

Supplementary Information

The structural transformation of metal-organic frameworks towards 2D carbon for desirable supercapacitor

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Experimental Section

Materials and Chemicals: Zn (NO₃)₂ 6H₂O, 1,3,5-Benzenetricarboxylic acid (BTC) and Potassium hydroxide (KOH) were purchased from Aladdin Biochemical Technology Co., Ltd.. Poly tetrafluoroethylene dispersion (PTFE, D210C) and acetylene black were purchased from Taiyuan LZY Technology Co. Ltd.. All reagents directly used without further purification. All the water used in the present study was deionized water.

Preparation of C-T: Synthesis of Zn-BTC: Zn (NO₃)₂ 6H₂O (8 g) and BTC (3.64 g) mixed in water (100 mL) with stirring 1h at 80 °C until precipitation finished. The resulting precipitation was collected by filter on commercial filter paper and washed thoroughly by deionized water. Finally, the precipitation was freeze-dried and white powers were prepared. The obtained samples were directly heated in an Ar atmosphere for 2h denoted as C-T, where T (700-1000 °C) indicates the pyrolysis temperature.

Characterizations: The morphologies of C-T samples were observed using a transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). The crystallographic structure of samples was determined by X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) where the samples were scanned from 10 to 90° at a scan speed of 0.02° s⁻¹. The carbon yield of Zn-BTC was probed by thermogravimetric analysis (TGA, Germany). Raman spectra were detected by the Renishaw inVia, UK Raman spectrometer system with a laser wavelength of 532 nm. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) methods and the pore size distribution was analyzed by the Barrett-Joyner-Halenda (BJH) model.

Electrochemical measurements: Three-electrode system: cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) curves of all samples were carried out on an electrochemistry workstation system (CHI 760E, CH Instruments Inc.) in a typical three-electrode system with Pt foil as the counter electrode, a Hg/HgO electrode as the reference electrode, and 6 M KOH aqueous solution as the electrolyte.

The working electrode was prepared as follows: carbon materials, acetylene black and PTFE were homogeneously mixed in ethanol/water mixture at a weight ratio of 8:1:1. Then the obtained slurry was pressed into the nickel foam (1 × 1 cm²), followed by drying at 50 °C for 12 h. The active material massing load of each electrode was approximately 2-4 mg cm⁻². CV tests were performed a potential window of -1~0 V at a scan rate from 10 to 100 mV s⁻¹. GCD tests were evaluated at different current densities of

0.5–20 A g⁻¹. EIS plot was recorded through the frequency range of 10000-0.01 Hz with a 10 mV sinusoidal voltage at open circuit potential. The specific capacitance of electrodes (C_s , F g⁻¹) was calculated from the discharge curves according to the following equation:

$$C_s = \frac{I \Delta t}{m \Delta V}$$

where I (A) is the constant current, Δt (s) is the discharge time, ΔV (V) represents the absolute discharge potential window, and m (g) corresponds to the total mass of the carbon materials.

For the test of two-electrode system, a symmetrical two-electrode device was fabricated in 6 M KOH electrolyte. The specific capacitance of the entire device (C_g , F g⁻¹), the energy density E (Wh kg⁻¹), power density P (W kg⁻¹) of the devices were calculated with the following equations:

$$C_g = \frac{I \Delta t}{m \Delta V}$$

$$E = \frac{C_g \Delta V^2}{7.2}$$

$$P = \frac{3600 E}{\Delta t}$$

where I (A) is the constant current, Δt (s) is the discharge time, ΔV (V) represents the absolute discharge potential window and m (g) corresponds to the total mass of the carbon samples.

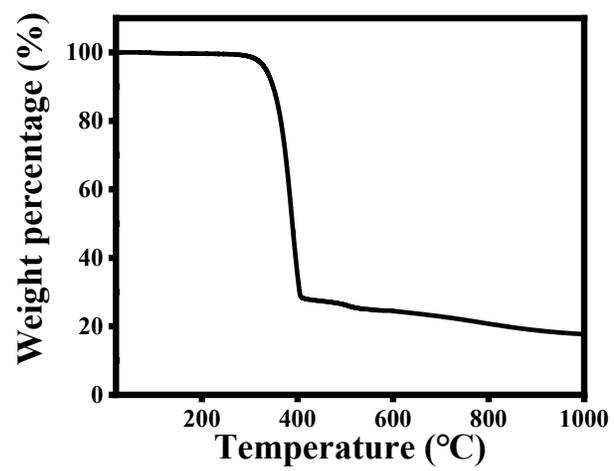


Figure S1. TGA curves of sample C-1000.

