

High-density active sites COFs with flower-like morphology for Energy storage application

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S1 Experimental Section

S1.1 Analysis and characterization

The morphologies of products were observed by using a field-emission scanning electron microscope (FESEM; ULTRA plus, Germany) and transmission electron microscope (TEM; JEM-2010, Japan). The crystallinity of the samples was tested on X-ray diffraction (D/Max-2400, Japan) at the Cu K α radiation ($\lambda=0.15418$ nm) in the 2θ range of 0° - 70° . The chemical structures of the samples were recorded on a Fourier transform infrared spectra (FT-IR, NEXUS 670, USA) with KBr pellets in the wavelength range of 4000 - 400 cm^{-1} . Thermogravimetric (TG) analysis was carried out using a Perkin-Elmer TG/DTA-6300 instrument in the temperature range of 20 - 800°C at heating rate of 5 $^\circ\text{C min}^{-1}$ under nitrogen atmosphere. The ^{13}C CP/MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe and with a sample spinning rate of 10.0 kHz; a contact time of 2 ms (ramp 100) and pulse delay of 4 s were applied.

S1.2 Materials

2, 6 Diaminoanthraquinone (97%, DAAQ) were obtained from Alfa Aesar Chemicals Co. Ltd., Shanghai, China. 1,3,5-triformylphloroglucinol (Tp) was purchased from Aladdin Industrial Corporation. *N, N*-Dimethylformamide (DMF), mesitylene, Ac (OH) and dioxane was purchased from Tianjin Damao Chemical Reagent (Tianjin, China). All the experiments were carried out using deionized (DI) water and analytical reagents.

S1.3 Electrochemical Characterizations

In the three-electrode system, the saturated calomel electrode (SCE) and platinum foil were used as the reference electrode and counter electrode, respectively. The working electrode was fabricated according to the literature ^[1, 2]. Typically, the acetylene black and active electrode material (16 mg) (weight ratio of 15:85) were completely dispersed into 0.4 mL Nafion solution (0.25 wt %) by sonication. Then the achieved suspension was dropped onto the glassy carbon electrode with the mass of 1.0 mg cm⁻² by a pipet gun and completely dried at room temperature. The electrochemical tests were carried out on a CHI 760E electrochemical workstation (CHI, Shanghai) in 1 mol L⁻¹ KOH or 1 mol L⁻¹ H₂SO₄ electrolyte at room temperature, including a working electrode, counter electrode (platinum plate) and reference electrode (SCE).

S1.4 Experimental section

Synthesis of COFs-M

1,3,5-triformylphloroglucinol (Tp, 10 mg, 0.048 mmol) and 2,6-diaminoanthraquinone (DAAQ, 17 mg, 0.071 mmol) were dissolved in 3 mL of mesitylene, charged in a glass tube (18 cm of length, 25 mL). The mixture was stirred for 1 h, then, 0.6 mL of 3 mol L⁻¹ Ac(OH) were successively added. The tube was sealed off and then heated at 120 °C for 3 days. The red precipitate was collected by filtration and rinsed with *N,N*-dimethylformylamide (DMF), tetrahydrofuran (THF) and ethanol in turn. The powders were collected and dried at 60 °C for 24 h.

Synthesis of COFs-D

1,3,5-triformylphloroglucinol (Tp, 10 mg, 0.048 mmol) and 2,6-diaminoanthraquinone (DAAQ, 17 mg, 0.071 mmol) were dissolved in 3 mL of dioxane, charged in a glass tube (18 cm of length, 25 mL). The mixture was stirred for

1 h, then, 0.6 mL of 3 mol L⁻¹ Ac(OH) were successively added. The tube was sealed off and then heated at 120 °C for 3 days. The red precipitate was collected by filtration and rinsed with *N,N*-dimethylformylamide (DMF), tetrahydrofuran (THF) and ethanol in turn. The powders were collected and dried at 60 °C for 24 h.

Synthesis of COFs-A

1,3,5-triformylphloroglucinol (**Tp**, 10 mg, 0.048 mmol) and 2,6-diaminoanthraquinone (**DAAQ**, 17 mg, 0.071 mmol) were dissolved in 3 mL of acetonitrile, charged in a glass tube (18 cm of length, 25 mL). The mixture was stirred for 1 h, then, 0.6 mL of 3 mol L⁻¹ Ac(OH) were successively added. The tube was sealed off and then heated at 120 °C for 3 days. The red precipitate was collected by filtration and rinsed with *N,N*-dimethylformylamide (DMF), tetrahydrofuran (THF) and ethanol in turn. The powders were collected and dried at 60 °C for 24 h.

