## **Electronic Supplementary Information**

## **Experimental section**

**Materials:** NH<sub>4</sub>Cl, N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, HNO<sub>3</sub>, HCl, C<sub>2</sub>H<sub>5</sub>OH, and Na<sub>2</sub>SO<sub>4</sub> were purchased from Chengdu Kelong Chemical Reagent Factory. NaOH, C<sub>7</sub>H<sub>5</sub>NaO<sub>3</sub>, NaClO, C<sub>5</sub>FeN<sub>6</sub>Na<sub>2</sub>O, para-(dimethylamino) benzaldehyde (p-C<sub>9</sub>H<sub>11</sub>NO), and stannic chloride pentahydrate (SnCl<sub>4</sub>·5H<sub>2</sub>O) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All the reagents were used as received without further purification. CC was purchased from Hongshan District, Wuhan Instrument Surgical Instruments business, and was pretreated in HNO<sub>3</sub>, then was sequentially cleaned in deionized water and C<sub>2</sub>H<sub>5</sub>OH several times by sonication to remove the surface impurities. The water used throughout all experiments was purified through a Millipore system.

**Preparation of SnO**<sub>2</sub>/**CC**: SnCl<sub>4</sub>·5H<sub>2</sub>O (0.84 mmol) and NaOH (10.08 mmol) were dissolved in deionized water (28 mL) in a 50 mL beaker. After being magnetically stirred for 20 min in air at room temperature, the mixture solution and a piece of CC (2 cm × 3 cm) were transferred to a Teflon-lined stainless-steel autoclave and maintained at 200 °C for 24 h. After the autoclave naturally cooled down to room temperature, the sample was taken out and thoroughly washed with deionized water and C<sub>2</sub>H<sub>5</sub>OH several times alternatively, then dried in air at 60 °C for 6 h. The loading for SnO<sub>2</sub> on CC was determined to be 2.25 mg cm<sup>-2</sup>.

**Characterizations:** XRD data were obtained from a Shimazu XRD-6100 diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. 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 with the exciting source of Mg. UV-Vis absorption spectra were recorded on a UV-Vis spectrophotometer (Shimadazu, UV-1800). Raman spectrum was collected on Renishaw with a 532 nm laser. A gas chromatograph (SHIMADZU, GC-2014C) equipped with MolSieve 5A column and Ar carrier gas was used for H<sub>2</sub> quantification. Gas-phase product was sampled every 1000 s using a gas-tight syringe (Hamilton). The N<sub>2</sub>-TPD spectrum was tested by TP-5076 TPD experimental device.

**Electrochemical measurements:** N<sub>2</sub> reduction experiments were carried out in a twocompartment cell under ambient conditions, which was separated by proton exchange membrane. The membrane was protonated by first boiling in ultrapure water for 1 h and treating in H<sub>2</sub>O<sub>2</sub> (5%) aqueous solution for another 1 h. And then, the membrane was treated in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 3 h and finally in water for 6 h. All steps were performed at 80°C.<sup>1</sup> Electrochemical measurements were performed in a standard three-electrode system by a CHI 660E electrochemical analyzer (CHI Instruments, Inc., Shanghai) using SnO<sub>2</sub>/CC ( $0.5 \times 0.5$ cm<sup>2</sup>) as working electrode, Ag/AgCl as reference electrode, and graphite rod as counter electrode. All experiments were carried out at room temperature (25 °C). For N<sub>2</sub> reduction experiments, the Na<sub>2</sub>SO<sub>4</sub> electrolyte (0.1 M) was bubbled with N<sub>2</sub> for 30 min before measurement.

**Determination of NH<sub>3</sub>:** Concentration of produced NH<sub>3</sub> was detected by UV-Vis absorption spectrophotometry with salicylic acid analysis method.<sup>2</sup> In detail, 4 mL electrolyte was taken from the cathodic chamber, then 50 µL oxidizing solution containing NaClO ( $\rho$ Cl = 4 ~ 4.9) and NaOH (0.75 M) was added into this solution. Subsequently, 500 µL coloring solution containing 0.4 M C<sub>7</sub>H<sub>5</sub>NaO<sub>3</sub> and 0.32 M NaOH, and 50 µL catalyst solution (0.1 g Na<sub>2</sub>[Fe(CN)<sub>5</sub>NO]·2H<sub>2</sub>O diluted to 10 mL with deionized water) were added into the above solution. After standing at 25 °C for 1 h, the UV-Vis absorption spectrum was measured at awavelength of 660 nm. The concentration-absorbance curve (y = 0.729x + 0.022, R<sup>2</sup> = 0.999) was calibrated using standard NH<sub>4</sub>Cl solution with NH<sub>3</sub> concentrations of 0.00, 0.01, 0.03, 0.05, 0.10, 0.20, and 0.30 µg mL<sup>-1</sup> in 0.1 M Na<sub>2</sub>SO<sub>4</sub> and it shows good linear relation of absorbances value with NH<sub>3</sub> concentrations by three times independent calibrations.

