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Supporting Information

Heteroatomic Interface Engineering in MOFs-Derived Carbon Heterostructures with Built-In Electric-Field Effect for High Performance Al-Ion Batteries

Caixia Li, Shihua Dong, Rui Tang, XiaoliGe, Zhiwei Zhang, Chengxiang Wang, Yupeng Lu and Longwei Yin* Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, School of Materials Science and Engineering, Shandong University, Jinan 250061, P. R. China

*To whom correspondence should be addressed. Tel.: + 86 531 88396970. Fax: + 86 531 88396970. E-mail: <u>yinlw@sdu.edu.cn</u>



FigureS1. The SEM images of as-synthesized UiO-66 derived porous carbonwith the diameter of about 200nm.



Figure S2.(a) XRD pattern and (b) Infrared spectras of theU, U@NU and U@NU@MPP samples. (c) XRD and (d) XPS spectrum of

C, N-C, N,P-C, C@N-C and C@N-C@N,P-Csamples.

Sample	C (at%)	N (at%)	P (at%)	O (%)
С	89	0	0	11
N-C	79	10	0	11
N,P-C	63	11	15	11
C@N-C	83	6	0	11
C@N-C@N,P-C	74	7	8	11

Table S1. The content of C, N and P forsamples.



Figure S3. The XPS spectrum of the C and C@N-C samples. (a) XPS spectra for C 1s of the C sample. XPS spectra for(b) C 1s and (c)N 1s of C@N-C respectively.

The XPS results exhibited that the atom ratio C:N:O=83:6:11 for the C@N-C sample, while the C@N-C@N,P-C is mainly composed of C (74 at%), O (11 at%), N (7 at%) and P (8 at%). The atom content for C, N, P and O atoms of C, N-C, N,P-C samples are also shown in **Figure S2 and Table S1**. To profoundly understand the chemical state of C, N and P elements, high-magnified XPS was provided. The C 1s spectrum of C sample (**Figure S3a**) displayed 4 peaks at 289.9, 287.9, 285.9, and 284.7 eV, which could be attributed to π - π *, O-C=C, C-O, sp2 carbon, respectively.¹ The strongest peak at 284.7 eV indicated that graphitic carbon is major species for

the MOFs derived porous carbon. The C 1s spectrum of C@N-C (**Figure S3b**), distinct from that of porous C without elemental doping (**Figure S3a**), was de-convoluted into 5 peaks. The peaks at 290.7, 288.3, 286.6, 285.8 and 284.8 eV correspond to the π - π *, O-C=C, C-O, C-N and sp2 carbon,² respectively. Correspondingly, the N 1s spectrum in **Figure S3c** certified the existence of the 4 chemical state for N and these 4 peaks for N 1s should be assigned to pyridic N (398.6 eV), pyrrolic N (400.3 eV), graphitic N (401.4 eV) and N-O (404.8 eV), indicating that N atoms are indeed inserted into the carbon lattice of C@N-C sample.³



Figure S4.The Raman spectrums of (a) C, (b) C@N-C and (c) C@N-C@N,P-C samples.Thetypical EDS spectrums of (d) C, (e) C@N-C and (f) C@N-C@N,P-C samples.



Figure S5 N₂ adsorption-desorption isotherms of (a) U, U@NU and the U@NU@MPP (b) C, C@N-C and C@N-C@N,P-C. Mesopore size distributions of (c) U, U@NU and the U@NU@MPP (d) C, C@N-C and C@N-C@N,P-C.Micro-pore size distributions of (e) U, U@NU and the U@NU@MPP (f) C, C@N-C and C@N-C@N,P-C.