Synthesis of COFs-F

1,3,5-triformylphloroglucinol (**Tp**, 10 mg, 0.048 mmol) and 2,6-diaminoanthraquinone (**DAAQ**, 17 mg, 0.071 mmol) were dissolved in 3 mL of mixed solution (dioxane/mesitylene, 1:1 in v/v), charged in a glass tube (18 cm of length, 25 mL). The mixture was stirred for 1 h, then, 0.6 mL of 3 mol L⁻¹ Ac(OH) were successively added. The tube was sealed off and then heated at 120 °C for 3 days. The red precipitate was collected by filtration and rinsed with *N,N*-dimethylformylamide (DMF), tetrahydrofuran (THF) and ethanol in turn. The powders were collected and dried at 60 °C for 24 h.

Synthesis of COFs-R

1,3,5-triformylphloroglucinol (**Tp**, 10 mg, 0.048 mmol) was mixed with 2,6-diaminoanthraquinone (**DAAQ**, 17 mg, 0.071 mmol) in a mortar-pestle. After the mixture was uniformly grinded for 3 minutes, few drops of 3 mol L⁻¹ Ac(OH) (~5-10 µL) was added. Continue to grind the mixture until the powder turns orange. Collect the above orange solids and put them into the glass pressure tube (18 cm of length, 25 mL). Add the 3mL mesitylene/dioxane = 1/1 (v/v) solution and 0.6 mL of 3.0 M Ac(OH) to the pressure tube. The tube was sealed off and then heated at 120 °C for 3 days. The red precipitate was collected by filtration and rinsed with

N,N-dimethylformylamide (DMF), tetrahydrofuran (THF) and ethanol in turn. The powders were collected and dried at 60 °C for 24 h.

Synthesis of TpPa-COFs-1

The TpPa-COFs-1 was fabricated according to the literature [3]. 1,3,5-triformylphloroglucinol (**Tp**, 10 mg) and P-phenylenediamine (**Pa**, 7.6 mg) were dissolved in 3 mL of mixed solution (dioxane/mesitylene, 1:1= v/v), charged in a glass tube (18 cm of length, 25 mL). The mixture was stirred for 1 h, then, 0.6 mL of 3 mol L⁻¹ Ac(OH) were successively added. The tube was sealed off and then heated at 120 °C for 3 days. The yellow precipitate was collected by filtration and rinsed with *N,N*-dimethylformylamide (DMF), tetrahydrofuran (THF) and ethanol in turn. The powders were collected and dried at 60 °C for 24 h.

Synthesis of TpPa-COFs-2

1,3,5-triformylphloroglucinol (**Tp**, 10 mg) was mixed with P-phenylenediamine (**Pa**, 7.6 mg) in a mortar-pestle. After the mixture was uniformly grinded for 3 minutes, few drops of 3 mol L⁻¹ Ac(OH) (~5-10 μL) was added. Continue to grind the mixture until the powder turns yellow. Collect the above solids and put them into the glass pressure tube (18 cm of length, 25 mL). Add the 3mL mesitylene/dioxane = 1/1 (v/v) solution and 0.6 mL of 3.0 M Ac(OH) to the pressure tube. The tube was sealed off and then heated at 120 °C for 3 days. The yellow precipitate was collected by filtration and rinsed with *N,N*-dimethylformylamide (DMF), tetrahydrofuran (THF) and ethanol in turn. The powders were collected and dried at 60 °C for 24 h.

S1.5 Calculations

In three-electrode system, we calculated the capacitances of the supercapacitors based on the GCD profiles.

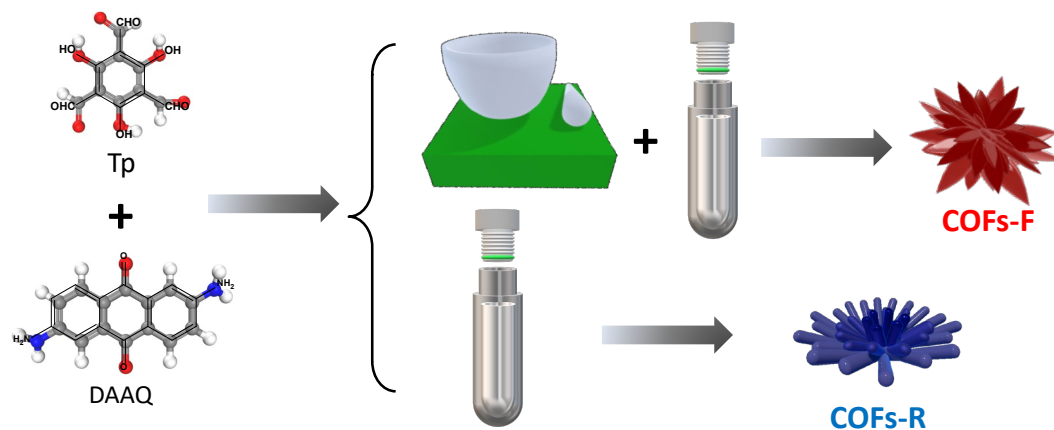
Specific capacitances derived from galvanostatic tests can be calculated from the equation:

$$C = I\Delta t / mV \quad (1)$$

where *m* (g) is the mass of active electrode material in the working electrode, *V* (V) is the potential drop during discharge, Δt (s) is the discharge time and *I* (A) is the

discharging current.

