Supporting Information

Large-Scale Fabrication of BCN Nanotube Architecture Entangled on Three Dimensional Carbon Skeleton for Energy Storage

Hassina Tabassum^{\$}, Chong Qu^{\$}, Kunting Cai, Waseem Aftab, Zibin Liang, Tianjie Qiu, Asif Mahmood, Wei Meng, Ruqiang Zou*

Beijing Key Lab of Theory and Technology for Advanced Battery Materials, Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China.

*E-mail: rzou@pku.edu.cn

^{\$} Equal contribution in this work

Experimental Section:

Chemicals: All chemicals were purchased and used without further purification. Boric acid (H₃BO₃) and urea were bought from Xilong Chemical Technology Co., Ltd. Polyethylene glycol (PEG) with different molecular weights was purchased from Beijing Yili Fine Chemical Co., Ltd. Commercial Melamine foam (MF) was used after washing with ethanol and water. Commercial graphene was bought from Alfa Aesar by thermo fisher scientist.

Synthesis of 3D-BCN Nanotubes : For the synthesis of 3D-BCN nanotubes architecture, colorless solution of PEG (0.15g), Urea (5.5g) and Boric acid (0.15g) in 50 mL water was sonicated for 30 min until a homogenous mixture was obtained. After that, a 3×4 cm² peices of commercial melamine foam was immersed in the solution and dried at 80°C in air for 5h. The enveloped melamine foam with BCN precursors was carbonized at 950°C temperature for 4h under the flow

of Ar. Afterward, 3D-BCN-950 nanotubes were obtained. For finding the effect of temperature on the growth of BCN nanotubes on the MF derived N doped carbon sekeleton at lower pyrolysis temperature 750 and 850°C. The product were named as 3D-BCN-750 and 3D-BCN-850. For comparatitve strudy, one sample was prepared without BCN precursors through the pyrolysis of MF at 950°C and named as 3D-CN-950. The MF free mono doped carbon based products (BC-950 and NC-950) were fabricated by using the Urea and Boric acid separately with PEG-2000 and pyrolyzed at 950 °C.

Fabrication of 65 Ni-MDH as positive electrode:

Synthesis of Ni-Co MOF-74: MOF-74 with different Ni: Co ion ratios were synthesized by a onepot solvothermal. Typically, 0.049 g of Ni(NO₃)₂· $6H_2O$ and 0.026 g of Co(NO₃)₂· $6H_2O$ along with 0.025 g of 2,5-dihydroxy-1,4-benzenedicarboxylic (DOBDC) were dissolved in a mixed solvent with 3.5 mL of dimethylformamide (DMF), 3.5 mL of ethanol, and 3.5 mL of deionized water under stirring. The solution was transferred into a Teflon-lined autoclave, tightly capped, and placed in an oven at 120 °C for 24 h. After cooling to room temperature, the parent liquor was decanted, the obtained material was washed thoroughly with methanol and DMF before immersed in anhydrous methanol for 3 days, during which the activation solvent was decanted and replaced once per day. The obtained material was then dried under vacuum at 80 °C for 24 h to remove the solvent and obtain as-synthesized MOF-74. For comparison, Ni-Co MOF-74 with different Ni: Co molar ratios were also fabricated by the same process.

Synthesis of MOF-74-derived Ni-Co double hydroxide (MDH): 5.0 mg of prepared Ni-Co MOF-74 were dispersed in a 2 M KOH solution (15 mL). The mixture was gently stirred for 2 h at room temperature and then transferred into a 30 mL Teflon-lined stainless autoclave. The autoclave was sealed and placed in an oven at 120 °C for 2 h. The as-obtained material was filtered and washed

repeatedly with ethanol and deionized water and then dried under vacuum at 80 °C for 24 h. the as obtained product was named as 65 Ni-MDH.

