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Electronic Supporting Information for

Efficient Lithium-Ion Storage Using Heterostructured Porous Carbon Framework and Its in situ Transmission Electron Microscopy Study

Minjun Kim,^{a,‡} Joseph F. S. Fernando,^{b,‡} Jie Wang,^{c,*} Ashok Kumar Nanjundan,^{a,*} Jongbeom Na,^a Md. Shahriar A. Hossain,^{a,d} Hiroki Nara,^c Darren Martin,^e Yoshiyuki Sugahara,^{c,f} Dmitri Golberg^{b,g,*} and Yusuke Yamauchi^{a,e,*}

- Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland, Brisbane,
 Queensland 4072, Australia
- b Centre for Materials Science and School of Chemistry and Physics, Queensland University of Technology (QUT), 2 George Street, Brisbane, Queensland, 4000, Australia
- c Kagami Memorial Research Institute for Science and Technology, Waseda University, 2-8-26 Nishi-Waseda, Shinjuku, Tokyo 169-0051, Japan
- d School of Mechanical and Mining Engineering, Faculty of Engineering, Architecture and Information Technology (EAIT), The University of Queensland, Brisbane, Queensland 4072, Australia
- e School of Chemical Engineering, Faculty of Engineering, Architecture and Information Technology (EAIT), The University of Queensland, Brisbane, Queensland 4072, Australia
- f Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
- g International Center for Materials Nanoarchitechtonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
- ‡ These authors equally contributed to this work.

Experimental Section

Preparation of ZIF-8 Polyhedra with an Average Particle Size of 225 nm: ZIF-8 polyhedra with an average particle size of 225 nm were prepared by previously reported method with minor modification.¹ Typically, 600 mg of $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 10 mL of water and 1.12 g of 2-methylimidazole (MeIM) and 2.0 mg of cetyltrimethylammonium bromide (CTAB) were dissolved in 10 mL of water by sonication. Then the solution of $Zn(CH_3COO)_2$ was added to the solution of MeIM and CTAB, and gently stirred for 10 s. The mixture was left undisturbed at room temperature (RT) for 2 h. The resulting ZIF-8 was washed with deionized (DI) water and was re-dispersed in DI water to prepare a suspension with a concentration about 15 mg mL⁻¹.

Preparation of PCF: GO was prepared *via* a modified Hummer's method. Fifteen mL of GO solution with a concentration of 2 mg mL⁻¹ were mixed with 2 mL of a ZIF-8 suspension and the mixture was stirred at RT for 12 h. The mixture was collected by filtration and then dried at 60 °C for 12 h. Then the obtained mixture was transferred to a tube furnace and calcinated at 900 °C for 4 h under an N₂ atmosphere with a heating rate of 2 °C min⁻¹. After cooling down to RT, the product was washed with 1 M HCl, DI water, and ethanol, respectively.

Preparation of ZIF-C: ZIF-C was prepared by direct pyrolysis of ZIF-8 at 900 °C for 4 h under a N_2 atmosphere with a heating rate of 2 °C min⁻¹. After cooling down to RT, the product was washed with 1 M HCl, DI water, and ethanol.

Characterization: The SEM images were obtained using a Hitachi S4800 SEM. The TEM images were obtained using a JEOL JEM-2100. *In situ* TEM measurements were conducted using a scanning tunneling microscopy (STM) type electrical TEM holder ("Zues" Zeptools, P.R. China). Raman spectroscopy was conducted on a HORIBA Scientific Lab RAM HR Raman spectrometer system with a 532.4 nm laser. The XPS analysis was carried out using a Perkin-Elmer PHI 550 spectrometer with Al-K α (1486.6 eV) as the X-ray source. The nitrogen adsorption–desorption measurements of the samples were performed on a Quantachrome Autosorb at 77 K. The specific surface area (SSA) was determined based on the BET method in the relative pressure range of 0.05–0.3. The pore size distribution curves were determined from the adsorption branches of the isotherm, according to the non-local density functional theory (NLDFT) assuming a mixed slit/cylinder pore model.

Electrochemical Performance Measurement: Electrochemical experiments were carried out using coin cells. The working electrodes were prepared by mixing the active materials, carbon black and poly(vinylidene difluoride), at a weight ratio of 8:1:1. The slurry was casted on pure Cu foil and dried in a vacuum oven at 120 °C for 12 h. The loading of active materials was about 1.0 mg cm⁻². A polypropylene film (Celgard 2320) was used as a separator. Pure lithium foil was used as counter and reference electrode. The electrolyte was 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 by volume). The assembling of the cell was performed in an argon-filled glove box. Galvanostatic discharge-charge measurements were carried out on a Land battery test system. Cyclic voltammogram was measured on a CHI660 electrochemical workstation.



Fig. S1. SEM image of ZIF-8 nanoparticles.



Fig. S2 A graphical description of synthetic routes for the preparation of PCF. a) Mixing of ZIF-8 and GO in a homogenous suspension. b) Electrostatic self-assembly of oppositely charged GO and ZIF-8 to generate GO-coated ZIF-8. c) GO/ZIF-8 hybrid composite. and d) PCF obtained *via* pyrolysis (Reproduced with permission.² Copyright 2019, Wiley-VCH).



