Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Synthesis of Co/CeO_2 hetero-particles with abundant oxygen-vacancies supported by carbon aerogels for ORR and OER

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1. Experimental

1.1. Materials and reagents

Cerium (III) chloride heptahydrate ($CeCl_3 \cdot 7H_2O$), potassium hexacyanocobaltate (III) ($K_3Co(CN)_6$) and chitosan (CS, 85% deacetylate) were bought from Alfa Aesar. Ruthenium dioxide (RuO_2) and commercial 20% Pt/C were purchased from Johnson Matthey Chemicals Ltd (Shanghai, China). All chemicals and reagents were utilized without further purification.

1.2. Preparation of Co-CeO_2/C aerogels

Typically, 2 mL $CeCl_3 \cdot 7H_2O$ (0.05 M) aqueous solutions were mixed with 2 mL $K_3Co(CN)_6$ (0.05 M) at room temperature, and then 10 mL aqueous solution containing chitosan (4 mg mL^{-1}) was added. The mixture was heated for 5 h at 50 ^oC after continuous ultrasonic treatment for 5 min, and then the homogeneous white $CeCl_3/K_3Co(CN)_6$-CS hydrogels were formed. Subsequently, the $CeCl_3/K_3Co(CN)_6$-CS hydrogels were freeze-dried for 24 h to obtain the $CeCl_3/K_3Co(CN)_6$-CS aerogels. Under a flow of 5% H_2/Ar with a heating rate of 5 ^oC min^{-1}, the obtained aerogels were annealed for 3 h at 700 ^oC. After being cooled down to room temperature, the products were laved using distilled water and absolute alcohol to get rid of KCl and subsequently dried at 40 ^oC to obtain the Co-CeO_2/C aerogels. Through the similar process of the preparation of Co-CeO_2/C aerogels, we also synthesized the Co/C aerogels and CeO_2/C aerogels for comparison.

1.3. Characterizations

The morphology and structure of products were examined on Hitachi S-4800 scanning electron microscopy (SEM) and JEOL JEM-2010 transmission electron microscopy (TEM). The phase purity and crystallinity of the products were identified by X-ray diffraction (XRD) on a Model D/max-rC X-ray diffractometer using Cu Kα radiation source (λ = 1.5406 Å) and operating at 40 kV and 100 mA. Energy-dispersive X-ray (EDX), high-angle annular dark-field scanning transmission electron

microscopy (HAADF-STEM) and elemental mapping measurements were performed on an FEI Tecnai G2 F20 microscope, which was built as an accessory on the JEOL JEM-2100F. The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution were measured at 77 K using a Micromeritics ASAP 2050 system. X-ray photoelectron spectroscopy (XPS) measurements carried out on a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Al Kα X-ray source (1486.6 eV photons). The binding energy was calibrated with respect to C1s at 284.6 eV. The Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet 520 SXFTIR spectrometer. Thermogravimetric analysis (TGA) of the product was carried out with a Netzsch STA 449C thermal analyser at a heating rate of 10 ^{o}C min^{-1} under air atmosphere.

1.4. Electrochemical measurements

All electrochemical tests were performed on the CHI 760E electrochemical workstation (CH Instruments, Shanghai Chenhua Co.). A standard three-electrode system was used, including a rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE) modified with catalysts as the working electrode (0.196 cm^2), a platinum foil as the auxiliary electrode and a saturated calomel electrode (SCE) protected by a Luggin capillary with a KCl solution as the reference electrode. All potentials were reported with respect to the reversible hydrogen electrode (RHE). The catalyst suspension was prepared by dispersing 5 mg of catalyst in 1 mL of solution containing 0.9 mL of distilled water and 0.1 mL of 0.5 wt.% Nafion solution followed by ultrasonication for 30 min. 10 μL of the catalyst suspension was dropped onto the electrode and dried at room temperature (loading density of ~255 μg cm^{-2}). The oxygen reduction reaction and oxygen evolution reaction measurements were performed in O_2-saturated 0.1 M KOH solution at a sweep rate of 5 mV s^{-1} with a rotation speed of 1600 rpm. The electron transfer number (n) is calculated based on the equation of $n = 4I_d/(I_d + (I_r/N))$, where I_d and I_r stand for the disk current and ring current, respectively, and N is the current collection efficiency of the Pt ring (0.37).

