Supporting information

Hydrogen-bonded organic framework-derived, flower-on-fiber-

like, carbon nanofiber electrode for supercapacitors

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Fig. S1. (a, b) SEM images of MCA.



Fig. S2. FT-IR spectra of MA, CUA, and MCA.



Fig S3. (a, b) SEM images of PAN nanofibers.



Fig. S4. SEM images of (a, b) PAN@MCA_{0.125}, (c, d) PAN@MCA_{0.375}, and (e, f) PAN@MCA_{0.5} nanofibers.



Fig. S5. (a, b) Raman spectra of MCA, PAN, and PAN@MCA nanofibers.



Fig. S6. Stress-strain curves of c-PAN@MCA nanofibers.



Fig. S7. (a, b) SEM images of c-PAN nanofibers.



Fig. S8. SEM images of (a, b) c-PAN@MCA $_{0.125}$, (c, d) c-PAN@MCA $_{0.375}$, and (e, f) c-PAN@MCA $_{0.5}$ nanofibers.



Fig. S9. TEM images of (a, b) c-PAN, (c, d) c-PAN@MCA $_{0.125}$, (e, f) c-PAN@MCA $_{0.375}$, and (g, h) c-PAN@MCA $_{0.5}$ nanofibers.



Fig. S10. (a) TGA curves of PAN, PAN@MCA nanofibers, and MCA. (b) Experimental and theoretical remaining weight at 700 °C with various MCA contents.



Fig. S11. XRD patterns at low angle and FWHM values of (a) c-PAN. (b) c-PAN@MCA_{0.125}, (c) c-PAN@MCA_{0.25}, (d) c-PAN@MCA_{0.375}, and (e) c-PAN@MCA_{0.5}.



Fig. S12. Contact angle measurements for (a) c-PAN, (b) c-PAN@MCA $_{0.125}$, and (c) c-PAN@MCA $_{0.25}$.



Fig. S13. Enlarged views of high-resolution XPS C1s spectra of (a) c-PAN, (b) c-PAN@MCA_{0.125}, (c) c-PAN@MCA_{0.25}, (d) c-PAN@MCA_{0.375}, and (e) c-PAN@MCA_{0.5}.



Fig. S14. (a) Nitrogen contents of c-PAN and c-PAN@MCA nanofibers from high-resolution XPS N1s spectra. (b) Oxygen contents of c-PAN and c-PAN@MCA nanofibers from high-resolution XPS O1s spectra.



Fig. S15. CV curves of (a) c-PAN, (b) c-PAN@MCA_{0.125}, (c) c-PAN@MCA_{0.375}, and (d) c-PAN@MCA_{0.5} at various scan rates.



Fig. S16. GCD curves of (a) c-PAN, (b) c-PAN@MCA_{0.125}, (c) c-PAN@MCA_{0.375}, and (d) c-PAN@MCA_{0.5} at various current densities.



Fig. S17. Relationships between the peak current and scan rate for (a) c-PAN, (b) c-PAN@MCA_{0.125}, (c) c-PAN@MCA_{0.375}, and (d) c-PAN@MCA_{0.5}.



Fig. S18. Capacitive contributions at a scan rate of 100 mV s⁻¹ for (a) c-PAN, (b) c-PAN@MCA_{0.125}, (c) c-PAN@MCA_{0.375}, and (d) c-PAN@MCA_{0.5}. (f) Capacitive contributions at various scan rates for (e) c-PAN, (f) c-PAN@MCA_{0.125}, (g) c-PAN@MCA_{0.375}, and (h) c-PAN@MCA_{0.5}.



Fig. S19. Electrochemical performances of c-PAN@MCA_{0.25} with different mass loadings measured in a three-electrode configuration in 6 M aqueous KOH electrolyte. (a) CV curves of c-PAN@MCA_{0.25} with different mass loadings at a scan rate of 100 mV s⁻¹. CV curves of c-PAN@MCA_{0.25} with mass loadings of (b) 2 mg cm⁻² and (c) 4 mg cm⁻² at various scan rates. (d) GCD curves of c-PAN@MCA_{0.25} with different mass loadings at a current density of 1 A g⁻¹. GCD curves of c-PAN@MCA_{0.25} with mass loadings of (e) 2 mg cm⁻² and (f) 4 mg cm⁻²

at various current densities. (g) Specific capacitances at various current densities for c-PAN@MCA_{0.25} with different mass loadings. (h, i) Nyquist plots of c-PAN@MCA_{0.25} with different mass loadings.



