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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

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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  $\pi$ - $\pi$ \*, O-C=C, C-O, sp2 carbon, respectively.<sup>1</sup> 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  $\pi$ - $\pi$ \*, O-C=C, C-O, C-N and sp2 carbon,<sup>2</sup> 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.<sup>3</sup>



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** N<sub>2</sub> 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, N<sub>2</sub> 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 m<sup>2</sup>g<sup>-1</sup> 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 cm<sup>3</sup> g<sup>-1</sup> 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 cm<sup>3</sup> g<sup>-1</sup> 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).<sup>5</sup>All the samples possess largeporevolumeand high surface area as shown in Table S1 which could offer efficient transport pathway for the AlCl<sub>4</sub>-anions, as well as more active sites for the electrochemical reactions.

![](_page_3_Figure_1.jpeg)

**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.

![](_page_4_Figure_0.jpeg)

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

Materials	Energy density (Wh kg <sup>-1</sup> )	Power density (W kg <sup>-1</sup> )	References				
Al   4 M LiPF <sub>6</sub> 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 <sub>2</sub>	241	/	9				

148

C@N-C@N,P-C

Table S2. Investigation of energy density and power density.

![](_page_4_Figure_4.jpeg)

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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.

![](_page_5_Figure_2.jpeg)

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.

![](_page_5_Figure_5.jpeg)

**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.

![](_page_6_Picture_0.jpeg)

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

![](_page_6_Figure_2.jpeg)

**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.

## References

- 1. W. Ai, W. Zhou, Z. Du, Y. Chen, Z. Sun, C. Wu, C. Zou, C. Li, W. Huang and T. Yu, *Energy Storage Materials*, 2017, **6**, 112-118.
- 2. K. Lu, Z. Hu, J. Ma, H. Ma, L. Dai and J. Zhang, Nat Commun, 2017, 8, 527.
- 3. Y. Liu, Y. Qiao, G. Wei, S. Li, Z. Lu, X. Wang and X. Lou, *Energy Storage Materials*, 2018, 11, 274-281.
- 4. Z. Li, C. Li, X. Ge, J. Ma, Z. Zhang, Q. Li, C. Wang and L. Yin, *Nano Energy*, 2016, 23, 15-26.
- M. C. Lin, M. Gong, B. Lu, Y. Wu, D. Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B. J. Hwang and H. Dai, *Nature*, 2015, 520, 325-328.
- 6. X. Zhang, Y. Tang, F. Zhang and C.-S. Lee, *Advanced Energy Materials*, 2016, 6, 1502588.
- D. Y. Wang, C. Y. Wei, M. C. Lin, C. J. Pan, H. L. Chou, H. A. Chen, M. Gong, Y. Wu, C. Yuan, M. Angell, Y. J. Hsieh, Y. H. Chen, C. Y. Wen, C. W. Chen, B. J. Hwang, C. C. Chen and H. Dai, *Nat Commun*, 2017, 8, 14283.
- 8. H. Chen, C. Chen, Y. Liu, X. Zhao, N. Ananth, B. Zheng, L. Peng, T. Huang, W. Gao and C. Gao, *Advanced Energy Materials*, 2017, **7**, 1700051.
- 9. Y. Hu, B. Luo, D. Ye, X. Zhu, M. Lyu and L. Wang, *Adv Mater*, 2017, **29**, 1606132.