Characterization: The morphology of 3D-BCN products were characterized by field emission electron microscopy (FESEM) by using a Hitachi S-4800 microscope, NOVA SEM coupled with elemental mapping and transmission electron microscopy (TEM) of FE1 Tecnai T20. Highresolution TEM images were recorded by Tecnai F20 and F30 microscope. The powder X-ray diffraction (PXRD) was conducted on the Bruker D8 advanced diffractometer using Cu K α radiation. Raman spectroscopy of 3D-BCN products were tested by using RENISHAW Raman spectrum equipment. The surface area was calculated using N₂ sorption test in Quantachrome autosorb-IQ gas adsorption analyzer at 77 K. All samples were evacuated at 150 °C for 5 h under dynamic vacuum before the adsorption test. Using sorption data, non-linear density functional theory (NL-DFT) was applied to calculate the pore size distribution while the pore volumes were calculated at relative pressure (P/Po) of 0.995. X-ray photoelectron spectroscopy (XPS) of 3D-BCN products was carried out by using an axis ultra-imaging photoelectron spectrometer with monochromatic Al K α line.

Electrochemical Testings:

Electrochemical measurement: The electrochemical measurements were carried out by using a electrochemical workstation in case of both three-electrode configuration and two-electrode device. For the working electrode of three-electrode system, a mixture slurry containing of 90 wt% active materials, and 10 wt% PTFE binder was prepared then rolled with the assistance of ethanol to form a uniform film with a typical areal mass of approximately 3.5 mg cm⁻² (We calculated the specific capacitance based on the mass of active materials in three-electrode configuration, while the specific capacitances of the ASC and SSC were calculated based on the total mass of the active

materials on both positive and negative electrodes). The film electrode was then pressed between two nickel foam, and dried under vacuum at 80 °C for 12 h. A platinum mesh electrode and an Ag/AgCl electrode prefilled with 4 M KCl aqueous solution saturated with AgCl were used as the counter and the reference electrodes, respectively. The cyclic voltammograms (CV) were acquired in a potential range between -1 and 0 V at different scan rates, and the charge-discharge processes were performed between -1 and 0 V at different current densities in a 2 M KOH aqueous electrolyte. Based on the galvanostatic discharge curve, the specific capacitance C(Fg^{-1}) was calculated as follows: ^[3]

C represents the galvanostatic charge-discharge (GCD) specific capacitance. \int^{Vdt} is the integral current area, where V is the potential with initial and final values of V_i and V_f, respectively. ${}^{i}m$ =I/m is the current density, where I is the current and m is the mass of active materials. The cyclic stability was evaluated by galvanostatic charge-discharge (GCD) measurements at a current density of 10 A g⁻¹.

The electrochemical measurements of the two-electrode devices with separator of MPF30AC-100 (Nippon Kodoshi Corporation, Kochi, Japan) in a split test cell (MTI Corporation) configuration were carried out in a 2 M KOH electrolyte. For the testing of 3D-BCN-950//65 Ni-MDH ASC, the positive electrode film was prepared with the same method described above with 80 wt% active material, 10 wt% Super P, and 10 wt% PTFE binder. The mass ratio of positive electrode to negative electrode is determined according to charge balance theory ($q^+ = q^-$). Based on the CV results from three-electrode system,

$$q = \int imdV/v \qquad \qquad S(2)$$

where q represents the charge, m is the mass of the active material, and $\int i dV/v$ is the integral area from CV.

In order to achieve charge balance,
$$m^+ \cdot \left(\int \frac{idV}{v}\right)_+ = m^- \cdot \left(\int \frac{idV}{v}\right)_-$$
, thus,

$$R = m^{+}:m^{-} = \left(\int \frac{idV}{v}\right)_{-}:\left(\int \frac{idV}{v}\right)_{+} \qquad S(3)$$

The CV was acquired in a potential range between 0 and 1.5 V at different scan rates, and the charge-discharge processes were performed by cycling the potential from 0 to 1.45 V at different current densities. The cyclic stability was evaluated by galvanostatic charge-discharge measurements at a current density of 10 A g^{-1} .

