Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2019

## **Supporting Information**

# Advanced sodium storage properties of porous nitrogen-doped

### carbon with NiO/Cu/Cu<sub>2</sub>O hetero-interface derived from bimetal-

### organic frameworks

Yan Zhang<sup>a, b#</sup>, Sana Ullah<sup>c#</sup>, Guang-Ping Zheng<sup>c\*</sup>, Xiu-Cheng Zheng<sup>a, b, c, d\*</sup>, Dan Li<sup>a, b\*</sup>

<sup>a</sup> College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

<sup>b</sup> Green Catalysis Center, College of Chemistry, Zhengzhou University Zhengzhou 450001, China

<sup>c</sup> Department of Mechanical Engineering, The Hong Kong Polytechnic University,

Hung Hom, Kowloon, Hong Kong, PR China

<sup>d</sup> Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education),

College of Chemistry, Nankai University, Tianjin 300071, PR China

\*Corresponding authors.

E-mail addresses: danli@zzu.edu.cn (D. Li), mmzheng@polyu.edu.hk (G.P Zheng),

zhxch@zzu.edu.cn (X.C. Zheng).

<sup>#</sup>Yan Zhang and Sana Ullah contributed equally to this work.

#### 1. Experimental

#### 1.1. Synthesis of Ni-Cu-MOF precursor and NCC composite

Nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 4.4 mg), copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 4.4 mg), 2, 2'-Bipyridine (BPY, 1.56 mg), and poly(4-vinylphenol) (PVP, 10.0 mg) were dissolved into 6.0 mL of the mixture of N, N-dimethylformamide (DMF) and ethanol (v : v = 3 : 1) in a 10 mL vial. Then a solution of tetra(4-carboxyphenyl)porphine (TCPP, 4.0 mg) dissolved in 2.0 mL of the mixture of DMF and ethanol (v : v = 3 : 1) was added dropwise into the aforementioned solution, which was then sonicated for 25 min. After that, the vial was capped and then heated at 80 °C for 24 h. The resulting Ni-Cu-MOFs precursor was washed twice with ethanol and collected by centrifuging. The Ni-Cu-MOFs precursor was calcined at 600 °C for 3 h in a tube furnace with a heating rate of 5 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere to obtain the NCC composite. For comparison, the nitrogen-doped carbon (N-doped carbon) was used as the reference sample, which was obtained by the calcination of polyvinyl pyrrolidone at a temperature of 650 °C.

#### 1.2. Materials characterization

The crystal structures of the samples were determined by X-ray diffraction (XRD, Bruker D8 advance) using Cu K $\alpha$  radiation over the range from  $2\theta = 10^{\circ}$  to 80°. Raman spectra (Micromeritics ASAP 2420) were recorded with a wavelength of 532 nm. The N<sub>2</sub> adsorption-desorption isotherms of the samples were measured by the Brunauer-Emmett-Teller using an ASAP 2420 instrument at 77 K. The morphologies and structures were observed by a FEI F50 field-emission scanning electron microscope (FESEM) and TECNAI G2 F20 and JEOL2100F transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS, EscaLab 250Xi) was used to determine the valences of the elements. The measurements of nitrogen and carbon contents were carried out by CHNS elemental analyses (Thermo Flash EA 1112, USA).

#### 1.3. Electrochemical measurements

The electrode slurry was coated on a copper foil by mixing the as-prepared material, acetylene black, and sodium carboxymethyl cellulose with a mass ratio of 8 : 1 : 1 in deionized water, and then dried at 120 °C for 12 h under vacuum. The loading mass of per electrode is around 1.3 mg cm<sup>-2</sup>. The electrolyte is composed of NaClO<sub>4</sub> (1 M) in a mixture of ethylene carbonate (EC) and diethyl carbonate DEC (v : v = 1 : 1) with 5% of fluoroethylene carbonate (FEC) as additive. The electrochemical performances were tested by the LAND CT2001A multi-channel battery testing system at a voltage range of 0.01-3 V. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) curves were performed on the CHI660E electrochemical workstations.



Fig. S1 XRD pattern of the as-prepared Ni-Cu-MOF precursor.



Fig. S2 XPS spectrum of O 1s in the NCC composite.

The high resolution XPS spectrum of O 1s can be divided into two peaks. The ones appeared at 532.5 and 530.8 eV are attributed to defect sites and metal-oxygen bond, respectively. <sup>1,2</sup>

 Table S1. The XPS element content of the NCC composite.

Element	С	Ν	Ni	Cu	0
Atomic (%)	80.72	2.94	1.18	4.07	11.09



Fig. S3 SEM images of the Ni-Cu-MOF precursor.



Fig. S4 HRTEM images of the NiO/Cu/Cu<sub>2</sub>O composite.