S2 Supplementary Figures



Scheme S1 Schematic diagram of the preparation of COFs-F and COFs-R.

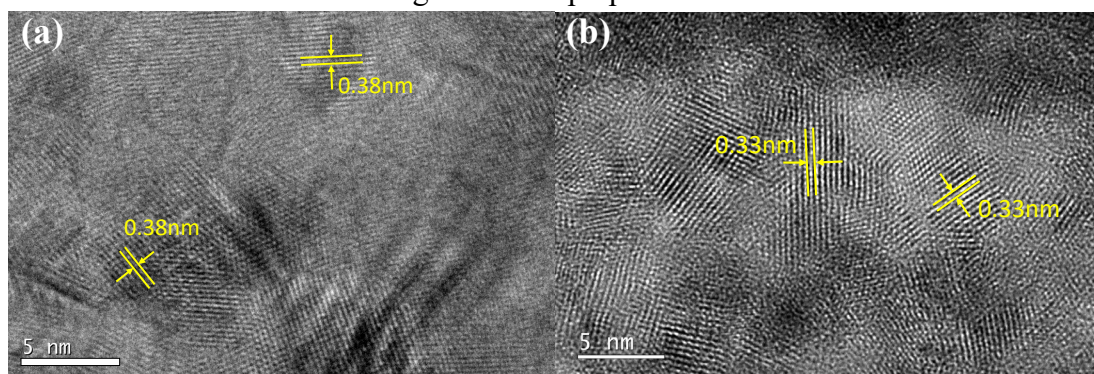


Figure S1 The HRTEM images of (a) COFs-F and (b) COFs-R.

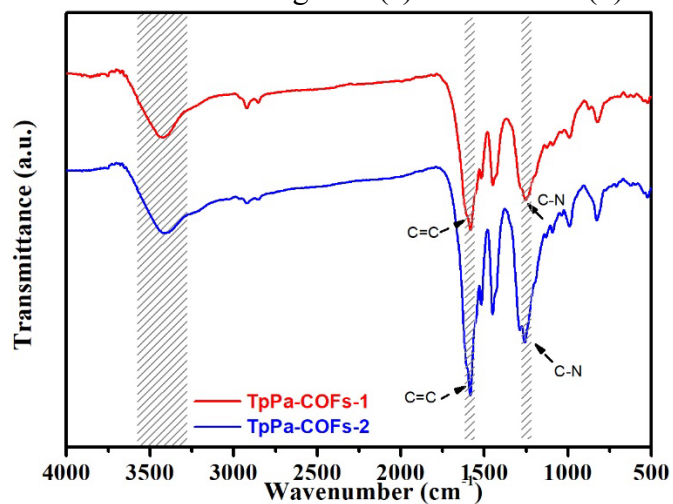


Figure S2 FT-IR spectra of the TpPa-COFs-1 and TpPa-COFs-2.

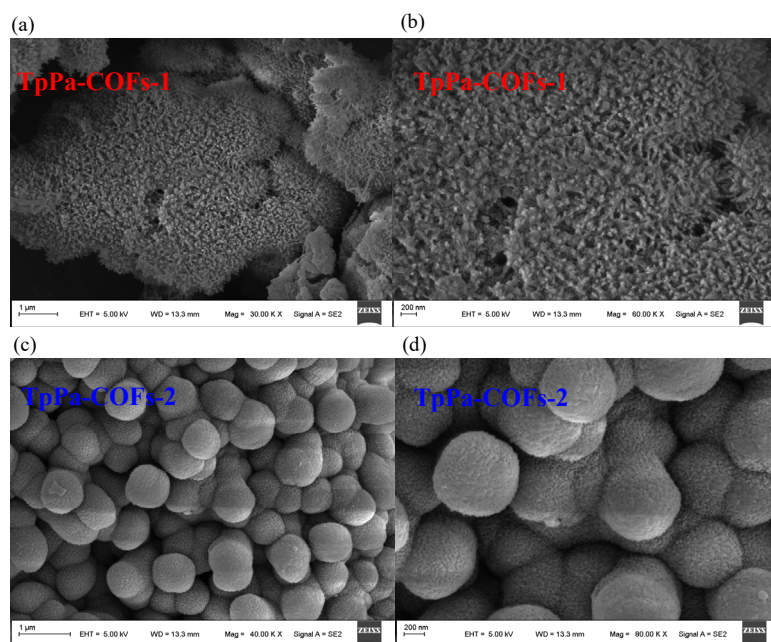


Figure S3 SEM images of the TpPa-COFs-1 (a) (b) and TpPa-COFs-2 (c) (d).

