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Flexible and Robust Bimetallic Covalent Organic Framework for Reversible Switching of Electrocatalytic Oxygen Evolution Activity

Zhi Gao[†a], Zhiwu Yu[†b], Yuxing Huang[†c], Xiangqing He[a], Xuemin Su[a], Longhui Xiao[a], Yi Yu[a], Xinhui Huang[a] and Feng Luo*[a]

[a] State key Laboratory of Nuclear Resources and Environment, School of Biology, Chemistry and Material Science, East China University of Technology, Nanchang, Jiangxi 330013, China

Email: ecitluofeng@163.com

[b] High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, Anhui, China

[c] School of Material Science and Engineering and Institute for Advanced Study, Nanchang University, Nanchang, Jiangxi, 330031, China

[†] These authors contributed equally to this work.

Experimental Section

Materials and Characterizations: All reagents were used as received without further purification. Powder X-ray diffraction (PXRD) analysis of all samples were taken on a Bruker AXSD8 Discover powder diffractometer with Cu Kα radiation (k = 0.154 nm). The simulated powder patterns were obtained by Materials Studio Forcite molecular dynamics module method. Infrared spectra (IR) were tested by a Bruker VERTEX70 spectrometer. Low temperature N_2 isotherms were recorded at 77 K on a Belsorp-max using ultrahigh-purity-grade (>99.999%) N_2. The morphologies of samples were determined by SEM measurement using a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were taken using a JEOL 2100 microscope operated at an accelerating voltage of 200 kV. High-angle annular dark-field scanning TEM-energy-dispersive X-ray spectroscopy (HAADF-STEM-EDX) image was recorded on a JEOL2010F instrument. Elemental analysis of metal in samples was determined on a Shimadzu ICPS-7500 inductively coupled plasma emission spectrometer (ICP-AES). X-ray photoelectron spectra (XPS) spectra were collected by Thermo Scientific ESCALAB 250 Xi spectrometer. The binding energy was carefully corrected, referring to C 1s at 284.6 eV.

Preparation of 2,4,6-triformylphloroglucinol: Firstly, phloroglucinol (6.014 g, 49 mmol) and hexamethylenetetraamine (15.098 g, 108 mmol) were simultaneously put into trifluoroacetic acid (90 mL) under N_2 atmosphere, followed by heating for 2.5 h at 100 ℃. After that, HCl (3 M, 150 mL) was added and the solution was sequentially heated for 1 h. After cooling to room temperature, the solution was filtered through

celite, extracted with 350 mL dichloromethane, dried by magnesium sulfate, and filtered. Rotary evaporation of the solution was performed to obtain 1.23 g off-white powder (5.87 mmol, 11 %) and the pure sample was obtained by sublimation. ^{1}H NMR (400 MHz, $CDCl_3$) data indicated about 99 % purity, giving 14.12 (s, 3H, OH), 10.15 (s, 3H, CHO) ppm. Element analysis: calculated value C, 51.44; H, 2.88; N, 0.00; Found: C 51.38; H 2.80; N, 0.00.

Synthesis of 2,5-diaminobenzenesulfonic acid: Firstly, p-phenylenediamine (2.7g, 25 mmol) was added into 20 % fuming sulfuric acid (33g, 66 mmol) and heated at 145 ℃ for 7 h. Then, 4 mL deionized water was added and the solution was heated at 135℃ for 3 h, followed by cooling to 30℃ through static crystallization for 2 h. After that, 2 mL deionized water was added and the pH value is adjusted to 4-5 using 30 % NaOH. Finally, the temperature was cooled down to 10 ℃ and a product of 3.8 g with purity greater than 98 % was obtained by filtration. ^{1}H NMR (400 MHz, DMSO) data for 2,5-diaminobenzenesulfonic acid: 7.39 (s, 1H), 6.94 (d, J = 8.5 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H). Element analysis: calculated value C, 38.29; H, 4.28; N, 14.88; S, 17.04; Found: C 38.22; H 4.32; N, 14.83; S, 17.00.

