Electronic Supplementary Information

From assembled metal-organic framework nanoparticles to hierarchically porous carbon for electrochemical energy storage

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1. Chemicals and Instrumentation

Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, Wako Pure Chemical Industries, Ltd.), triethylamine (TEA, Chameleon reagent) and 2-methylimidazole (MeIM, Tokyo Chemical Industry Co., Ltd.) were used as received.

A bath sonicator (VELVO, VS-N100S, 100 W, 40 kHz) was used for the experiments with ultrasonication. Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku Rint 2000 X-ray diffractometer with Cu Kα. Scanning electron microscopic SEM images were recorded on a JEOL JSM-6390 scanning electron microscope. Transmission electron microscope (TEM, FEI TECNAI G^2) and energy-dispersive X-ray spectroscopy (EDS) were applied for the detailed microstructure and composition information.

2. Experimental Section

2.1 Preparation of S-ZIF-8: A methanolic solution (500 mL) of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, 7.4350 g, 25 mmol) was added into a methanolic solution (500 mL) of 2-methylimidazole (2.0520 g, 25 mmol) and triethylamine (3.2675 g, 36 mmol) in 2 min with ultrasonication at ambient temperature, giving a turbid solution. The turbid solution was allowed to stand for 4 h and then centrifuged to give a white solid, which was washed for five times with methanol and then dried at 80 °C for 4 h to afford S-ZIF-8.

2.2 Preparation of sonicated ZIF-8-derived carbon (S-ZC-800): The S-ZIF-8 sample (4.0 g) was transferred into a ceramic boat and placed into a temperature-programmed furnace under an argon flow, heated from room temperature to 800 °C in 1 h, and then kept at 800 °C for 10 h and cooled down to room temperature. The resultant black material was washed several times with a HCl (5 vol% in water) solution, followed by washing with plenty of distilled water and dried at 80 °C for 12 h to afford S-ZIF-8-derived carbon, S-ZC-800.

2.3 Preparation of sonicated ZIF-8-derived and activated carbon (AS-ZC-800): The above prepared S-ZC-800 (1.0 g) and KOH (2.0 g) were mixed in water (10 mL) and allowed to stand for 4 h, followed by drying at 80 °C for 4 h to give the S-ZC-800/KOH composite, which was then transferred into a temperature-programmed furnace and heated to 800 °C with a heating rate of 10 °C min^{-1} under an argon flow. The composite was kept at 800 °C for 1 h and then cooled down to room temperature in the argon atmosphere. The obtained material was washed with plenty of water and dried at 80 °C for 12 h to afford S-ZIF-8-derived and activated carbon, AS-ZC-800.

2.4 Preparation of ZIF-8: A methanolic solution (500 mL) of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, 7.4350 g, 25 mmol) was added into a methanolic solution (500 mL) of 2-methylimidazole (2.0520 g, 25 mmol) and triethylamine (3.2675 g, 36 mmol) in 2 min with stirring at ambient temperature, giving a turbid solution. The turbid solution was allowed to stand for 4 h and

then centrifuged to give a white solid, which was washed for five times with methanol and then dried at 80 °C for 4 h to afford ZIF-8.

2.5 Preparation of ZIF-8-derived carbon (ZC-800): The ZIF-8 sample (4.0 g) was charged into a ceramic boat and placed into a temperature-programmed furnace under an argon flow, heated from room temperature to 800 °C in 1 h, and then kept at 800 °C for 10 h and cooled down to room temperature. The resultant black material was washed for several times with a HCl (5 vol% in water) solution, followed by washing with plenty of distilled water and dried at 80 °C for 12 h to afford ZIF-8-derived carbon, ZC-800.

2.6 Preparation of ZIF-8-derived and activated carbon (A-ZC-800): The above prepared ZC-800 (1.0 g) and KOH (2.0 g) were mixed in water (10 mL) and allowed to stand for 4 h, followed by drying at 80 °C for 4 h to give the ZC-800/KOH composite, which was then transferred into a temperature-programmed furnace and heated to 800 °C with a heating rate of 10 °C min^{-1} under an argon flow. The composite was kept at 800 °C for 1 h and then cooled down to room temperature in the argon atmosphere. The obtained material was washed with plenty of water and dried at 80 °C for 12 h to afford ZIF-8-derived and activated carbon, A-ZC-800.

