Cu/Cu$_x$O@C nanocomposites as efficient electrodes for high-performance supercapacitor devices

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Experimental Section

Materials. All chemicals (analytical grade) were purchased from commercially-available sources and directly used as reagents. Water was purified with the Millipore system (18.2 MΩ cm).

Synthesis of TP-Na and BTC-Na

Terephthalic acid (TP) (4.15 g) and NaOH (2 g) were put together and introduced into 50ml ultrapure water. After stirring and dissolving, TP-Na solution was obtained. Trimesic acid (BTC) (5.25 g) and NaOH (3 g) were put together and introduced into 50ml ultrapure water. After stirring and dissolving, BTC-Na solution was obtained.

Synthesis of precursor (TP-PRE and BTC-PRE)

0.5M $Cu(OAc)_2$ was prepared by dissolve $Cu(OAc)_2.H_2O$ (4.99 g) in 50ml ultrapure water. A mixture of TP-Na (5 mL), 0.5M $Cu(OAc)_2$ (5 mL) in 40 ml anhydrous ethanol was placed in a 50 mL beaker and stirred magnetically for 30min with magnetons. The blue precipitates (TP-PRE) obtained by centrifugation were washed in the order of deionized water, deionized water/ethanol (1:1), ethanol, and finally vacuumed freeze-drying overnight. Similarly, if TP-Na was replaced by BTC-Na, blue powder (BTC-PRE) could be obtained.

Preparation of electrode active materials

The TP-PRE and BTC-PRE samples were annealed in a tube furnace filled with N_2 at 800 ºC for 2 h at a heating rate of 3 ºC per minute. Then, the calcined samples were annealed in an air-filled muffle furnace at 250 ºC for 4 h at a heating rate of 2 ºC per minute to obtain black powder, named as 800-TP and 800-BTC separately. In a similar process, when the calcination temperature in the tube furnace was raised to 900 ºC, the as-obtained black powders were named as 900-TP and 900-BTC, respectively.

Instruments.

The chemical composition of as-prepared samples was characterized by using SEM (JSM-7800F, JEOL), TEM (Tecnai G2 F30, FEI), EDS (JSM-7800F, JEOL), XPS including Auger Energy spectrum (Thermo Fisher Nexsa). TGA was performed on the HTG HQG thermogravimetric analyzer of the Beijing Henven Scientific Instrument Factory. Raman spectra were recorded on a Thermo Fischer DXR Raman spectrometer employing a 514 nm laser beam. The specific surface and porosity of the sample were analyzed by Micromeritics ASAP2460 specific surface and porosity analyzer (the sample is degassed and activated under vacuum at 100 ºC for 3 h before the N_2 adsorption-desorption test). The samples were examined by powder X-ray diffraction (PXRD) on a MiniFlex600 diffractometer (RIGAKU, Japan) with a Cu Kα radiation source ($\lambda = 1.5406$ nm).

Electrochemical measurements.

I) Electrode preparation

The working electrode was prepared by mixing the active material, acetylene black and polytetrafluoroethylene (PTFE) in a mass ratio of 75:15:10. Then, the isopropanol was used to make the black paste. After stirring for 12 hours, the working electrode was pasted onto Ni foam (1×1 cm^2), and was dried at 80 ºC in the oven for 2h.

The activated carbon (AC) capacitive electrode was prepared by mixing AC, acetylene black and polyvinylidene difluoride (PVDF) in a mass ratio of 75:15:10. Then, the N-methyl-2-pyrrolidone (NMP) was used to make the black paste. After stirring for 12 hours, the working electrode was pasted onto Ni foam (1×1 cm^2), and was dried at 75 ºC in a vacuum oven overnight.

II) Three electrode test

The working electrode, Hg/HgO as a reference electrode, and platinum wire as a counter electrode in an aqueous KOH electrolyte (6 M) under electrochemical workstation CHI660e to examine the electrochemical performance of the material by the test of Cyclic Voltammetry (CV), Chronopotentiometry (CP), and Electrochemical Impedance Spectroscopy (EIS).

III) Two electrode test

AC as a capacitive electrode, the working electrode as a battery type electrode, and other conditions are the same as the three-electrode test.

IV) LED experiment

The carbon cloth was heated and refluxed with nitric acid at 80 °C for two hours, and then the carbon cloth was placed in deionized water and anhydrous ethanol successively for 15 min, and the as-obtained carbon cloth was dried in a vacuum drying oven at 45 °C. Then, the dried carbon cloth was cut into several small discs with a diameter of 14 mm using a slicer. Then, the slurry made of active material was applied into the discs. The as-fabricated films were put in a vacuum drying oven and dried at 80 °C for 12 h. Then, electrode sheets coated with active material or activated carbon were obtained. The battery-type capacitor was assembled in the following order: positive electrode shell, electrode sheet coated with active material, two filter paper separators with a diameter of 19 mm, electrode sheet coated with a negative electrode material, stainless steel gasket, shrapnel, negative electrode shell, on the front and back of the separator. After an appropriate amount of electrolyte (6 mol L^{-1} KOH) was added, the device was sealed using a button battery sealing machine.