Synthesis of COF-SO_3H: Firstly, 2,5-diaminobenzenesulfonic acid (0.45 mmol, 84.7 mg), 2,4,6-triformylphloroglucinol (0.3 mmol, 63 mg) and a mixed solvent of 1.5 mL butyl alcohol and 1.5 mL 1,2-dichlorobenzene were added into a Pyrex tube. After the ultrasound for 20 min, aqueous acetic acid (3 M, 0.5 mL) was added and the tube was degassed by freeze-pump-thaw cycles for several times, sealed under vacuum and heated at 120 °C for 3 days. The resulting reaction mixture was cooled to

room temperature and washed with deionized water, dimethylacetamide and acetone for three times. The obtained dark red powder was dried at 120 °C under vacuum for 12 hours.

Synthesis of NH_4@COF-SO_3: 50 mg COF-SO_3H was poured into 20 mL glass bottles with 10 mL (1 wt%) ammonium hydroxide and stirred for 30 hours. Then the formed materials were washed by deionized water, acetone and methanol. The resulting dark red powder was dried at 60 °C under vacuum for 12 hours.

Synthesis of Co_xV_{1-x}@COF-SO_3 (x = 0, 0.2, 0.5, 0.8, 1.0): 20 mg NH_4@COF-SO_3, x mL $CoCl_2 \cdot 6H_2O$ (Co^{2+}, 1000 ppm) and (1-x) mL VCl_3 (V^{3+}, 1000 ppm) were added into 5 mL glass bottles, followed by stirring for 1 h under room temperature. Afterward, the resulting suspension was centrifuged, washed thoroughly and dried in a vacuum oven at 60 °C for 12 h. The final precipitate was denoted as Co_xV_{1-x}@COF-SO_3 (x = 0, 0.2, 0.5, 0.8, 1.0).

Electrochemical Measurements: All electrochemical experiments were carried out at room temperature on a CHI660E electrochemical workstation (CH Instruments Inc., Shanghai) in a standard three-electrode system in 1 M KOH electrolyte. The catalyst inks were prepared by adding 3 mg catalyst into 1 mL solution including 0.95 mL ethyl alcohol and 50 μL Nafion solution, followed by ultrasonication for 30 min. Finally, 50 μL of above ink was dripped on the carbon paper and then dried at room temperature. Carbon electrode, saturated calomel electrode and the as-prepared catalyst were used as counter electrode, reference electrode and working electrode, respectively. The linear sweep voltammetry (LSV) was conducted in an O_2-saturated

1.0 M KOH at a scan rate of 5 mV s^{-1} to obtain the polarization curves. Electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range from 100 kHz to 0.1 Hz at the overpotential of 318 mV. The electrochemically active surface area (ECSA) of different catalysts was determined based on the double-layer capacitance (C_{dl}) using a simple cyclic voltammetry method in a non-Faradic potential range of 1.23-1.33 V vs RHE. By plotting the capacitive density at 1.28 V vs RHE against the scan rate (20, 20, 40, 60 and 100 mV s^{-1}), a linear trend was observed. The slope of the fitted line was the twice of C_{dl}. The chronoamperometric curves were recorded at a constant overpotential of 366 mV to determine the stability of $Co_{0.5}V_{0.5}$@COF-SO_3. The Faradaic efficiency was determined from the total amount of charge Q (*C*) passed through the cell and the total amount of the produced O_2 n_{O2} (mol): Faradaic efficiency = $4F \times n_{O2}/Q$, where F is the Faraday constant, assuming the four electrons are needed to produce one oxygen molecule.

