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1 Supporting Information

² Solvent-assisted Structural Phase Transition of Zn-MOF from 2D to 3D

- ³ and its Microflower Superstructural Carbon for Supercapacitors
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19 1. Experimental

20 Materials

21 Zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, 99.0%), 2-Aminoterephthalic acid (BDN, 99%), methanol
22 (CH₃OH, 99.8%), ethanol (C₂H₅OH, 99.8%), 1-Propanol (C₃H₇OH, 99.5%), butyl alcohol (C₄H₉OH, 99.5%),

23 1-Hexanol (C₆H₁₃OH, 99.5%), 1-Octanol (C₈H₁₇OH, 99%), 1-Decanol (C₁₀H₂₁OH, 98%) were purchased

24 from Sigma-Aldrich. Deionized water was supplied by Sinopharm Chemical Reagent Co., Ltd. (China).

25 Preparation of ultrathin ZBN-M

In a typical process, 2-aminoterephthalic acid (0.054 g, 0.3 mmol) was ultrasonicated to dissolve in 20 mL of methanol and sonicated to form a transparent solution, followed by the addition of a solution of zinc acetate dihydrate (0.22 g, 1 mmol) in methanol (50 mL) and sonicated for 30 min. The precursor (P-ZBN) was centrifuged, washed with water and methanol three times separately (10 mL water or methanol every time), and then dispersed directly in the methanol (30 mL). The mixture was transferred into a Teflon-lined autoclave (50 mL capacity) and heated at 130 °C for 12 h. The solid products were collected by centrifugation, dried under vacuum at 80 °C, and denoted as ZBN-M.

For comparison, samples were prepared with other solvents, such as ethanol, n-propanol, n-butanol, and 1nonanol, instead of methanol, and the obtained products were named ZBN-E, ZBN-P, ZBN-B, and so on (shown in Table S1).

36 Preparation of ZBN-M-derived carbon

The products were placed in a ceramic boat and sintered in a tube furnace. The samples were pyrolyzed in N_2 atmosphere at 900 °C for 1 h at a ramping rate of 2 °C min⁻¹ and cooling down naturally. The black products were refluxed with hydrochloric acid (6.0 M, 10 mL), followed by washing with plenty of water, and marked as ZBN-M-900.

41 Characterization

42 The morphologies of the products were characterized by a scanning electron microscope (SEM, ZEISS Sigma-43 500) and transmission electron microscope (TEM, JEM-2100F). The crystallinity of the samples was 44 determined with a MAX250V13H X-ray powder diffractometer (PXRD, Rigaku) using Cu-K α radiation at a 45 scanning rate of 5° min⁻¹. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical states using a Thermo Fisher Scientific Escalab 250 Xi spectrometer, which equipped with a high-performance Al
Kα monochromatic x-ray source (1486.68 eV). Fourier transform infrared spectroscopy (FTIR, Nicolet 5700)
was applied to obtain the infrared absorption of the samples in the region 4000-650 cm⁻¹. Nitrogen (N₂)
adsorption-desorption data were obtained at 77 K using BELSORP-maxII.

50 1.4. Electrochemical measurements

Electrochemical tests were evaluated in a three-electrode or two-electrode system with a CHI-660E electrochemical workstation and a LAND battery tester (CT3002). A platinum (Pt) plate and a saturated calomel electrode (SCE) were employed as the counter and the reference electrodes, respectively. The working electrode was fabricated by homogeneously mixing the active material, acetylene black, and polytetrafluorethylene (PTFE) at a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone. The mixture was applied to a carbon fiber paper (CFP) with an area of 1 cm⁻² and then dried under vacuum at 80 °C for 12 h.

57 The specific capacitance (C_{sp} , F g⁻¹) was determined using the following equation in a three-electrode system:

$$C_{sp} = \frac{I \times \Delta t}{m \times \Delta E} \tag{1}$$

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59 Here, I/m (A/g) indicated the discharge current density, Δt (s) represented the discharge time, ΔE (V) showed 60 the potential window.

61 For the two-electrode system, the specific capacitance (C_{sp} , F g⁻¹) was calculated with the equation:

$$C_{sp} = \frac{4I \times \Delta t}{m \times \Delta E} \tag{2}$$

63 Where Δt (s), I/m (A/g), and ΔE (V) were the discharge time, the discharge current density, and the voltage 64 window, respectively.