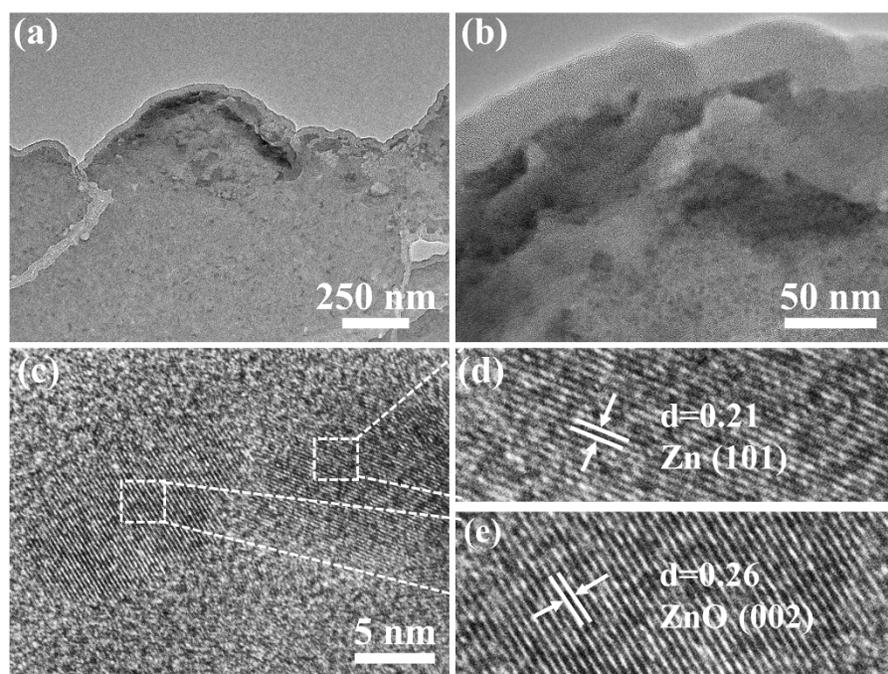


Figure S2. Typical TEM images of sample C-700 under different magnifications.

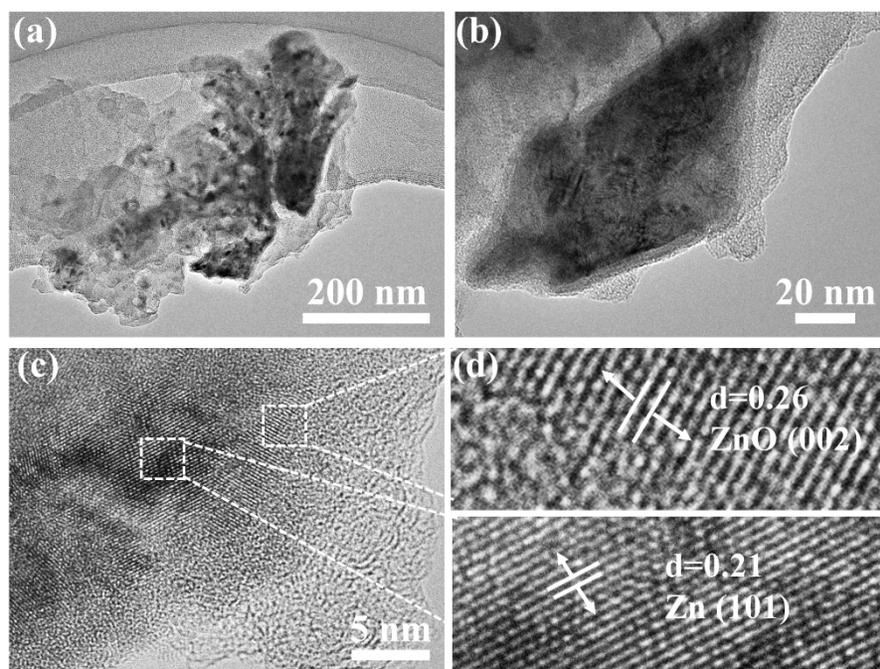


Figure S3. Typical TEM images of sample C-800 under different magnifications.