Fig. S3. SEM image of GO/ZIF-8 composite.



Fig. S4. Raman spectra of PCF and ZIF-C.

Supplementary Note in Fig. S4: To compare the structural characteristics of PCF and ZIF-8 derived carbon (ZIF-8-C), Raman spectra were recorded as presented in Fig. S4. The Raman bands at 1352 and 1626 cm⁻¹ are assignable to the D band and G band, respectively.^{3,4} As such, the degree of graphitization can be referred by the intensity ratio between the D and G bands (I_D/I_G). The PCF has lower I_D/I_G of 1.99 (calculated by the integrated area) than ZIF-8-C ($I_D/I_G = 2.33$), indicating that it exhibits higher graphitization level.



Fig. S5. a) C1s and b) N1s XPS spectra of PCF. c) C1s and d) N1s XPS spectra of ZIF-C.

Supplementary Note in Fig. S5: The high-resolution XPS (HRXPS) for C 1*s* is deconvoluted into C–C (*sp*²), C=C (*sp*³), C–O, C–OOH, and π – π * at 284.8, 285.8, 287, 288.9, and 290.9 eV, respectively (**Fig. S5**).⁵ The PCF contains C-C (*sp*²) at 73.8 % of the total carbon content, as compared to 58.0 % of the total carbon content is C-C (*sp*²) in ZIF-8-C The higher graphitization level of PCF demonstrated by Raman spectroscopy and HRXPS can therefore be attributed to the existence of reduced GO (rGO) in the porous framework. As PCF and ZIF-8-C also contain 5.6 and 13.7 at. % of nitrogen, respectively, the profiles of different nitrogen species in their carbon networks were investigated. XPS for N 1*s* (**Fig. S5**) was deconvoluted into pyridinic, pyrrolic, graphitic nitrogen species at 398.5, 400.3, 401.2, and 402.9 eV, respectively. The pyridinic and graphitic nitrogen species improve the capacitive performances of LIBs by acting as electrochemical active sites, and the graphitic nitrogen species contribute to increase the electrical conductivity of the material.^{6,7} Along with nitrogen species, oxygen-containing groups in the PCF are also expected to undergo the Faradaic reaction with Li ions, therefore, contributing to the enhancement in storage capacity.⁸

Sample	C (%)					N (%)			
	C-C (<i>sp</i> ²)	C-C (<i>sp</i> ³)	C=O	С-ООН	π-π*	Pyridinic N	Pyrrolic N	Graphitic N	Oxidized N
ZIF-C	58.0	21.7	11.1	5.5	3.7	61.5	25.4	8.5	4.6
PCF	73.8	15	4.7	3.2	3.3	46.4	19.4	24.1	10.1

Table S1 Percentages of each-type carbon and nitrogen atoms in ZIF-C and PCF.



Fig. S6. a) Nitrogen adsorption-desorption isotherms and b) pore size distribution curves of PCF.

Supplementary Note in Fig. S6: Nitrogen adsorption/desorption measurements were conducted to study the porosity of PCF. In both cases, a rapid initial nitrogen adsorption at low relative pressure (P/P_0) indicates the presence of micropores (**Fig. S6a**). The pore size distribution curves derived by the nonlocal density functional theory (NLDFT) method identify the presence of micropores less than 2 nm (**Fig. S6b**). This micropores were derived from MOF-derived carbon layers on the rGO surface. The surface area and pore volume of PCF were calculated to be 643 m² g⁻¹ and 0.35 cm³ g⁻¹, respectively. Although hierarchically porous structure is generally beneficial to electrochemical applications, an appropriate distribution of pore sizes is of paramount importance in achieving the high-performance anode material for LIBs. Typically, micropores act as reservoirs for the Li ions, while meso/macropores mitigate the transport resistance by providing efficient transport channels to Li ions. The optimized hierarchical porosity distribution is therefore required to achieve high-performance anode electrode material in LIBs. The overall electrochemical performance of PCF as anode material in LIB was investigated to understand the effect of its hierarchically pore structures.



Fig. S7. Selected area for SAED acquisition of PCF cluster 1 after lithiation.



Fig. S8. 1D diffraction profiles generated from SAED patterns acquired before and after lithiation of PCF cluster 1. The conversion was performed using the DiffTools script in Gatan Digital Micrograph software.⁹



Fig. S9. TEM and corresponding inverse FFT images (after masking the amorphous region). a) after 1st lithiation and b) after 1st de-lithiation of PCF cluster 2.

Davaus aarban matarials	Current density	Charge capacity	Cuele number	References	
r orous carbon materiais	(mA g ⁻¹)	(mA h g ⁻¹)	Cycle number		
N-doped porous carbon network	100	523	180	10	
Pomegranate-like hollow carbon	100	484.2	100	11	
Hollow carbon	100	568	100	12	
Interconnected hollow carbon	37.2	630	50	13	
N-doped porous carbon	100	540	100	14	
COF derived N-doped porous carbon	100	488	100	15	
N-doped carbon nanotube	100	397	100	16	
Graphite powder	100	353.9	100	17	
3D Porous carbon framework	100	594	300	This work	

Table S2. Comparison of the performances of different porous carbon materials in LIBs.

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