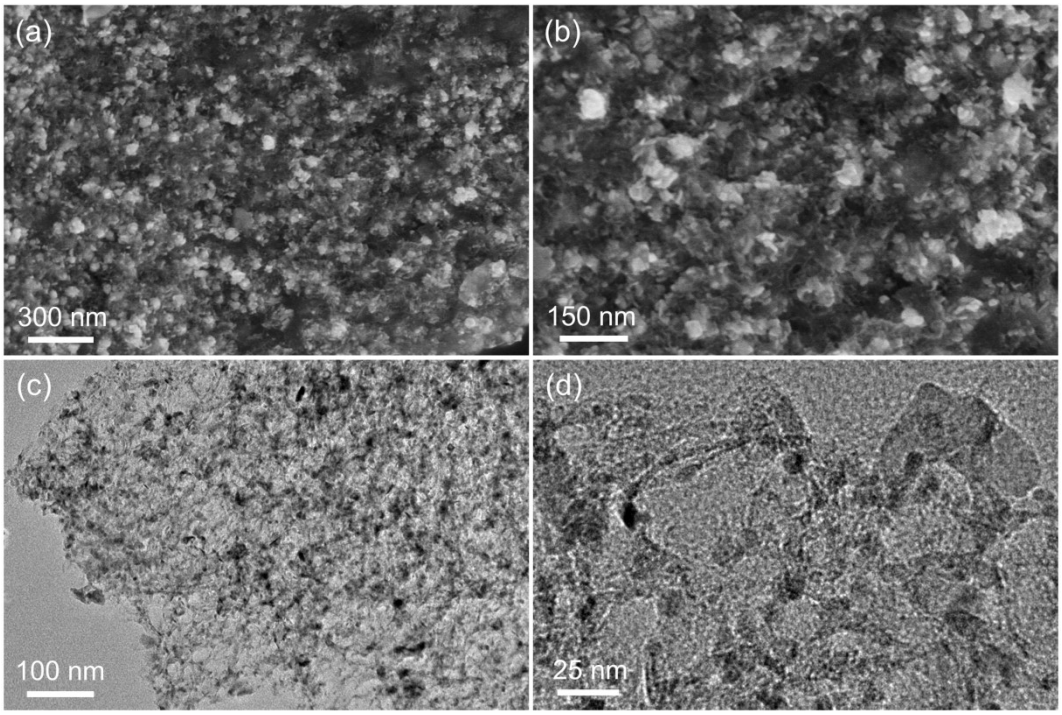

Fig. S1 Typical (a-b) SEM images and (c-d) TEM images of the Co-CeO_2/C aerogels at different magnifications.

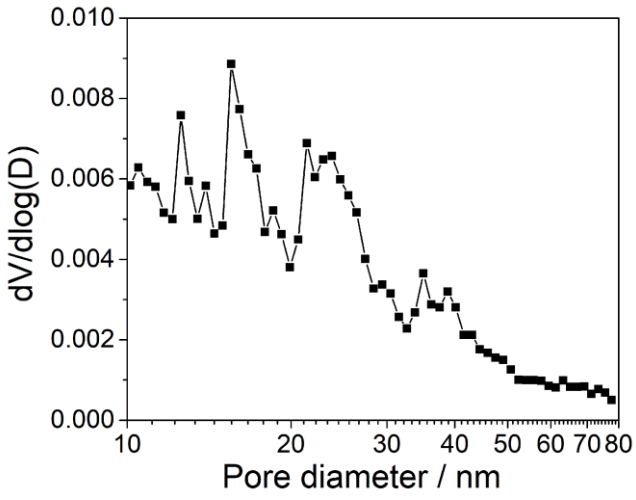

Fig. S2 Pore distribution curves of the Co-CeO_2/C aerogels.

