Electronic Supplementary Information

Nanoporous CeO_2 nanowire array by acid etching preparation： An efficient electrocatalyst for ambient N_2 reduction

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Content:

Experimental section

Materials: Nariño (5 wt%) solution, salicylic acid, ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), sodium citrate, sodium hypochlorite (NaClO), sodium nitroferricyanide ($C_5FeN_6Na_2O$), para-(dimethylamino) benzaldehyde, and aniline were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) and ethanol were purchased from Aladdin Ltd. (Shanghai, China). Nafion 115 membrane (DuPont) was purchased from HESEN Co., Ltd. (Shanghai, China). Ultrapure water used throughout all experiments was purified through a Millipore system.

Preparation of MnO_2-CeO_2/TM and np-CeO_2/TM: MnO_2-CeO_2/TM was prepared as follows. 24 mmol of $CO(NH_2)_2$, 4 mmol of $Ce(NO_3)_2\cdot 6H_2O$, 4 mmol of $Mn(NO_3)_2\cdot 4H_2O$ and 10 mmol of NH_4F were mixed (70 mL) together under stirring. Then the solution and a piece of Ti mesh (1 cm × 4 cm in size) were put into a Teflonlined autoclave and kept at 120 °C for 5 h. When the autoclave cooled down naturally, the resulting sample was dried 2 h at 60 °C in air and followed by calcination at 300 °C under Ar atmosphere in the presence of nw for 120 min. To prepare np-CeO_2/TM, the resulting MnO_2- np-CeO_2/TM was put in 0.6 M oxalic solution for 1.5 h and then dried for 4 h at 60 °C.

Preparation of np-CeO_2/GCE: To prepare the np-CeO_2/GCE, 30 mg CeO_2 and 45 μL 5wt% Nafion solution were dispersed in 960 μL ethanol followed by 30 min sonication to form a homogeneous ink. 10 μL ink was loaded onto a GCE (1*1 cm^2) and dried under ambient condition.

Characterizations: XRD patterns were obtained from a Shimazu XRD-6100 diffractometer with Cu Kα 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 absorbance data of spectrophotometer were measured on SHIMADZU UV-1800 ultraviolet-visible

(UV-Vis) spectrophotometer.

Electrochemical measurements: Before NRR tests, the Nafion 115 membrane was pre-treated by heating in 5% H_2O_2 solution and ultrapure water at 80 °C for 1 h, respectively. Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CHI Instruments, Inc., Shanghai) in a standard three-electrode system using Mo_2N/GCE 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_2 reduction experiments, the HCl electrolyte (0.1 M) was bubbled with N_2 for 30 min before the measurement.

Nafion resistance analysis: To evaluate the resistance of Nafion membrane, two kinds of conditions were conducted: one compartment cell testing and two compartment cell testing. The resistance of Nafion membrane can be regarded as the resistance of solution, which is denoted as R_{Ω}.. From Fig. S1, the resistance of Nafion membrane is the difference of two values of R_{Ω}. That is 9.75 Ω at -0.3 V (the best NRR rate), and the current is 0.2 mA. The difference in potential loss is 9.75×0.2 = 2 mV. Thus, the resistance of Nafion membrane can be ignored. Meanwhile, the fitting values of one-compartment cell are R_{s1}=2.21 ohm, R_{ct1}=1.66 ohm, and C_{dl}=0.0639 F. The fitting values of two-compartment cell are R_{s2}=24.9 ohm, R_{ct2}=2.68 ohm, and C_{d2}=0.0428 F.

Determination of NH_3: The produced ammonia was estimated by indophenol blue method by ultraviolet spectroscopy. In detail, 2 mL of post-tested solution was got from the electrochemical reaction vessel. Then, 2 mL of 1 M NaOH solution (contains 5 wt% salicylic acid and 5 wt% sodium citrate) was followed by addition of 1 mL of 0.05 M NaClO and 0.2 mL of $C_5FeN_6Na_2O$ (1 wt%). After standing at 25 °C for 2 h, the UV-Vis absorption spectrum was measured. The concentration of indophenol blue was determined using the absorbance at awavelength of 655 nm. The concentration-absorbance curve was calibrated using standard ammonia chloride solution with a serious of concentrations. The fitting curve ($Y=0.336X+0.018$, $R^2=0.999$) shows good linear relation of absorbance value with NH_4Cl concentration by three times independent calibrations.

