Metalloporphyrin-based highly conjugated three-dimensional covalent organic frameworks for electrochemical hydrogen evolution reactions

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Supporting Information

Table of Contents

1. Supplementary Methods

1.1. Materials and Methods

Organic solvents were purchased from Adamas-beta, and used as received. Fuming nitric acid and acetic anhydride were purchased from Sinopharm and used as received. Palladium on activated carbon was purchased from Acros Organics and used as received. Hydrogen stored in the high-pressure gas cylinder was ordered from Dehai Gas, Qingdao.

Solid-state NMR spectra were measured at ambient temperature on a Agilent DD2 600M spectrometer. FT-IR spectra were measured on a Bruker Tensor 27 Spectrometer. PXRD patterns were obtained on a Rigaku Smart lab X-Ray diffractometer with Cu Kα line focused radiation at 40 kV and 40 mA from $2\theta = 3.0°$ up to $45°$ with $0.02°$ increment. TGA from 30-800 °C was carried out on an American TA-Q20 under a nitrogen atmosphere using a 10 °C/min ramp without equilibration delay. SEM (JEOL, JSM-7500F, Japan) was used to investigate the structure of the **3D-Por-SP-COF** at an accelerating voltage of 5.0 kV. Samples were prepared by dispersing the material onto conductive adhesive tapes attached to a flat aluminum sample holder and then coated with gold. N_2 physisorption isotherms were measured up to 1 bar at 77 K using a Micrometrics ASAP 2460 surface area analyzer. Prior to measurements, samples were degassed for over 12 h at 100 °C. UHP grade N_2 were used for measurements. Oil-free vacuum pumps and oil-free pressure regulators were used for measurements to prevent contamination of the samples during the degassing process and isotherm measurement. SEM images were collected using a scanning electron microscope (JEOL, JSM-7500F) at an accelerating voltage of 5.0 kV. TEM was performed on a JEM-2100 electron microscope with an accelerating voltage of 200 kV. The ultraviolet, visible and near-infrared absorbance was measured by an Ultraviolet-visible near-infrared spectrophotometer (Agilent, cary5000). XPS was performed on a Thermo Scientific ESCA Lab 250Xi instrument. The parameters were as follows: Al Kα (1486.6 eV, 150 W) radiation was used as the X-ray source, the vacuum degree of the chamber was 3.6

$\times$ 10^{-9} mbar and the scan range was -10~1350 eV. The spectra were analyzed using Avantage Software. A typical three-electrode system (CHI 760E, CH Instruments, Inc. Shanghai) was used for all electrochemical measurements.

1.2 Synthesis

Synthesis of 3D-Por-SP-COF: 9,9'-spirobifluorene-3,3',6,6'-tetraamine (11.4 mg, 0.03 mmol) and 5,10,15,20-tetrakis(4-benzaldehyde)porphyrin (21.8 mg, 0.03 mmol), were added into the mixture of 1.8 mL o-dichlorobenzene, 0.2 mL butanol, and 0.2 mL aqueous acetic acid (6 M) in a glass tube. After being degassed for three times and sealed under vacuum, the tube was heated at 120 °C for 7 days. Then, the resulting precipitate was filtered off, washed by Soxhlet extractions with tetrahydrofuran for 24 h and dried at 80 °C under vacuum for 12 h. The **3D-Por-SP-COF** was obtained as a dark purple powder in 72% yield.

Synthesis of Co@3D-Por-SP-COF: A well-dispersed suspension of **3D-Por-SP-COF** (10 mg) and $Co(OAc)_2$ (20 mg) in DMF (3 mL) was stirred at 75 °C for 24 hours. After the reaction was completed, the **Co@3D-Por-SP-COF** was obtained by filtration, washed with EtOH, H_2O and DCM, and dried under vacuum.

1.3 Electrochemistry

Electrochemical experiments were conducted at a CHI760E electrochemical workstation of Shanghai Chenhua instrument, using a traditional three-electrode battery system. In all electrochemical tests, the platinum sheet (1×1 cm^2) electrode was used as the counter electrode. To prepare the working electrode, catalyst (2 mg) and Nafion solution (DuPont 5 wt%, 40 μL) were dispersed in a 300 μL mixture solution consisting of deionized water (150 μL) and EtOH (150 μL). The obtained uniform catalyst solution (50 μL) was decorated onto a 1 × 1 cm carbon cloth and dried at room temperature affording the desired working electrode (loading content: 0.29 g/cm^2).