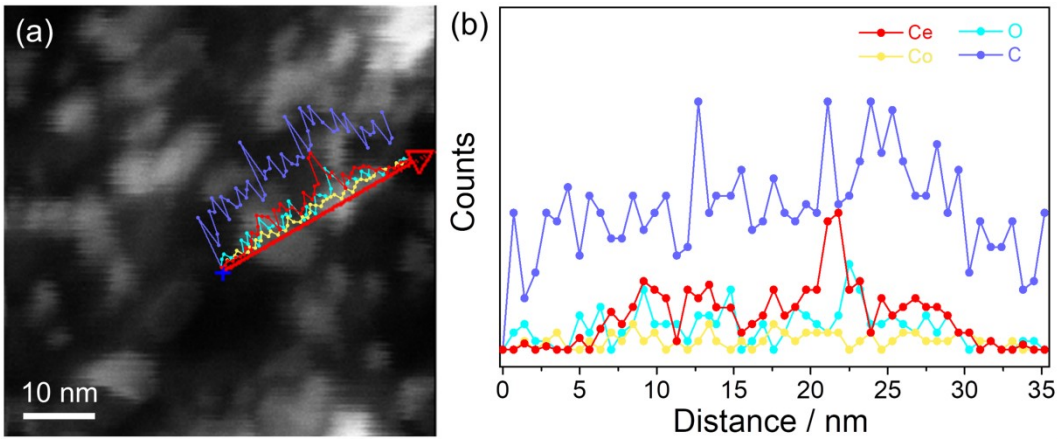

Fig. S3 (a) STEM image and (b) EDX line scanning profile of the Co-CeO_2/C aerogels.

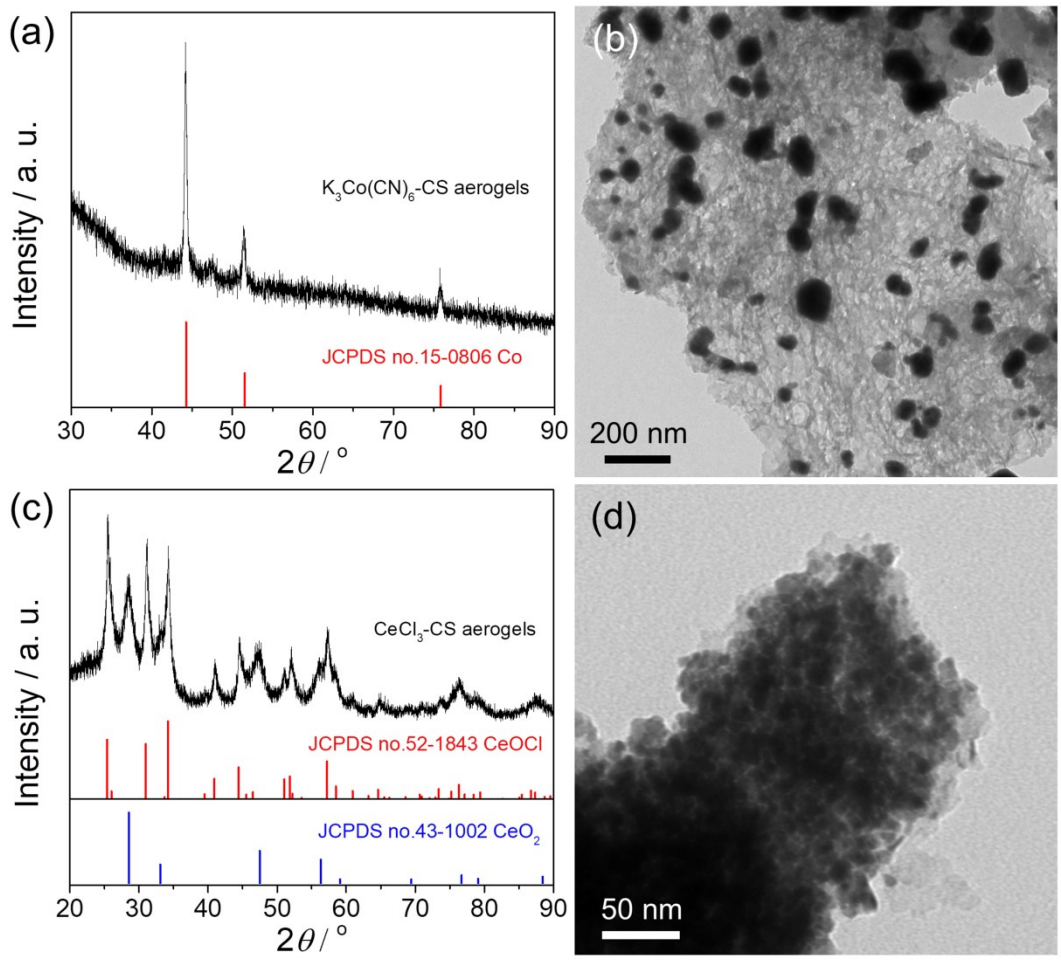

Fig. S4 (a) XRD pattern and (b) TEM image of the Co/C aerogels. (c) XRD pattern and (d) TEM image of the CeO_2/C aerogels.

