Supporting Information

Hybrid Architecture of Porous Polypyrrole Scaffold Loaded with Metal-Organic Frameworks for Flexible Solid-State Supercapacitor

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■ Experimental Section

Synthesis of three-dimensional porous PPy (p-PPy). The synthesis of p-PPy was established according to the procedure reported by Liu et al.[1] Pyrrole was distilled and kept refrigerated in the dark before use. 0.05 g of perfluorotetradecanoic acid (PFTA) was ultrasonically dispersed in 2 ml of ethanol for 15 minutes, and then 9 ml of water was added with magnetically stirring for 1 hour. 62 μl of pyrrole monomer was added into the solution and vigorously stirred for 2 hours. Subsequently, 0.18 g of ammonium persulfate dissolved in 1 ml of deionized water was added dropwise to the above solution, and the solution gradually formed into a black jelly. After staying for 1 h, the above solution was placed in the lined stainless steel autoclaves at 150 °C for 8 h. The obtained gel was immersed in 500 ml of 1 M HCl/ethanol (1:1, v:v) for 5 days to exclude the PFTA template, and then soaked in DI water until the soaking solution is neutral. Final sample of p-PPy was obtained after freeze-drying.

Synthesis of p-PPy scaffold loaded with Cu-CAT MOF (p-PPy/Cu-CAT). The preparation of Cu-CAT MOF was according to the report of Hmadeh et al.[2] Typically, copper acetate monohydrate (0.6 mmol, 120 mg) and 2, 3, 6, 7, 10, 11-hexahydroxytriphenylene (HHTP) (0.3 mmol, 97.5 mg) were added into the mixture solvent of water/DMF (v: v = 1:1) in a 20 mL glass vial. Subsequently, after vigorously stirring and ultrasonication for 20 min, the mixture solution was turned into dark. Then p-PPy was immersed into the above solution and heated in an oven at 85 °C for 6 h. After the reaction finished and the mixture cooled down to room temperature, the product was taken out and washed by DI water and DMF for several times in order to remove unreacted reactants and soluble impurities. The obtained p-PPy/Cu-CAT was immersed into acetone for 2 days at 80 °C accompanied with solvent-exchange, and then dried in a vacuum oven at 60 °C. Similarly, Cu-CAT powders were synthesized by the same procedure just without the addition of p-PPy.

Preparation of the flexible p-PPy/Cu-CAT electrodes. The p-PPy/Cu-CAT electrode was prepared by the traditional slurry coating method. The active materials were mixed with polyvinylidene fluoride and

conductive carbon (80:10:10, w/w/w) in N-methyl-2-pyrrolidene solution by stirring into a sticky slurry. Then the slurry was coated onto the carbon cloth and dried at 50 °C overnight under vacuum. The mass loading of p-PPy/Cu-CAT is about 2.8 mg cm^{-2}. Both the electrodes of active material p-PPy and Cu-CAT with the same mass loading are respectively assembled by the similar method.

Assembly of symmetric flexible all-solid-state supercapacitor. The gel electrolyte was prepared by mixing 2 g polyvinyl alcohol (PVA) and 4.25 g of LiCl in 20 mL DI water at 85 °C with stirring into a homogeneous, clear and sticky gel solution. Two pieces of identical p-PPy/Cu-CAT electrodes were immersed into the above solution and then lifted up. Symmetrical two electrodes were allowed to assemble into a flexible supercapacitor device. The PVA/LiCl gel was acted as both the electrolyte and separator. Furthermore, to avoid moisture from the air, Paramembrane® was used to seal the supercapacitor device.

Characterizations. SEM and EDX were performed with a field-emission scanning electron microscope (FESEM, Nova NanoSEM 450) at an accelerating voltage of 10 kV. XRD patterns is conducted on a PANalytical B.V. x'pert3 powder X-ray diffractometer with Cu Kα radiation (λ = 1.5405 Å) at 30 kV and 20 mA from 3° to 30° with a scanning increment of 0.02°. TEM and high-resolution TEM images were obtained with a Tecnai G2 20 scope at an acceleration voltage of 200 kV. N_2 adsorptions experiments were measured on a Quantachrome Autosorb-1 automatic volumetric instrument. A liquid nitrogen bath (77 K) was used for isotherm measurements. Ultra-high purity grade N_2 was used to the adsorption experiments. XPS spectra was collected by a monochromatic Al-Kα X-ray source (hv = 1486.6 eV, Kratos, AXIS-ULTRA DLD-600W). Thermogravimetric analysis (TGA) was performed on a Pyris 1 TGA (PerkinElmer Instruments) under air atmosphere at a heating rate of 5 °C min^{-1}. Infrared Spectroscopy (IR) was conducted on Equinox55 equipment.

