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Supplementary Information

N-doped hierarchically porous carbon derived from heterogeneous core-shell ZIF-L(Zn)@ZIF-67 for supercapacitor application

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Experimental

Materials and chemicals

All chemicals were used as received without further purification.

Synthesis of ZIF-L(Zn) nanoleaves

ZIF-L(Zn) nanoleaves were prepared by mixing aqueous solution of zinc nitrate hexahydrate (2 mmol, 5 mL) and aqueous solution of 2-methylimidazole (MeIm) (20 mmol, 50 mL) with agitation for 2 hours and the reaction was aged for 12 hours at room temperature. The white product was centrifuged and washed with deionized water twice, and finally dried in a vacuum oven at 50 °C for 12 hours.

Synthesis of ZIF-67 crystals with different sizes

In a typical synthesis, large-sized ZIF-67 crystals (~4 μ m) were synthesized by mixing aqueous solution of cobalt nitrate hexahydrate (2 mmol, 5 mL) and aqueous solution of 2-methylimidazole (MeIm) (100 mmol, 250 mL) with agitation for 2 hours and the reaction was aged for 12 hours at room temperature. Small-sized ZIF-67 crystals (250 nm~800 nm) were synthesized by mixing methanol solution of cobalt nitrate hexahydrate (4 mmol, 10 mL) and methanol solution of MeIm (160 mmol, 200 mL) as the same procedure with the synthesis of large-sized ZIF-67 in aqueous solutions. The purple product was centrifuged and washed with deionized water twice, and finally dried in a vacuum oven at 50 °C for 12 hours.

Preparation of core-shell ZIF-L(Zn)@ZIF-67 nanoleaves

Core seeds of ZIF-L(Zn) were synthesized by the above method of ZIF-L(Zn) nanoleaves without procedure of drying after washing with deionized water twice, then the shell of ZIF-67 was fabricated according to the synthesis of large-sized ZIF-67 crystals (~4 μ m), firstly aqueous solution of 2-methylimidazole (MeIm) (100 mmol, 250 mL) was added to disperse the wet seeds, after stirring 5minutes, aqueous solution of cobalt nitrate hexahydrate (2 mmol, 5 mL) was injected. Subsequently, the reaction was kept stirring for 2 hours, aged for 12 hours at room temperature. The final product was collected by centrifugation, washed twice with deionized water, and dried in a vacuum oven at 50 °C for 12 hours. The investigation of the interaction between the thickness and feeding molar ratio of OC²⁺/Zn²⁺ was carried out by changing feeding molar ratio of Co²⁺/Zn²⁺ from 0.25 to 2.

Carbonization of core-shell ZIF-L(Zn)@ZIF-67 nanoleaves

Core-shell ZIF-L(Zn)@ZIF-67 nanoleaves with different size derived from vary feeding molar ratio of Co^{2+}/Zn^{2+} from 0.25 to 2, were carbonized under nitrogen condition at 750 °C for 3 h, with a heating rate of 2 °C·min⁻¹. In addition, single ZIF-L(Zn) and ZIF-67 were also carbonized under the same thermal conditions as a control experiment. Subsequently, all the as-prepared porous carbons were washed by HF solution (10 wt %) to remove the residual Zn and Co species.

Materials characterization

The crystal phases were determined by a Cu K α radiation powder X-ray diffractometer (XRD, Rigaku D/MAX 2500 VL). The morphology of products was examined by field-emission scanning electron microscopy (FESEM, Hitachi SU8020) and high resolution transmission electron microscopy (HRTEM, JEOL JEM 2100). The X-ray photoelectron spectrum (XPS) was recorded on an ESCALAB250Xi spectrometer (Thermo Fisher) with its energy analyzer working in the pass energy mode at 50 eV, and the Mg K α line was used as the excitation source. Raman spectra were collected using a Micro-Raman spectrometer (LabRAM HR Evolution). N₂ adsorption/desorption isotherm and the BET surface area were measured using a Quantachrome Autosorb IQ instrument with liquid nitrogen at 77 K. The total pore volumes and pore-size distributions were calculated from the adsorption branches of isotherms based on the density functional theory (DFT) method. Thermogravimetric analysis (TGA) was performed by using a simultaneous thermal analyzer (STA, STA449F3).