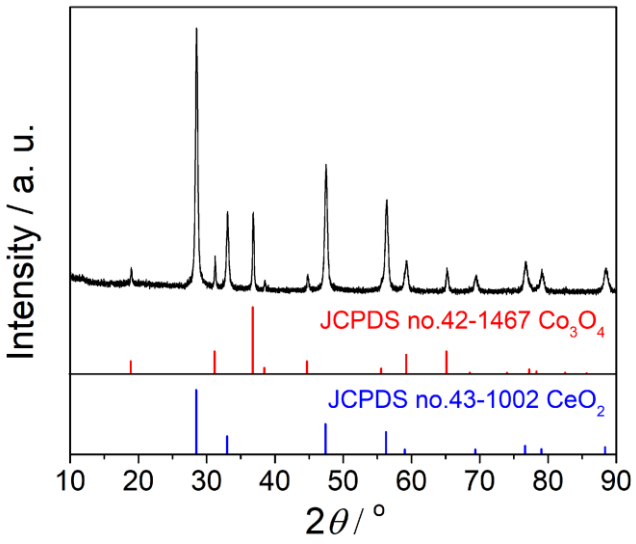

Fig. S5 XRD pattern of the Co-CeO_2/C aerogels after TGA measurement.

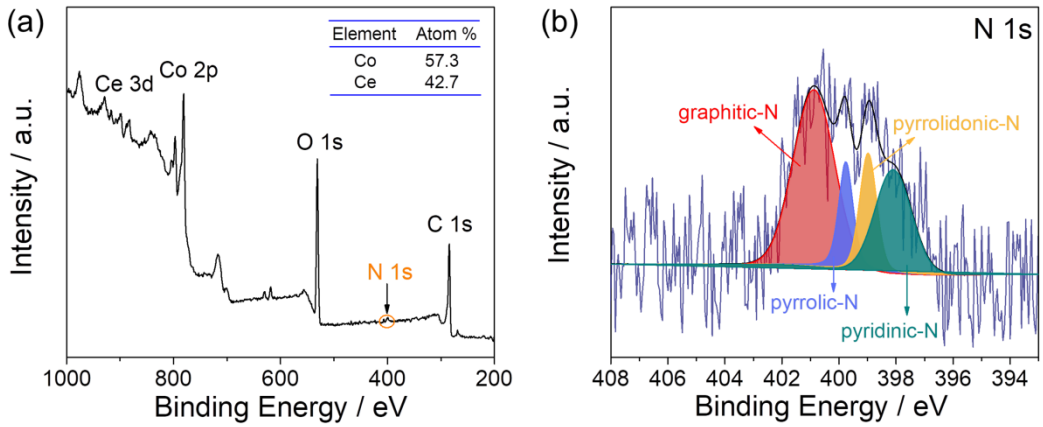

Fig. S6 (a) XPS survey scan spectrum of the Co-CeO_2/C aerogels. (b) High-resolution XPS spectrum of N 1s region in Co-CeO_2/C aerogels.