Electrochemical measurements. The electrochemical performance of these electrodes was studied in a three-electrode cell in 3 M KCl aqueous electrolytes with Ag/AgCl and Pt plate as the reference electrode

and counter electrode, respectively. All electrochemical measurements were performed on a CHI 660E electrochemical workstation. The gravimetric and areal capacitances were calculated using the following equations (1) to (4). Electrochemical performance of assembled flexible supercapacitor device were tested in a two-electrode configuration and the areal energy (E) and power densities (P) were calculated using the following equations (5) to (6). The LED light used in the test was a cap-shape red LED lamp bead with a diameter of 5 mm, whose working potential is 1.8-2.2 V, working current is 15-20 mA, and rated power is 0.04 W.

Gravimetric capacitance

$$C_m(\mathrm{F\ g^{-1}}) = \int \frac{I_1 \mathrm{d}U}{2vmU} \qquad (1)$$

$$C_m(\mathrm{F\ g^{-1}}) = \frac{I_2 t}{mU} \qquad (2)$$

Areal capacitance

$$C_s(\mathrm{F\ cm^{-2}}) = \int I_1 \mathrm{d}U/2vSU \qquad (3)$$

$$C_s(\mathrm{F\ cm^{-2}}) = I_2 t/SU \qquad (4)$$

where I_1 (A) is the response current of CV, U (V) is voltage window (voltage drop IR drop has been considered for galvanostatic charging/discharging), v (V s^{-1}) is the scan rate, I_2 (A) is the discharging current, t (s) is the discharging time, and m (g) and S (cm^2) are the weight and area of the electrode or the supercapacitor device.

$$E = \frac{CU^2}{(2 \times 3600)} \qquad (5)$$

$$P = E \times \frac{3600}{t} \qquad (6)$$

■ Supplementary Figures

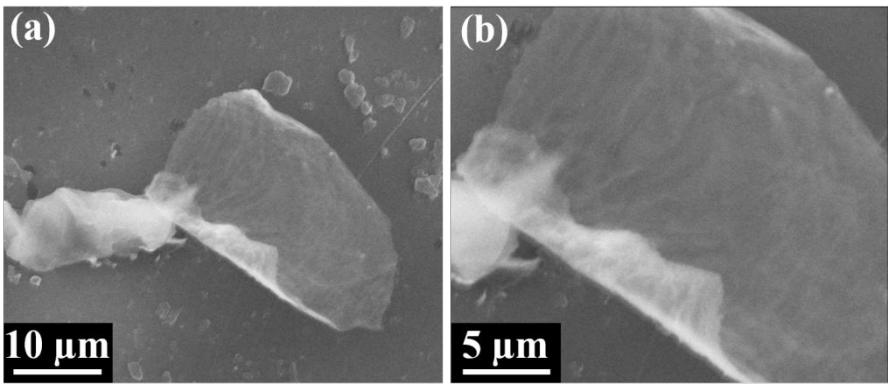

Figure S1. (a, b) SEM images of different multiples for PFTA template. (The PFTA solution in ethanol/H_2O was dripped onto a piece of silicon slice and then dried for the SEM characterization of PFTA template.)

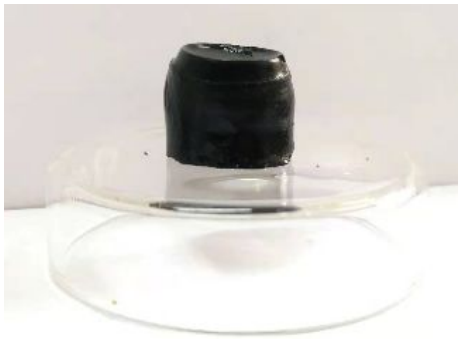

Figure S2. Photograph of PPy/PFTA hydrogel.