The energy density E (Wh kg⁻¹) and power density P (W kg⁻¹) in Ragone plot were calculated with the following equations,

$$P = 3600 \cdot \frac{E}{\Delta t} \tag{5}$$

Where *C* is the specific gravimetric capacitance (F g⁻¹), ΔV is the potential window (V), and Δt is the discharge time (s).

Additional Figures



Figure S1 (a,b). Higher magnification FESEM images of 3D-BCN-950 nanotubes architecture.



Figure S2. (a-b) FESEM and (c-d) TEM images of 3D-BCN-750 architecture.



Figure S3. (a-b) FESEM and (c-d) TEM images of 3D-BCN-850 nanotubes architecture.



Figure S4. FESEM images of MF derived 3D-CN.



Figure S5. PXRD of 3D-BCN architecture and 3D-CN.



Figure S6. XPS survey spectra of 3D-BCN architecture.



Figure S7. B1s and N1s of (a, b) 3D-BCN-850 and (c, d) 3D-BCN-750 architecture.



Figure S8. Charge-Discharge behavior of (a) 3D-BCN-850 and (b) 3D-BCN-750 architecture.



Figure S9. (a,b) FESEM images of BC-950 and NC-950, (c) CV and (d) charge-discharge

curves of CN-950, BC-950 and commercial graphene.



Figure S10. (a) PXRD and (b) SEM image of 65 Ni-MDH electrodes.



Figure S11. (a) CV and (b) of 65 Ni-MDH electrodes in three electrode system exhibit the capacitance of 1740 Fg⁻¹ at 1Ag⁻¹.



Figure S12. Compatibility of 3D-BCN-950 and 65 Ni-MDH electrodes.



Figure S13. (a) CV and (b) charge-Discharge behavior of 3D-BCN-950//65 Ni-MDH.



Figure S14. Series connection of 3D-BCN-950//65 Ni-MDH to enlighten the commercial

LED.

Samples name	B / %	C / %	N /%	O /%
3D-BCN-950	3.89	75.1	7.85	13.15
3D-BCN-850	10.45	69.64	9.35	10.55
3D-BCN-750	13.33	74.65	4.99	7.02

 Table S1. XPS Elemental distribution in 3D-BCN architecture.

 Table S2. N2 sorption study of 3D-BCN architecture.

Sample Name	S _{BET} / m ² g ⁻¹
3D-BCN-950	649
3D-BCN-850	460
3D-BCN-750	140

Table S3. Comparison of ASC performance regarding negative electrodes for ASC with current

 literature.

ASC device	Active mass loading	Negative	Energy	Power	Ref.
	on negative	Electrode	Density	density	
	electrodes/ mg/cm ²		(Whkg-1)		
				(Wkg ⁻¹)	
MnO ₂ /CF0.2	4	Carbon foam	86.2	174.8	1
Co ₃ O ₄ //carbon	1	Porous carbon	7.9	450	2
NiCo ₂ O ₄ /Porou	2	Porous carbon	21	424.5	3

s carbon						
MoO ₃ -	2.4	PPy	21.03	22	4	
PPy//CNTs-						
MnO ₂						
AC//LiMn ₂ O ₄	3	Activated	33.12	90	5	
		Carbon				
rGO/Ag/Ni ₃ S ₂	2.5	Reduced	28.7	425	6	
		Graphene				
		oxide				
NiFe ₂ O ₄ @MnO	2.5	Activated	45.2	174	7	
2//AC		Carbon				
FeCo ₂ O ₄ @Mn	6	Activated	22.68	406.01	8	
O ₂ //AC		Carbon				
Co ₃ O ₄ /NHCSs	3.8	nitrogen-doped	34.5	753	9	
		carbon hollow				
		spheres				
Co ₉ S ₈ @Ni(OH)	2	Active Carbon	31.35	252.8	10	
_{2/} Active		film				
Carbon film						
Ni ₃ S ₂ /CoNi ₂ S ₄	5	Activated	50.7	1594.1	11	
/NF//AC/NF		Carbon				
Fe ₂ O ₃ /GH//GH	2.5	GH nanosheets	25.6	347	12	