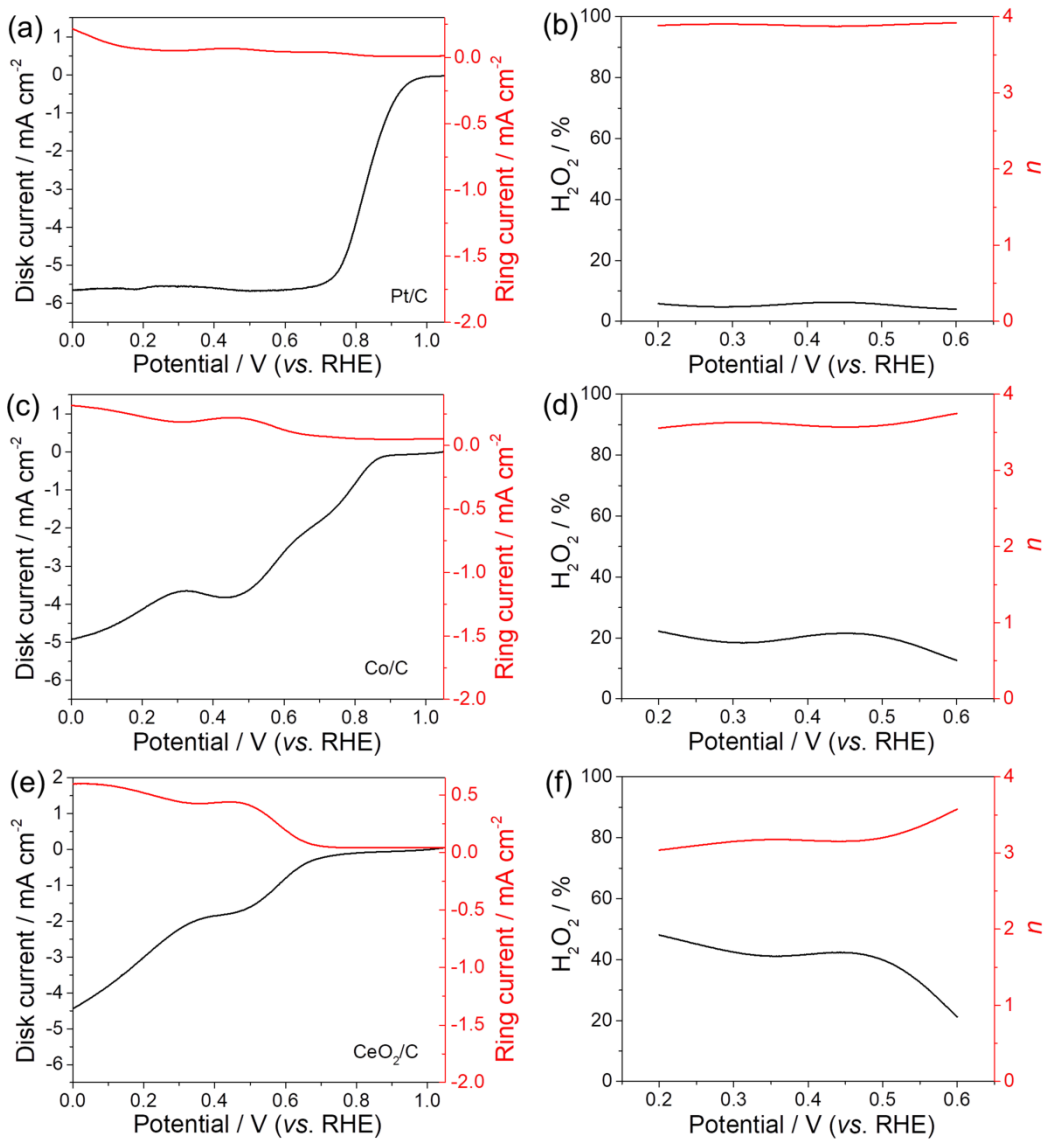

Fig. S7 RRDE tests of (a-b) the commercial Pt/C catalysts, (c-d) the Co/C aerogels, and (e-f) the CeO_2/C aerogels in O_2-saturated 0.1 M KOH solution at a sweep rate of 5 mV s^{-1} and a rotation rate of 1600 rpm: (a, c, e) polarization curves; (b, d, f) H_2O_2 yield and electron transferred number *n*.

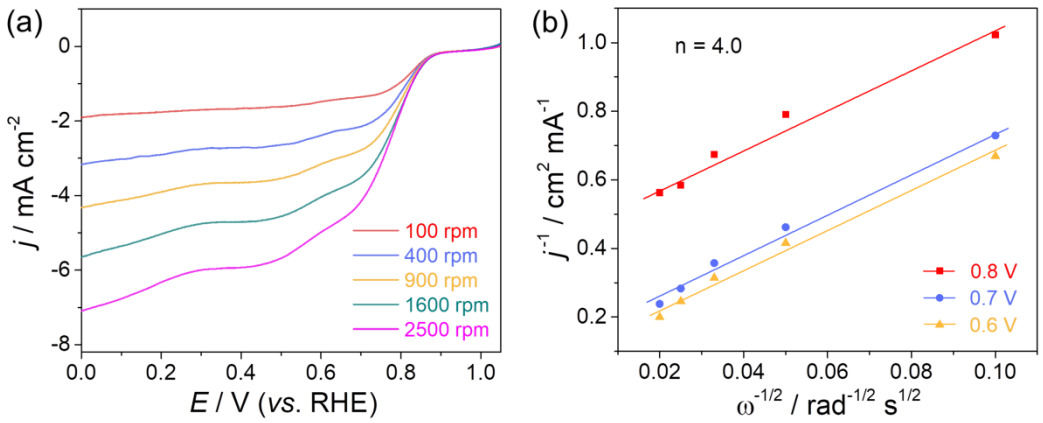

Fig. S8 (a) Rotation rate-dependent current-potential curves. (b) Koutecky-Levich plots at different potentials for Co-CeO_2/C aerogels.