**Determination of N**<sub>2</sub>**H**<sub>4</sub>: N<sub>2</sub>H<sub>4</sub> presented was estimated by the method of Watt and Chrisp.<sup>3</sup> p-C<sub>9</sub>H<sub>11</sub>NO (5.99 g), HCI (30 mL), and C<sub>2</sub>H<sub>5</sub>OH (300 mL) were mixed and used as a color reagent. Calibration curve was plotted as follows. We prepared a series of 5 mL standard N<sub>2</sub>H<sub>4</sub> solutions with the concentrations of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5  $\mu$ g mL<sup>-1</sup> in 0.1 M Na<sub>2</sub>SO<sub>4</sub>, and separately mixed with 5 mL above prepared color reagent. After stirring the mixed solution for 10 min at room temperature, the absorbance of the resulting solution was measured at 455 nm, and the yields of N<sub>2</sub>H<sub>4</sub> were estimated from a standard curve.

Calibration curve (y = 1.198 x + 0.0519,  $R^2 = 0.999$ ) shows good linear relation of absorbance with N<sub>2</sub>H<sub>4</sub> concentration by three times independent calibrations.

**Calculations of NH<sub>3</sub> yield rate and FE:** NH<sub>3</sub> yield rate is calculated using the following equation:

NH<sub>3</sub> yield rate = 
$$(c_{NH3} \times V) / (17 \times t \times A)$$
 (1)

FE is calculated according to following equation:

 $FE = 3 \times F \times c_{NH3} \times V / (17 \times Q)$ <sup>(2)</sup>

Where  $c_{NH3}$  is the measured NH<sub>3</sub> concentration; V is the volume of the cathodic reaction electrolyte; t is the potential applied time; A is the geometric area of the cathode (0.5 × 0.5 cm<sup>2</sup>); F is the Faraday constant; and Q is the quantity of applied electricity.



Fig. S1. SEM images for bare CC.



Fig. S2. FE-SEM image for SnO<sub>2</sub>/CC.



Fig. S3. TEM image for SnO<sub>2</sub>.



Fig. S4. N<sub>2</sub> TPD profile of SnO<sub>2</sub>.



Fig. S5. LSV curves of  $SnO_2/CC$  in Ar- and  $N_2$ -saturated 0.1 M  $Na_2SO_4$  with a scan rate of 5 mV s<sup>-1</sup>.



Fig. S6. CV curves of  $SnO_2/CC$  in Ar- and  $N_2$ -saturated 0.1 M  $Na_2SO_4$ .



**Fig. S7.** (A) UV-Vis absorption spectra of various NH<sub>3</sub> concentrations after incubated for 1 h at room temperature. (B) Calibration curve used for calculation of NH<sub>3</sub> concentrations.



Fig. S8. (A) The amount of evolved  $H_2$  at each given potential. (B) The calculated FEs of HER.



**Fig. S9.** UV-Vis absorption spectra of 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte stained with NH<sub>3</sub> color agent before and after 2 h electrolysis at -0.7 and -0.8 V in Ar atmosphere on the SnO<sub>2</sub>/CC electrode.



Fig. S10. UV-Vis absorption spectra of 0.1 M  $Na_2SO_4$  electrolyte stained with  $NH_3$  color agent before and after 2 h electrolysis in  $N_2$  atmosphere on the  $SnO_2/CC$  electrode at opencircuit potential under ambient conditions.



**Fig. S11.** UV-Vis absorption spectra of 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte (before and after using CC as working electrode at -0.7 V for 2 h in 0.1 M Na<sub>2</sub>SO<sub>4</sub>) after incubated with NH<sub>3</sub> color agent under ambient conditions.



Fig. S12. (A) 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. S13.** UV-Vis absorption spectra of 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte (after cycling stability test at -0.7 V for 2 h) after incubated with NH<sub>3</sub> color agent.



Fig. S14. FE-SEM images of  $SnO_2/CC$  after NRR stability test in 0.1 M  $Na_2SO_4$ .



Fig. S15. TEM image of  $SnO_2$  after stability test in 0.1 M  $Na_2SO_4$ .



Fig. S16. XRD pattern of SnO<sub>2</sub>/CC after stability test.



Fig. S17. XPS spectra for  $SnO_2$  in (A) Sn 3d and (B) O 1s regions after stability test.

