

Electronic Supplementary Information

Experimental Section

Materials: Juncus was obtained from the local Changsheng Pharmacy (Nanchang, China). CP was purchased from Shenzhen Green and Creative Environmental Science and Technology Co., Ltd. Cerous nitrate (99.99%), sodium hydroxide (99.0%), ammonium chloride (99.5%), sodium salicylate (AR), p-dimethylaminobenzaldehyde (AR), sodium nitroferricyanide dehydrate (AR), NaOH (AR) and sodium hypochlorite solution (AR) were purchased from Aladdin Co., Ltd. (Shanghai, China). Nafion (5 wt%) solution was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Hydrogen peroxide (36%), hydrazine monohydrate (AR) and ethyl alcohol (75%) were purchased from Beijing Chemical Corp. The ultrapure water used throughout all experiments was purified through a Millipore system. All reagents were analytical reagent grade without further purification.

Synthesis of JDC: Juncus was prewashed with distilled water under ultrasonic cleaning for 2 h, and then dried at 60 °C for 24 h under vacuum. JDC was calcinated at 800 °C for 2 h with a heating speed of 2 °C min⁻¹ in Ar atmosphere.

Synthesis of CeO₂@JDC: 0.15 g of prewashed Juncus was immersed in 40 mL 0.1 M Ce(NO₃)₂·2H₂O solution for 24 h and dried at 60 °C for another 24 h under vacuum. Subsequently, it was annealed at 800°C with a heating speed of 2 °C min⁻¹ for 2 h in Ar atmosphere. The weight of the obtained CeO₂@JDC is about 0.53 g, thus the mass percentage of CeO₂ in CeO₂@JDC is about 45.8%.

Synthesis of CeO₂ nanoparticles: Typically, 0.88 g of Ce(NO₃)₃·6H₂O was dissolved in 20 mL of H₂O with stirring. Then 15 mL of 14 M NaOH was dropwise added to the Ce(NO₃)₃ solution under stirring for 30 min. The mixed solution was transferred into a 50 mL of Teflon-lined autoclave for heating at 100 °C for 24 h. After the reaction, the obtained white precipitate was collected and washed with deionized water and ethanol. Finally, the sample was calcined in a tube furnace under Ar atmosphere at 500 °C for 4 h to obtain CeO₂ nanoparticles.

Characterizations: X-ray diffraction (XRD) analysis was performed with a Haoyuan DX-2700BH diffractometer. Copper K α radiation (1.54 Å) was generated with a tube voltage of 40 kV and a tube current of 30 mA. SEM measurements were carried out on a GeminiSEM 300 scanning electron microscope (ZEISS, Germany) at an accelerating voltage of 5 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer was measured on UV-vis spectrophotometer. The ion chromatography data were collected on Metrohm 940 Professional IC Vario. Transmission electron microscopy (TEM) images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. After ultrasonic dispersion of the samples for 20 min, the samples were prepared using a double membrane.

Electrochemical measurements: All electrochemical measurements were carried on a CHI760E electrochemical workstation (Shanghai, Chenhua) using a standard three-electrode setup. Electrolyte solution was N₂/Ar-saturated 0.1 M Na₂SO₄, using CeO₂@JDC/CP (1 × 1 cm²) as the working electrode, a carbon rod as the counter electrode and Ag/AgCl as the reference electrode. Nafion@117 Membrane used to separate the H-type electrolytic cell was protonated by boiling in ultrapure water, H₂O₂ (5%) aqueous solution and 0.5 M H₂SO₄ at 80 °C for 1 h, respectively. All the potentials reported in our work were converted to reversible hydrogen electrode (RHE) via the calibration equation: E (RHE) = E (vs. Ag/AgCl) + 0.0591 × pH + 0.197. Before the measurements, the electrolyte was purged with feeding gas for 0.5 h.

Preparation of the working electrode: 6 mg of the catalyst and 30 μL of 5 wt% Nafion were dispersed in 1170 μL of a deionized water/ethanol solution (v/v = 1:3) by sonicating for 2 h to get a homogeneous catalyst ink. Then, the ink was dropped onto a 1 cm² of carbon paper with a mass loading of 0.1 mg cm⁻² and then dried at 80 °C for 1 h.