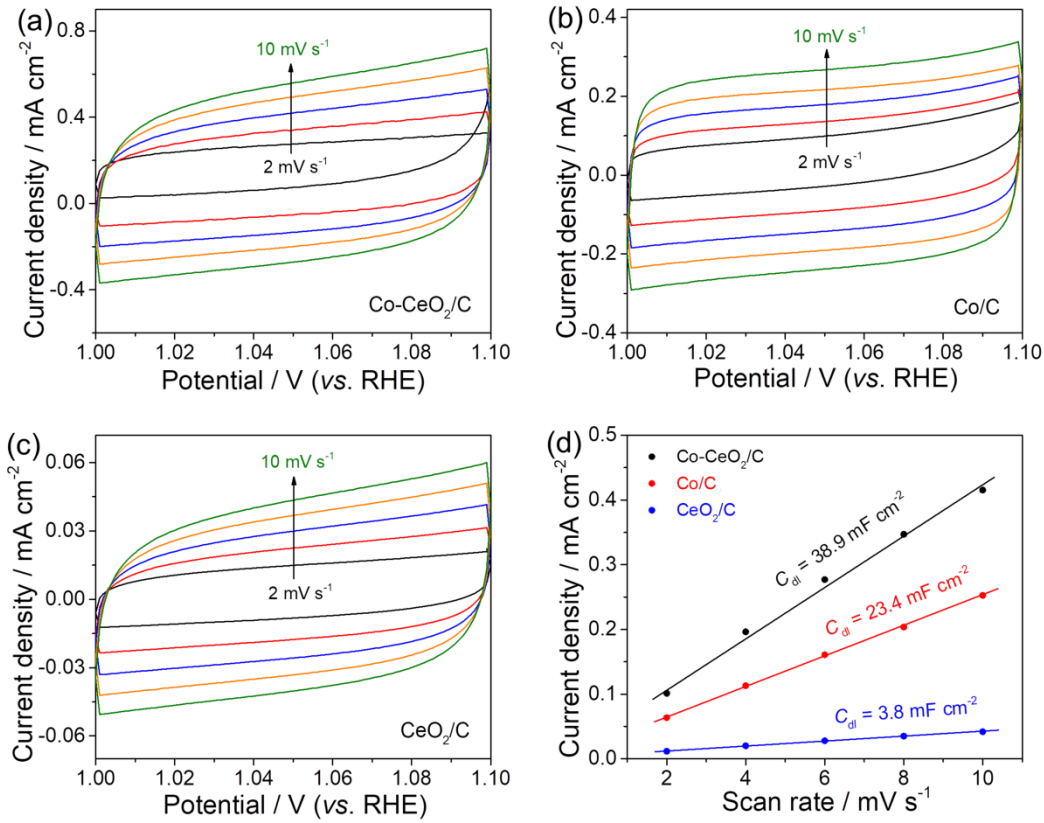

Fig. S9 CVs of (a) Co-CeO_2/C, (b) Co/C and (c) CeO_2/C at different sweeping rates from 2 mV s^{-1} to 10 mV s^{-1} in 0.1 M KOH solution. (d) The C_{dl} values of Co-CeO_2/C, Co/C and CeO_2/C.

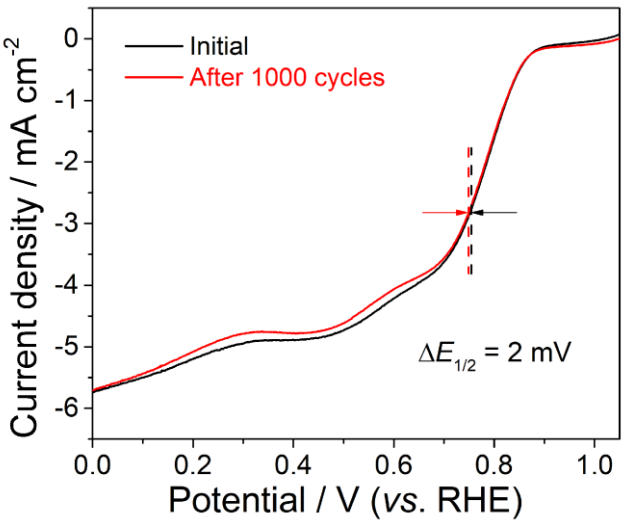

Fig. S10 ORR polarization curves of the Co-CeO_2/C aerogels before and after 1000 cycles.