In the hydrogen evolution reaction (HER) test, the catalyst-modified carbon cloth, mercury/mercury oxide electrode (Hg/HgO, MOE) and 1.0 M KOH solution were used as the working electrode, reference electrode and electrolyte, respectively. The

conversion of potential is based on the following equation, $E_{RHE} = E_{Hg/HgO} + 0.0592$ pH + 0.098. All linear sweep voltammetry (LSV) measurements were recorded at a scan rate of 5 mV/s. The long-term stability of HER is achieved through the chronoamperometry experiment. To estimate the electrochemical surface area (ECSA) of the prepared catalyst, the electrochemical double-layer capacitance (Cdl) was determined based on the double-layer charging curves using CVs records at different scanning speeds of 20, 40, 60, 80 and 100 mV/s. The electrochemical impedance spectroscopy (EIS) was performed with a frequency range of 10^{-1} to 10^5 Hz at open-circuit voltage.

1.4 Structural simulation and analysis

Structural modeling of **3D-Por-SP-COF** and **Co@3D-Por-SP-COF** were performed in the Materials Studio 2020 software package. The space groups were obtained from the Reticular Chemistry Structure Resource. The theoretical models were then optimized by the Forcite module.

Pawley refinements of the PXRD patterns were done in the Reflex module using data from 3 to 25°. The integrated intensities were extracted using the Pseudo-Voigt profile. The unit cell parameters a, b, c, FWHM parameters U, V, W, profile parameters NA, NB, and zero point were refined. The background was refined with 20th-order polynomial.
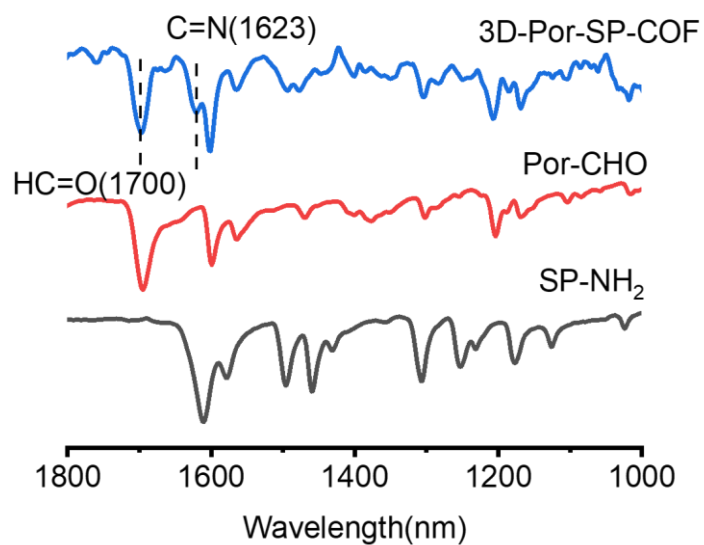
Fig. S1 FT-IR spectra of **3D-Por-SP-COF** (blue), 5,10,15,20-tetrakis(4-benzaldehyde)porphyrin (**Por-CHO**) and 3,3',6,6'-tetraamine-9,9'-spirobifluorene (**SP-NH₂**).
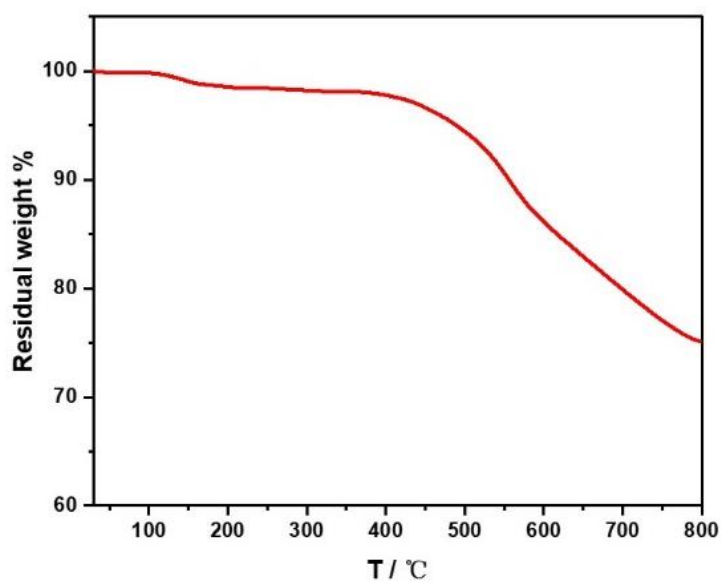