Fig. S20. Electrochemical performances of c-PAN@MCA_{0.25} with different annealing temperatures measured in a three-electrode configuration in 6 M aqueous KOH electrolyte. (a) CV curves of c-PAN@MCA_{0.25} with different annealing temperatures at a scan rate of 100 mV s⁻¹. CV curves of c-PAN@MCA_{0.25} with annealing temperatures of (b) 600, (c) 800, and (d) 900 °C at various scan rates. (e) GCD curves of c-PAN@MCA_{0.25} with different annealing temperatures at a current density of 1 A g⁻¹. GCD curves of c-PAN@MCA_{0.25} with mass loadings of (f) 600, (g) 800, and (h) 900 °C at various current densities. (i) Specific capacitances at various current densities for c-PAN@MCA_{0.25} with different annealing temperatures.



Fig. S21. (a, b) Nyquist plots of c-PAN@MCA_{0.25} with different annealing temperatures.



Fig. S22. (c, b) SEM images of ground c-PAN@MCA_{0.25} nanofiber.



Fig. S23. Electrochemical performance measured in a two-electrode configuration in 1 M aqueous Na₂SO₄ electrolyte. (a) CV curves for free-standing and ground c-PAN@MCA_{0.25}-based symmetric SC at a scan rate of 100 mV s⁻¹, respectively. (b) CV curves of ground c-PAN@MCA_{0.25}-based symmetric SC at various scan rates. (c) GCD curves for free-standing and ground c-PAN@MCA_{0.25}-based symmetric SC at a current density of 1 A g⁻¹, respectively. (d) GCD curves of ground c-PAN@MCA_{0.25}-based symmetric SC at various current densities. (e) Specific capacitances of free-standing and ground c-PAN@MCA_{0.25}-based symmetric SC at various and ground c-PAN@MCA_{0.25}-based symmetric SC at various current densities, respectively. (f) Ragone plot for free-standing and ground c-PAN@MCA_{0.25}-based symmetric SCs, respectively.

To measure the electrochemical performance of powder-type c-PAN@MCA_{0.25}, ground c-PAN@MCA_{0.25} was mixed uniformly with carbon black, and poly(vinylidene fluoride) with a mass ratio of 8:1:1 and then pasted onto the nickel foam (1 x 2 cm²). The active mass in each electrode was fixed at 1 mg cm⁻².

| | $S_{\rm BET} ({ m m}^2 { m g}^{-1})$ | $V_{\text{total}} \left(\text{cm}^3 \text{ g}^{-1} \right)$ | $V_{\rm micro} ({\rm cm}^3 {\rm g}^{-1})$ | $V_{\rm meso} ({\rm cm}^3 {\rm g}^{-1})$ |
|----------------------------|--------------------------------------|--|---|--|
| c-PAN | 7.1 | 0.027 | 0.026 | 0.001 |
| c-PAN@MCA _{0.125} | 335.1 | 0.211 | 0.084 | 0.127 |
| c-PAN@MCA _{0.25} | 403.1 | 0.358 | 0.212 | 0.146 |
| c-PAN@MCA _{0.375} | 368.5 | 0.321 | 0.187 | 0.134 |
| c-PAN@MCA _{0.5} | 347.6 | 0.463 | 0.346 | 0.117 |

Table S1. BET surface area (S_{BET}), total pore volume (V_{total}), micropore volume (V_{micro}) and mesopore volume (V_{meso}) of c-PAN and c-PAN@MCA nanofibers.

| | C (at%) | N (at%) | O (at%) |
|----------------------------|---------|---------|---------|
| c-PAN | 87.8 | 8.8 | 3.4 |
| c-PAN@MCA _{0.125} | 83.4 | 11.9 | 4.7 |
| c-PAN@MCA _{0.25} | 82.1 | 13.5 | 4.4 |
| c-PAN@MCA _{0.375} | 81.3 | 14.7 | 4.0 |
| c-PAN@MCA _{0.5} | 80.6 | 15.4 | 4.0 |