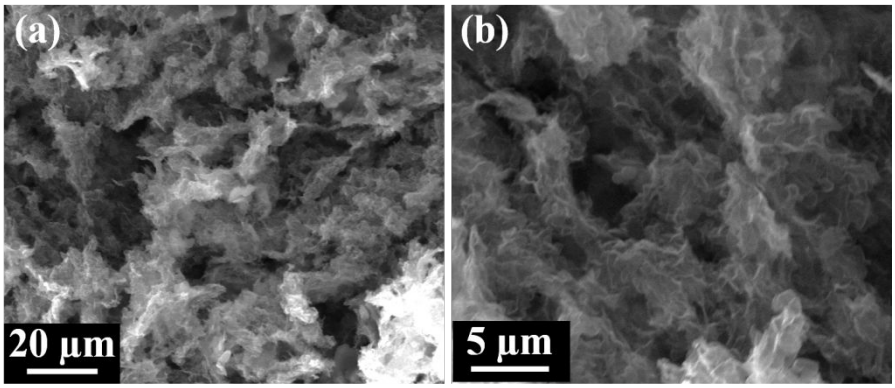

Figure S3. (a, b) SEM images of different multiples for PPy/PFTA hydrogel.

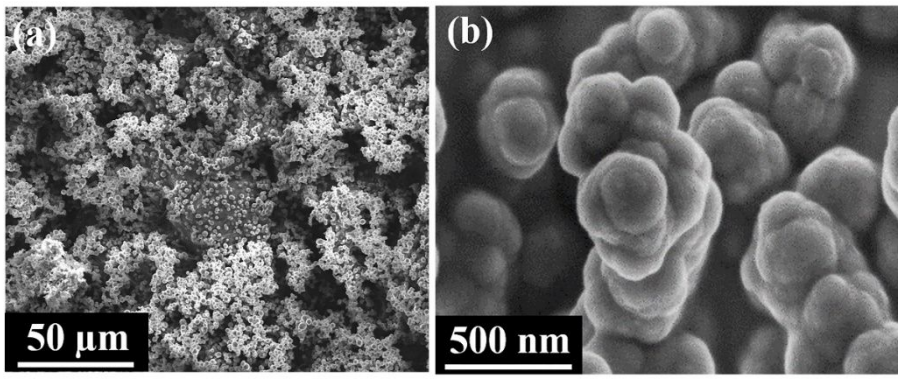

Figure S4. (a, b) SEM images of different multiples for typical PPy without PFTA template.

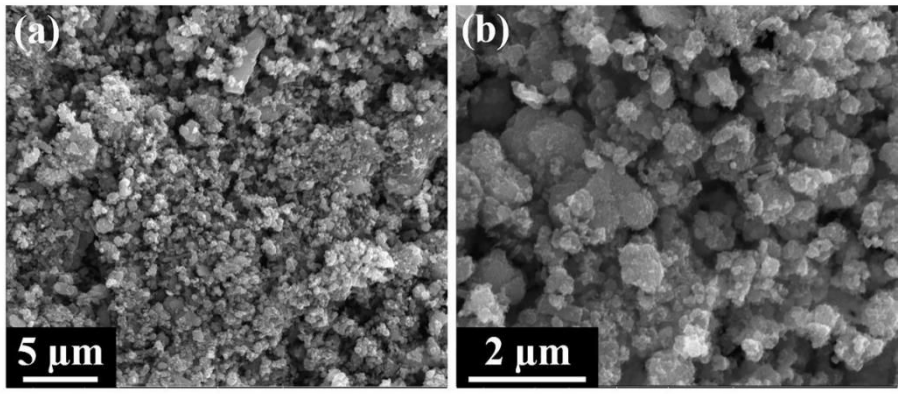

Figure S5. (a, b) SEM images of different multiples for Cu-CAT particles synthesized without p-PPy.

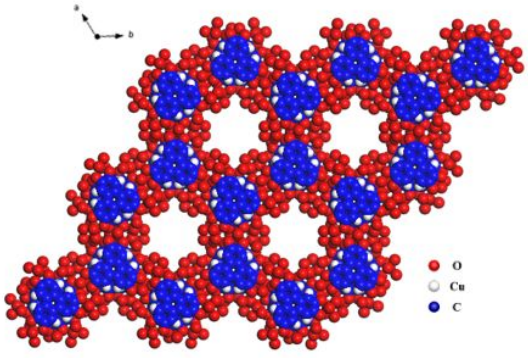

Figure S6. Simulated crystal structure of Cu-CAT.