3. Electrochemical Measurements

3.1 Capacitor Construction: All electrochemical measurements were carried out in a two-electrode cell (capacitor) with an aqueous solution of sulfuric acid (1.0 M) as electrolyte (each electrode containing 2.0 mg carbon without adding any binder and conductive agents), in which a glassy paper separator was sandwiched between two electrodes and platinum plates were used as electronic collectors. Two identical electrodes were adopted as cathode and anode for the cell configuration.

3.2 Electrochemical Measurements: The electrochemical experiments were performed under ambient conditions. Before the measurements, the capacitor cell was evacuated for 3 h to allow the active material fully soaked in the electrolyte. Cyclic voltammograms at different sweep rates for the capacitor were carried out on a Solartron electrochemical workstation (S1 1287). The specific capacitance is calculated according to the following equation (**1**):

$$C = 2 \times \Delta Q / (\Delta V \times m) \qquad (\mathbf{1})$$

where ΔQ is the charge integrated from the whole voltage range, ΔV is the whole voltage difference, and m is the mass of carbon on an electrode. Galvanostatic charge/discharge examinations at various current densities were performed on a Solartron electrochemical workstation (S1 1287) and a voltage range of 0 to 1 V was set. Specific capacitance of each electrode was calculated according to the following equation (**2**):

$$C = 2 \times I \times \Delta t / (\Delta V \times m) \qquad (\mathbf{2})$$

where I is the discharge current, Δt is the discharge time from 1 to 0 V, ΔV is the voltage difference within the discharge time Δt, and m is the mass of carbon on an electrode. The factor of two in these equations comes from the fact that the total capacitance measured from the test cells is the sum of two equivalent single electrode capacitors in series.