The marked lattices with *d*-spacing were measured to be 0.206 and 0.130 nm, which match well with the (111) and (220) plans of Cu, respectively. While the *d*-spacing of 0.103 and 0.096 nm correspond to the (400) plane of NiO and (620) plane of Cu<sub>2</sub>O, demonstrating the formation of hetero-interface, which can enhance electrochemical reaction kinetics and electrical conductivity of the NCC composite.



Fig. S5 EDS spectrum of the NCC composite.



**Fig. S6** (a) A STEM image of N-doped carbon, theelemental mapping images of (b) N and (c) C in the N-doped carbon, (d) EDS spectrum of the N-doped carbon, (e) CV curves of the N-doped carbon for the first three cycles at a scan rate of 0.1 mV s<sup>-1</sup>, (f) cycling performance of the N-doped carbon at a current density of 0.5 A g<sup>-1</sup>, (g) rate capabilities of the N-doped carbon.

The nitrogen-doped carbon (N-doped carbon) was used as the reference sample, which was obtained by the calcination of polyvinyl pyrrolidone at high temperature at 650 °C. The SEM image, elemental mapping images, and EDS spectrum of the N-doped carbon sample are shown in Fig. S6a-S6d. Fig. S6e exhibits the CV curves of the N-doped carbon electrode at 0.1 mV s<sup>-1</sup> for the first three cycles. In the first discharge process, the irreversible reduction peak at 1.2 V is ascribed to the decomposition of the electrolyte and the formation of SEI. The broad peaks at 0-0.5 V are attributed to the insertion of Na<sup>+</sup> in the N-doped carbon. During the anodic scan, a peak at around 0.01 V corresponds to the extraction of Na<sup>+</sup>. The cycling performance of the N-doped carbon at 0.5 A g<sup>-1</sup> is presented in Fig. S6f, showing the lower special capacity of 138 mA h g<sup>-1</sup> over 100 cycles than 280 mA h g<sup>-1</sup> for the NCC composite. The rate capability of the N-doped carbon is depicted in Fig. S6g. The reversible capacities of 162, 159, 143, 129, 117, 103, and 146 mA h g<sup>-1</sup> were achieved at 0.1, 0.2, 0.5, 1.0, 2.0, and 5 A g<sup>-1</sup>, respectively.

Materials	Current density (A g <sup>-1</sup> )	Cycle number	Specific capacity (mA h g <sup>-1</sup> )	references
<b>Carbon nanocups</b>	1.5	1000	212	3
HC microspherules	0.1	200	272	4
Carbon nanosheets (bacterial cellulose)	0.2	300	~159	5
Carbon nanosheets (shaddock peel)	0.1	500	232	6
Phenolic resin carbon	0.3	600	188	7
Carbon membrane	0.04	200	~240	8
HC macrotubes	0.1	100	305	9
Amorphous carbon (pitch derived)	0.1	100	~266	10
<b>Carbon Nanowires</b>	0.05	400	206.3	11
N-doped carbon nanosheets	0.5	200	217.1	12
Graphene nanosheets	0.1	300	189	13
N-doped carbon sheets	about 1.7	2000	<100	14
N-doped Graphene	0.1	150	235	15
S-doped reduced graphene	1	4000	145	16
Hard carbon/CNT	0.1	160	151.7	17
NP-CNFs	0.05	300	174	18
P-doped carbon	0.1	300	300	19
Porous carbon	0.5	200	290.6	This work
(MOFs derived)	1.5	600	256.3	1 IIIS WORK

Table S2. Comparison of the electrochemical performances of carbon anode materials for SIBs.



**Fig. S7** Nyquist plots of the NCC electrode tested at a current density of 0.5 A g<sup>-1</sup> after 1 and 100 cycles.

 Table S3. Equivalent circuit parameters of the NCC electrode.

Element (Unit)	R <sub>e</sub> /Ohm	R <sub>ct</sub> /Ohm	CPE-T	CPE-P
After 1 cycle	3.879	435.9	6.2061E-6	0.83114
After 100 cycles	7.924	194.8	1.8507E-5	0.79429



Fig. S8 The linear fitting of Warburg impedance of the NCC composite.

The Na<sup>+</sup> diffusion coefficient can be calculated based on EIS according to Eq (1-3),

$$\omega = 2\pi f$$
(1)  

$$Z_{re} = R_s + R_{ct} + R_f + \sigma \omega^{-1/2}$$
(2)  

$$D = \frac{0.5R^2T^2}{S^2n^4F^4\sigma^2C^2}$$
(3)

where *R* is gas constant, *S* is the surface area of electrode, *T* is absolute temperature, *F* is Faraday's constant, *n* is charge transfer number during electrochemical reaction, and *C* is Na<sup>+</sup> ion concentration. <sup>20</sup> Among these factors,  $\sigma$  can be calculated based on Eq (2), as shown in Fig. S6. Thus the Na<sup>+</sup> diffusion coefficient of the NCC composite is calculated to be  $3.26 \times 10^{-17}$  cm<sup>2</sup> s<sup>-1</sup>.