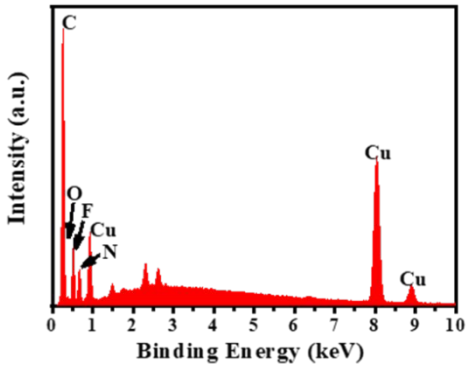

Figure S7. Energy dispersive X-ray (EDX) spectroscopy of p-PPy/Cu-CAT.

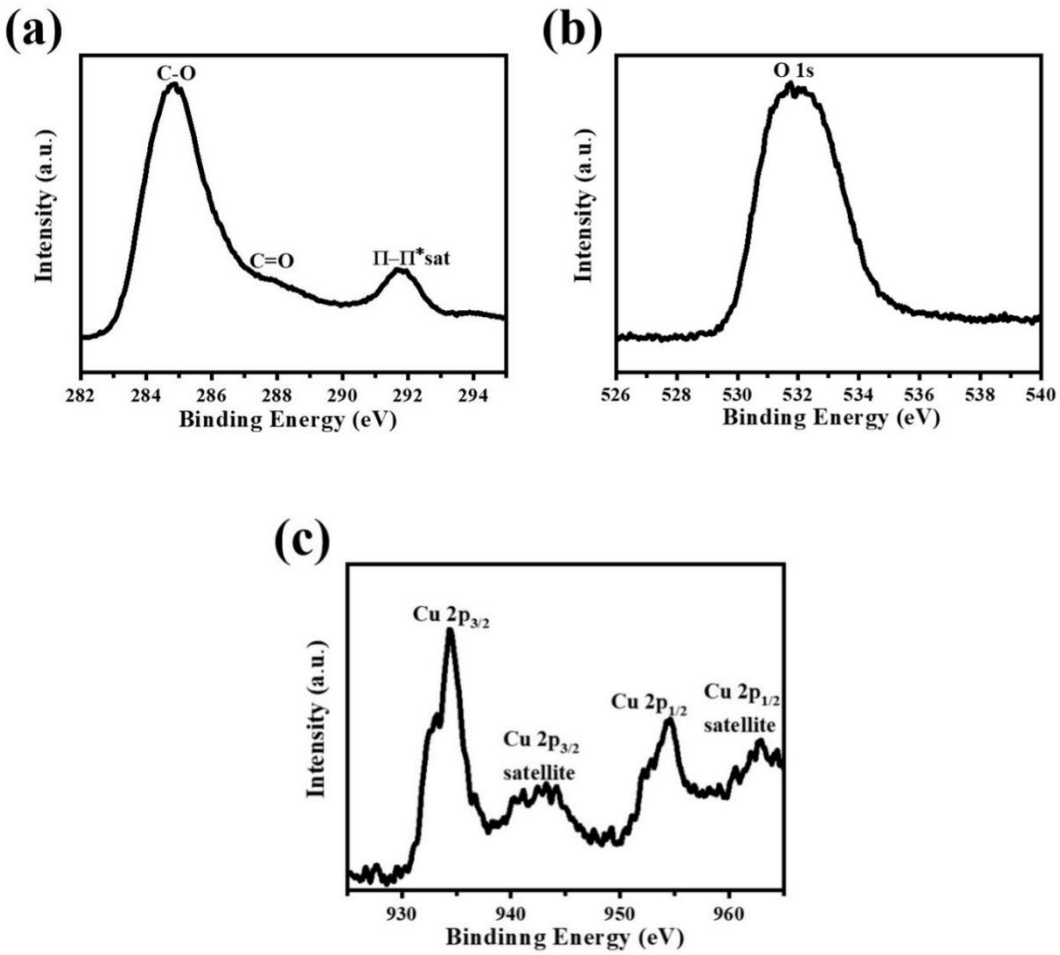

Figure S8. XPS spectra of (a) C 1s, (b) O 1s and (c) Cu 2p of p-PPy/Cu-CAT.