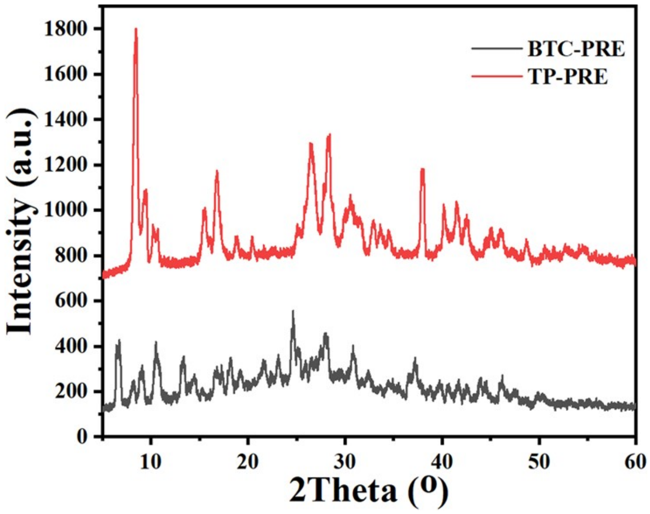


Figure S1 Comparison of XRD patterns of BTC-PRE and TP-PRE

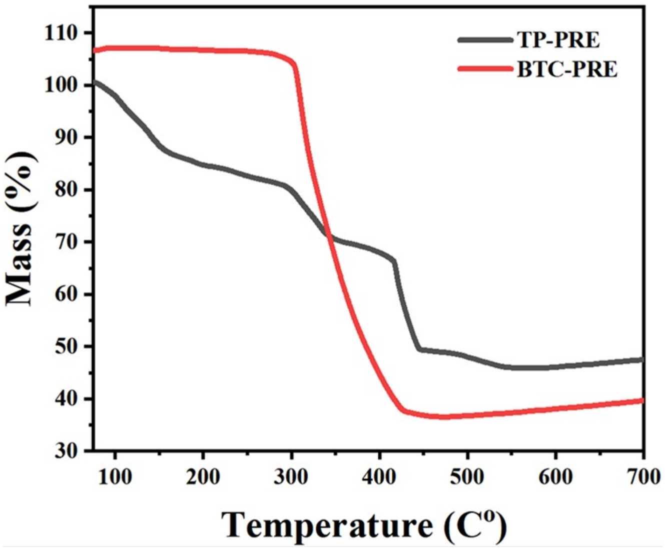
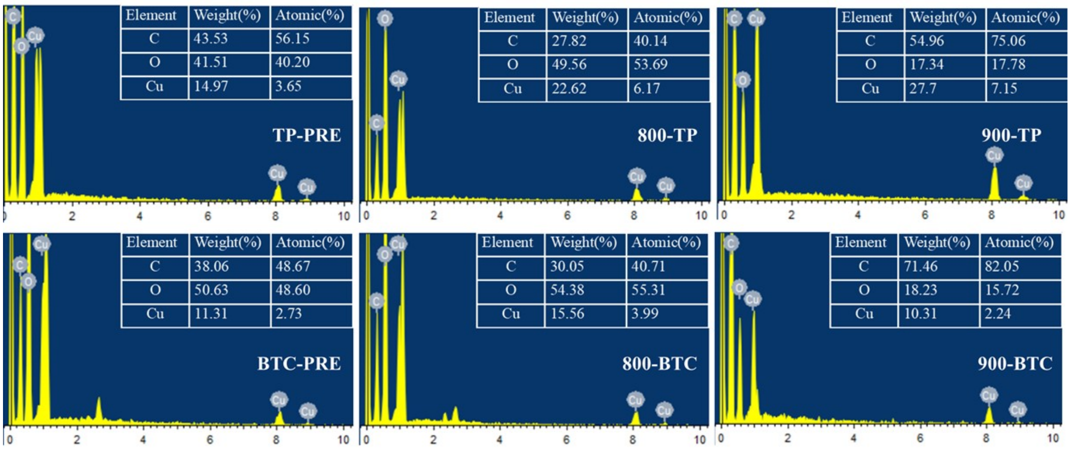


Figure S2 The TGA curves of TP-PRE and BTC-PRE.



TP-PRE

Element	Weight(%)	Atomic(%)
C	43.53	56.15
O	41.51	40.20
Cu	14.97	3.65

800-TP

Element	Weight(%)	Atomic(%)
C	27.82	40.14
O	49.56	53.69
Cu	22.62	6.17

900-TP

Element	Weight(%)	Atomic(%)
C	54.96	75.06
O	17.34	17.78
Cu	27.7	7.15

BTC-PRE

Element	Weight(%)	Atomic(%)
C	38.06	48.67
O	50.63	48.60
Cu	11.31	2.73

800-BTC

Element	Weight(%)	Atomic(%)
C	30.05	40.71
O	54.38	55.31
Cu	15.56	3.99

900-BTC

Element	Weight(%)	Atomic(%)
C	71.46	82.05
O	18.23	15.72
Cu	10.31	2.24

Figure S3 EDS analysis of TP-PRE, 800-TP, 900-TP, BTC-PRE, 800-BTC, 900-BTC

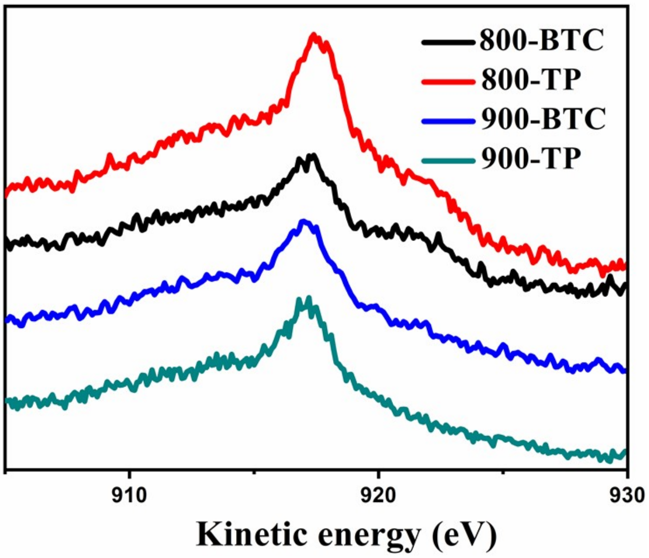


Figure S4 Auger energy spectra of 900-BTC, 900-TP, 800-BTC and 800-TP, respectively.

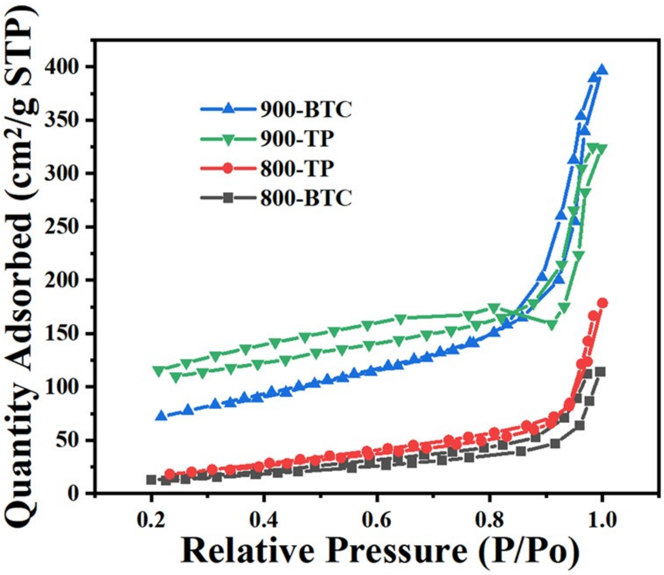


Figure S5 Nitrogen adsorption-desorption isotherm and pore-size distribution of calcined samples