Electrochemical measurements

About 9 mg obtained porous carbon materials was mixed with poly (vinylidine difluoride) (1 mg) and then dissolved in N-methylpyrrolidinone solvent (0.1 mL). Subsequently, the obtained slurry was homogenized by ultrasonication and stirring, then smeared onto a graphite substrate (2 cm²), and dried in a vacuum oven at 50 °C for 4 hours to form the thin film on the electrodes. The electrochemical properties were investigated by cyclic voltammetry (CV), and galvanostatic charge-discharge in 2 M KOH solution by using an electrochemical workstation (Autolab PGSTAT 302N) conducted in a standard three-electrode electrochemical cell. The KCl saturated Ag/AgCl was used as the reference electrode, and Pt rod was used as the counter electrode. EIS measurements were tested in the frequency range from 0.01Hz to 100 kHz at open circuit potential with an ac perturbation of 0.1 V. The specific capacity (C_s, F g⁻¹) was calculated by using following equation (galvanostatic charge/discharge curves):

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

Where C_s is the specific capacity (F g⁻¹), *I* is the discharge current (A), m is the mass of the active materials (g), ΔV is the potential drop excluding the IR drop (V) and Δt is the total discharge time (s).



Fig. S1 SEM images of ZIF-L(Zn) nanoleaves (a) and large-sized ZIF-67 crystals (b).



Fig. S2 SEM images of small-sized ZIF-67 crystals (a) and core-shell ZIF-L(Zn)@ZIF-67 nanoleaves adopting the reaction condition of small-sized ZIF-67 crystals to prepare the shell (b).



Fig. S3 Photograph of ZIF-L(Zn) nanoleaves, ZIF-67 crystals and core-shell ZIF-L(Zn)@ZIF-67(x) nanoleaves prepared by using different feeding molar ratios of Co^{2+}/Zn^{2+} from 0.25 to 2.

Fig No.	Feeding molar ratio of Co^{2+}/Zn^{2+}	Shell thickness (nm)
Fig. 1a-c	0.25	5
Fig. 1d-f	0.5	60
Fig. 1g-i	1	220
Fig. 1j-l	2	320

Table S1 Summary on shell thicknesses of core-shell ZIF-L(Zn)@ZIF-67(x) nanoleaves with different feeding molar ratios of Co^{2+}/Zn^{2+} shown in Fig 1.



Fig. S4 XRD patterns of ZIF-L(Zn) nanoleaves (a), core-shell ZIF-L(Zn)@ZIF-67(0.25) nanoleaves (b), core-shell ZIF-L(Zn)@ZIF-67(0.5) nanoleaves (c), core-shell ZIF-L(Zn)@ZIF-67(1) nanoleaves (d), core-shell ZIF-L(Zn)@ZIF-67(2) nanoleaves (e) and ZIF-67 crystals (f).



Fig. S5 The SEM images, TEM images and elemental mappings of core-shell ZIF-L(Zn)@ZIF-67(20) crystals (a, b, c) and core-shell ZIF-L(Zn)@ZIF-67(40) crystals (d, e, f).



Fig. S6 TG curves of ZIF-L(Zn) nanoleaves, ZIF-67 crystals and core-shell ZIF-L(Zn)@ZIF-67(x) nanoleaves.



Fig. S7 XRD patterns (a) and high-resolution N 1s spectra (b) of N-C@GC(0.25)/CNTs, N-C@GC(0.5)/CNTs and N-C@GC(2)/CNTs.



Fig. S8 Raman spectra of N-doped C, N-C@GC(x)/CNTs and N-doped GC.