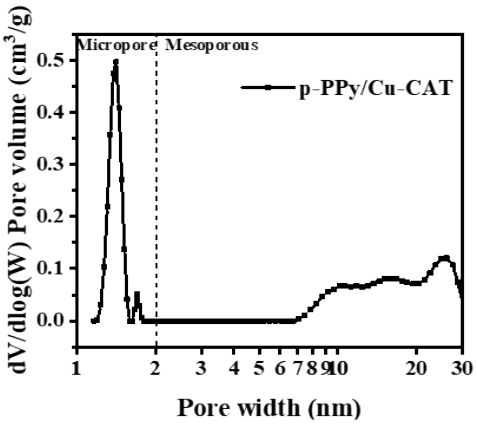

Figure S9. Pore-size distribution of p-PPy/Cu-CAT.

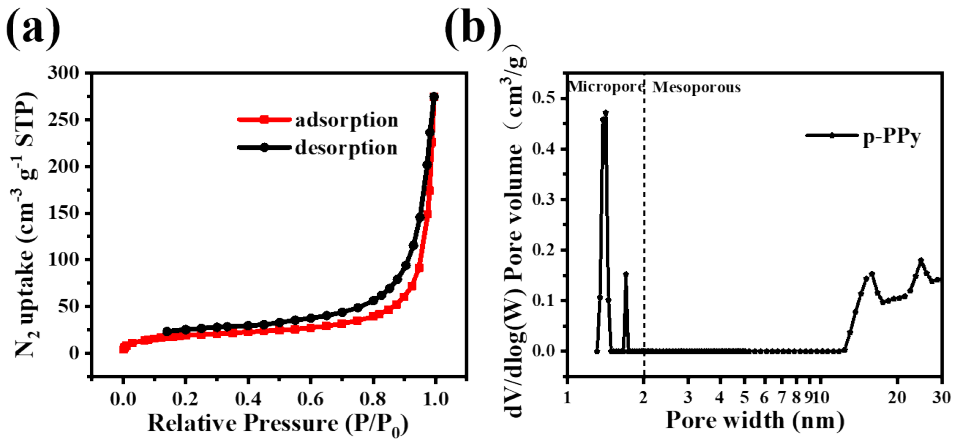

Figure S10. (a) N_2 sorption isotherms and (b) pore-size distribution of p-PPy.

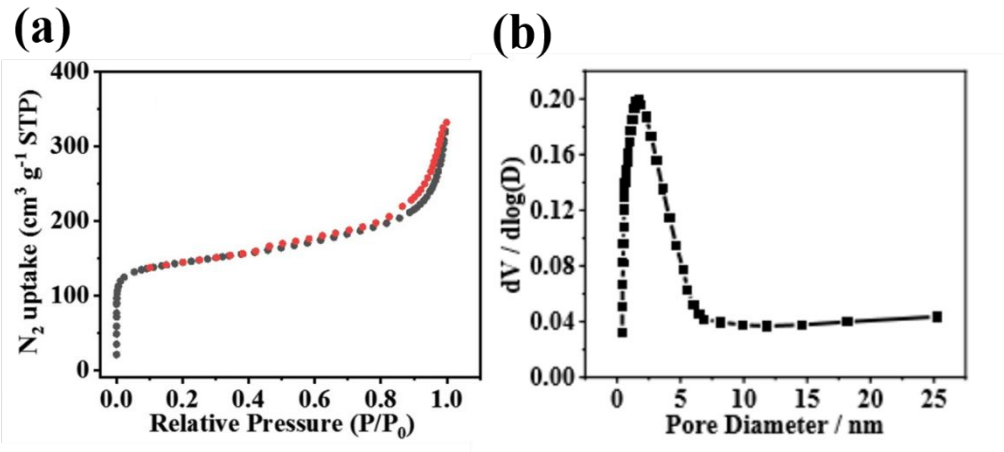

Figure S11. (a) N_2 sorption isotherms and (b) pore-size distribution of Cu-CAT nanowires.[3]