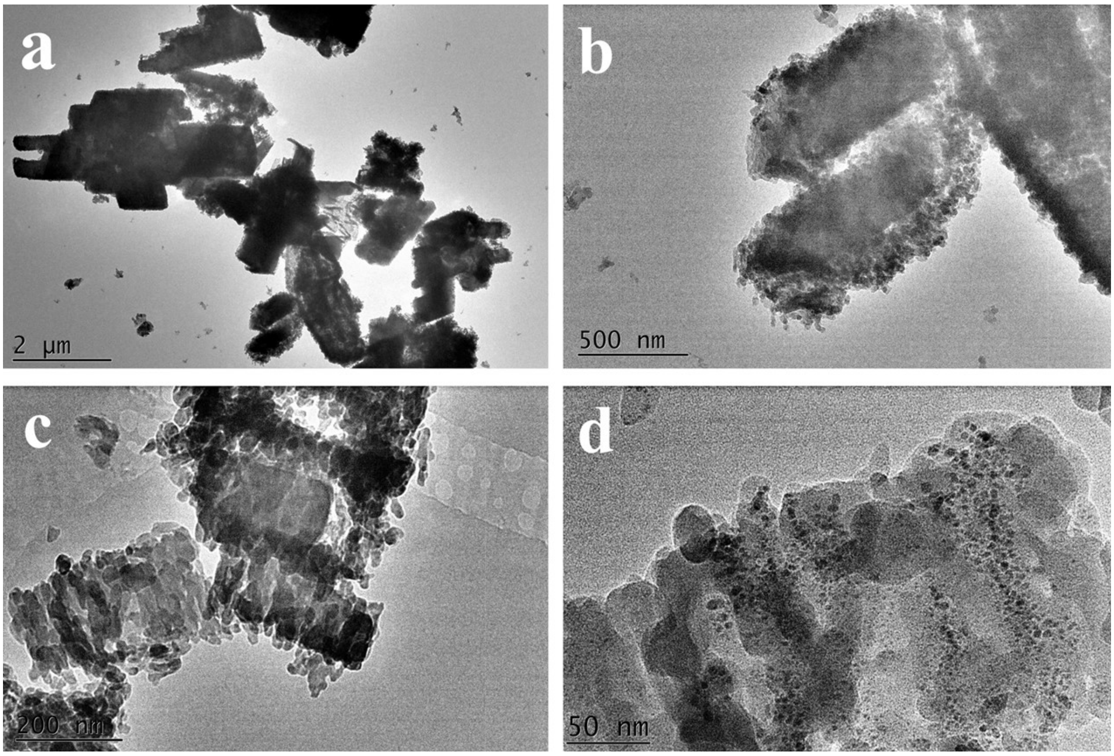


Figure S6 The TEM images of the TP-PRE precursor

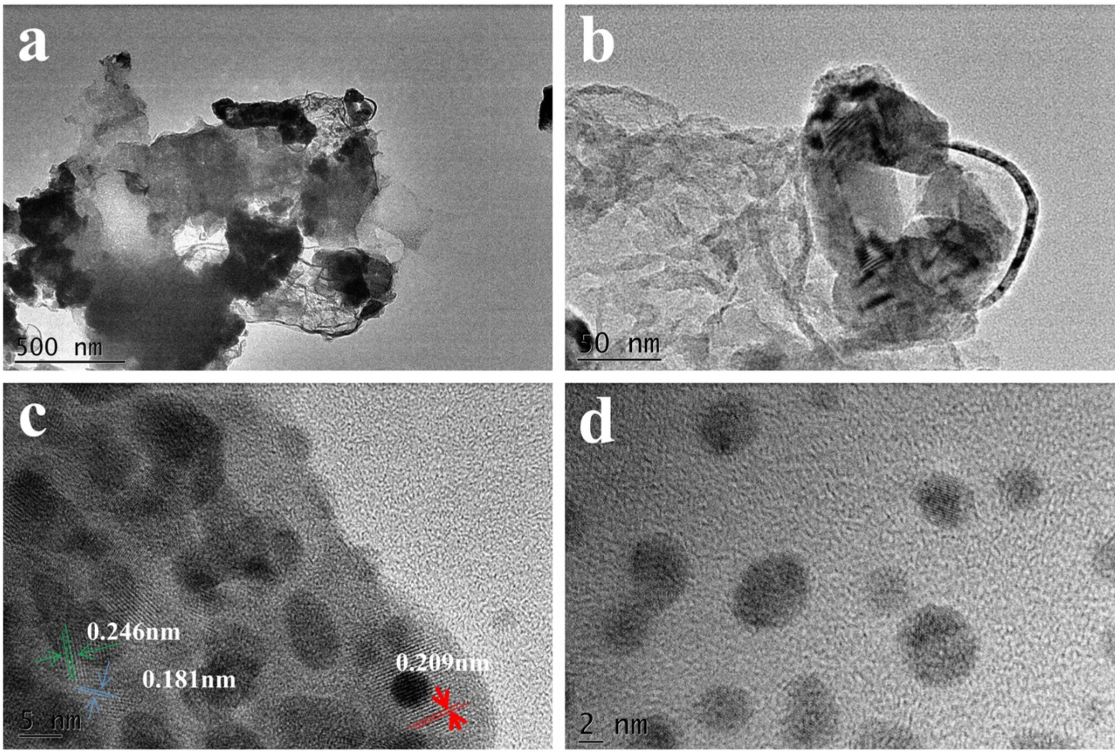


Figure S7 The TEM images of 800-TP sample

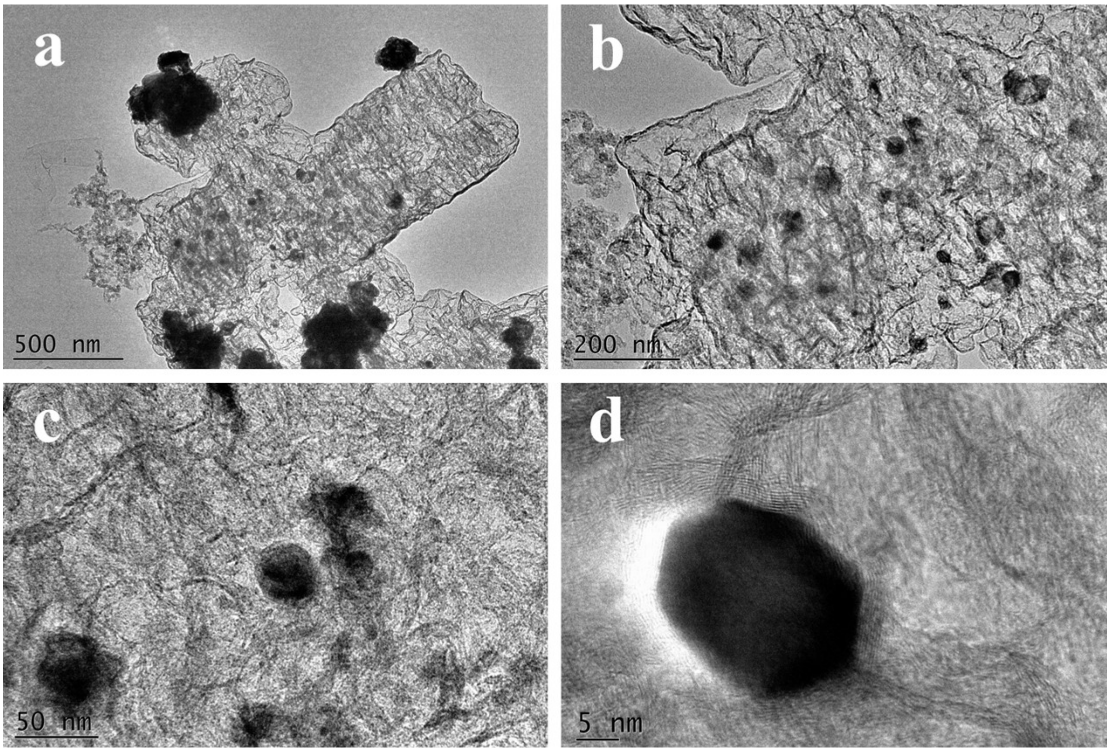