Determination of NH₃: The indophenol blue method was employed to quantify the

concentrations of produced NH_3 . Firstly, 2 mL of electrolyte was pipetted from the cathodic chamber and mixed with 2 mL of 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate. Then, 1 mL of 0.05 M NaClO and 0.2 mL of 1% $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$ were added to the above solution in turn. Finally, after standing for 120 minutes at room temperature, the absorbance measurements were performed in the range of 500 nm to 800 nm. The absorbance value at 655 nm was employed to calculate the NH_3 concentration through the calibration curve. The concentration-absorbance curves were calibrated by measuring a series of standard solution with different NH_4Cl concentrations. The fitting curve of NH_3 is $y=0.583x+0.020$, $R^2=0.999$.

Determination of N_2H_4 : The N_2H_4 content in the electrolyte was determined by the method of Watt and Chrisp. 3 mL of concentrated HCl, 30 mL of $\text{C}_2\text{H}_5\text{OH}$, and 0.6 g of *p*- $\text{C}_9\text{H}_{11}\text{NO}$ were evenly mixed as a color reagent. Typically, 2 mL of electrolyte was pipetted from the cathodic chamber and mixed with 2 mL of the above prepared color reagent. After standing for 10 minutes, the UV-vis spectra were collected at a wavelength of 455 nm. The concentration-absorbance curves were plotted by measuring a series of standard solution with different N_2H_4 concentrations. The fitting curve is $y=0.287x+0.085$, $R^2=0.998$.

Calculations of NH_3 yield and Faradaic efficiency (FE):

NH_3 yield (V_{NH_3}) was calculated as follows:

$$V_{\text{NH}_3} = c(\text{NH}_3) \times V / (t \times m_{\text{cat}}) \quad (1)$$

The amount of NH_3 produced was calculated as follows:

$$m_{\text{NH}_3} = c(\text{NH}_3) \times V \quad (2)$$

FE was calculated as follows:

$$\text{FE} = 3F \times c(\text{NH}_3) \times V / (17 \times Q) \times 100\% \quad (3)$$

Where F is the Faraday constant (96485 C mol^{-1}); c_{NH_3} is the calculated NH_3

concentration ($\mu\text{g mL}^{-1}$); V is the volume of the electrolyte (35 mL) in the cathodic compartment; t is the reduction time (2 hours); Q is the quantity of electricity; m_{cat} is the loading quality of $\text{CeO}_2@\text{JDC}$ (0.1 mg cm^{-2}).

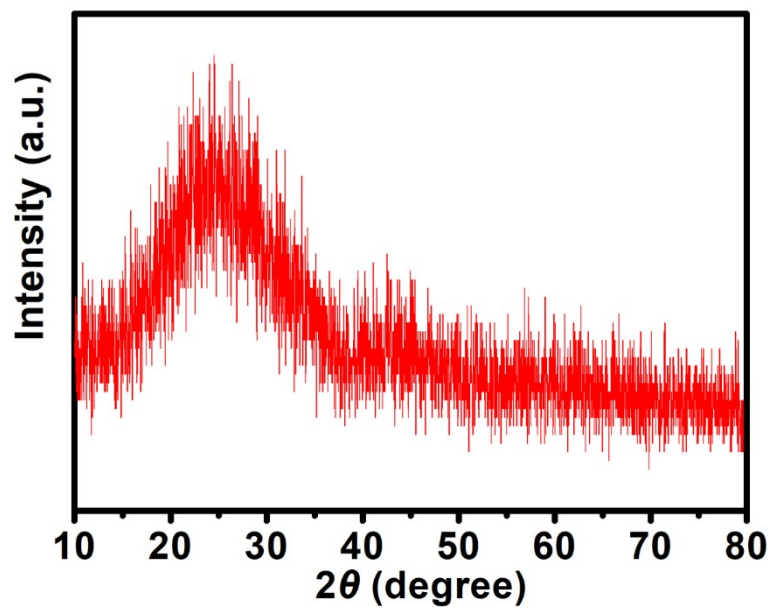


Fig. S1. XRD pattern of bare JDC.