Determination of N_2H_4: The N_2H_4 present in the electrolyte was determined by the method of Watt and Chrisp. The p-$C_9H_{11}NO$ (5.99 g), HCI (30 mL), and C_2H_5OH (300 mL) were mixed and used as a color reagent. In detail, 5 μL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL prepared color reagent and stirred 15 min at 25 °C. The obtained calibration curve of N_2H_4 is $Y=0.552X + 0.044$, $R^2=0.995$.

Calculations of NH_3 formation rate and FE: Ammonia formation was calculated using the following equation:

$$\text{Ammonia formation rate} = [NH_4^+]\times V/(m\times t)$$

FE was calculated according to following equation:

$$FE = 3\times F\times[NH_4^+]\times V/(17\times Q)$$

Where $[NH_4^+]$ is the measured NH_4^+ ion concentration; V is the volume of the cathodic reaction electrolyte; t is the potential applied time; m is the loaded quality of catalyst; F is the Faraday constant; and Q is the quantity of applied electricity.

Calculations of H_2 amount and FE: The FE was calculated by comparing the amount of measured H_2 generated by cathodal electrolysis with calculated H_2 (assuming 100% FE). GC analysis was carried out on GC–2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second.

FE was calculated according to following equation:

$$FE = 2\times F\times n/Q$$

Where F is the Faraday constant; n is the actually produced H_2(mol), and Q is the quantity of applied electricity.

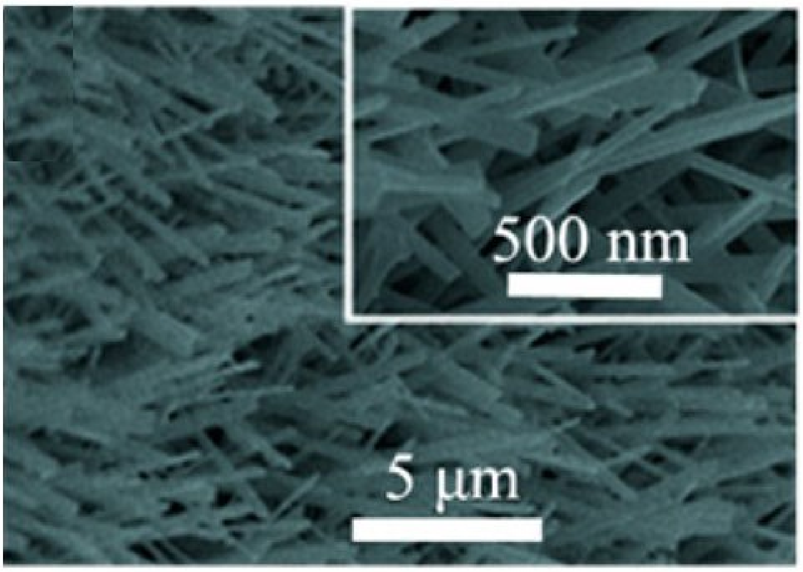

Fig. S1. The SEM image for MnO_2-CeO_2.

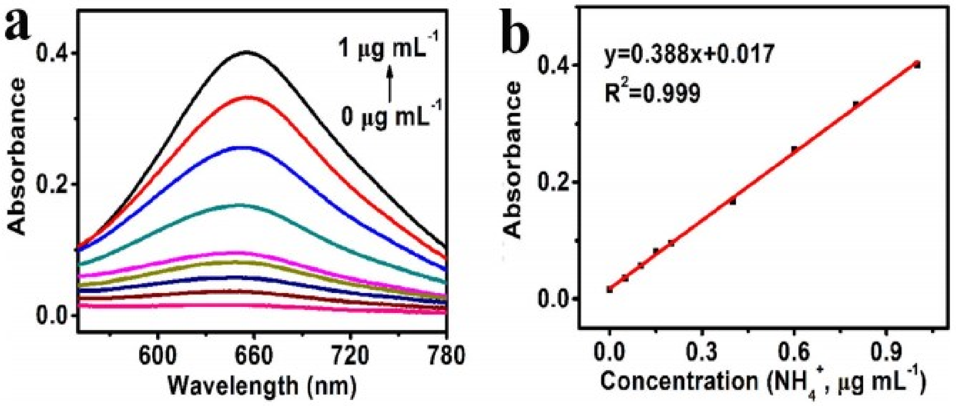

Fig. S2. (a) UV-Vis spectra of indophenol assays with NH_4^+ ions after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_4Cl.