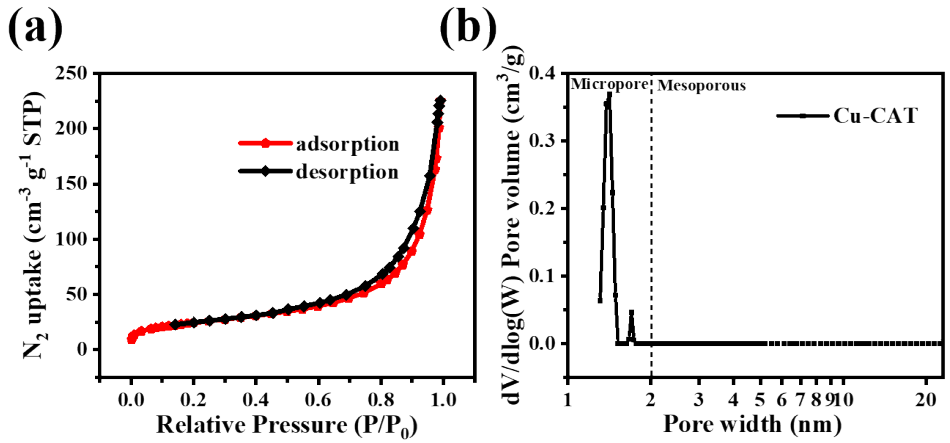

Figure S12. (a) N_2 sorption isotherms and (b) pore-size distribution of Cu-CAT particles.

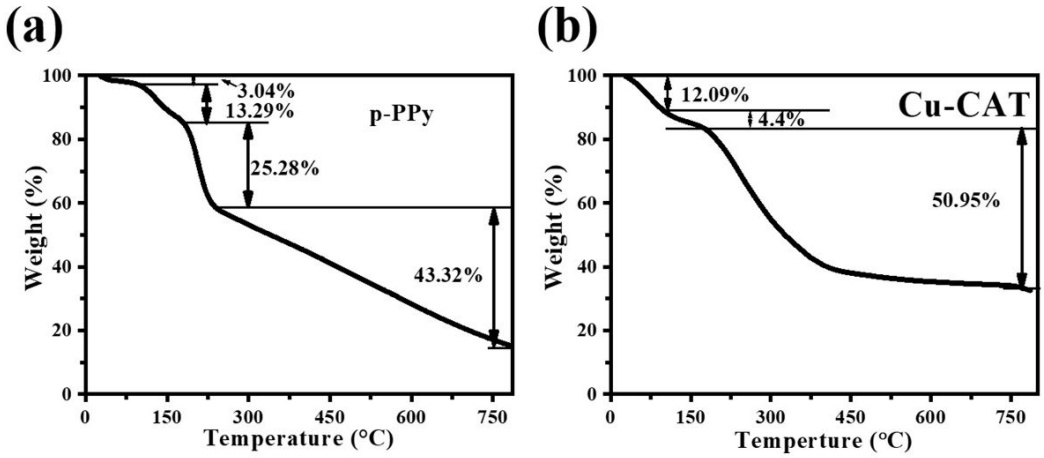

Figure S13. Thermal gravimetric analysis of (a) p-PPy and (b) Cu-CAT.

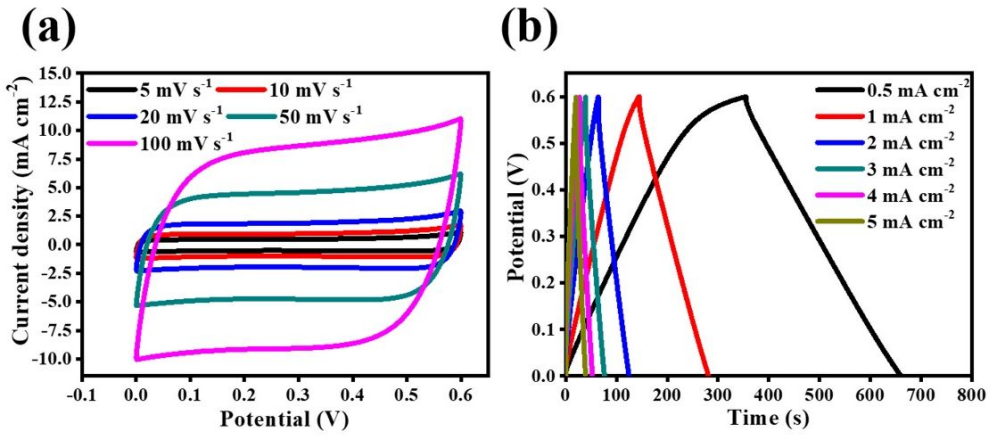

Figure S14. (a) CV at various scan rates and (b) GCD at diverse current densities of single p-PPy.