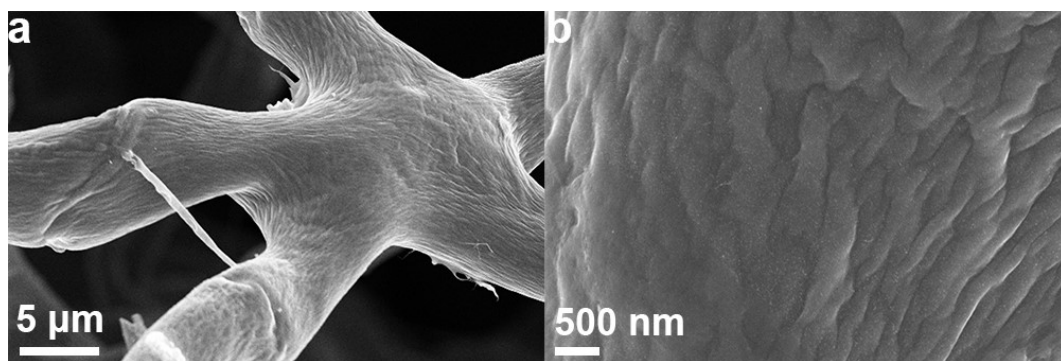


Fig. S2. (a) Low- and (b) high-magnification SEM images of JDC.

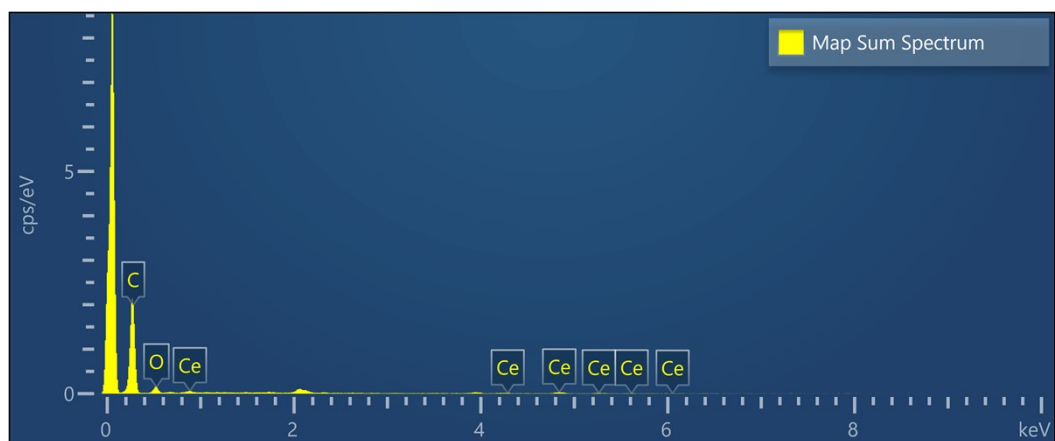


Fig. S3. EDX spectrum of CeO₂@JDC.

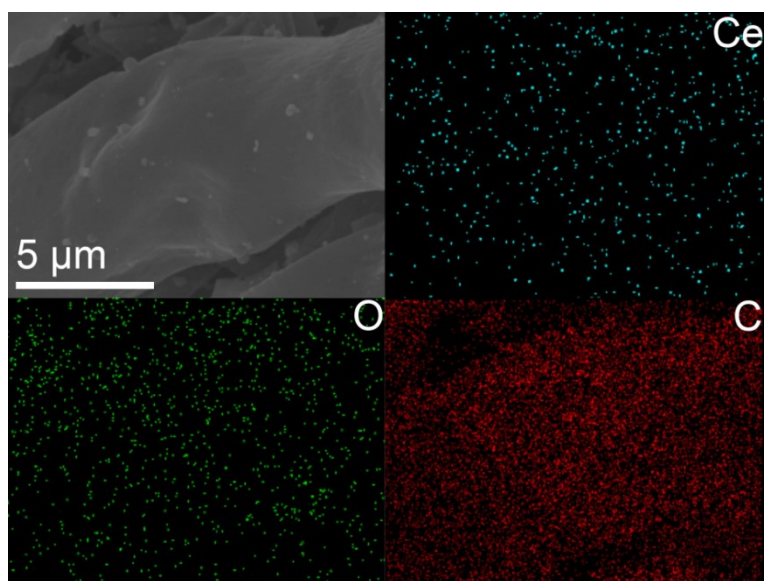


Fig. S4. SEM image and EDX mapping images of Ce, O and C elements in $\text{CeO}_2@\text{JDC}$.