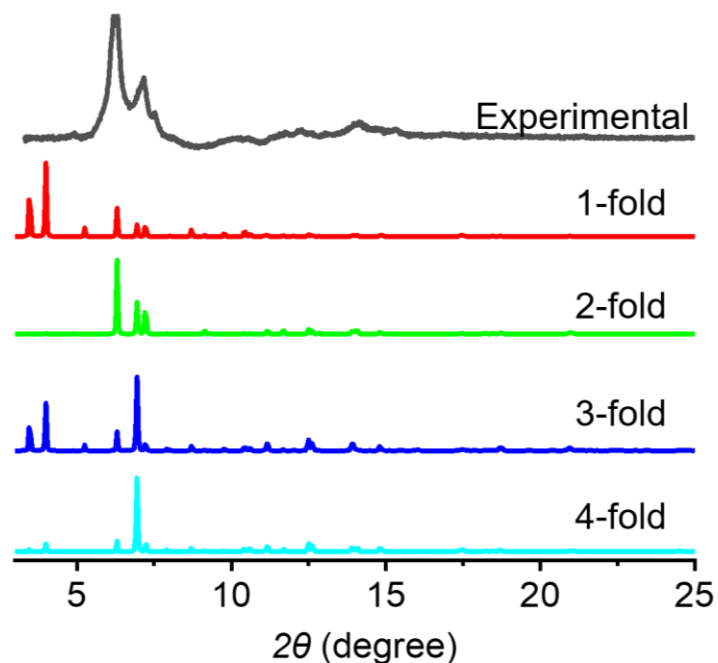**Fig. S2** TGA spectra of **3D-Por-SP-COF**.