Switching OER Property Determination: 20 mg $Co_{0.5}V_{0.5}$@COF-SO_3 and 10 mL HCl (6 M) were added into 20 mL glass bottles and then stirred under room temperature for 1h. The resulting suspension was centrifuged, washed thoroughly and dried in a vacuum oven at 60 °C for 12 h to obtain the precipitate denoted as COF-SO_3H turn off first. Then, 3 mg as-obtained precipitate was added into 1 mL solution containing 0.95 mL ethyl alcohol and 50 μL Nafion solution to prepare working electrode using carbon paper as support. The corresponding LSV tested was carried out at a scan rate of 5 mV s^{-1}. Afterwards, the carbon paper was removed from

electrolyte and dried in a vacuum oven at 60 °C for 12 h, followed by immersing in 10 mL (1 %) ammonium hydroxide for 30 hours. The resultant paper was washed thoroughly by deionized water, followed by immersing in the mixed solution of $CoCl_2 \cdot 6H_2O$ and VCl_3 to obtained $Co_{0.5}V_{0.5}$@COF-SO_3 turn on first. The corresponding LSV plot was obtained. The whole process was repeated twice to obtain COF-SO_3H turn off second and $Co_{0.5}V_{0.5}$@COF-SO_3 turn on second, as well as COF-SO_3H turn off third and $Co_{0.5}V_{0.5}$@COF-SO_3 turn on third, respectively.

Turnover Frequency Calculation: Turnover frequency (TOF) value of catalysts was calculated based on the equation: $TOF=(J \times A)/(4 \times F \times n)$, where J (mA/cm^2) is the current density at an overpotential of 300 mV; A is the surface area of electrode (1 cm^2); F is the Faraday constant (96485 C/mol); n is molar number of active sites on the electrode. In this work, both Co and V in Co_xV_{1-x}@COF-SO_3 samples (x = 0, 0.2, 0.5, 0.8, 1) are regarded as active sites.

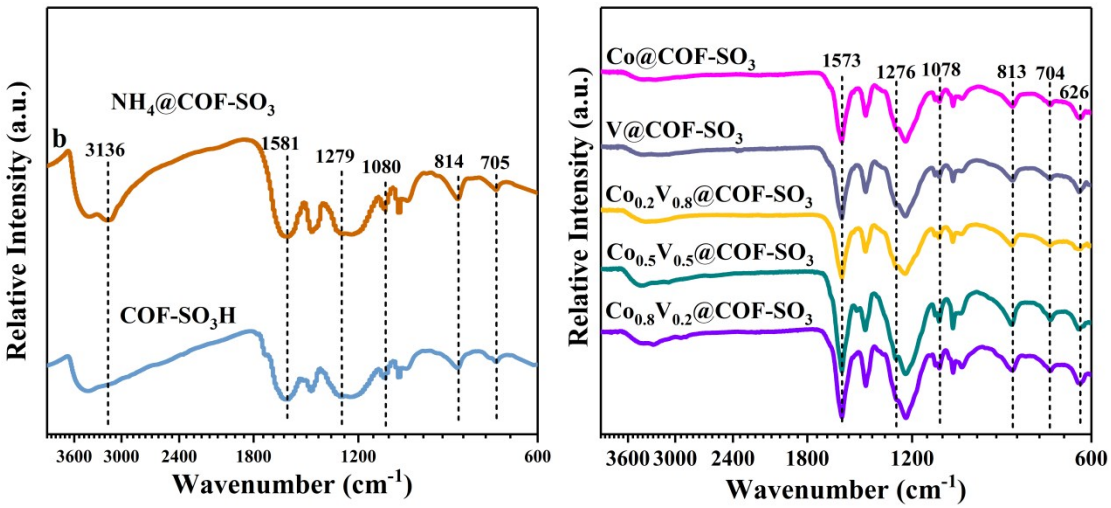

Fig. S1 IR spectrum of different samples.