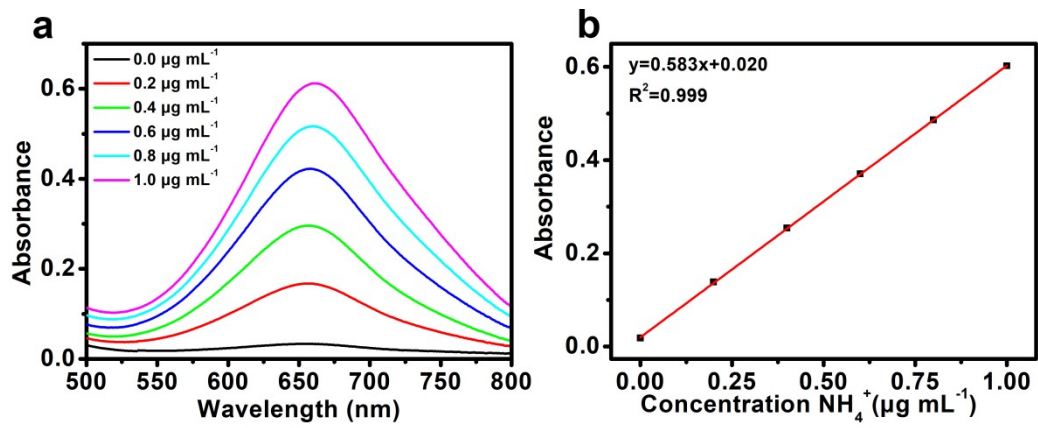


Fig. S5. (a) UV-Vis spectra and (b) corresponding calibration curve for calculation of NH_4^+ concentration.

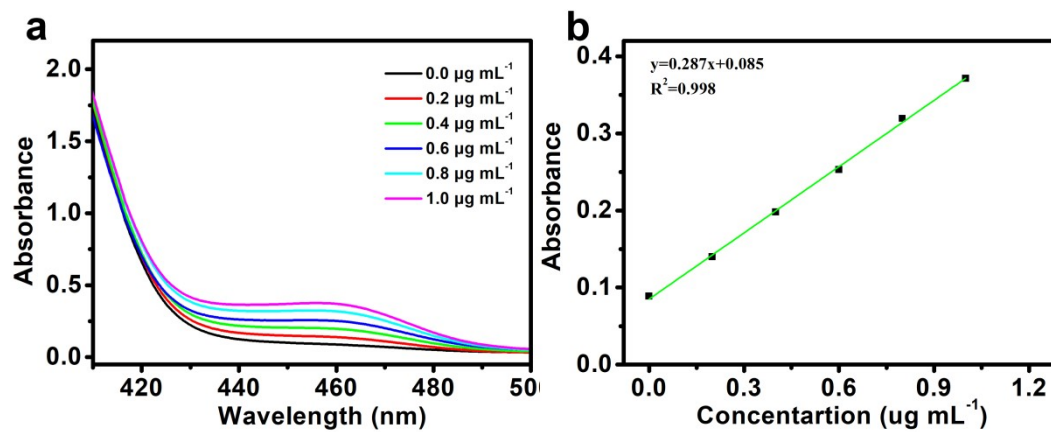


Fig. S6. (a) UV-Vis spectra and (b) corresponding calibration curve for calculation of N_2H_4 concentration.