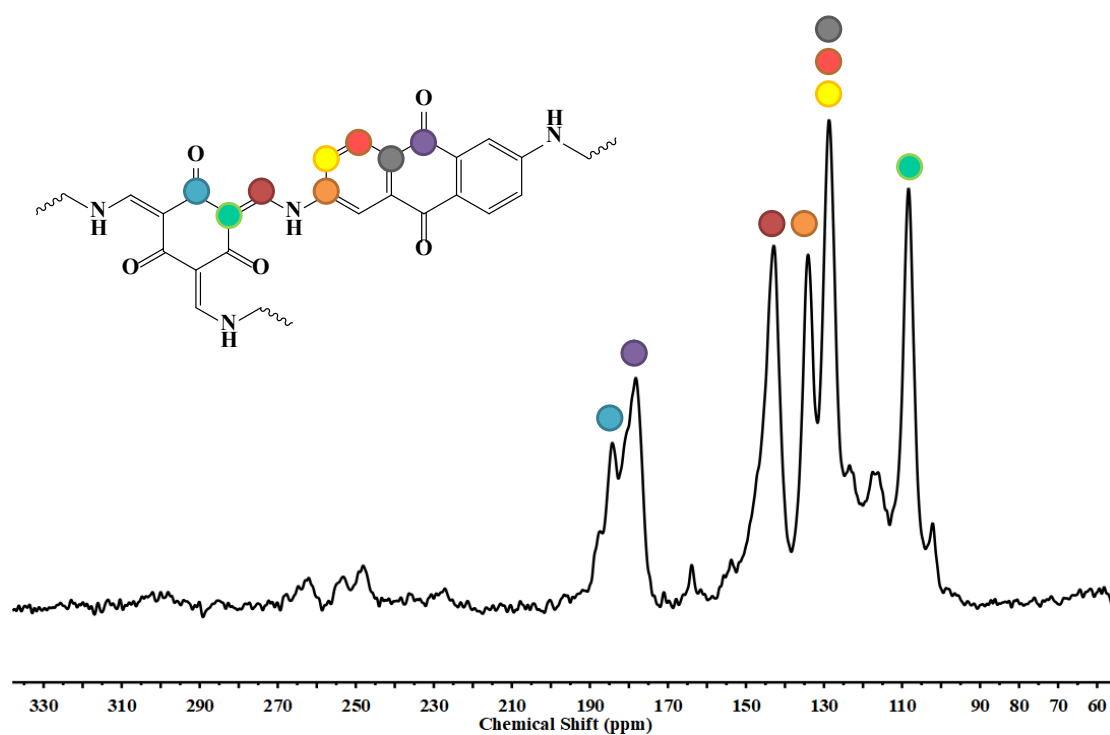


Figure S4 ^{13}C CP/MAS NMR spectra of DAAQ-Tp COFs

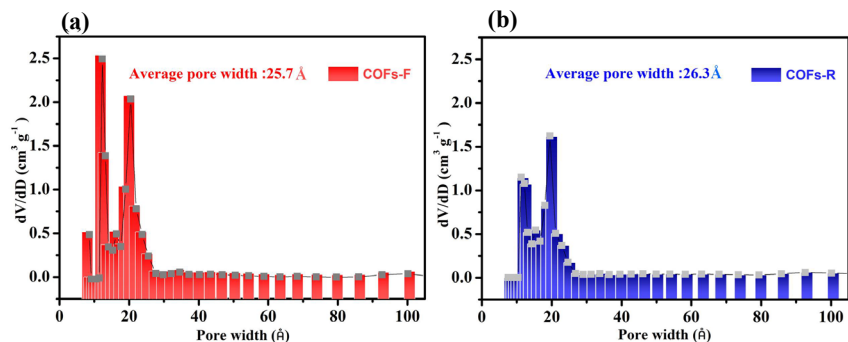


Figure S5 Pore size distributions of COFs-F (a) and COFs-R (b).