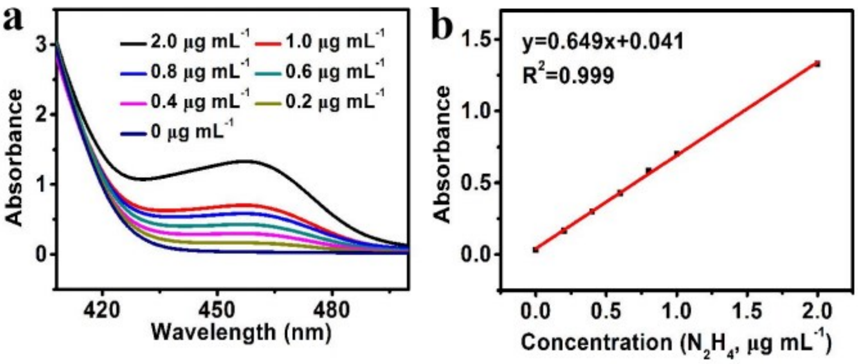

Fig. S3. (a) UV-Vis spectra of various N_2H_4 concentrations after incubated for 15 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations.

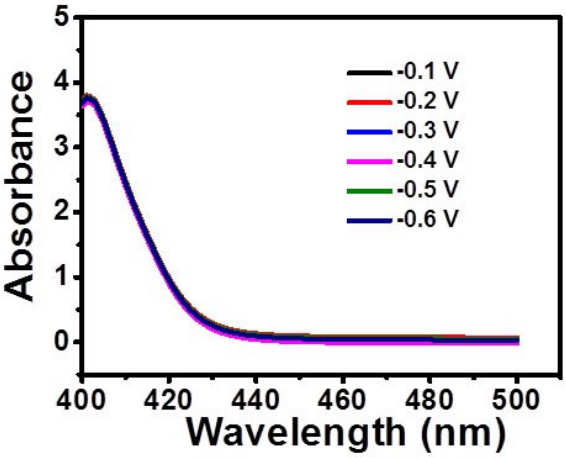

Fig. S4. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp after 2-h electrolysis at each given potential under ambient conditions.

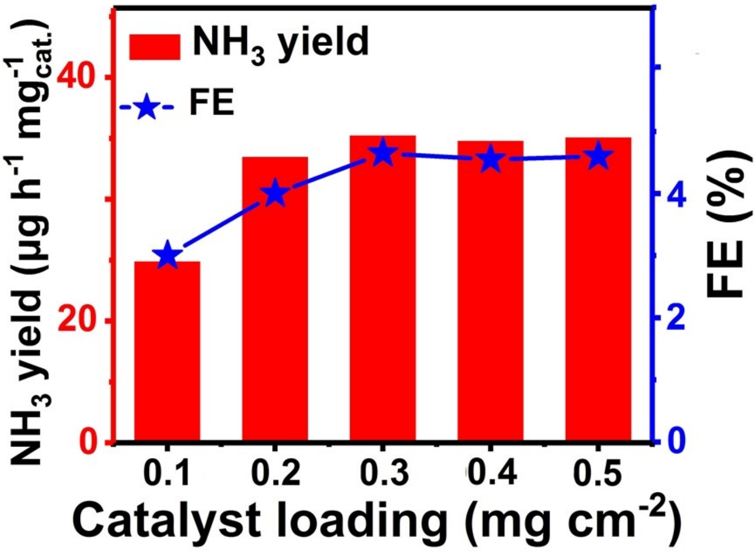

Fig. S5. The NH$_3$ yields and FEs for np-CeO$_2$ with different catalyst loadings.