Fig. S3 Experimental and calculated PXRD patterns of **3D-Por-SP-COF**. Calculated data for 1-fold mode (red curve), 2-fold mode (greed curve), 3-fold mode (blue curve) and 4-fold mode (cyan curve). Obviously, the calculated diffraction patterns of the 2-fold stacking model matched well with the experimental PXRD patterns, suggesting that the **3D-Por-SP-COF** adopted a 2-fold stacking structure.
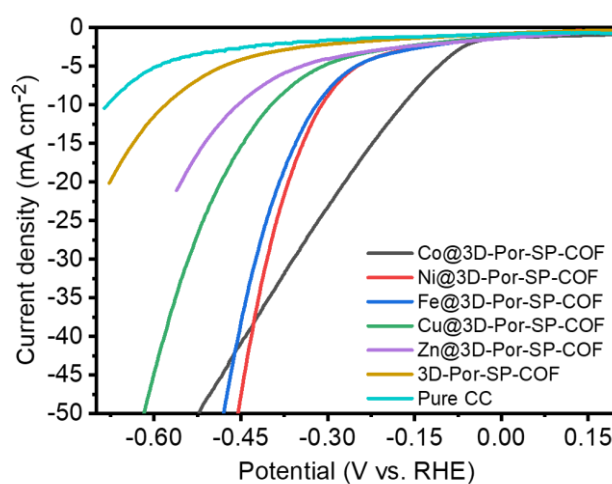
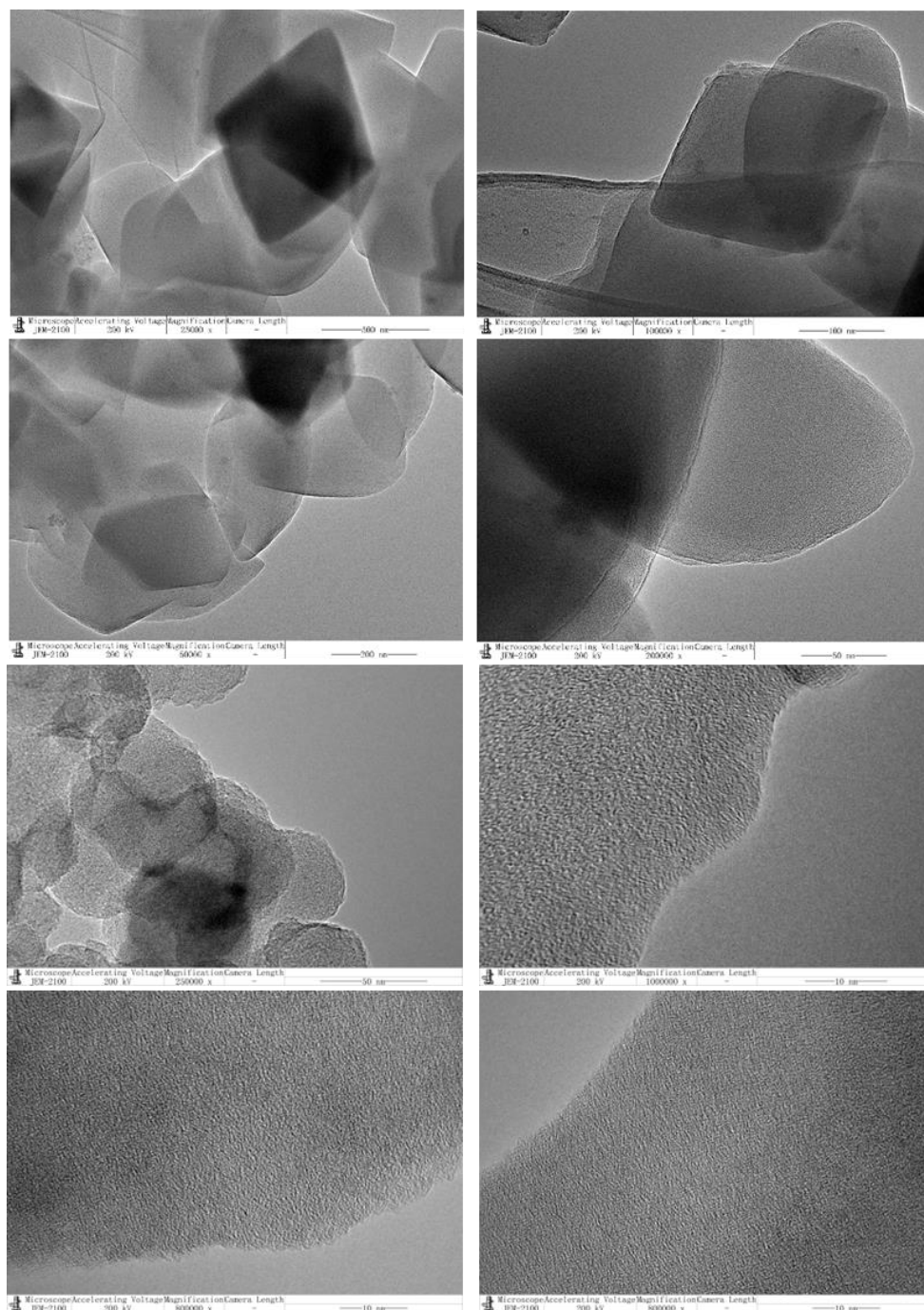**Fig. S4** The corresponding HER LSV curves of different metals in **3D-Por-SP-COF**.