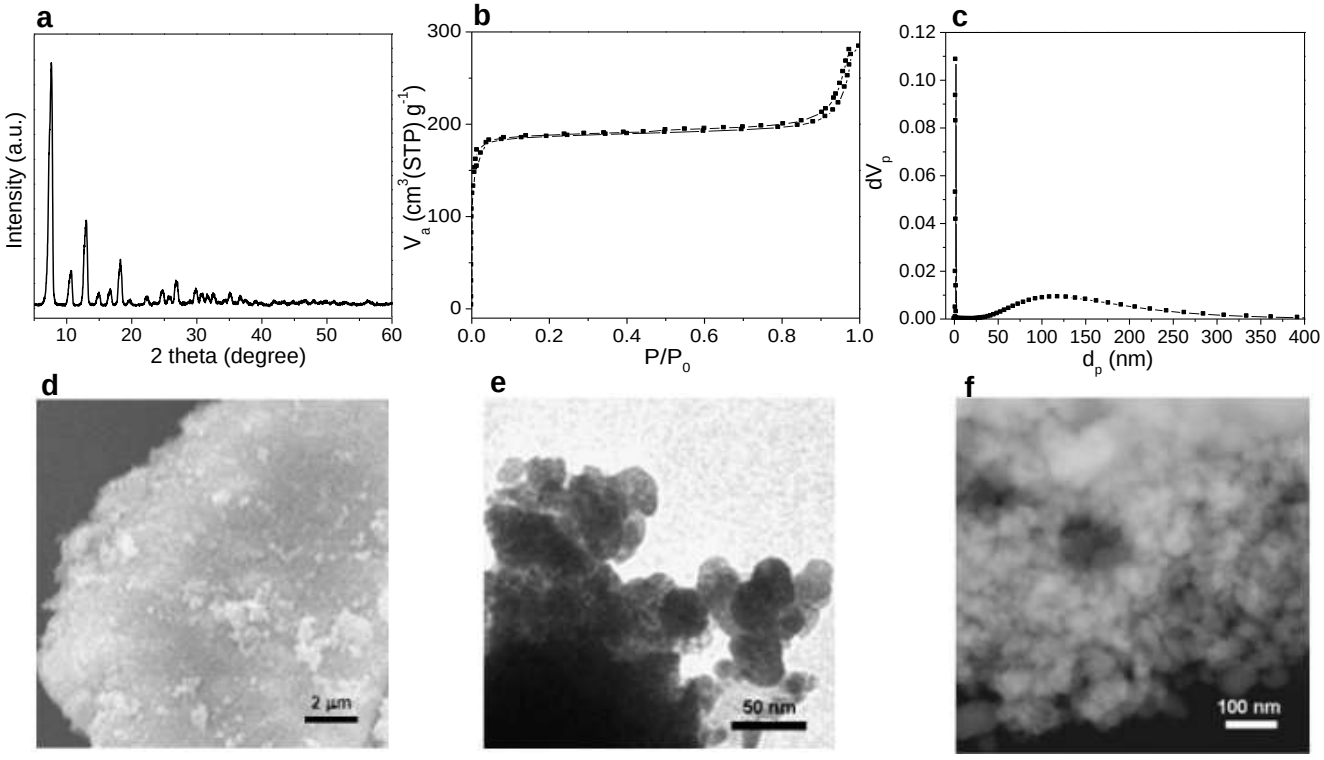

Fig. S1 (a) PXRD, (b) N_2 adsorption-desorption isotherms at 77 K, (c) the corresponding NL-DFT pore size distribution, and (d) SEM, (e) TEM and (f) HAADF-STEM images of S-ZIF-8, the ZIF-8 prepared with ultrasonication.