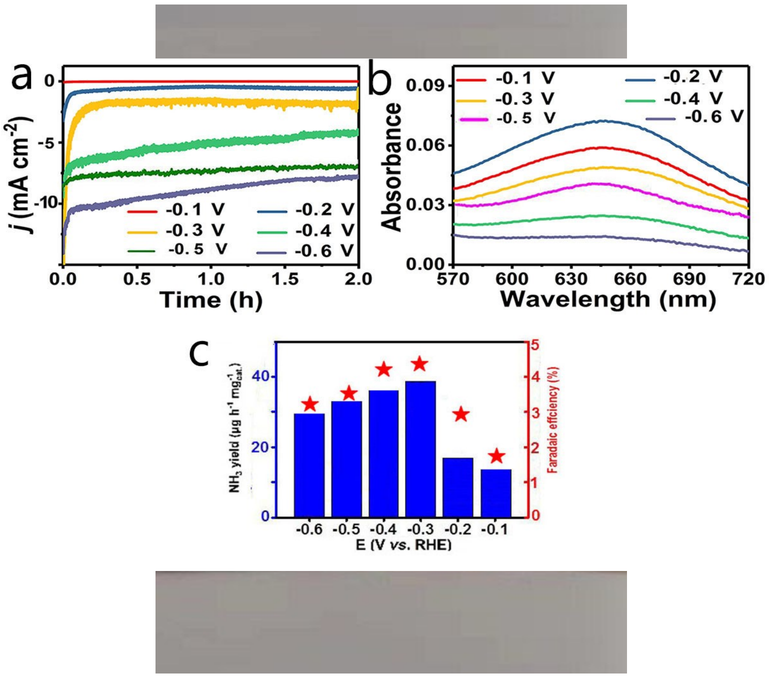

Fig. S6. Photographs of pH test papers in 0.1 M HCl before and after 24 h electrolysis.

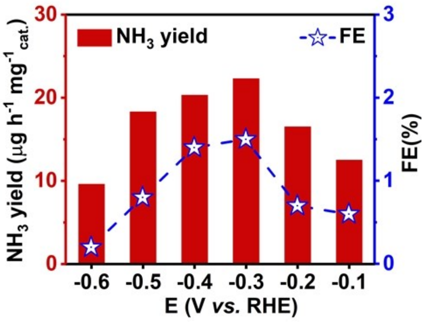

Fig. S7. (a) Time-dependent current density curves for CeO_2 at different potentials in 0.1 M HCl. (b) UV-Vis absorption spectra of the 0.1 M HCl electrolytes stained with indophenol indicator after electrolysis at a series of potentials. (c) NH_3 yields and FEs at a series of potentials.

Fig. S8. NH_3 yield and FE of the MnO_2-CeO_2.

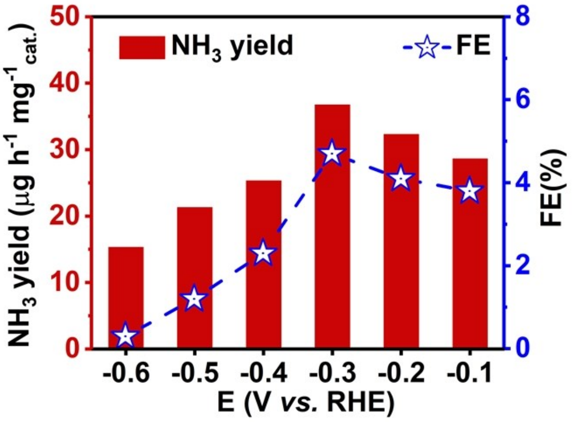

Fig. S9. NH_3 yield and FE of the np-CeO_2 when testing in H_2SO_4.