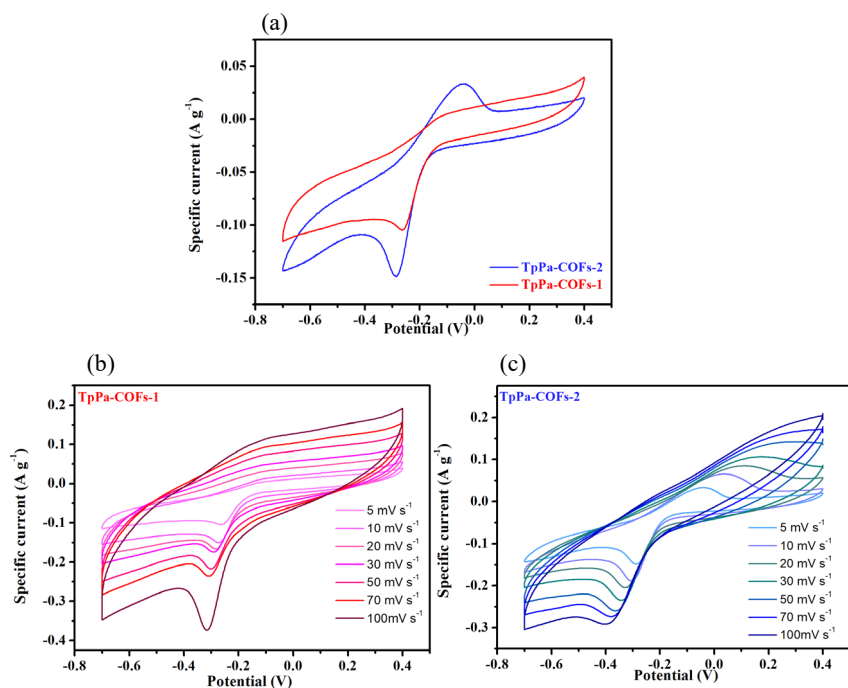


Figure S6 The CV curves of TpPa-COFs-1 and TpPa-COFs-2 at 5 mV s⁻¹ (a). The CV curves of TpPa-COFs-1 (b) and TpPa-COFs-1 (c) at different scan rates.

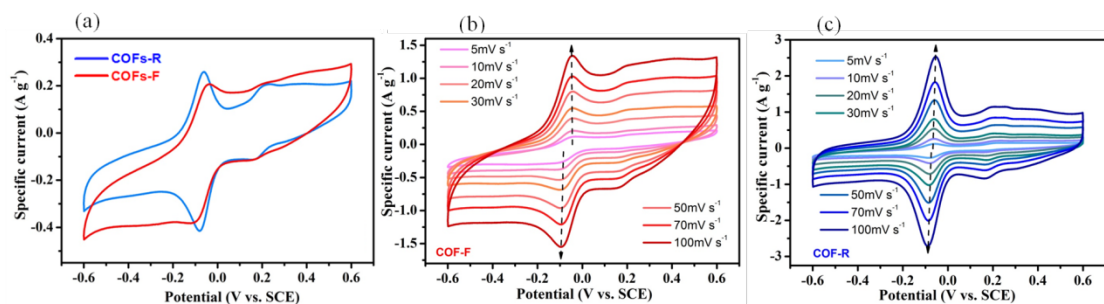


Figure S7 The CV curves of COFs-F and COFs-R at 5 mV s⁻¹ (a). The CV curves of COFs-F (b) and COFs-R (c) at different scan rates in 1M H₂SO₄.

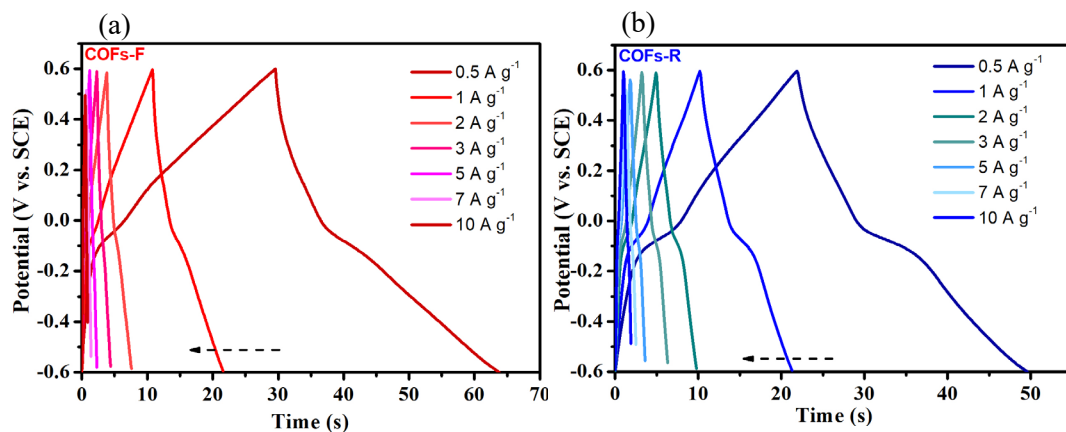


Figure S8 The galvanostatic charge-discharge curves of COFs-F (a) and COFs-R (b).