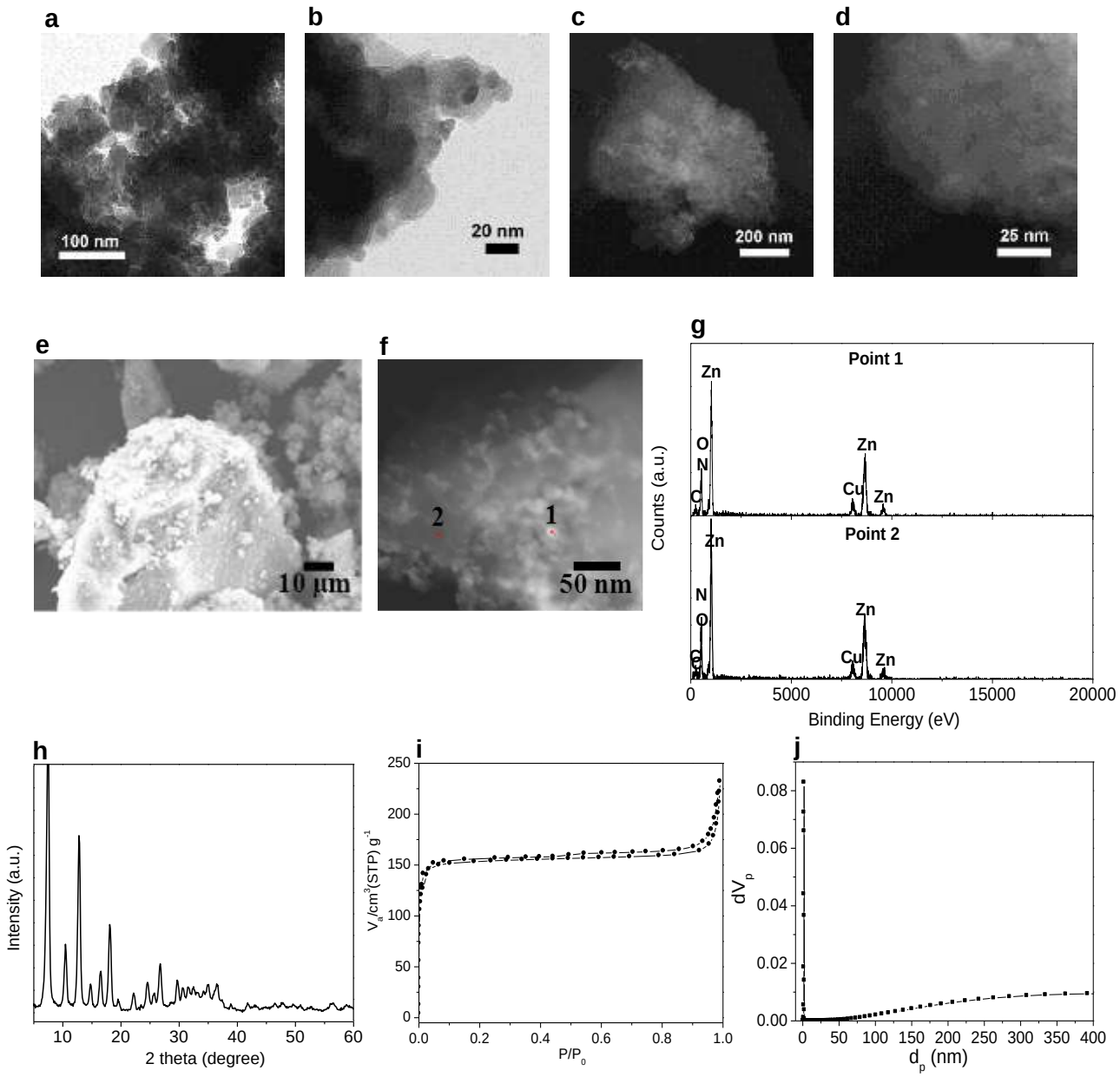

Fig. S2 (a, b) TEM, (c, d, f) HAADF–STEM and (e) SEM images and (g) the corresponding EDS spectra for selected points in (f), (h) PXRD, (i) N_2 adsorption-desorption isotherms at 77 K, and (j) the corresponding NL-DFT pore size distribution of ZIF-8. The copper peaks in (g) arise from the TEM grid.