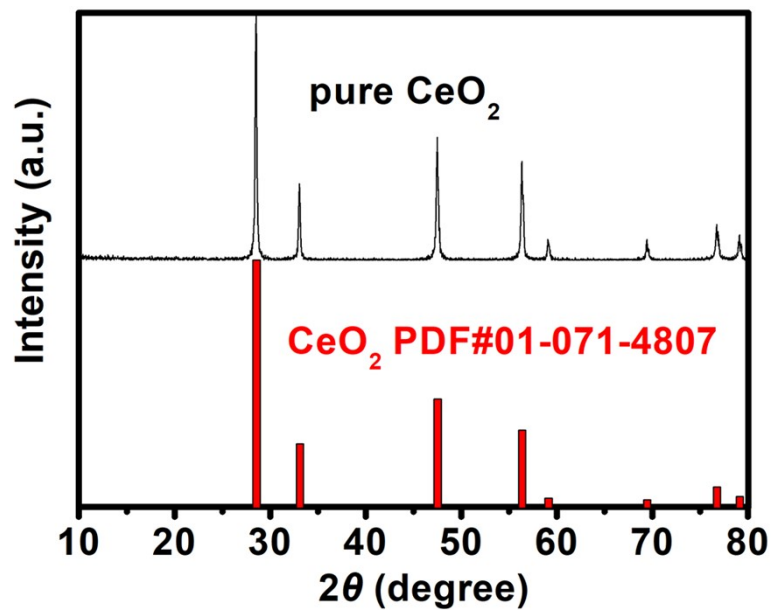


Fig. S7. XRD pattern of pure CeO₂

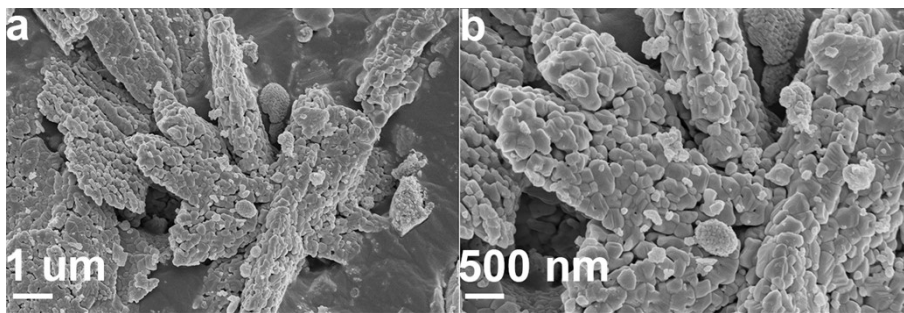


Fig. S8. (a) Low- and (b) high-magnification SEM images of pure CeO₂ particles.

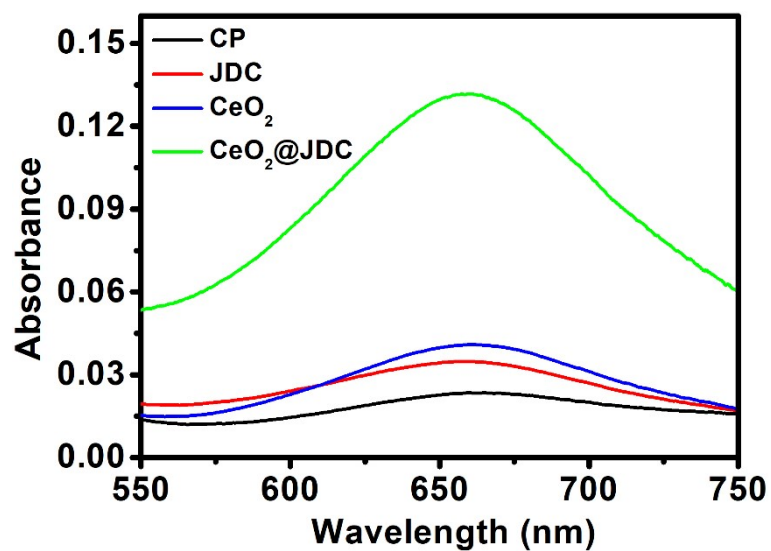


Fig. S9. UV-vis spectra of the electrolytes stained with indophenol indicator for the CeO₂@JDC, CeO₂, JDC and bare CP electrodes after 2-h electrolysis at -0.6 V in N₂-saturated 0.1 M Na₂SO₄.