-III					
e NiCo-	2.29	activated	89.7	456.8	13
LDH@CNT/N		polyaniline			
F//APDC/NF		derived carbon			
GF@PPy@Mn	0.08	GF@PPy@Mn	28	508	14
O ₂ //GF@PPy@		O ₂			
MnO ₂					
$NiCo_2S_4@Ni_3V_2$	2.5	activated	42.7	200	15
O ₈ //activated		carbon			
carbon					
ZnO	2.5	porous N-	23.6	847	16
QDs/carbon/C		doped			
NTs//porous N-		carbon/CNTs			
doped					
carbon/CNTs					
3D-BCN-	2.5	3D-BCN-950	72	896	This
950//65 Ni-					work
MDH					

References

- S1. S. He and W. Chen, J. Power Sources, 2014, 262, 391-400.
- S2. R. R. Salunkhe, J. Tang, Y. Kamachi, T. Nakato, J. H. Kim and Y. Yamauchi, ACS Nano, 2015, **9**, 6288-6296.
- S3. W. Wang, J. Qi, Y. Sui, Y. He, Q. Meng, F. Wei and Y. Jin, J. Nanosci. Nanotechnol., 2018, 18, 5600-5608.
- P. C. Du, W. L. Wei, D. Liu, H. X. Kang, C. Liu and P. Liu, J. Mater. Sci., 2018, 53, 5255-5269.
- H. W. Xiao, Y. R. Wang, K. Xie, S. Q. Cheng and X. Z. Cheng, J. Alloys Compd., 2018, 738, 25-31.
- S6. J. Q. Qi, Y. Chang, Y. W. Sui, Y. Z. He, Q. K. Meng, F. X. Wei, Y. J. Ren and Y. X. Jin, Adv. Mater.Interface, 2018, 5, 201700985.
- S7. X. Zhang, Z. Zhang, S. Sun, Q. Sun and X. Liu, Dalton Trans., 2018, 47, 2266-2273.
- S8. F. F. Zhu, Y. Liu, M. Yan and W. D. Shi, J. Colloid Interface Sci., 2018, 512, 419-427.
- S9. T. Liu, L. Zhang, W. You and J. Yu, Small 2018, 201602868.
- S10. F. F. Zhu, M. Yan, Y. Liu, H. Shen, Y. Lei and W. D. Shi, J. Mater. Chem.A, 2017, 5, 22782-22789.
- S11. W. He, C. Wang, H. Li, X. Deng, X. Xu and T. Zhai, Adv. Energy Mater., 2017, 7, 1700983.
- S12. H. Zhang, Q. M. Gao, K. Yang, Y. L. Tan, W. Q. Tian, L. H. Zhu, Z. Y. Li and C. X. Yang,
 J. Mater. Chem.A, 2015, 3, 22005-22011.
- S13. X. Li, J. Shen, W. Sun, X. Hong, R. Wang, X. Zhao and X. Yan, J. Mater. Chem.A, 2015, 3, 13244-13253.
- S14. T. Qin, B. Liu, Y. Wen, Z. Wang, X. Jiang, Z. Wan, S. Peng, G. Cao and D. He, J. Mater. Chem.A, 2016, 4, 9196-9203.

- S15. L. Niu, Y. Wang, F. Ruan, C. Shen, S. Shan, M. Xu, Z. Sun, C. Li, X. Liu and Y. Gong, J. Mater. Chem.A, 2016, 4, 5669-5677.
- S16. Y. Zhang, B. Lin, J. Wang, J. Tian, Y. Sun, X. Zhang and H. Yang, J. Mater. Chem.A, 2016, 4, 10282-10293.