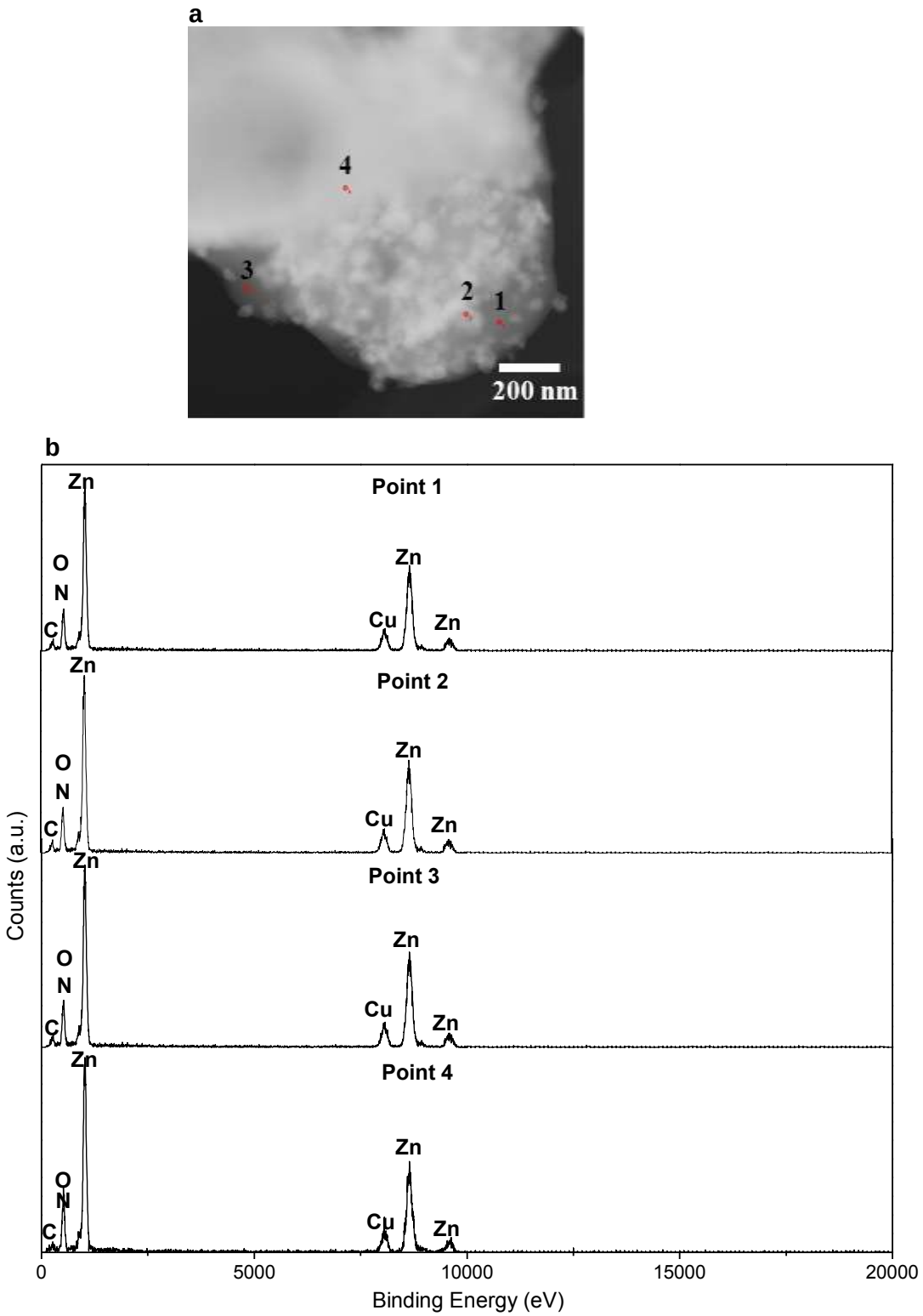

Fig. S3 (a) HAADF–STEM image of S-ZIF-8 and (b) the corresponding EDS spectra for selected points in (a). The copper peaks arise from the TEM grid.