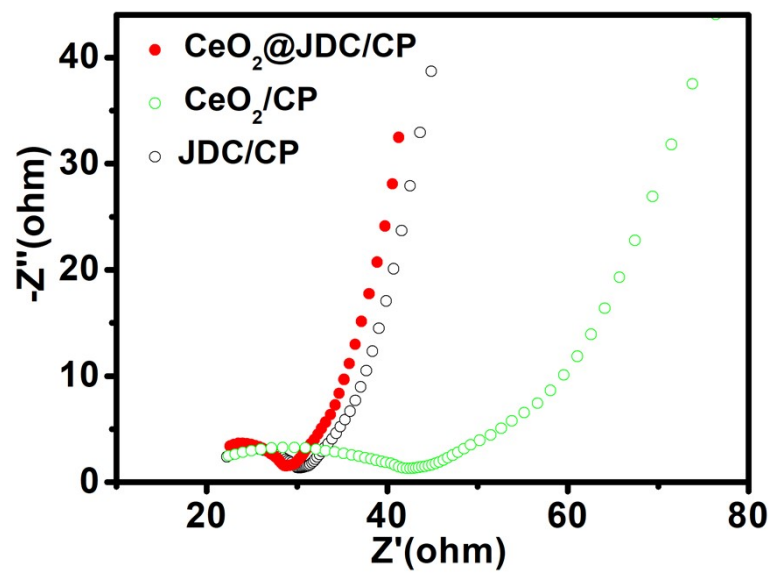


Fig. S10. Nyquist plots of CeO₂@JDC/CP, CeO₂/CP and JDC.

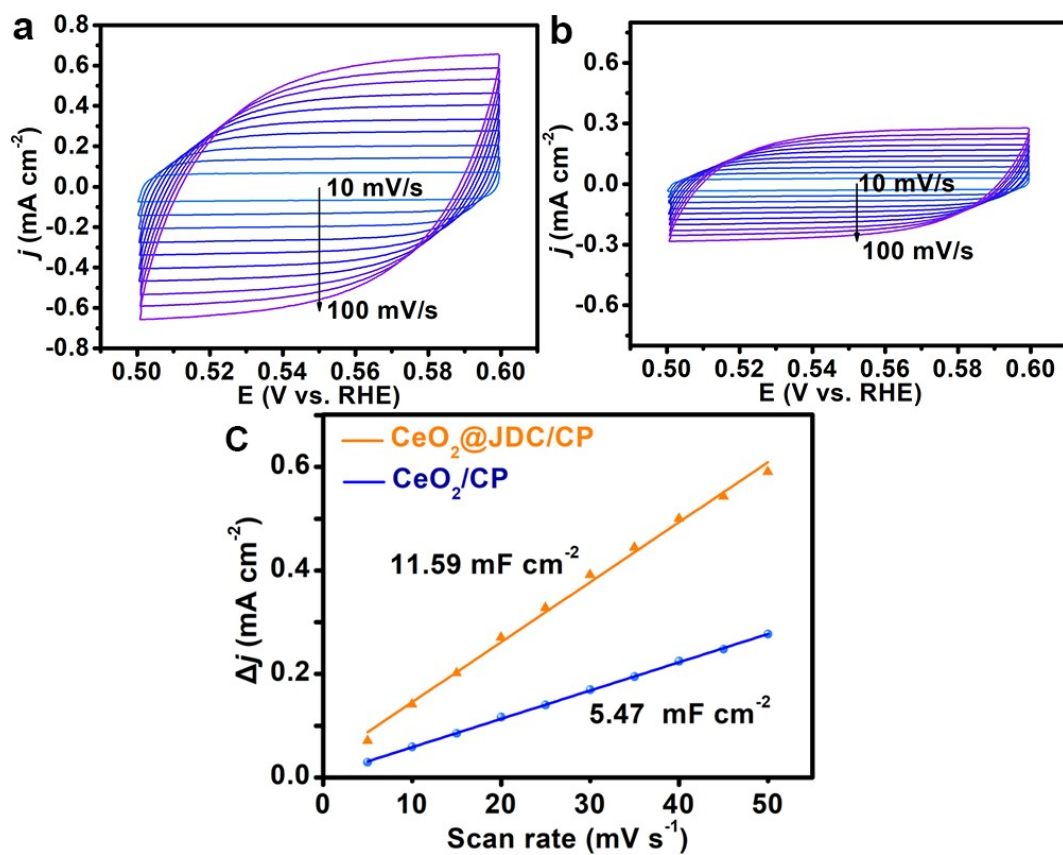


Fig. S11. CV curves of (a) CeO₂@JDC/CP and (b) CeO₂/CP with various scan rates (10–100 mV s⁻¹). (c) The corresponding C_{dl} of CeO₂@JDC/CP and CeO₂/CP.