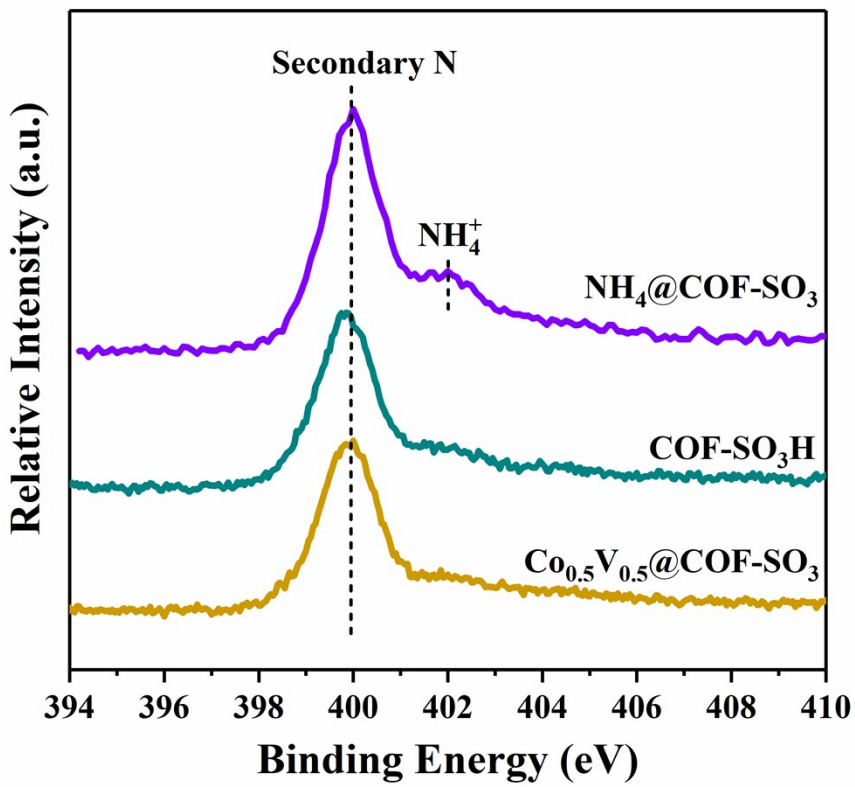

Fig. S2 N 1s spectra of different samples.