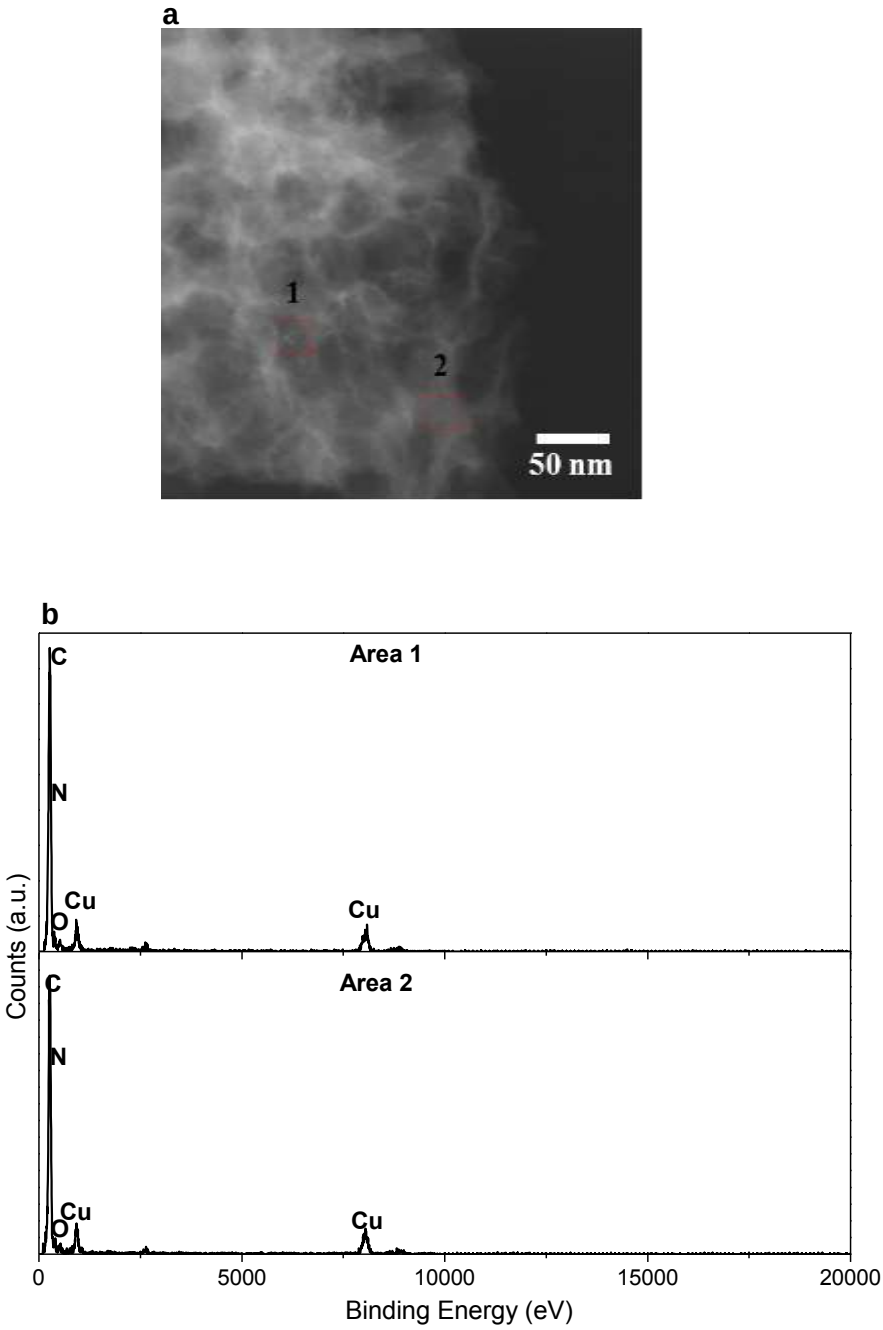

Fig. S4 (a) HAADF–STEM image of S-ZC-800, and (b) the corresponding EDS spectra for selected areas in (a). The copper peaks arise from the TEM grid.

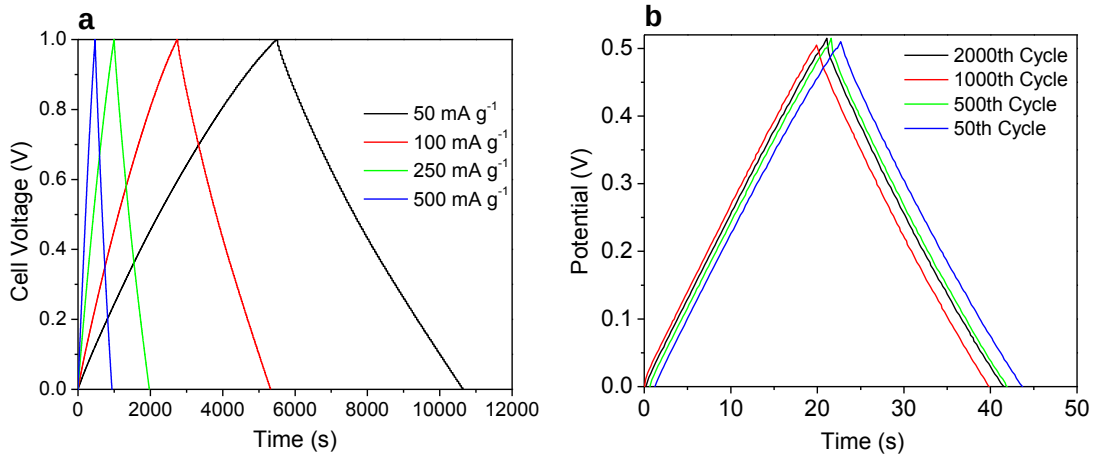

Fig. S5 Galvanostatic charge/discharge curves for AS-ZC-800 (a) at low current densities, and (b) for various cycles at current density 5A g^{-1}.

Table S1 Specific capacitance at different sweep rates for supercapacitor based on AS-ZC-800 with 1.0 M H_2SO_4 solution as electrolyte.

Sweep rate ($mV\ s^{-1}$)	Specific capacitance ($F\ g^{-1}$)
5	214
10	211
20	210
50	208
100	206
200	200
300	196
400	187