Table S2. Atomic concentrations for c-PAN and c-PAN@MCA nanofibers.

| Electrode sample name | Specific capacitance (three-electrode configuration) | Energy density | Power density | Mass loading | Reference |
|---------------------------|--|---------------------------|-------------------------|--------------------------------------|-----------|
| | 338.6 F g ⁻¹ (1 A g ⁻¹) | 11.4 Wh kg ⁻¹ | 344 W kg ⁻¹ | 1 mg cm ⁻² | |
| c-PAN@MCA _{0.25} | 285.7 F g ⁻¹ (1 A g ⁻¹) | N/A | N/A | 2 mg cm ⁻² | This work |
| | 257.8 F g ⁻¹ (1 A g ⁻¹) | N/A | N/A | 4 mg cm ⁻² | |
| CLCF | 223.8 F g ⁻¹ (0.5 A g ⁻¹) | 5.9 Wh kg ⁻¹ | 1200 W kg ⁻¹ | 1.2 mg cm ⁻² | 1 |
| MCF | 105 F g ⁻¹ (5 mV s ⁻¹ , two- electrode configuration) | 5.1 Wh kg ⁻¹ | 242 W kg ⁻¹ | 0.44 mg cm ⁻² | 2 |
| P-CNF | 104 F g ⁻¹ (0.2 A g ⁻¹) | 3.22 Wh kg ⁻¹ | 600 W kg ⁻¹ | 0.51 mg cm ⁻² | 3 |
| PHCNF30 | 239 F g ⁻¹ (1 A g ⁻¹) | 5.28 Wh kg ⁻¹ | 500 W kg ⁻¹ | 2 mg cm ⁻² | 4 |
| C67 ₁₄ @PAN-OC | 270 F g ⁻¹ (1 A g ⁻¹) | 9.64 Wh kg ⁻¹ | 550 W kg ⁻¹ | N/A | 5 |
| NHCF | 302 F g ⁻¹ (0.5 A g ⁻¹) | N/A | N/A | 1 mg cm ⁻² | 6 |
| UT-CNF | 243 F g ⁻¹ (1 A g ⁻¹) | N/A | N/A | 1.2-1.4 mg cm ⁻² | 7 |
| CACNF | 202 F g ⁻¹ (0.1 A g ⁻¹) | N/A | N/A | 1.5 mg cm ⁻² | 8 |
| NFMCNF | 252.6 F g^{-1} (0.5 A g^{-1}) | 8.07 Wh kg ⁻¹ | 248 W kg ⁻¹ | N/A | 9 |
| N-CNT@CF | 367 F g ⁻¹ (0.5 A g ⁻¹) | 5.5 Wh kg ⁻¹ | 254 W kg ⁻¹ | 1.0-1.2 mg cm ⁻² | 10 |
| NC-800 | 264 F g ⁻¹ (1 A g ⁻¹) | N/A | N/A | 1.5 mg cm ⁻² | 11 |
| N-PCNFA | 279 F g ⁻¹ (0.5 A g ⁻¹) | N/A | N/A | N/A | 12 |
| PAN/NOC (7:3) | 394 F g ⁻¹ (1 A g ⁻¹) | 13.6 Wh kg ⁻¹ | 500 W kg ⁻¹ | 1.67 mg cm ⁻² (powder) | 13 |
| HPCNFs-N | 307.2 F g ⁻¹ (1 A g ⁻¹) | 10.96 Wh kg ⁻¹ | 250 W kg ⁻¹ | 1.0 mg cm ⁻² (powder) | 14 |
| NSCPCNF-800 | 396 F g ⁻¹ (1 A g ⁻¹) | 14.3 Wh kg ⁻¹ | 250 W kg ⁻¹ | 1.0 mg cm ⁻² | 15 |

Table S3. Summary of the electrochemical performance of c-PAN@MCA $_{0.25}$ and the state-of-the-art carbon nanofiber electrodes.

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Supplementary movie 2_c-PAN@N