Fig. S9 The survey XPS spectrum of the NCC electrode material after 600 cycles at 1.5 A g<sup>-1</sup>.

#### References

- X.F. Lu, D.J. Wu, R.Z. Li, Q. Li, S.H. Ye, Y.X. Tong, G.R. Li, *J. Mater. Chem. A*, 2014, 2, 4706–4713.
- 2. Y.H. Ma, Y.K. Li, D. Li, Y.S. Liu, J.M. Zhang, J. Alloy. Compd., 2019, 771, 885–891.
- X. Jian, H. Wang, G.F. Rao, L.Y. Jiang, H.N. Wang, C.M. Subramaniyam, A. Mahmood, W.L. Zhang, Y. Xiang, S.X. Dou, Z.W. Zhou, D. Hui, K. Kalantar-Zadeh, N. Mahmood, *Chem. Eng. J.*, 2019, 364, 578–588.
- Y.M. Li, S.Y. Xu, X.Y. Wu, J.Z. Yu, Y.S. Wang, Y.S. Hu, H. Li, L.Q. Chen, X.J. Huang, J. Mater. Chem. A, 2015, 3, 71–77.
- 5. N. Sun, H. Liu, B. Xu, J. Mater. Chem. A, 2015, 3, 20560–20566.
- T.Y. Zhang, J.T. Chen, B.J. Yang, H.X. Li, S.L. Lei, X. Ding, *RSC Adv.*, 2017, 7, 50336– 50342.
- 7. P. Lu, Y. Sun, H.F. Xiang, X. Liang, Y. Yu, Adv. Energy Mater., 2018, 8, 1702434.
- H.B. Li, F. Shen, W. Luo, J.Q. Dai, X.G. Han, Y.N. Chen, Y.G. Yao, H.L. Zhu, K. Fu, E. Hitz, L.B. Hu, ACS Appl. Mater. Interfaces, 2016, 8, 2204–2210.
- 9. Y.M. Li, Y.S. Hu, M.M. Titirici, L.Q. Chen, X.J. Huang, *Adv. Energy Mater.*, 2016, 6, 1600659.
- Y.M. Li, L.Q. Mu, Y.S. Hu, H. Li, L.Q. Chen, X.J. Huang, *Energy Storage Mater.*, 2016, 2, 139–145.
- Y.L. Cao, L.F. Xiao, M.L. Sushko, W. Wang, B. Schwenzer, J. Xiao, Z.M. Nie, L.V. Saraf, Z.G. Yang, J. Liu, S, *Nano Lett.*, 2012, 12, 3783–3787.
- 12. Z.G. Luo, J. Zhou, X.X. Cao, S.N. Liu, Y.S. Cai, L.R. Wang, A.Q. Pan, S.Q. Liang, *Carbon*, 2017, **122**, 82–91.
- X.F. Luo, C.H. Yang, Y.Y. Peng, N.W. Pu, M.D. Ger, C.T. Hsieh, J.K. Chang, J. Mater. Chem. A, 2015, 3, 10320–10326.
- 14. T.Z. Yang, T. Qian, M.F. Wang, X.W. Shen, N. Xu, Z.Z. Sun, C.L. Yan, *Adv. Mater.*, 2016, **28**, 539.
- 15. J.T. Xu, M. Wang, N.P. Wickramaratne, M. Jaroniec, S.X. Dou, L.M. Dai, *Adv. Mater.*, 2015, **27**, 2042–2048.
- 16. Y.S. Yun, H.J. Jin, Sulfur-doped, Mater. Lett., 2017, 198, 106–109.
- L.Y. Suo, J.H. Zhu, X.Y. Shen, Y.Z. Wang, X. Han, Z.Q. Chen, Y. Li, Y.R. Liu, D. Wang, Y.W. Ma, *Carbon*, 2019, **151**, 1–9.
- Y.H. Qu, M.M. Guo, F.Y. Zeng, C.W. Zou, C.L. Yuan, X.H. Zhang, Q. Li, H. Lu, Solid State Ionics, 2019, 337, 170–177.
- Q. Zhao, Y. Meng, L.C. Yang, X. He, B. He, Y.H. Liu, D. Xiao, J. Colloid Interf. Sci., 2019, 551, 61–71.
- J. Bai, H. M. Wu, S. Q. Wang, G. X. Zhang, C. Q. Feng and H. K. Liu, *Appl. Surf. Sci.*, 2019, 488, 512-521.