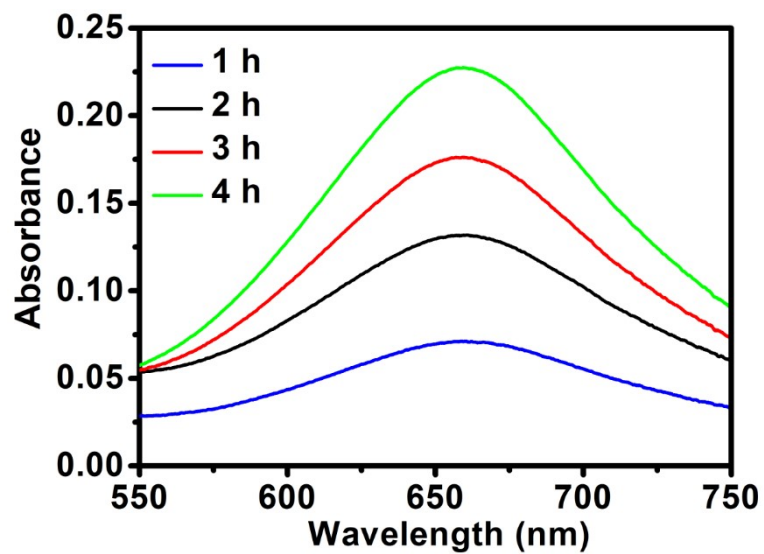


Fig. S12. UV-vis spectra of the electrolytes with different electrolysis time at -0.6 V on the $\text{CeO}_2@\text{JDC}$.

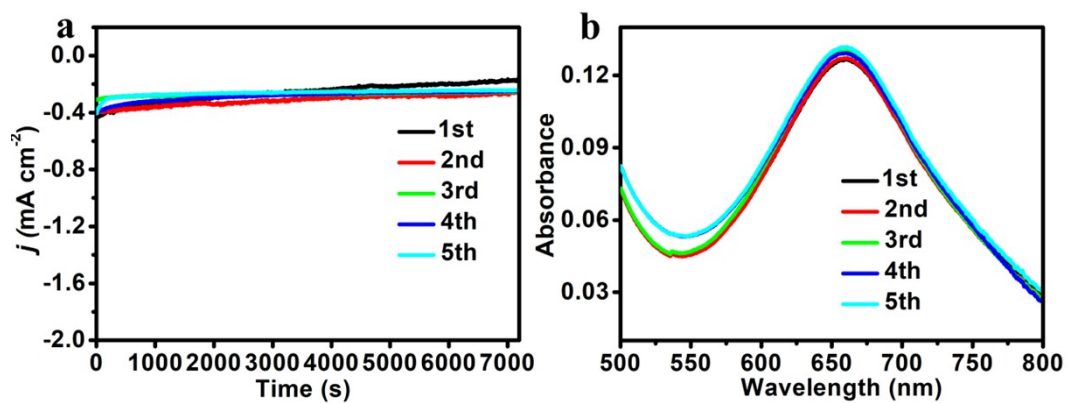


Fig. S13. (a) Chronoamperometry curves of CeO₂@JDC at -0.6 V for 5 cycles. (b) UV-vis absorption spectra of the electrolytes stained with indophenol indicator after cycling tests.

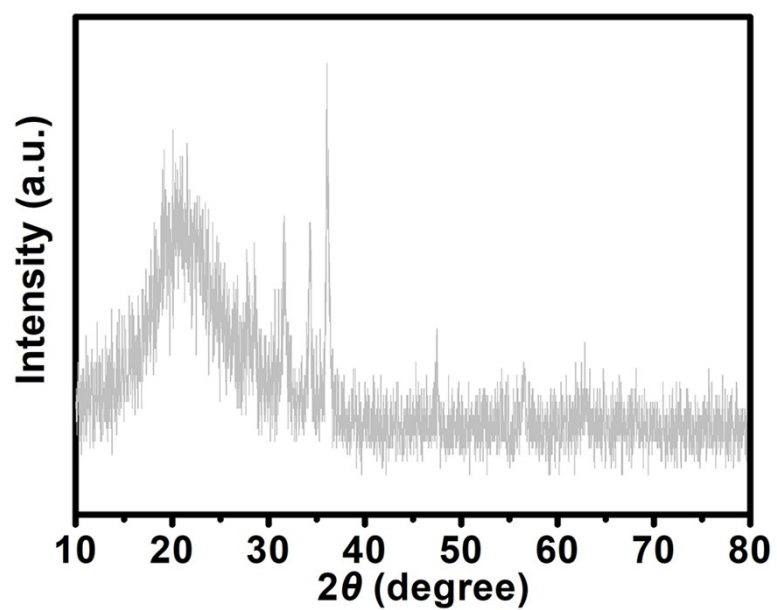


Fig. S14. XRD pattern of after electrolytic CeO₂@JDC/CP.