65 The energy density (E, W h kg⁻¹) and the power density (P, kW kg⁻¹) of the symmetric supercapacitor cell 66 were calculated using the following equations:

$$E = \frac{1}{2 \times 3.6} C_T V^2 \tag{3}$$

$$P = \frac{E \times 3600}{\Delta t}$$
(4)

69 where C_T (F g⁻¹) was the specific capacitance of the supercapacitor cell, V (V) was the voltage change during

70 the discharge process, and Δt (s) was the discharge time.

71 **Table S1.** The preparation conditions for all samples synthesized in this work.

	S.		Temperature	Reaction time	
Sample	Source	Solvent	(°C)	(h)	
ZBN-DMF	P-ZBN	DMF	130	12	
ZBN-Water	P-ZBN	H ₂ O 130		12	
ZBN-Acetone	P-ZBN	Acetone	130	12	
ZBN-Toluene	P-ZBN	Toluene	130	12	
ZBN-M	P-ZBN	Methanol	130	12	
ZBN-E	P-ZBN	Ethanol	130	12	
ZBN-P	P-ZBN	1-Propanol	130	12	
ZBN-B	P-ZBN	1-Butanol	130	12	
ZBN-H	P-ZBN	1-Hexanol	130	12	
ZBN-O	P-ZBN	1-Octanol	130	12	
ZBN-Decanol	P-ZBN	1-Decanol	130	12	
ZBN-M-90	P-ZBN	Methanol	90	12	
ZBN-M-110	P-ZBN	Methanol	110	12	
ZBN-M-150	P-ZBN	Methanol	150	12	
ZBN-M-0.5	P-ZBN	H ₂ O	130	0.5	
ZBN-M-1	P-ZBN	H ₂ O	130	1.5	
ZBN-M-3.5	P-ZBN	H ₂ O	130	3.5	
ZBN-M-6	P-ZBN	H ₂ O	130	6	
ZBN-M-24	P-ZBN	H ₂ O	130	24	



Fig. S2. SEM images and particle size distribution histogram of as-synthesized ZBN-M microflowers.



Fig. S3. N₂ adsorption-desorption isotherm curves of (a) P-ZBN and (b) ZBN-M.



87 Fig. S4. FTIR spectra of ZBN-M.

Note: FTIR spectrum of ZBN-M presents weak adsorptions around 3300-3100 cm⁻¹, suggesting that the presence of amine groups and those peaks around 1600-1300 cm⁻¹ could be ascribed to carboxyl groups' symmetric and asymmetric vibrations.^{S1, S2}

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95 Fig. S5. (a) Survey XPS spectrum of ZBN-M. High-resolution XPS spectra for (b) C 1s and (c) N1s of 96 ZBN-M.



Fig. S6. Refined XRD spectra of (a) P-ZBN, (b) ZBN-M-1.0h, (c) ZBN-M-3.5h, and (d) ZBN-M. (e) 101 Calculated ratio of crystal phase in each sample.



- 105 Fig. S7. SEM images of ZBN-M synthesized in methanol for 0.5 h.



110 Fig. S8. SEM images of samples synthesized in (a) DMF, (b) Water, (c) Acetone, and (d) Toluene.



115 Fig. S9. SEM images and particle size distribution histogram of as-synthesized ZBN-M-900.



Fig. S12. Thermogravimetric pattern of ZBN-M under a nitrogen atmosphere.

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133 Fig. S13. SEM images of (a) ZBN-M-800, (b) ZBN-M-850, (c) ZBN-M-950 and (d) ZBN-M-1000.







147 Fig. S15. N₂ adsorption-desorption isotherm curves of (a) ZBN-M-800, (b) ZBN-M-850, (c) ZBN-M-950 and

148 (d) ZBN-M-1000.

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Fig. S17. Electrochemical performance of ZBN-M-900 (a-b) CV curves at 10 mV s⁻¹ and GCD curves at 1 A g^{-1} in (a-b) 1.0 M H₂SO₄, (c-d) 1.0 M Na₂SO₄, (e-f) 1.0 M KOH.