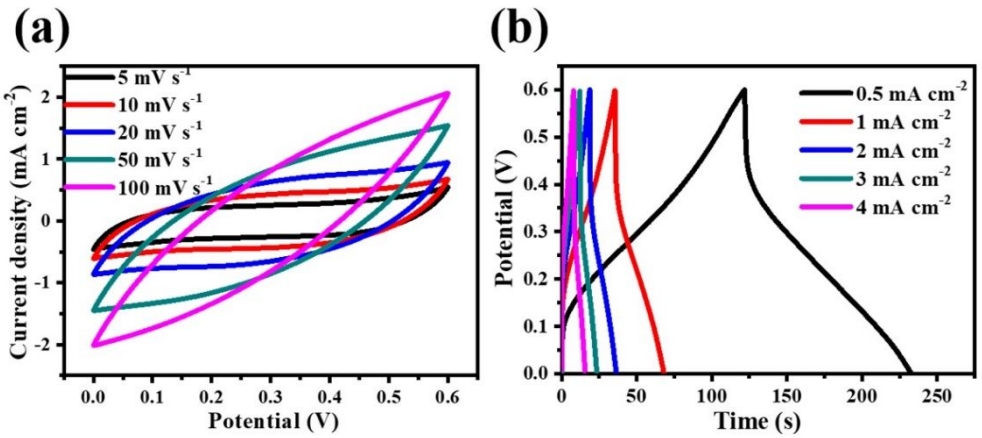

Figure S15. (a) CV at various scan rates and (b) GCD at diverse current densities of single Cu-CAT.

Figure S16. Equivalent circuit of the electrodes. R_s is electrolyte resistance; CPE_{dl} is electrical double-layer capacitance; R_{ct} is charge transfer resistance; W_s is Warburg diffusion process; CPE_f is pseudocapacitance.

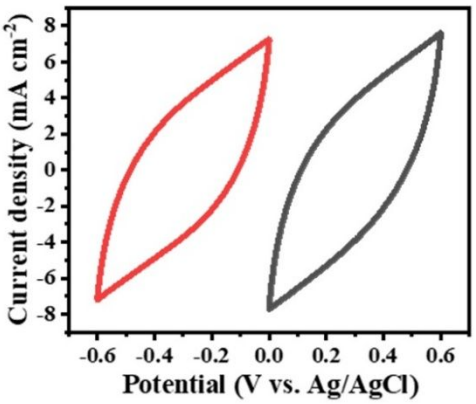

Figure S17. CV curves collected over diverse potentials of p-PPy/Cu-CAT electrode in a three-electrode system at a scan rate of 10 mV s^{-1}.

Table S1. Typical results for some MOFs and MOF-conducting polymer hybrids based supercapacitors.

Supercapacitor	Specific capacitance (mF cm^{-2})	Scan rate / Current density	Energy density (μWh cm^{-2})	Power density (mW cm^{-2})	Specific surface area (m^2 g^{-1})	Ref.
$Ni_3(HITP)_2$	15.69	0.10 mA cm^{-2}	48.8	45.54	-	4
Cu–CAT NWAs	0.022	0.5 A g^{-1}	2.6 (W h kg^{-1})	0.2 (kW kg^{-1})	540	5
PEDOT-GO/UiO-66	30	5 mV s^{-1}	2.2	0.2	623 (UiO-66)	6
PANI-ZIF-67-CC	35	0.05 mA cm^{-2}	16.1	245	73	7
CC/ZIF-67/PPy	180.7	1 mA cm^{-2}	-	-	-	8
CFs@UiO-66/PPY	206	5 mV s^{-1}	12.8	2.102	125	9
ZIF–PPy-2	225.8	0.4 mA cm^{-2}	11.3	1.44	518.8	10
Cu-CAT-NWAs/PPy	252.1	1.25 mA cm^{-2}	22.4	1.1	468 (Cu-CAT nanowire)	3
This work	233	0.5 mA cm^{-2}	12	1.5	107	-

■ References

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