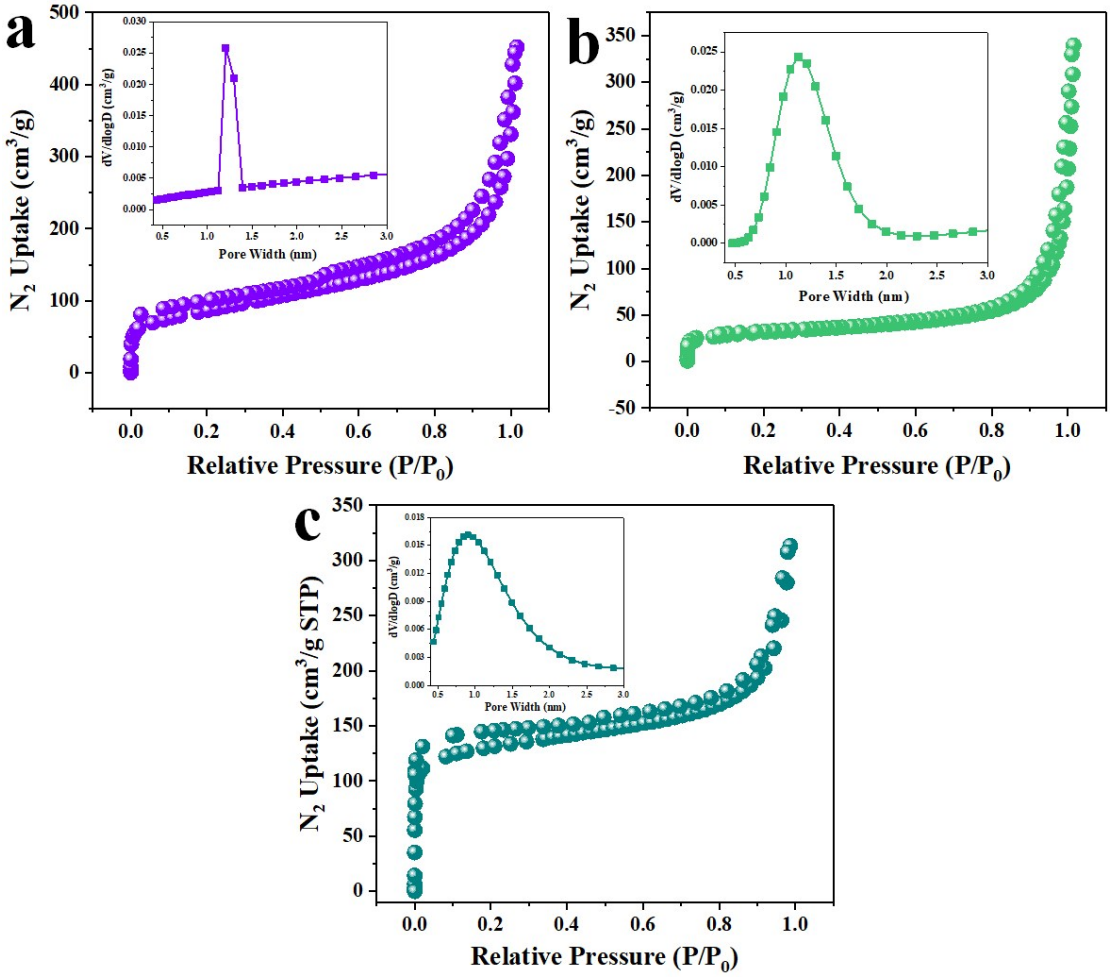

Fig. S3 77 K nitrogen adsorption isotherm of COF-SO_3H (a), NH_4@COF-SO_3 (b) and $Co_{0.5}V_{0.5}$@COF-SO_3 (c) with the inset for the distribution of pore size.

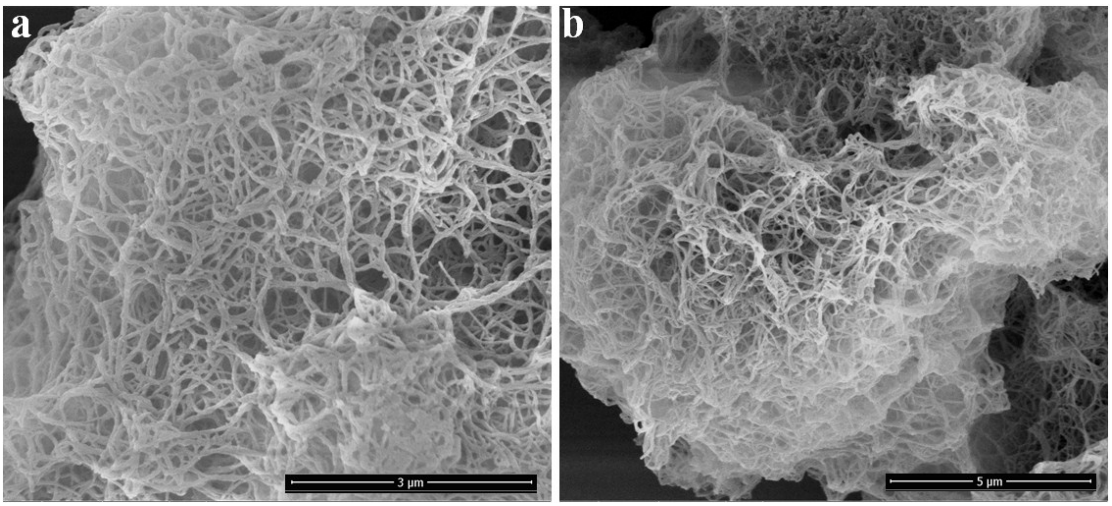

Fig. S4 SEM images of COF-SO_3H (a) and NH_4@COF-SO_3 (b).