Figure S8 The TEM images of 900-TP sample

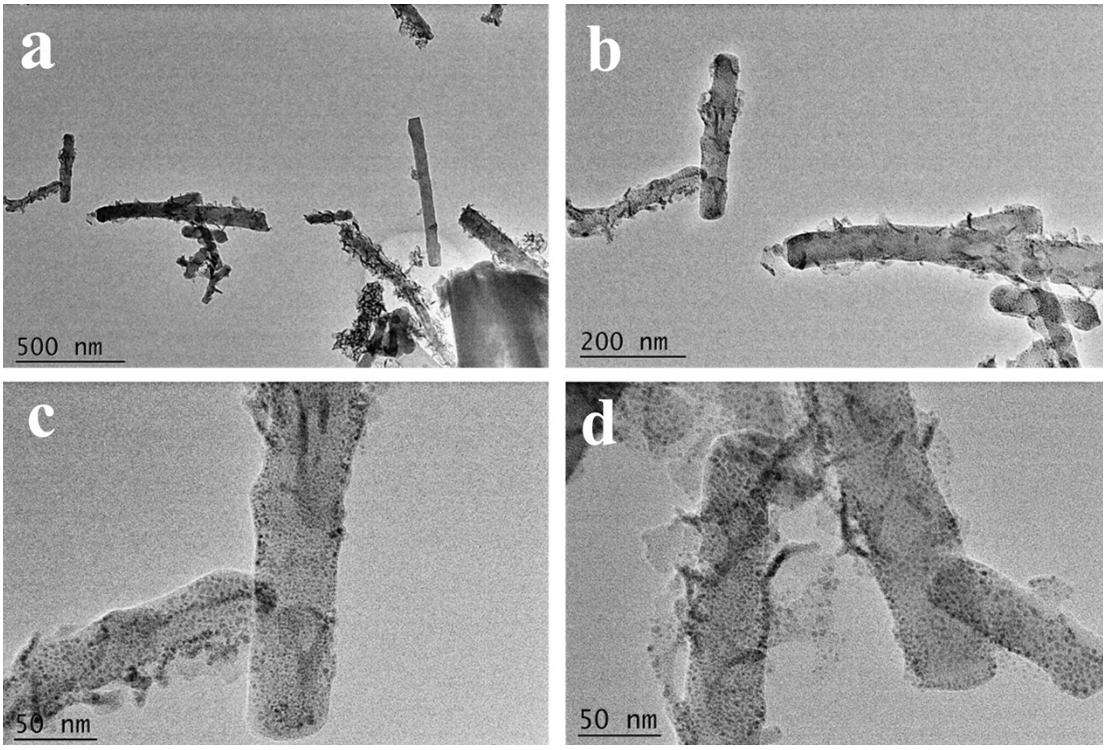


Figure S9 The TEM images of BTC-PRE precursor

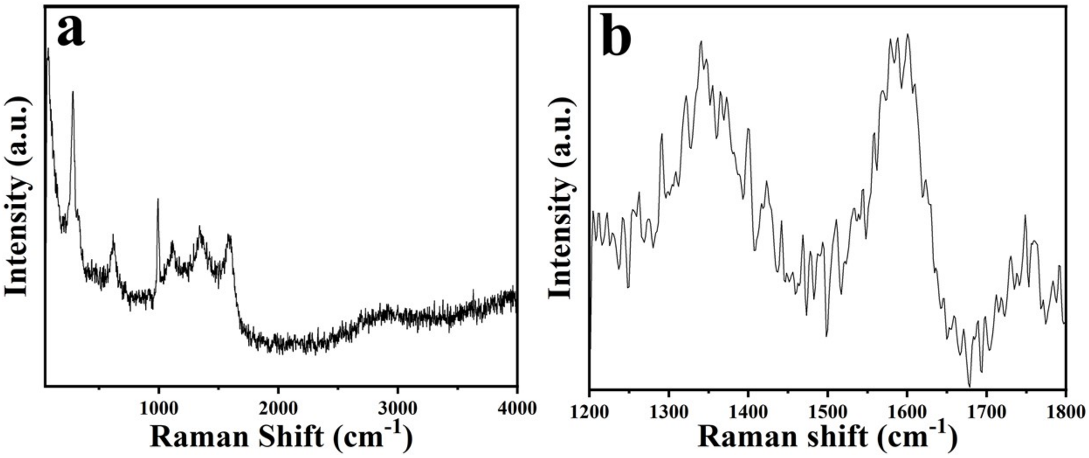


Figure S10 (a) The Raman curve of BTC-900 from 50 cm^{-1} to 4000 cm^{-1} Raman shift