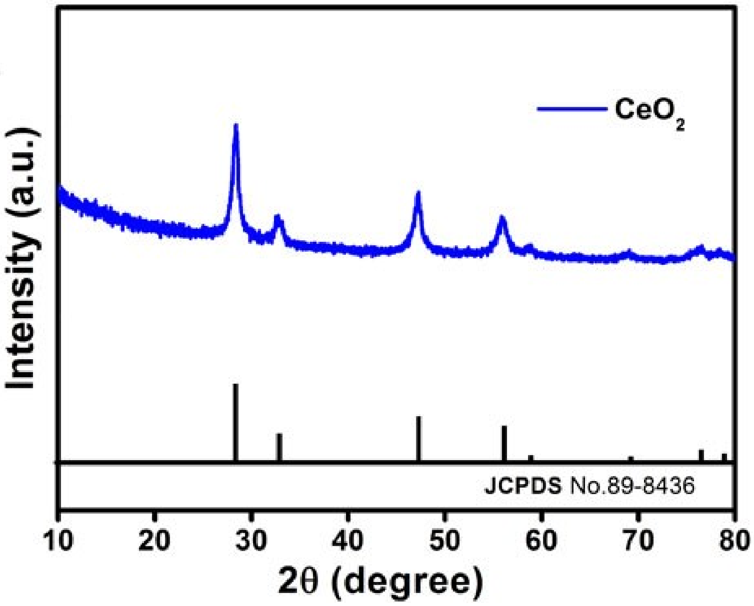

Fig. S10. XRD patterns for CeO$_2$ after the long stability test.

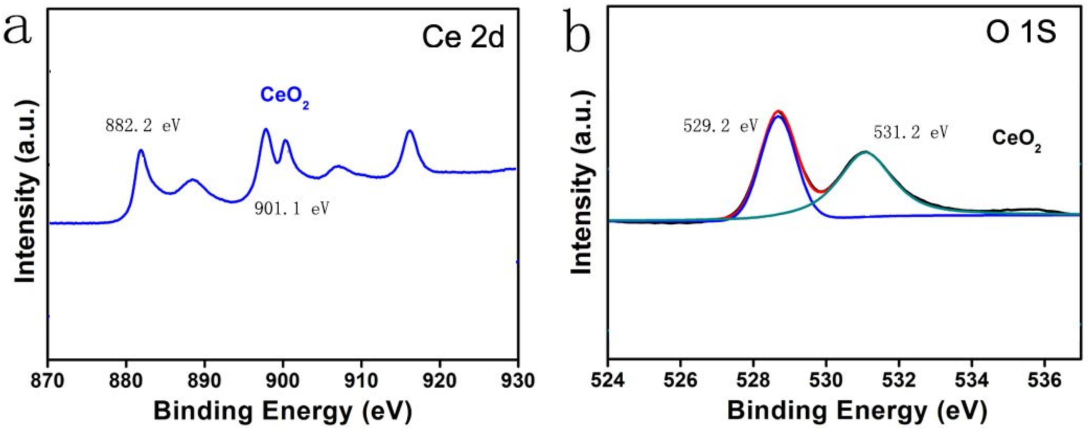

Fig. S11. XPS spectra for CeO_2 after the long stability test.

Table S1. Comparison of the NH_3 electrosynthesis activity for np-CeO_2/GCE with other NRR catalysts under ambient conditions.

Catalyst	R NH_3	FE%	Ref
np-CeO_2/GCE	**38.6 μg h^{-1} mg^{-1}**	**4.7%**	**This work**
MoO_3 nanosheet	29.43 μg h^{-1} $mg^{-1}_{cat.}$	1.9%	1
$Bi_4V_2O_{11}/CeO_2$	23.21 μg h^{-1} $mg^{-1}_{cat.}$	10.16%	2
TA-reduced Au/TiO_2	21.4 μg h^{-1} $mg^{-1}_{cat.}$	8.11%	3
α-Au/CeO_x-RGO	8.31 μg h^{-1} $mg^{-1}_{cat.}$	10.1%	4
Au nanorod	6.042 μg h^{-1} $mg^{-1}_{cat.}$	~4.0%	5
γ-Fe_2O_3	0.212 μg h^{-1} $mg^{-1}_{cat.}$	1.9%	6
N-doped nanocarbon	27.2 μg h^{-1} $mg^{-1}_{cat.}$	1.42%	7
TiO_2-rGO	15.13 μg h^{-1} $mg^{-1}_{cat.}$	3.3%	8
Mn_3O_4-rGO	17.4 μg h^{-1} $mg^{-1}_{cat.}$	3.52%	9
R-WO_3 nanosheet	17.28 μg h^{-1} $mg^{-1}_{cat.}$	7.0%	10
$Pd_{0.2}Cu_{0.8}$-rGO	2.8 μg h^{-1} $mg^{-1}_{cat.}$	0.6%	11
PdRu tripods	37.23 μg h^{-1} $mg^{-1}_{cat.}$	1.85%	12
Au flowers	25.57 μg h^{-1} $mg^{-1}_{cat.}$	4.05%	13

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