To investigate thestructure, such as surface area, pore size distribution and pore volume, N₂ adsorptiondesorption analysis was performed as shown in Figure S5. For all the samples in Figure S5a-b, typical type I isotherms were shown corresponding with the rapid rise of the adsorption at a low pressure range $(P/P_0 \sim 0)$ reveals the presence of a large amount of microspores. The samples possessed high surface area of 1261, 1112 and 1342 m^2g^{-1} for U, U@NU and U@NU@MPPrespectively, which was a bit lower than that of the corresponding carbonization product C, C@N-C and C@N-C@N,P-C (1408, 1268, 1410 m²g⁻¹ respectively) as shown in Table S1.4From the pore-sizedistribution curve based on the BJH method in FigureS5c-d, theBJH curvespresenta narrow pore-size distribution of 2.0 nm, indicating that there is large amount of mesopores with diameter of 2 nm in the samples before and after carbonization. Actually, the values of mesopore volume are 0.12, 0.12 and 0.22 cm³ g⁻¹ for U, U@NU and U@NU@MPP samples, respectively. After pyrolysis process, the pore volume of corresponding sample increase to 0.17, 0.16 and 0.23 cm³ g⁻¹ for C, C@N-C and C@N-C@N,P-C. Moreover, all of the samples demonstrated relatively coincident micro-pore distribution with the peak at about 0.60 nm for U, U@NU and U@NU@MPP in Figure S5e. Besides, the C, C@N-C and C@N-C@N,P-C displayed even narrower peaks at about 0.67 nm in the curves in Figure S5f. It should be mentioned that, the average diameter of the C, C@N-C and C@N-C@N,P-C is about 1 nm, which is much larger than the size of $AlCl_4^-$ (0.528 nm).⁵All the samples possess largeporevolumeand high surface area as shown in Table S1 which could offer efficient transport pathway for the AlCl₄-anions, as well as more active sites for the electrochemical reactions.



Figure S6. (a) The structure of the AIBs. Ni foams were used to support and protect the cell integrality. (b) The illustration of electrochemical process for AIBs in this system.



Figure S7. The cycling performance of N-C and N,P-C at 5 A g^{-1} .

Materials	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)	References				
Al 4 M LiPF ₆ in EMC	222	132	6				
Graphite	150	1200					
Graphite	40	3000	5				
Natural Graphite	68.7	/	7				
High Quality Graphene	40	3000	8				
Graphene/SnS ₂	241	/	9				

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C@N-C@N,P-C

Table S2. Investigation of energy density and power density.



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This work

Figure S8.Cycling performance of Al-C@N-C@N, P-C cell.

	$\rm S_{BET}$	V Meso-pore	V Micro-pore	V Pore	D Pore
	$(m^2 g^{-1})$	$(cm^{-3} g^{-1})$	$(cm^{-3} g^{-1})$	$(cm^{-3} g^{-1})$	(nm)
U	1261	0.12	0.48	0.58	0.92
U@NU	1112	0.12	0.43	0.52	0.95
U@NU@MPP	1342	0.22	0.52	0.71	1.07
С	1408	0.17	0.56	0.69	0.98
C@N-C	1268	0.16	0.51	0.63	1.00
C@N-C@N,P-C	1410	0.23	0.57	0.73	1.04

Table S3 the surface area and pore size distribution.



Figure S9. CV curves of the Al-ion batteries with cathode of (a) C and (b)C@N-C.

The CV curve of the cell (**Figure S9**) showed broad cathode peaks at about 1.46 V in the first cycle for the C and C@N-Ccorresponding with the intercalation of $AlCl_4$ and the chemical combination with C atoms in porous carbon which shift to lower potential in the following cycles.



Figure S10. Raman spectrum for (a) charged to 2.3V at a fully charged status. (b) Partially discharged to 0.8V. (c) Fully discharged at 0.5V.



Figure S11. Structure characterization of C@N-C@N,P-C after 100 cycles at fully charged state at 2.3 V by SEM.



Figure S12. Structure characterization of C@N-C@N,P-C after 100 cycles at fully charged state at 2.3 V byTEM.(a-f) TEM images of C@N-C@N,P-C and the corresponding elemental mappings of C, N, P, Al and Cl elements.

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