Fig. S5 High-resolution TEM images of **Co@3D-Por-SP-COF**.
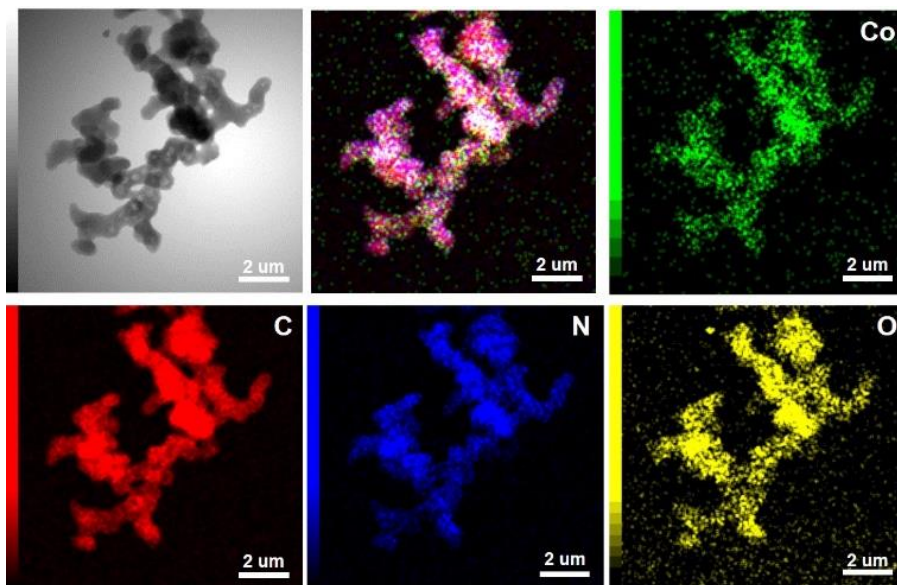
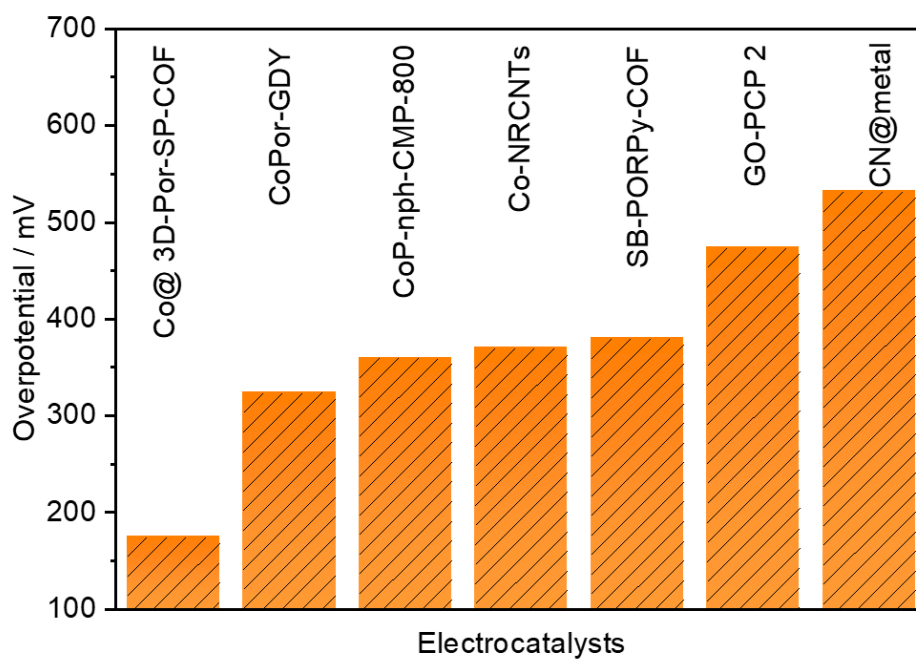**Fig. S6** EDX elemental mappings of **Co@3D-Por-SP-COF**.