156 Note to Fig. S17:

157 CV and GCD were employed to investigate the electrolyte effect on the specific capacitance. A high specific 158 capacitance of 292 F g^{-1} was achieved in 1.0 M H_2SO_4 compared to 118 F g^{-1} and 186 F g^{-1} in 1.0 M Na_2SO_4

159 and 1.0 M KOH, respectively.



161 **Fig. S18.** Electrochemical performance of ZBN-M-*x* carbonized at different temperatures (*x* denotes the 162 carbonization temperature; 800, 850, 900, 950 and 1000 °C). (a) CV curves at 10 mV s⁻¹, (b) GCD curves at 163 1 A g⁻¹ in 1.0 M H₂SO₄, (c) the histogram of specific capacitances.

164 Note to Fig. S18:

165 CV and GCD were employed to investigate the contribution of calcination temperatures to the specific 166 capacitance.



Fig. S19. Electrochemical performance of synthesized samples calcined at 900 °C. CV curves at 10 mV s⁻¹,
GCD curves at 1 A g⁻¹ in 1.0 M H₂SO₄ and the histogram of specific capacitances: (a-c) different solvents,
(d-f) different alcohols, (g-i) different hydrothermal temperatures, (j-1) different reaction time.



Fig. S20. (a-d) SEM images of IRMOF-3. Electrochemical performance of IR-MOF-3 calcined at 900 °C: (e)
CV curves at scan rates from 1 mV s-1 to 20 mV⁻¹, (f) GCD curves and (g) specific capacitances at varying
current densities.



193 Fig. S21. SEM image of ZBN-M-900 (a-c) before and (d-f) after cycling tests.



198 Fig. S22. XRD patterns of ZBN-M-900 (a) before and (b) after cycling tests.

		Current	Specific	Energy	Power	
Sample	Electrolyte	density	capacitance	density	density	Reference
		(A g ⁻¹)	(F g ⁻¹)	(Wh kg ⁻¹)	(W kg-1)	
ZBN-M-900	1.0 M H ₂ SO ₄	0.5	308.25	43.29	499.98	This work
B, N dual-doped hierarchical porous carbon	1.0 M H ₂ SO ₄	1	236.9	33.3	212.5	[S3]
nitrogen-rich mesoporous carbons	6.0 M KOH	0.5	300	8.3	1105	[S4]
nitrogen-doped hierarchical porous carbon nanosheets	6.0 M KOH	0.5	347	25.7	90	[85]
N, S, and O-doped carbon	1.0 M Na ₂ SO ₄	1	352	25.2	180	[S6]
Nitrogen-doped carbon nanospheres	6.0 M KOH	1	432	9.2	23240	[S7]
O, N co-doped activated carbon aerogels	3.0 M H ₂ SO ₄	2	342	3.8	246	[S8]
N/P co-doped carbon	6.0 M KOH	0.5	212	10.61	400	[S9]
B/S co-doped porous carbon	1.0 M Na ₂ SO ₄	0.5	290	16.65	450	[S10]
Hierarchical porous carbon nanorods	6.0 M KOH	0.5	274	6.77	100	[S11]
N-doped carbon nanotubes	6.0 M KOH	1	336	17.2	300	[812]
Carbon nanorod	2.0 M H ₂ SO ₄	0.5	198	22	2030	[S13]
Porous carbon nanowires	$1.0 \text{ M} \text{H}_2\text{SO}_4$	1	185	13.9	1000.8	[S14]
Defects-rich porous carbon nanosheets	6.0 M KOH	1	277	5.54	50000	[S15]



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Fig. S23. SEM images (a-b) and XRD patterns (c) of samples in SSC after cycling tests, Cycle test of SSC at a current density of 10 A g^{-1} (Inset: the first and last 20 cycles of 10,000 cycles).

Note: Fig. S23a shows that the capacitive retention is 99.4% after 10000 charge-discharge cycles and the inset shows similar cycling curves during the first and last 20 periods, which revealing the cycling reliability of the ZBN-M-900 in SSC device. This was further proved with the SEM images (Fig. S23b,c) and XRD analysis (Fig. S23d) after the test, which showed no significant changes in the morphology or structure.

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