Fig. S9 The TEM images and elemental mappings of N-doped C (a, b), N-C@GC(0.25)/CNTs (c, d), N-C@GC(0.5)/CNTs (e, f), N-C@GC(1)/CNTs (g, h), N-C@GC(2)/CNTs (i, j) and N-doped GC (k, l).



Fig. S10 The N₂ adsorption/desorption isotherms (a) and the pore-size distribution curves (b) of N-C@GC(0.25)/CNTs , N-C@GC(0.5)/CNTs and N-C@GC(2)/CNTs.

Table S2 Summary on surface areas and total pore volumes of N-doped C, N-C@GC(x)/CNTs and N-doped GC.

Sample	$S_{\rm BET} ({ m m}^2~{ m g}^{-1})$	$S_{\rm meso} ({\rm m}^2 {\rm g}^{-1})$	$S_{ m meso}/S_{ m BET}$ (%)	$V_{\text{pore}} (\text{cm}^3 \text{ g}^{-1})$
N-doped C	2	2	-	0.009
N-C@GC(0.25)/CNTs	13	13	-	0.08
N-C@GC(0.5)/CNTs	59	33	55.9	0.11
N-C@GC(1)/CNTs	359	160	44.6	0.26
N-C@GC(2)/CNTs	372	122	32.8	0.30
N-doped GC	313	57	18.2	0.2



Fig. S11 The CV curves of N-doped C (a), N-C@GC(0.25)/CNTs (b), N-C@GC(0.5)/CNTs (c) , N-C@GC(1)/CNTs (d), N-C@GC(2)/CNTs (e) and N-doped GC (f) at the potential scan rate of 10, 20, 40, 60, 80, 100, 150 and 200 mV S⁻¹.



Fig. S12 The GCD plots of N-doped C (a), N-C@GC(0.25)/CNTs (b), N-C@GC(0.5)/CNTs (c) , N-C@GC(1)/CNTs (d), N-C@GC(2)/CNTs (e) and N-doped GC (f) at different current densities.



Fig. S13 Nyquist plots of N-doped C, N-C@GC(1)/CNTs, N-C@GC(2)/CNTs and N-doped GC in the frequency range from 0.01Hz to 100 kHz at open circuit potential with an ac perturbation of 0.1 V.

Materials	Nitrogen content (wt%)	Electrolyte	Potential range (V)	Current density (A g ⁻¹)	Capacitance (F g ⁻¹)	Ref.
N-C@GC/CNTs	13.57	2 M KOH	1.0	2.0	252.1 F g ⁻¹	This work
Nitrogen enriched mesoporous carbon spheres	10.0	1 M H ₂ SO ₄	0.8	1.0	211 F g ⁻¹	Electrochem. Commu. 2007, 9, 569.
Nitrogen-doped porous nanofibers	7.2	6 M KOH	1.0	1.0	202 F g ⁻¹	ACS Nano, 2012, 6, 7092.
Hetroatom-doped carbon	0.7	1 M H ₂ SO ₄	1.0	2.0	245 F g ⁻¹	Adv. Funct. Mater. 2013, 23, 1305.
Nitrogen-doped hollow carbon spheres	6.0	2 M H ₂ SO ₄	0.8	2.0	245 F g ⁻¹	J. Mater. Chem. 2012, 22, 13464.
Nanoporous GC	0.8	0.5 M H ₂ SO ₄	0.8		238 F g ⁻¹	Chem. Eur. J. 2014, 20, 7895.
Hierarchically flower-like N-doped porous carbon	1.9	6 M KOH	1.0	0.5	149 F g ⁻¹	Inorg. Chem. 2016, 55, 6552.
Exfoliated Carbon Nanosheets	6.13	6 M KOH	1.0	0.5	265 F g ⁻¹	ACS Appl. Mater. Interfaces 2017, 9, 17317.
Nitrogen and boron co-doped graphene	3.0	1 M H ₂ SO ₄	0.8		215 F g ⁻¹	Adv. Mater. 2012, 24, 5130.

Table S3 Comparison of specific capacitances of N-doped porous carbon materials reported in the representative literatures.