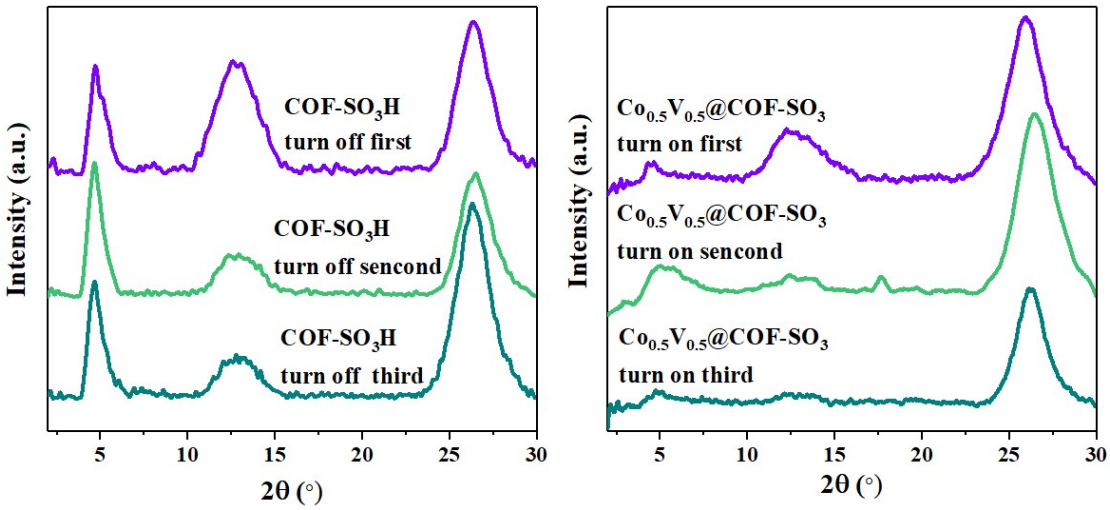

Fig. S5 PXRD patterns of different samples.