Catalyst	Electrolyte	Temperatur e	NH <sub>3</sub> yield rate	Ref.
SnO <sub>2</sub> /CC	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	$\begin{array}{c} 1.47 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2} \\ (4.03 \ \mu\text{g h}^{-1} \ \text{mg}^{-1}_{\text{cat.}}) \end{array}$	This work
Fe <sub>2</sub> O <sub>3</sub> -CNT	diluted KHCO <sub>3</sub> aqueous solution	25 °C	$3.58 \times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2}$	2
AuHNCs	0.5 M LiClO <sub>4</sub>	25 °C	$6.37 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	4
β-FeOOH	0.5 M LiClO <sub>4</sub>	25 °C	23.32 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	5
MoS <sub>2</sub> /CC	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	$8.08 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	6
TiO <sub>2</sub>	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	$9.16 \times 10^{-11} \text{ mol s}^{-1} \cdot \text{cm}^{-2}$	7
Li <sup>+</sup> - incorporated PEBCD/C	0.5 M Li <sub>2</sub> SO <sub>4</sub>	25 °C	$2.58 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	8
Fe <sub>3</sub> O <sub>4</sub> /Ti	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	$5.6 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	9
Mo nanofilm	0.01 M H <sub>2</sub> SO <sub>4</sub>	25 °C	$3.09 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	10
hollow Cr <sub>2</sub> O <sub>3</sub> microspheres	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	$25.3 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	11
DR MoS <sub>2</sub> nanoflower	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	29.28 µg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	12
Fe <sub>2</sub> O <sub>3</sub> nanorods	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	$15.9 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	13
TiO <sub>2</sub> -rGO	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	$15.13 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	14
Bi <sub>4</sub> V <sub>2</sub> O <sub>11</sub> /CeO <sub>2</sub>	0.1 M HCl	25 °C	23.2 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	15
MoO <sub>3</sub>	0.1 M HCl	25 °C	29.43 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	16
Mo <sub>2</sub> N	0.1 M HCl	25 °C	78.4 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	17
Nb <sub>2</sub> O <sub>5</sub> nanofiber	0.1 M HCl	25 °C	43.6 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	18
VN/TM	0.1 M HCl	25 °C	$8.40 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	19
MoN NA/CC	0.1 M HCl	25 °C	$3.01 \times 10^{-10} \text{ mo1 s}^{-1} \text{ cm}^{-2}$	20
Ag nanosheet	0.1 M HCl	25 °C	$4.62 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	21
B <sub>4</sub> C	0.1 M HCl	25 °C	$26.57 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	22
Au nanorods	0.1 M KOH	25 °C	$2.69 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	23

**Table S1.** Comparison of the  $NH_3$  yield of  $SnO_2/CC$  with other reported aqueous-based NRR electrocatalysts.

Pd <sub>0.2</sub> Cu <sub>0.8</sub> /rGO 0.1 M KOH 25 °C 2.80 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	24
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Catalyst	Electrolyte	Temperature	FE	Ref.
SnO <sub>2</sub> /CC	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	2.17%	This work
Fe <sub>2</sub> O <sub>3</sub> -CNT	diluted KHCO <sub>3</sub> aqueous solution	25 °C	0.15%	2
MoS <sub>2</sub> /CC	$0.1 \text{ M} \text{ Na}_2 \text{SO}_4$	25 °C	1.17%	6
TiO <sub>2</sub>	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	2.5%	7
Li <sup>+</sup> -incorporated PEBCD/C	0.5 M Li <sub>2</sub> SO <sub>4</sub>	25 °C	2.85%	8
Fe <sub>3</sub> O <sub>4</sub> /Ti	$0.1 \text{ M} \text{ Na}_2 \text{SO}_4$	25 °C	2.6%	9
Mo nanofilm	0.01 M H <sub>2</sub> SO <sub>4</sub>	25 °C	0.72%	10
hollow Cr <sub>2</sub> O <sub>3</sub> microspheres	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	6.78%	11
DR MoS <sub>2</sub> nanoflower	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	8.34%	12
Fe <sub>2</sub> O <sub>3</sub> nanorods	0.1 M Na <sub>2</sub> SO <sub>4</sub>	25 °C	0.94%	13
TiO <sub>2</sub> -rGO	$0.1 \text{ M} \text{ Na}_2 \text{SO}_4$	25 °C	3.3%	14
Bi <sub>4</sub> V <sub>2</sub> O <sub>11</sub> /CeO <sub>2</sub>	0.1 M HCl	25 °C	10.16%	15
MoO <sub>3</sub>	0.1 M HCl	25 °C	1.9%	16
Mo <sub>2</sub> N	0.1 M HCl	25 °C	4.5%	17
Nb <sub>2</sub> O <sub>5</sub> nanofiber	0.1 M HCl	25 °C	9.26%	18
VN/TM	0.1 M HCl	25 °C	2.25%	19
MoN NA/CC	0.1 M HCl	25 °C	1.15%	20
B <sub>4</sub> C	0.1 M HCl	25 °C	15.95%	22
N-doped porous C	0.05 M H <sub>2</sub> SO <sub>4</sub>	25 °C	1.42%	25
N-doped porous C	0.1 M HCl	25 °C	1.45%	26
Rh nanosheets nanoassemblies	0.1 M KOH	25 °C	0.217%	27
γ-Fe <sub>2</sub> O <sub>3</sub>	0.1 M KOH	25 °C	1.96%	28
CP <sub>2</sub> TiCl <sub>2</sub>	H <sub>2</sub> O	25 °C	0.23%	29

**Table S2.** Comparison of FE of  $SnO_2/CC$  for NRR with other reported aqueous-based NRR electrocatalysts.

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