Fig. S7 Comparison of the HER performances of **Co@3D-Por-SP-COF** with reported catalysts.
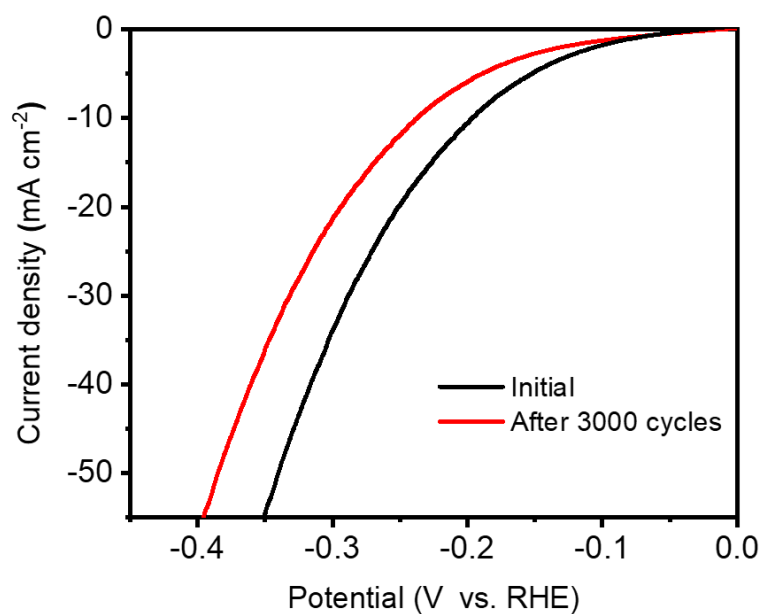
Fig. S8 The polarization curves of **Co@3D-Por-SP-COF**. Before and after 3000 cycling tests for HER in 1.0 M KOH condition.
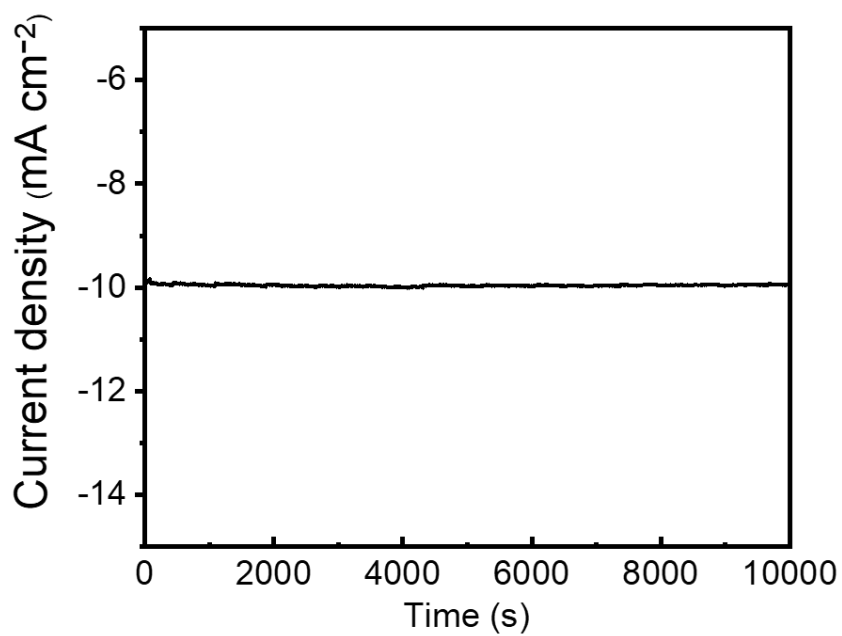

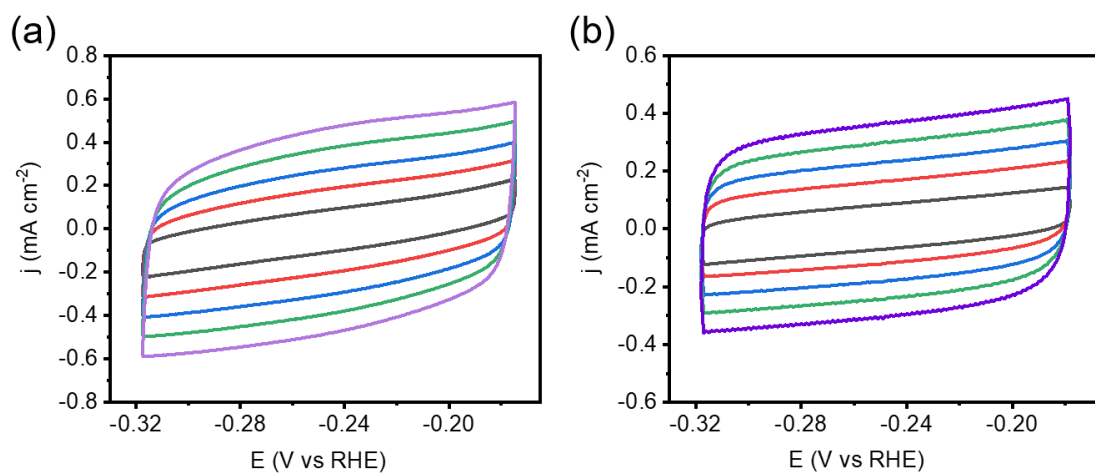**Fig. S9** The long-term stability the current density of **Co@3D-Por-SP-COF**.

Fig. S10 The CVs of the (a) **Co@3D-Por-SP-COF** and (b) pure **3D-Por-SP-COF** for Cdl measurements.