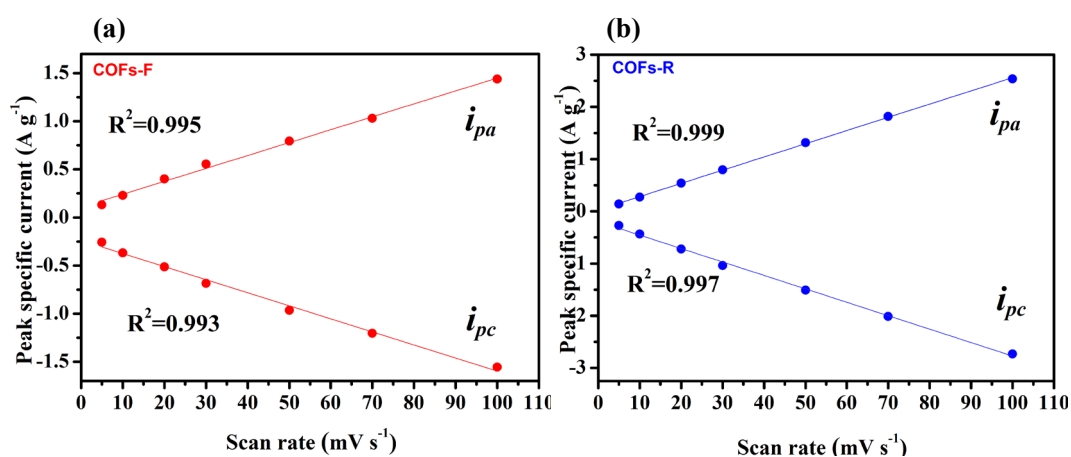


Figure S9 The relationship between peak specific current (i) and scan rate (v) of the COFs-F (a) and COFs-R (b) in 1M H₂SO₄.

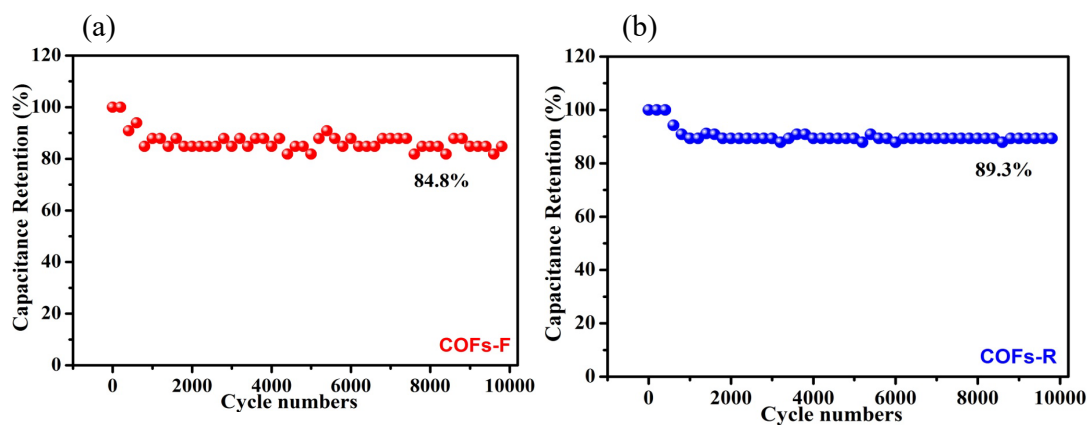


Figure S10 The cycling stability of COFs-F (a) and COFs-R (b) in 1M H₂SO₄.