(b) The Raman curve of BTC-900 from 1200 cm^{-1} to 1800 cm^{-1} Raman shift

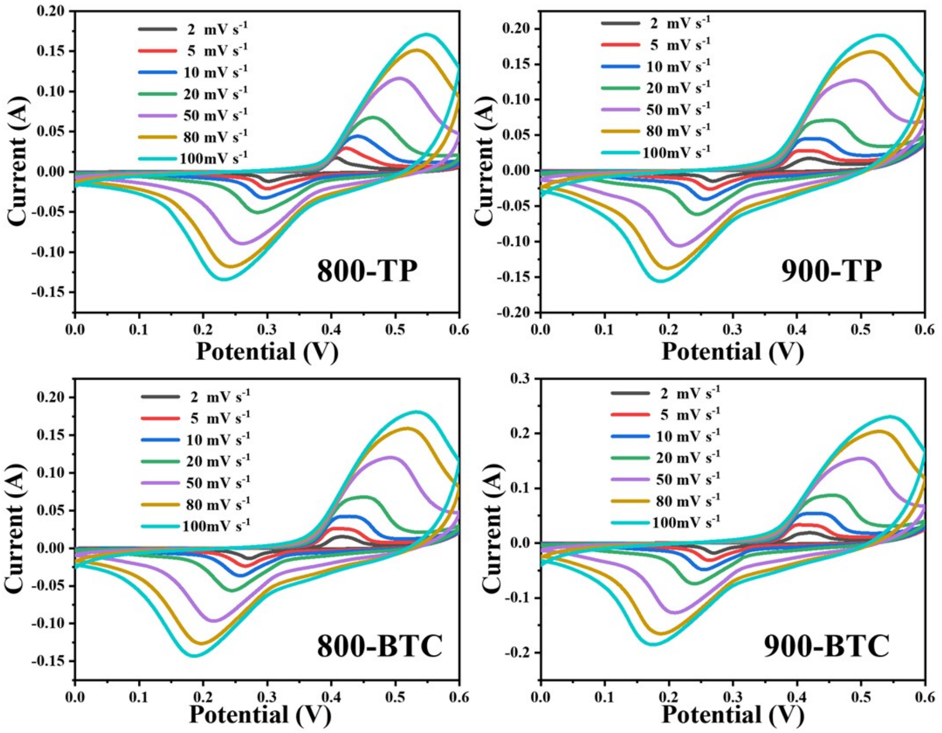


Figure S11 CV curves of 800-TP, 900-TP, 800-BTC and 900-BTC electrodes at different scan rates

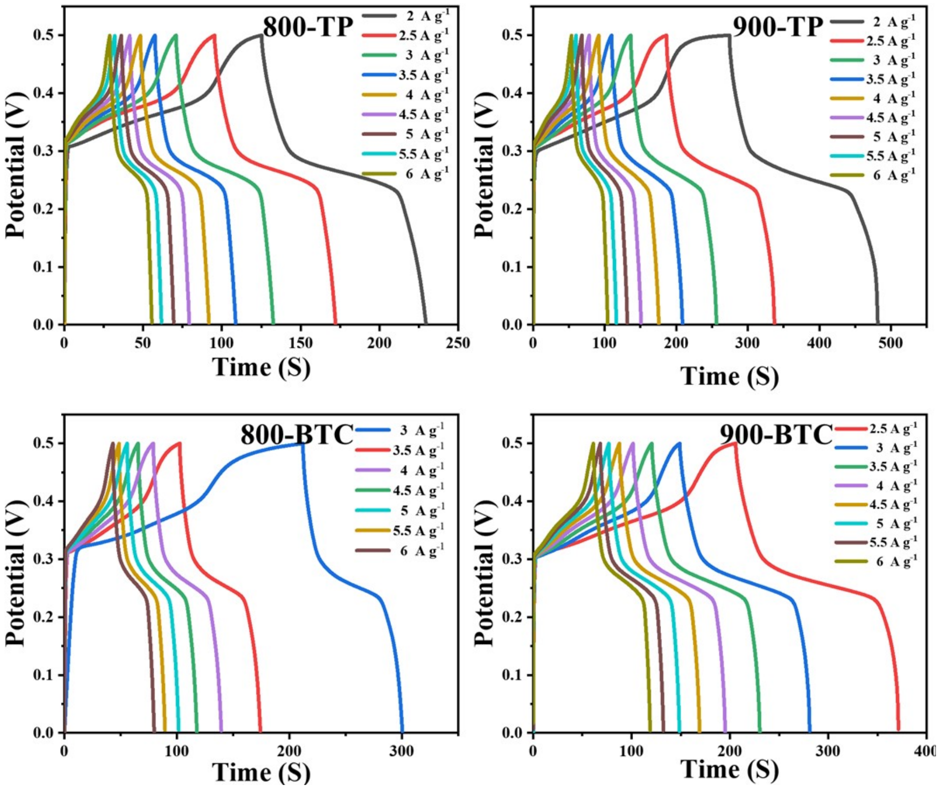


Figure S12 CP curves of 800-TP, 900-TP, 800-BTC and 900-BTC electrodes at different scan rates

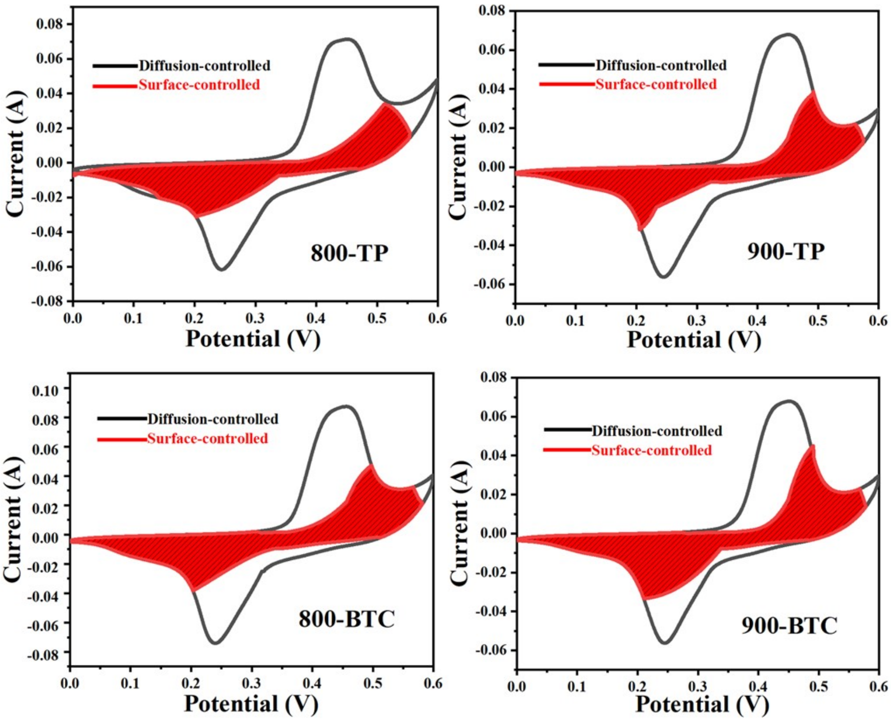


Figure S13 Voltammetric response for the as-prepared calcined sample electrodes at a sweep rate of 20 mV s^{-1}