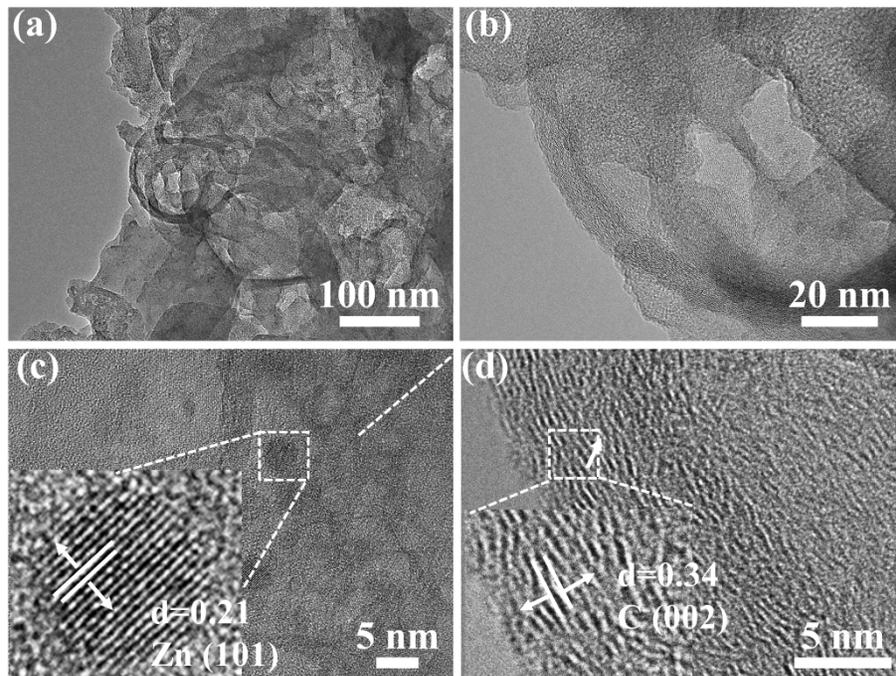


Figure S4. Typical TEM images of sample C-900 under different magnifications.

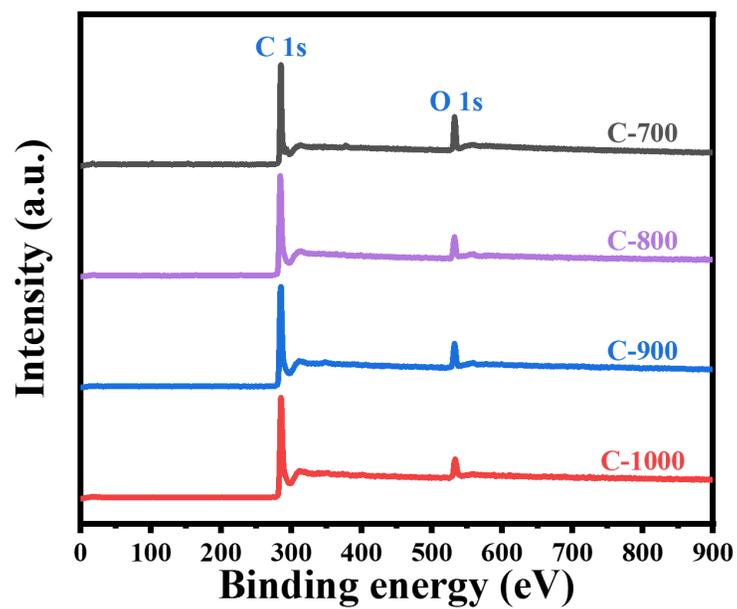


Figure S5. XPS survey spectra of samples C-700, C-800, C-900 and C-1000.