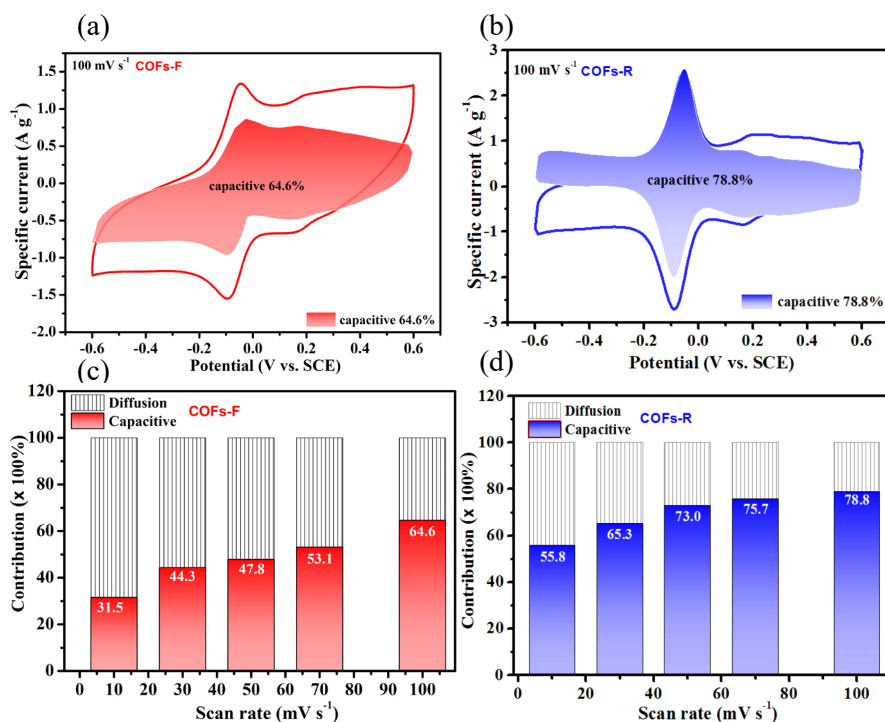


Figure S11 Capacitive and diffusion-controlled contributions to charge storage of the COFs-F (a) and COFs-R (b) at 100 mV s⁻¹ in 1M H₂SO₄. The pseudocapacitance contribution of the (c) COFs-F and (d) COFs-R electrode at different scan rates.

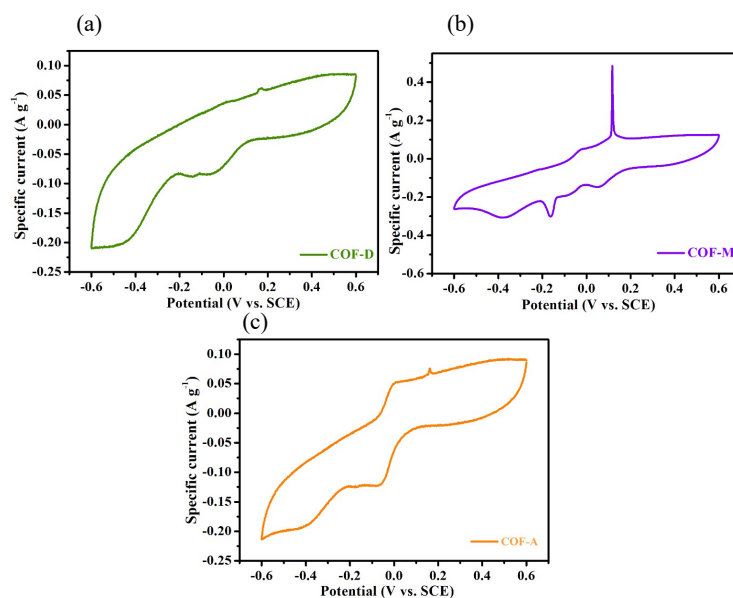


Figure S12 The CV curves of COFs-D (a), COFs-M (b) and COFs-A (c) at 5mV s⁻¹.

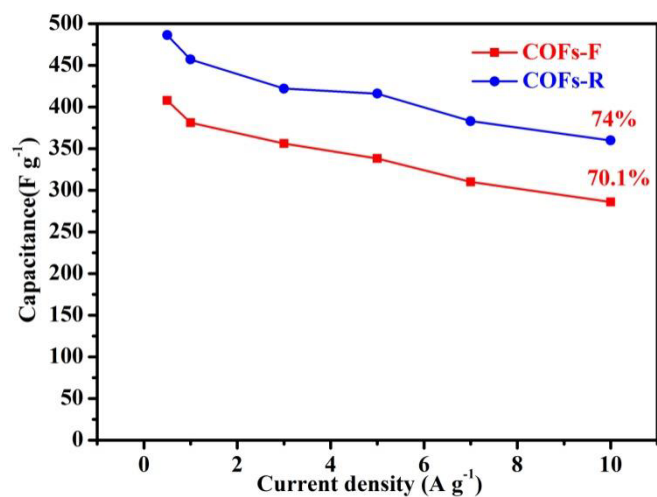


Figure S13 Specific capacitances versus current densities of COFs-F and COFs-R from 1 to 10 A g⁻¹.

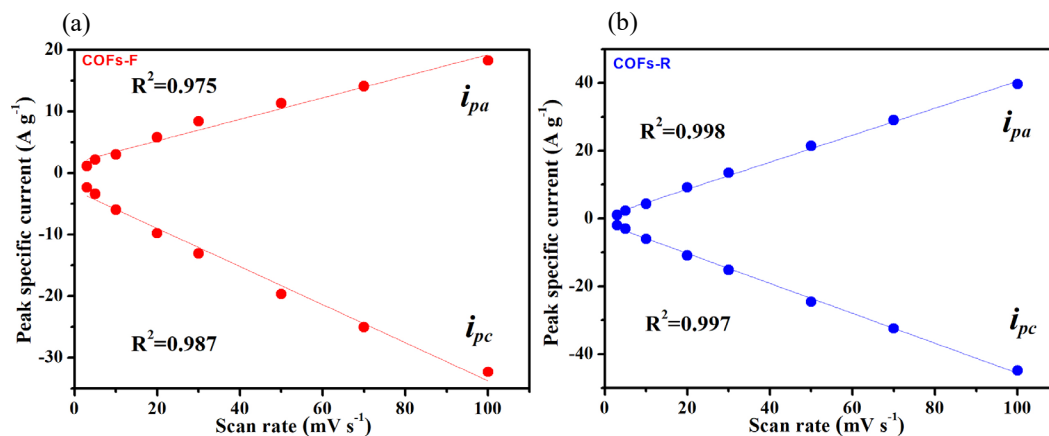


Figure S14 The relationship between peak specific current (i) and scan rate (v) of the COFs-F (a) and COFs-R (b) in KOH.