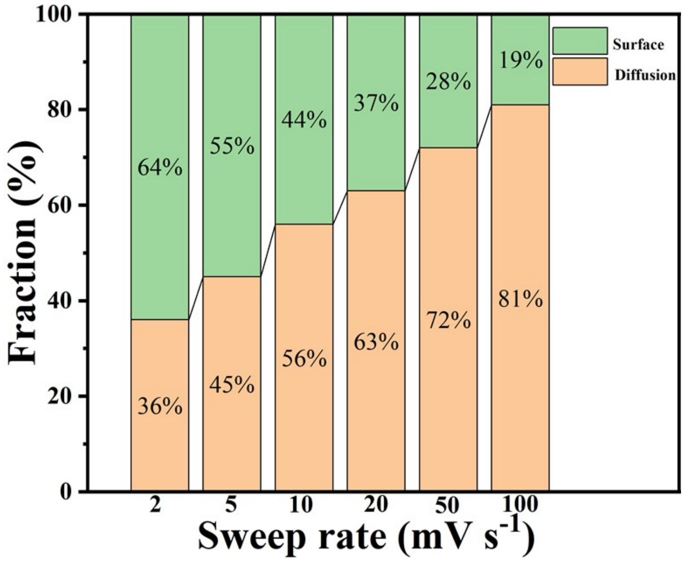


Figure S14 Normalized contribution ratio of surface/diffusion-controlled currents at various scan rates for 900-BTC

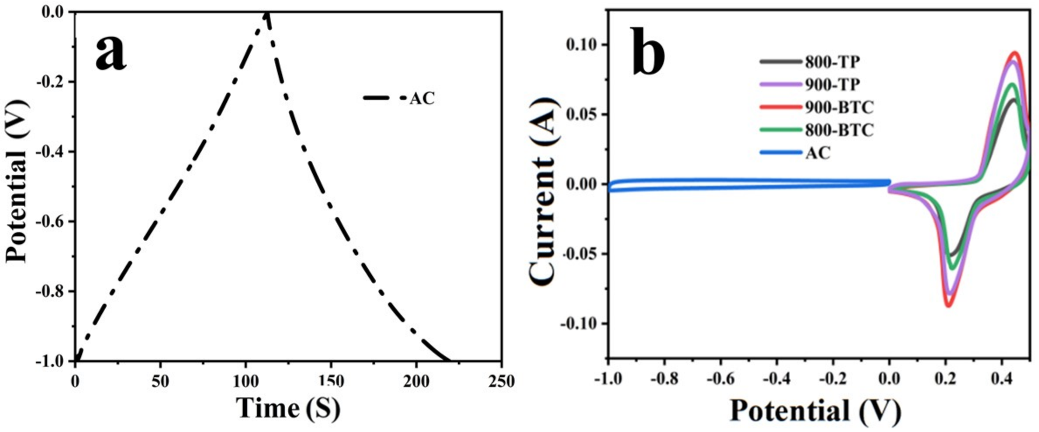


Figure S15 (a) CP curves of AC at a current density of 1 A g^{-1} in 6 mol L^{-1} KOH (b) CV curves of AC and calcined sample at a scan rate of 20 mV s^{-1}

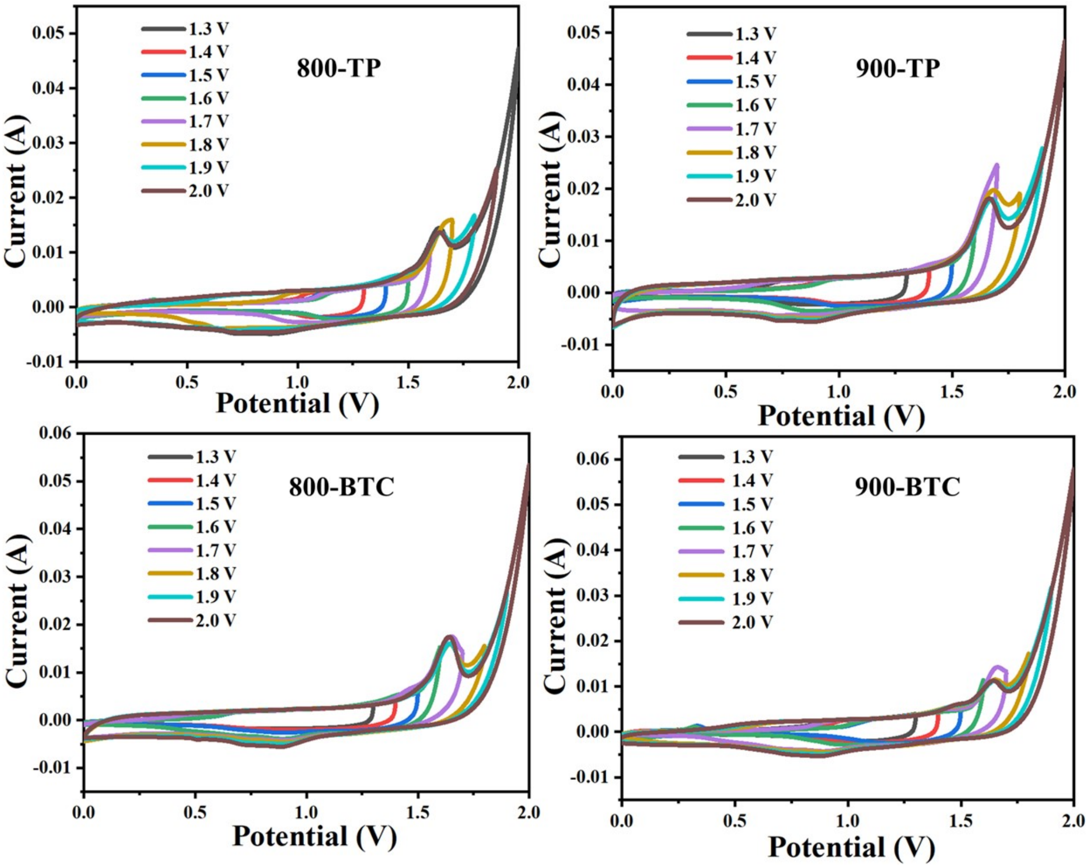


Figure S16 Polarization curves of 800-TP//AC, 900-TP//AC, 800-BTC//AC and 900-BTC//AC, respectively.