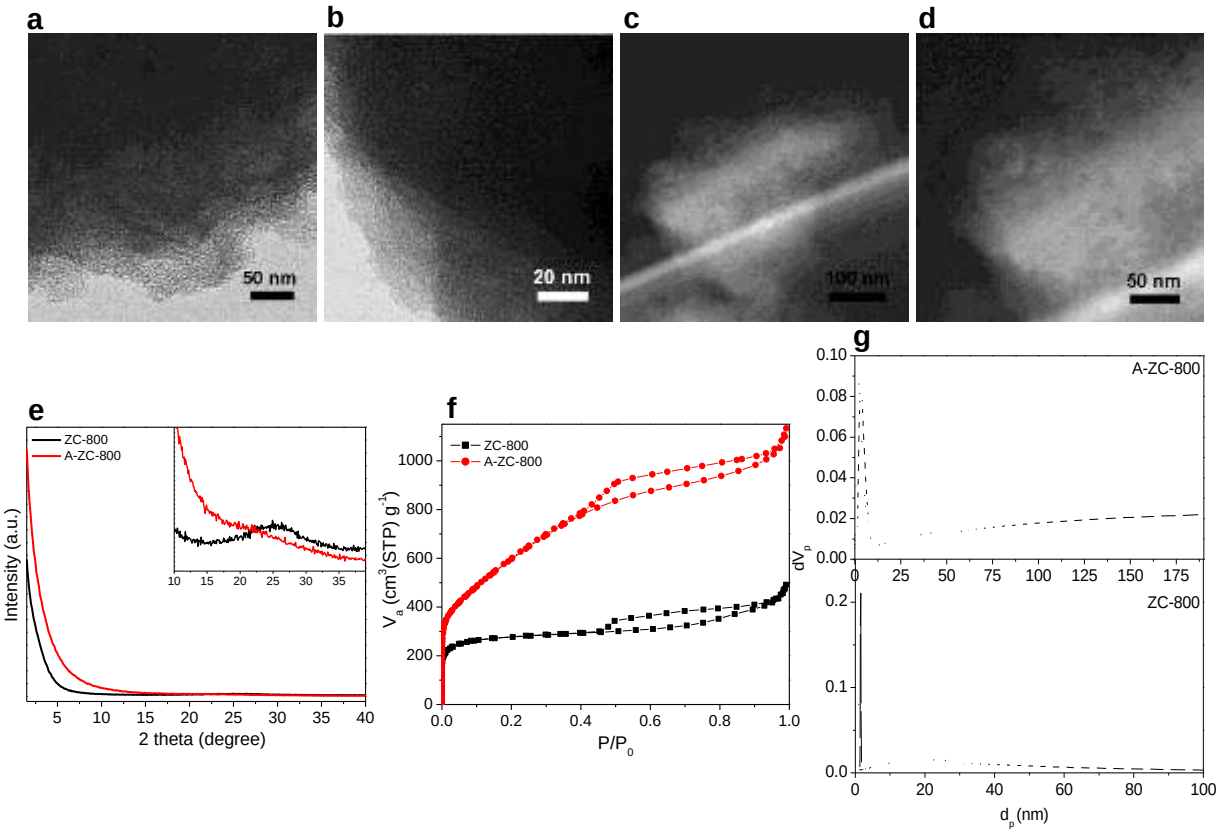

Fig. S6 (a, b) TEM and (c, d) HAADF–STEM images of ZC-800 and (e) PXRD patterns (inset: enlarged view to show the diffraction from the 002 plane of carbon), (f) N_2 adsorption-desorption isotherms at 77 K, and (g) the corresponding NL-DFT pore size distributions of ZC-800 and A-ZC-800.