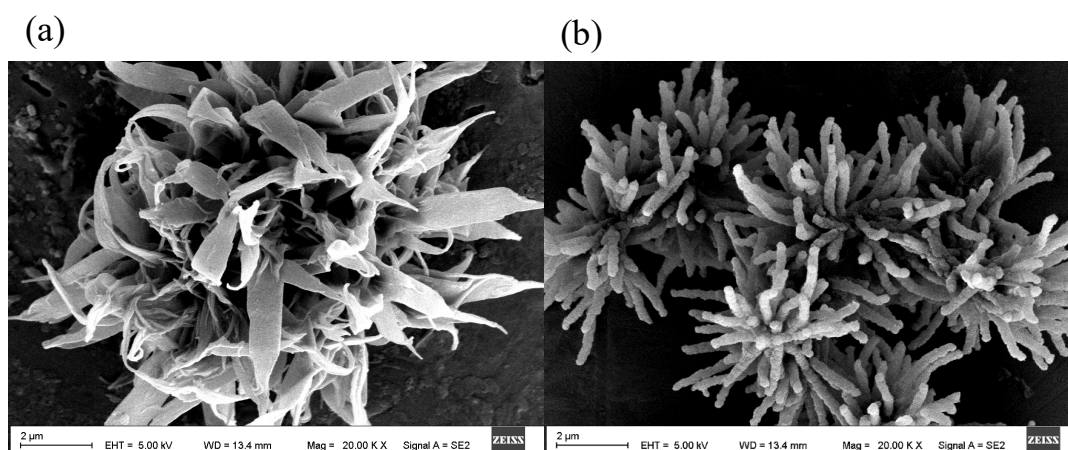


Figure S15 The SEM images of COFs-F (a) and COFs-R (b) in KOH after activation.

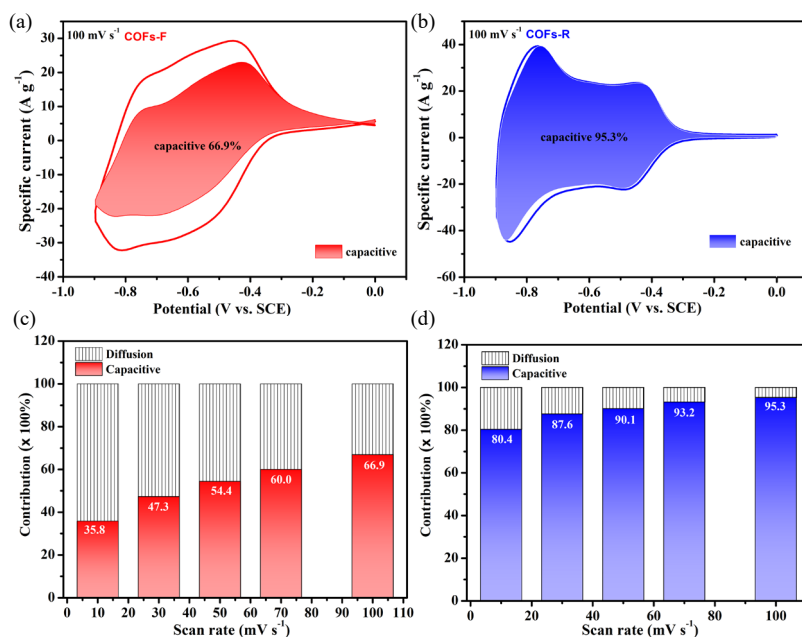


Figure S16 Capacitive and diffusion-controlled contributions to charge storage of the COFs-F (a) and COFs-R (b) at 100 mV s⁻¹ in KOH. The capacitance contribution of the (c) COFs-F and (d) COFs-R electrode at different scan rates.

Supplementary References

1. He, Y.; Yang, X.; An, N.; Wang, X.; Yang, Y.; Hu, Z. *New J. Chem.*, 2019, **43**, 1688-1698.
2. Kang, S.; Qiao, S.; Hu, Z.; Yu, J.; Wang, Y.; Zhu, J. *J. Mater. Sci.*, 2019, **54**, 6410-6424.
3. Zhang, X.; Wang, Z.; Yao, L.; Mai, Y.; Liu, J.; Hua, X.; Wei, H. *Materials Letters*, 2017, **213**, 143-147.