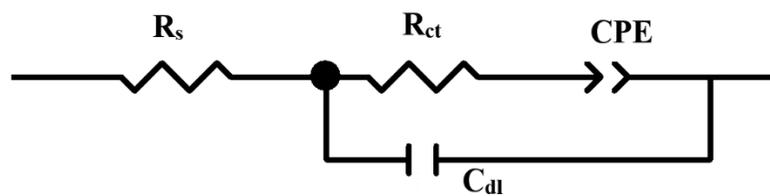


Figure S6. Equivalent circuit model for Nyquist plots of samples C-700, C-800, C-900 and C-1000.

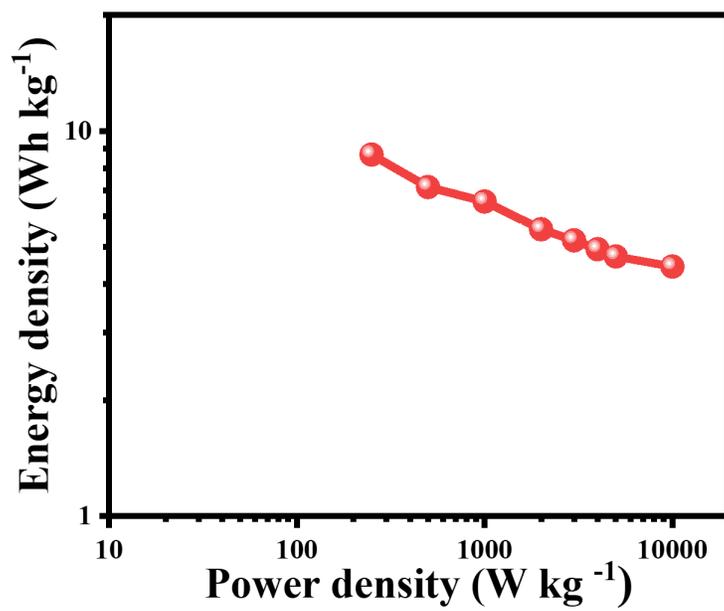


Figure S7. Ragone plots of SCs based on sample C-1000.

Table S1. Overview of the cycling stability of typical symmetric supercapacitors based on carbon electrodes ever reported.

Electrode materials	Current density (A/g)	Cycle number	Retention (%)	Rf.
PIC ₂ -24h	1	20000	94	1
Pc/SWCNTs.	3	5000	88.7	2
1-900	5	5000	90.4	3
Zn ₇ -1000	10	10000	96	4
SAC-MnO	5	5000	79.4	5
KDPC-20-600	20	10000	99	6
GPAC	10	10000	96.27	7
Ti ₃ C ₂ T _z /CNT@MnO ₂	10	10000	92.2	8
C-1000	4	30000	96	This work

SI Reference

1. X. Cui, G. Xu, Z. Gao, S. Zhu, Y. Zhao, X. Mo, Z. Gao, Z. Zheng and J. Zhang, *Energy Fuels*, 2023, **37**, 4038-4047.
2. L. Tong, T. Wang, Y. Chen, G. Lin, L. He and X. Liu, *Diam. Relat. Mater.* 2023, **134**, 109787.
3. Y. F. Wang, Y. Liang, Y. F. Wu, J. Yang, X. Zhang, D. Cai, X. Peng, M. Kurmoo and M. H. Zeng, *Angew Chem Int Ed. Engl*, 2020, **59**, 13232-13237.
4. T. Li, Y. F. Wang, Z. Yin, J. Li, X. Peng and M. H. Zeng, *Chem Sci*, 2022, **13**, 10786-10791.
5. H. Wang, H. Chen, X. Hou, H. Ye, Z. Guo, Z. Chen, Y. Jin, Y. Du and P. Ren, *Diam. Relat. Mater.*, 2023, **136**, 109888.
6. Q. Yin, X. Li, X. Yong, P. Sha, Q. Zhang, H. Dong, J. Sui, J. Yu, L. Yu and L. Dong, *Diam. Relat. Mater.*, 2023, **134**, 109798.
7. Y. Zeng, F. Zhang, J. Wu and J. Huang, *Mater. Adv.*, 2023, **4**, 2192-2200.
8. S. Li, Z. Peng, Y. Huang, L. Tan and Y. Chen, *J. Mater. Chem. A*, 2022, **10**, 23886-23895.