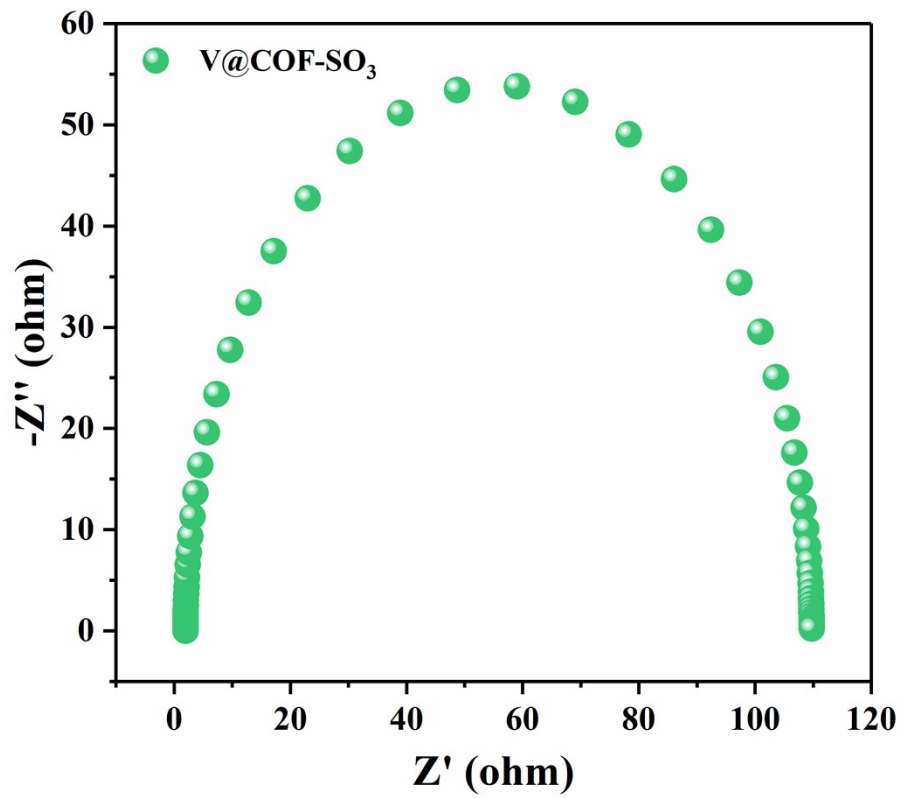

Fig. S6 Nyquist plot of V@COF-SO_3 at the overpotential of 300 mV.

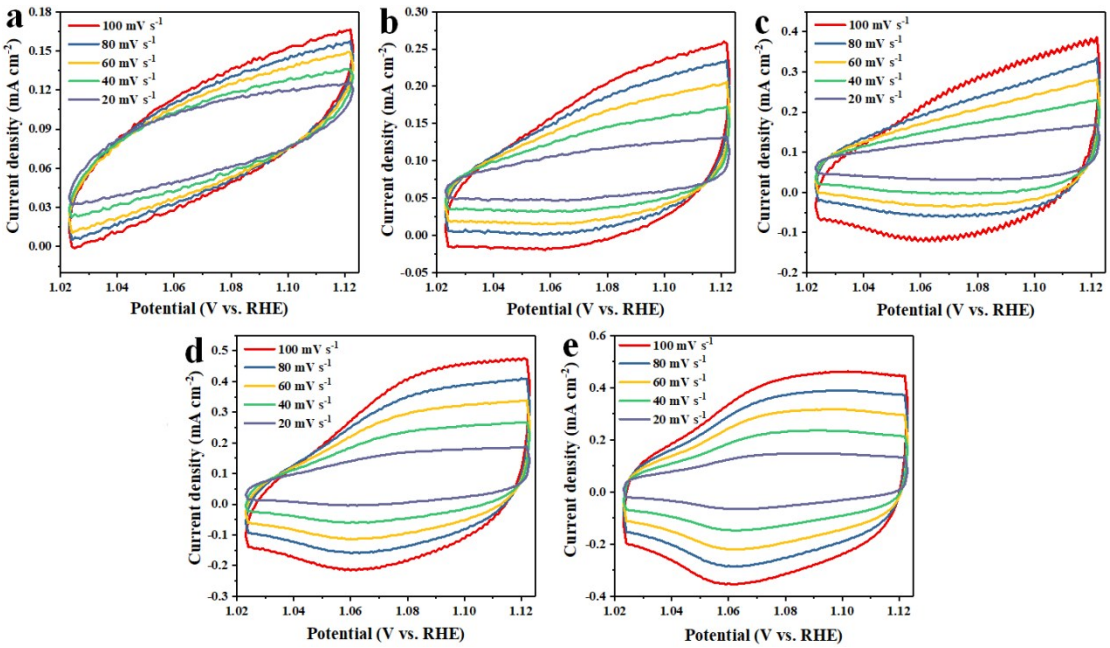

Fig. S7 CV plots of V@COF-SO_3 (a), Co@COF-SO_3 (b), $Co_{0.2}V_{0.8}$@COF-SO_3 (c), $Co_{0.8}V_{0.2}$@COF-SO_3 (d) and $Co_{0.5}V_{0.5}$@COF-SO_3 (e) tested at various scan rates from 20 to 100 mV s^{-1}.