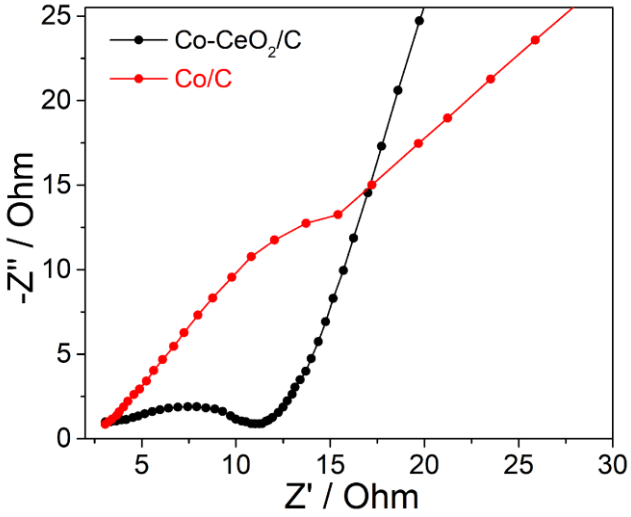

Fig. S11 EIS Nyquist plots of the Co-CeO_2/C aerogels and Co/C catalyst.

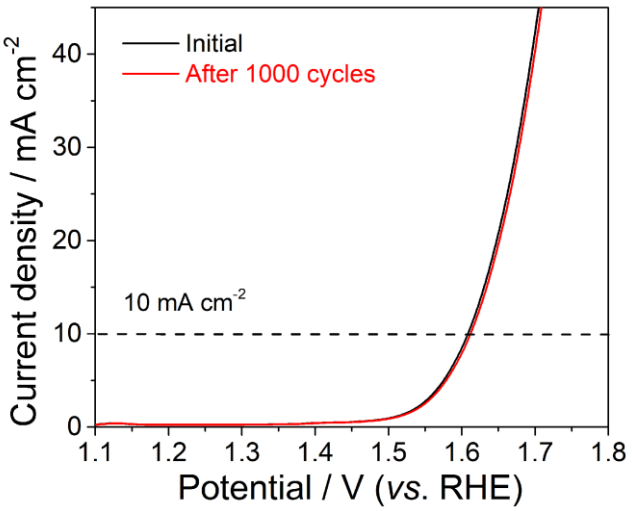

Fig. S12 OER polarization curves of the Co-CeO_2/C aerogels before and after 1000 cycles.