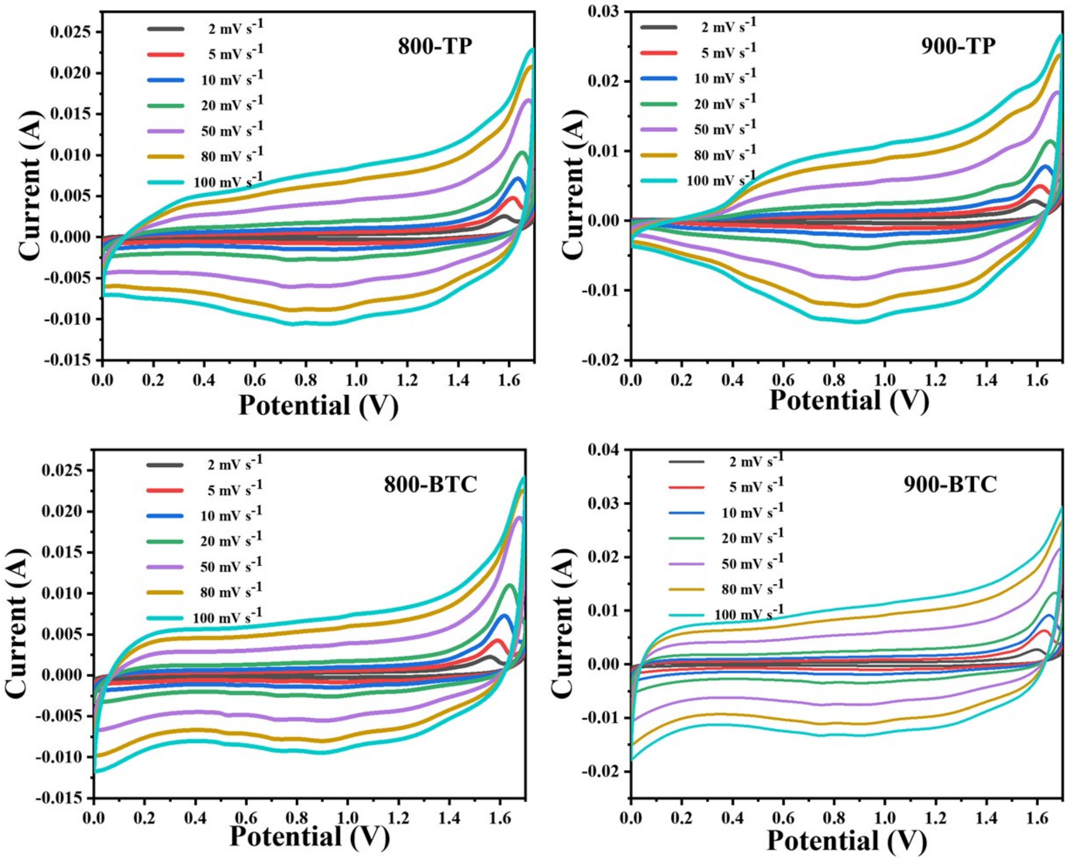


Figure S17 CV curve of 800-TP//AC, 900-TP//AC, 800-BTC//AC and 900-BTC//AC

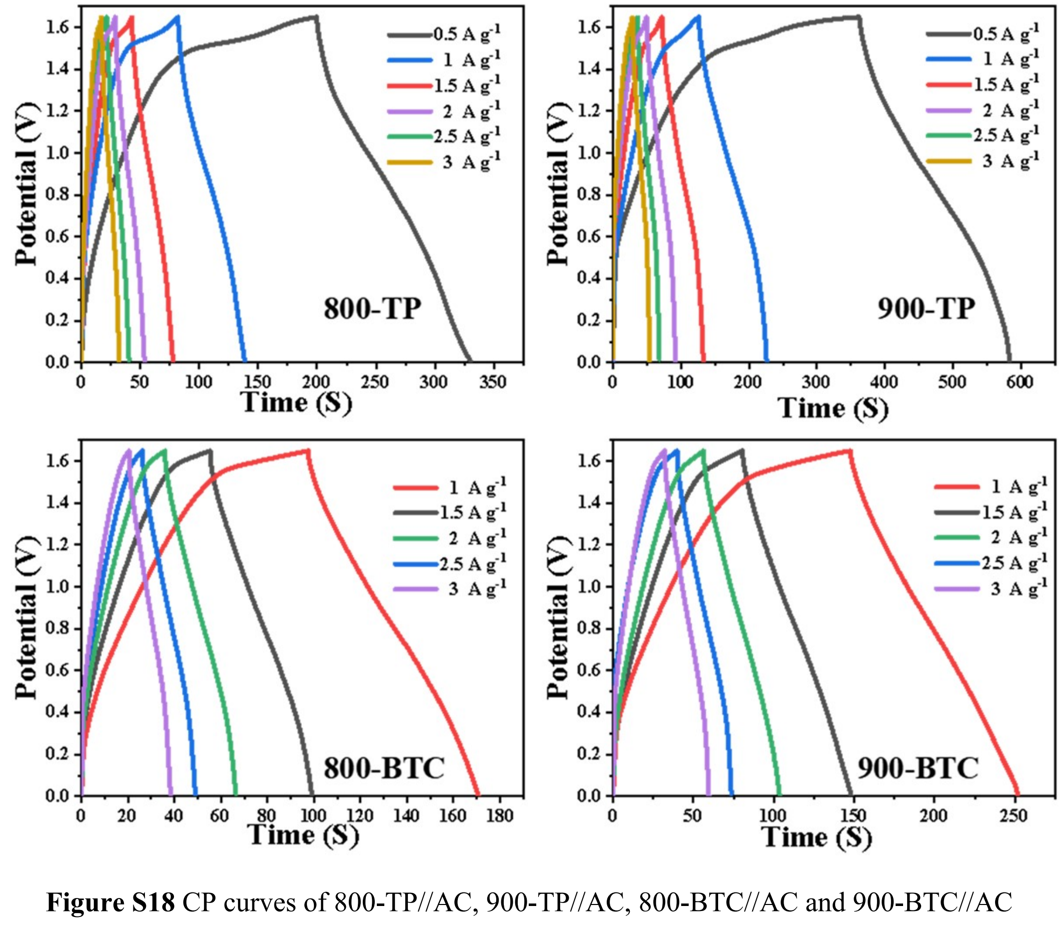


Figure S18 CP curves of 800-TP//AC, 900-TP//AC, 800-BTC//AC and 900-BTC//AC

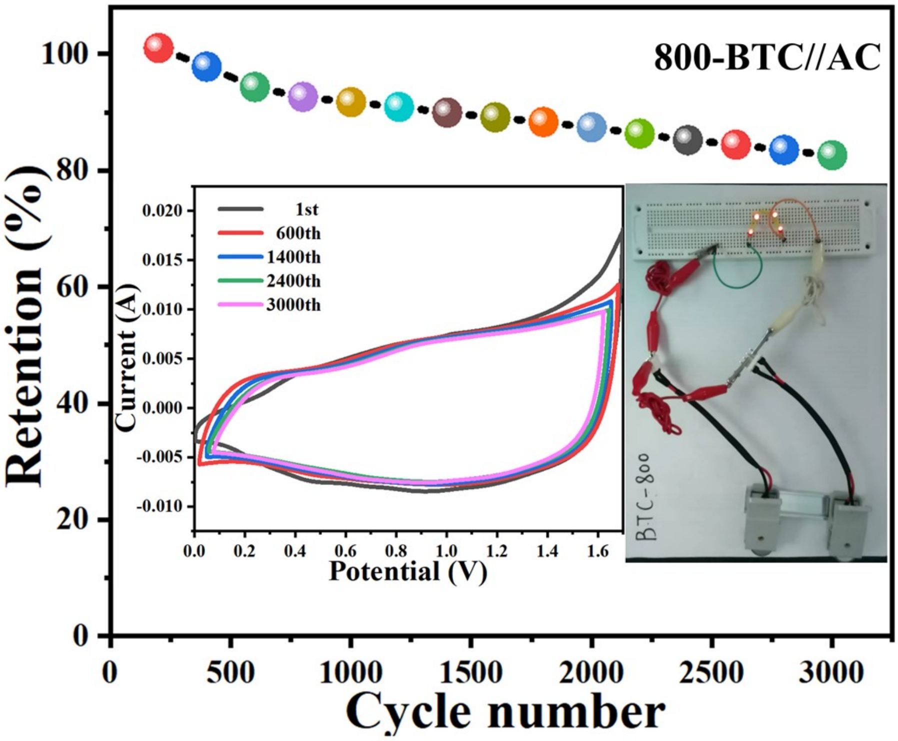


Figure S19 The endurance tests of the 800-BTC//AC device for 3000 cycles at 30 mV s^{-1}. Inset: CV curves at different cycles.

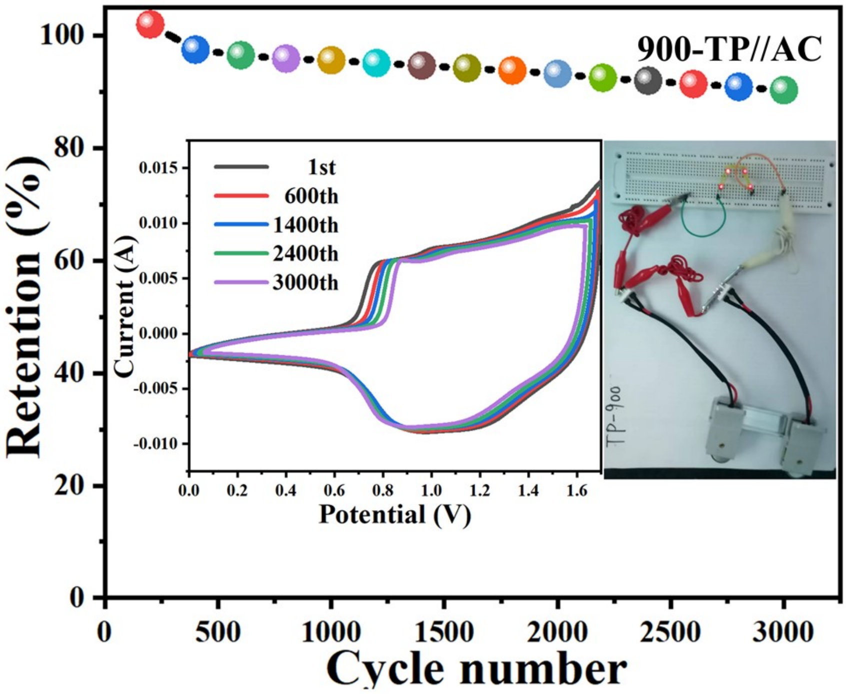


Figure S20 The endurance tests of the 900-TP//AC device for 3000 cycles at 30 mV s^{-1}. Inset: CV curves at different cycles.

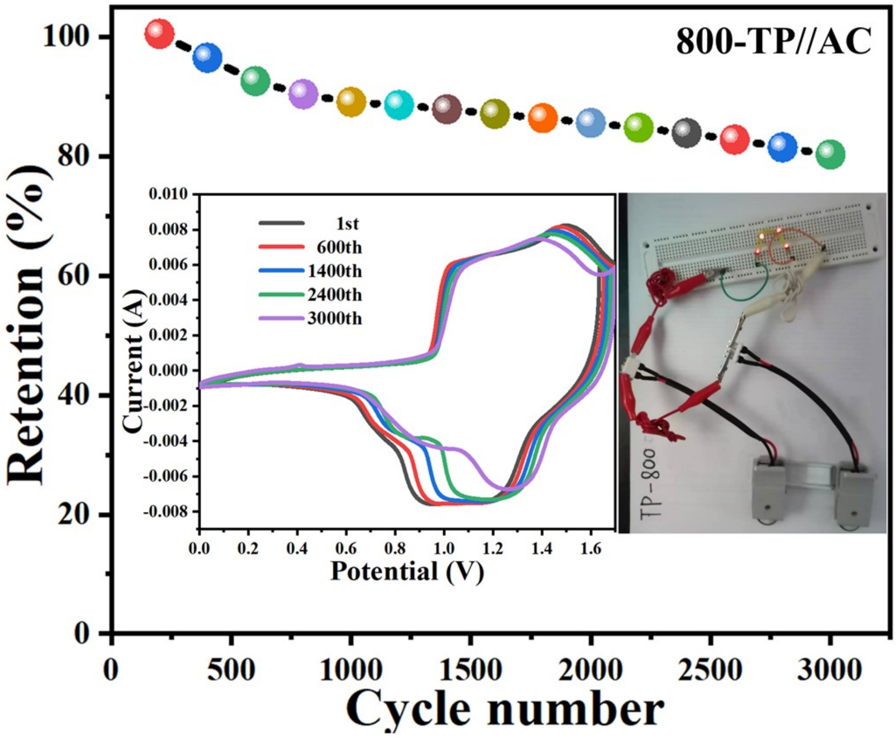


Figure S21 The endurance tests of the 800-TP//AC device for 3000 cycles at 30 mV s^{-1}. Inset: CV curves at different cycles.

Table S1 Carbon contents in the as-obtained MOFs-derived samples

Sample	C (At%)	O (At%)	Cu (At%)
800-TP	43.85	46.73	9.42
800-BTC	51.18	43.32	5.51
900-TP	80.36	13.67	5.97
900-BTC	82.10	13.78	4.12

Table S2 Comparison of specific surface area and pore-size of materials

	800-BTC	900-BTC	800-TP	900-TP
BET surface (m^2 g^{-1})	43.97	394.01	64.60	248.88
Average pore size (nm)	15.20	4.88	14.40	9.48

Table S3 The *b* values obtained from Dunn's equation

	800-BTC	900-BTC	800-TP	900-TP
The values of *b*	0.76	0.63	0.82	0.67

Table S4 Comparison of electrochemical properties of four materials

Sample	Specific Capacity (3A g^{-1})	Energy Density (825 W Kg^{-1})
800-TP	186 C g^{-1}	13.04 W h kg^{-1}
800-BTC	267 C g^{-1}	16.86 W h kg^{-1}
900-TP	364 C g^{-1}	22.89 W h kg^{-1}
900-BTC	396 C g^{-1}	24.01 W h kg^{-1}