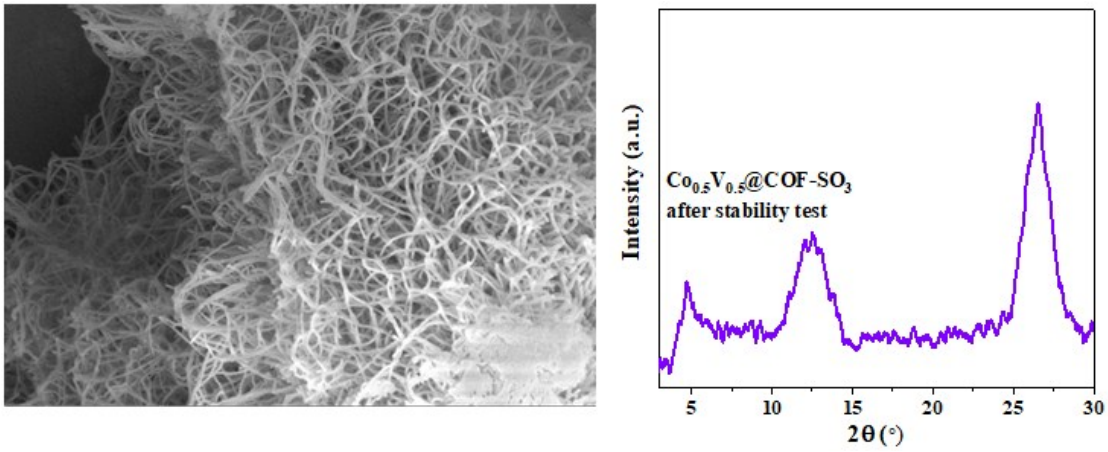

Fig. S8 SEM image and XRD pattern of $Co_{0.5}V_{0.5}$@COF-SO_3 after chronoamperometric test.

Table S1 ICP-AES results of different COFs.

Catalyst	Content (wt.%)		Co/V mass ratio
	Co	V	
Co@COF-SO_3	4.87	0	4.87/0
V@COF-SO_3	0	5.17	0/5.17
$Co_{0.2}V_{0.8}$@COF-SO_3	1.20	4.69	0.2/0.78
$Co_{0.5}V_{0.5}$@COF-SO_3	2.88	2.50	0.5/0.43
$Co_{0.8}V_{0.2}$@COF-SO_3	4.53	1.12	0.8/0.2

Table S2. Comparison of the OER activities of some recently reported highly active Co-based electrocatalysts in 1.0 KOH.

Catalysts	Overpotential at 10 mA cm^{-2} (mV vs. RHE)	Tafel slope (mV dec^{-1})	Reference
$Co_{0.5}V_{0.5}$@COF-SO_3	318	62	This work
macro-TpBpy-Co	380	54	J. Am. Chem. Soc. 2019, 141, 6623-6630
Electrode 1	313	162±0.7	Angew. Chem. Int. Ed. 2019, 58, 4644-4648
Fe@BIF-91	350	71	Adv. Sci. 2019, 6, 1801920
NTs@NiCoP/C	297	57.35	Nanoscale, 2018, 10, 13555-13564.
Co/CoP-5	340	79	Adv. Energy Mater. 2017, 7, 1602355.
metal-ion (Fe, V, Co, and Ni)-doped MnO_2 ultrathin nanosheet/CFP	390	104.4	Adv. Funct. Mater. 2017, 27, 1704083
MAF-X27-OH	303	83	J. Am. Chem. Soc. 2016, 138, 8336.
CoO_x-ZIF	318	70.3	Adv. Funct. Mater. 2017, 27, 1702546

Table S3 ICP-AES results of different COFs.

Catalyst	Content (wt.%)	
	Co	V
COF-SO_3H turn off first	0	0
COF-SO_3H turn off second	0	0
COF-SO_3H turn off third	0	0
$Co_{0.5}V_{0.5}$@COF-SO_3 turn on first	2.91	2.49
$Co_{0.5}V_{0.5}$@COF-SO_3 turn on second	2.88	2.50
$Co_{0.5}V_{0.5}$@COF-SO_3 turn on third	2.90	2.50