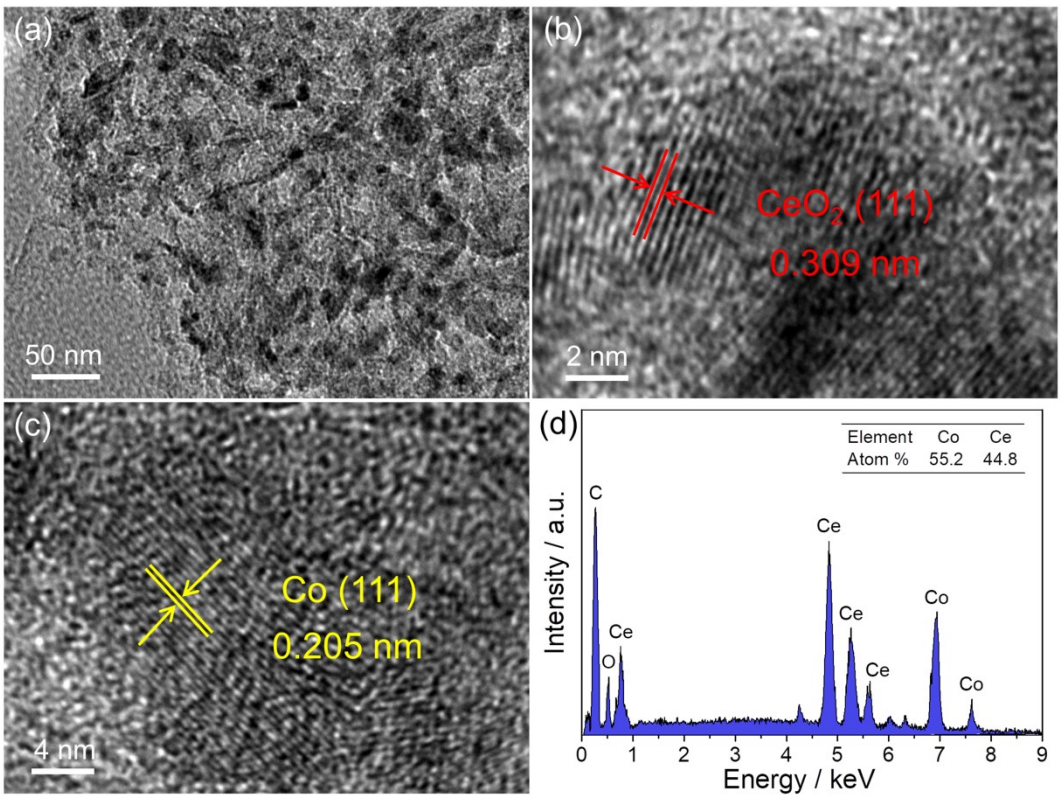

Fig. S13 Morphological and compositional characterizations of the Co-CeO_2/C aerogels after long duration test. (a) TEM image, (b-c) HRTEM images, and (d) EDX spectrum.

Table S1. Comparison of the ORR activity of the Co-CeO_2/C aerogels with other electrocatalysts previously reported.

Catalyst	E_0 / V	$E_{1/2}$ / V	Electrolyte	Loadings (mg cm^{-2})	Ref
Co_3O_4/2.7Co_2MnO_4	0.90	0.68	0.1 M KOH	0.09	Nanoscale 2013, 5, 5312.
$NiCo_2O_4$/G	0.89	0.56	0.1 M KOH	0.41	J. Mater. Chem. A 2013, 1, 4754.
Co/N-C-800	0.83	0.74	0.1 M KOH	0.25	Nanoscale 2014, 6, 15080.
CeGS	0.90	0.81	0.1 M KOH	0.12	J. Mater. Chem. A 2017, 5, 6656.
Co-NiO	0.92	0.79	0.1 M KOH	0.20	Appl. Catal. B: Environ. 2019, 250, 71-77.
Co@NC-600	0.94	0.835	0.1 M KOH	0.15	Nanoscale 2020, 12, 22718-22734.
CoO_x/CeO_2/RGO	~	0.83	0.1 M KOH	0.35	J. Energy Chem. 2021, 59, 615-625.
Co porphyrins 1/CNTs	~	0.81	0.1 M KOH	0.25	J. Energy Chem. 2021, 53, 77-81.
Co/C	0.89	0.62	0.1 M KOH	0.255	This work
CeO_2/C	0.80	0.30	0.1 M KOH	0.255	This work
Co-CeO_2/C	0.92	0.75	0.1 M KOH	0.255	This work

Table S2. Comparison of the OER activity of the Co-CeO_2/C aerogels with other electrocatalysts previously reported.

Catalyst	Overpotential / V (10 mA cm^{-2})	Electrolyte	Loadings (mg cm^{-2})	Ref
Co_3O_4/2.7Co_2MnO_4	0.54	0.1 M KOH	0.09	Nanoscale 2013, 5, 5312.
$NiCo_2O_4$-graphene	0.46	0.1 M KOH	2.00	ACS Nano 2013, 7, 10190.
Co@Co_3O_4/NC-1	0.42	0.1 M KOH	0.21	Angew. Chem. 2016, 55, 4087.
$LaCoO_3$	0.49	0.1 M KOH	~	Nat. Common. 2016, 7, 11510.
NiCo@N-C 2	0.53	0.1 M KOH	0.4	Adv. Funct. Mater. 2018, 28, 1705094.
NiCo@N-C 3	0.55	0.1 M KOH	0.4	Adv. Funct. Mater. 2018, 28, 1705094.
CoO_x/CeO_2/RGO	0.36	0.1 M KOH	0.35	J. Energy Chem. 2021, 59, 615-625.
Co porphyrins 1/CNTs	0.407	1 M KOH	0.25	J. Energy Chem. 2021, 53, 77-81.
Co/C	0.58	0.1 M KOH	0.255	This work
CeO_2/C	0.60	0.1 M KOH	0.255	This work
Co-CeO_2/C	0.38	0.1 M KOH	0.255	This work