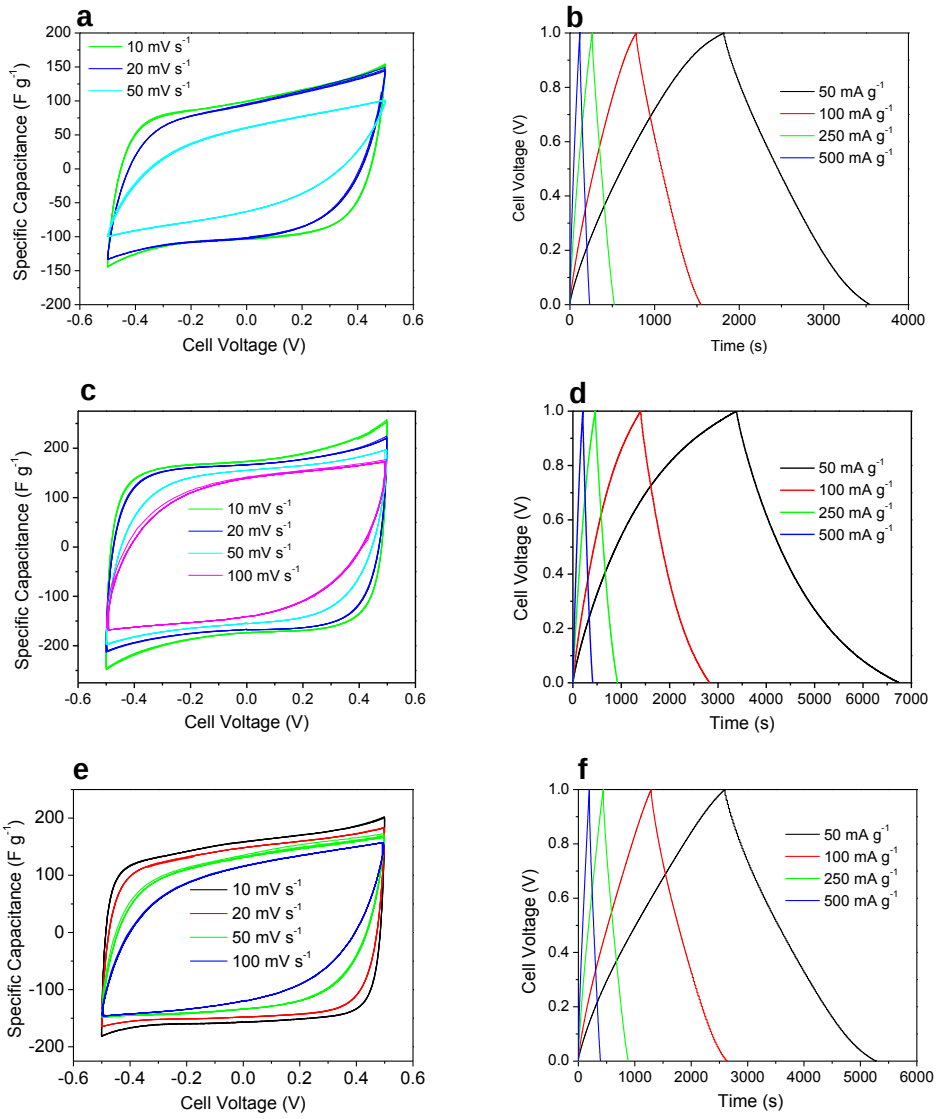

Fig. S7 Cyclic voltammograms at different scan rates and galvanostatic charge/discharge curves at different current densities for (a, b) ZC-800, (c, d) A-ZC-800, and (e, f) S-ZC-800, respectively.

Table S2. Specific capacitance at different sweep rates for supercapacitors based on various carbons with 1.0 M H_2SO_4 solution as electrolyte.

Sweep rate ($mV\ s^{-1}$)	Specific capacitance ($F\ g^{-1}$)			
	ZC-800	S-ZC-800	A-ZC-800	AS-ZC-800
10	104	158	170	211
20	96	148	165	210
50	63	136	155	208
100	-	116	141	206

Table S3. Specific capacitance at different current densities in various carbon based supercapacitors with 1.0 M H_2SO_4 solution as electrolyte.

Sample	Current Density ($A\ g^{-1}$)	Specific capacitance ($F\ g^{-1}$)
ZC-800	0.250	63
S-ZC-800	0.250	107
A-ZC-800	0.250	112
AS-ZC-800	0.250	251
AS-ZC-800	50	204

Table S4. Summary of the surface areas and pore volume distributions for the obtained materials.

Sample	Surface area[a] ($m^2 g^{-1}$)	Total pore volume[b] ($cm^3 g^{-1}$)	Meso-Macropore volume[c] ($cm^3 g^{-1}$)	Micropore volume[d] ($cm^3 g^{-1}$)
ZIF-8	811	0.4335	0.1052	0.3283
S-ZIF-8	655	0.3544	0.2356	0.1188
ZC-800	1051	0.7580	0.1895	0.5685
S-ZC-800	1955	1.2057	1.0424	0.1633
A-ZC-800	1341	1.3321	0.3233	1.0087
AS-ZC-800	2972	2.5590	1.7851	0.7739

[a] Calculated from the BET surface area analysis.

[b] Calculated from the BET surface area analysis.

[c] Calculated using t-plot (FHH) method.

[d] Calculated by subtracting the total pore volume with the meso-/macropore volumes.