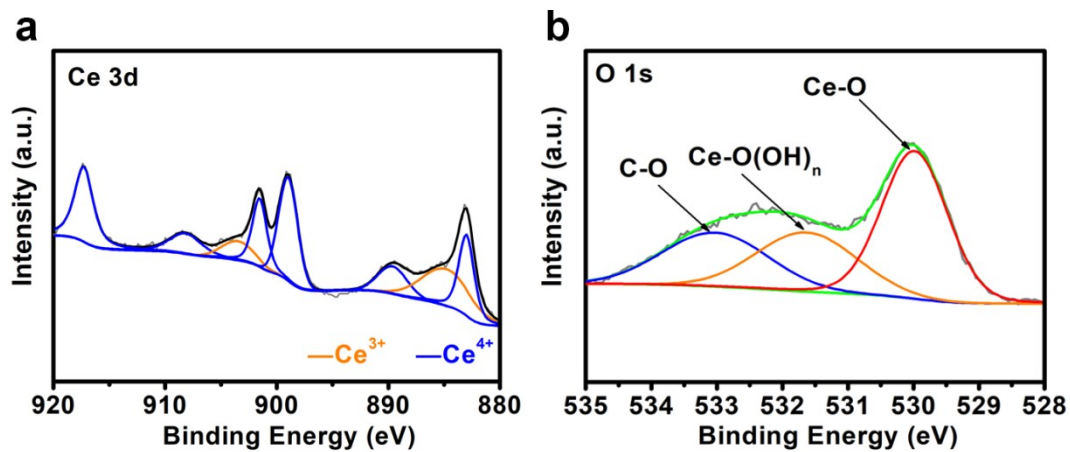


Fig. S15. XPS spectra in (a) Ce 3d and (b) O 1s regions of CeO₂@JDC after long-term NRR electrolysis.

Table S1. Comparison of the NH₃ electrosynthesis activity for CeO₂@JDC/CP with other NRR catalysts under ambient conditions.

Catalyst	Electrolyte	NH ₃ yield ($\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$)	FE (%)	Ref.
CeO₂@JDC	0.1 M Na₂SO₄	33.4	6.1	This work
Bi-doped CeO ₂	0.1 M Na ₂ SO ₄	17.83	1.61	1
r-CeO ₂ /CP	0.1 M Na ₂ SO ₄	16.4	3.7	2
Bi ₄ V ₂ O ₁₁ /CeO ₂	0.1 M HCl	23.21	10.16	3
Co-PCN	0.1 M Na ₂ SO ₄	49.69	32.2	4
Ce-Bi ₂ WO ₆	0.1 M HCl	22.5	15.9	5
Mo-W ₁₈ O ₄₉	0.1 M Na ₂ SO ₄	5.3	12.1	6
FeSC	0.1 M KOH	8.8 ± 1.3	6.1 ± 0.9	7
h-BNNS	0.1 M HCl	22.4	4.7	8
Au NPs/CoO _x	0.05 M H ₂ SO ₄	15	19	9
Fe-MoS ₂	0.5 M K ₂ SO ₄	8.63	18.8	10
CRP NRs/NF	0.1 M Na ₂ SO ₄	15.4	9.4	11
LaFeO ₃	0.1 M HCl	18.59	8.77	12
ZnO/RGO	0.1 M Na ₂ SO ₄	17.7	6.4	13
NiFeB	0.1 M KOH	3.24	3.19	14
Au(111)@Bi ₂ S ₃	0.1 M Na ₂ SO ₄	45.57	3.10	15
MoS ₂ /C ₃ N ₄	0.1 M Na ₂ SO ₄	19.86	6.87	16
Mo ₂ N nanorod	0.1 M HCl	78.4	4.5	17
Fe-MoS ₂	0.5 M K ₂ SO ₄	8.63	18.8	18
B-Mo ₂ C/NC	0.5 M K ₂ SO ₄	52.1	36.9	19

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