral media at ambient conditions.

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