Fabrication of nitrogen-rich three-dimensional porous carbon

composites with nanosheets and hollow spheres for efficient

supercapacitor

Jinghua Liu^a, Xiaohui Ren^a, Xu Kang^b, Xiong He^a, Peicheng Wei^a, Yan Wen^b and Xin Li^a

^aMIIT Key Laboratory of Critical Materials Technology for New Energy Conversion

and Storage, School of Chemistry and Chemical Engineering, State Key Lab of Urban

Water Resource and Environment, Harbin Institute of Technology, Harbin 150090,

China.

^bSchool of Environment, Harbin Institute of Technology, Harbin 150090, China

*Corresponding author: Tel.: +86-0451-86282153.

E-mail address: lixin@hit.edu.cn (X. Li)

As shown in Fig. S1a, diffraction peak at 27.4° can be indexed as the respective (002) plane of g-C₃N₄, indicating the presence of g-C₃N₄ in the intermediate calcined at 550 °C[1]. In addition, the FT-IR spectrum further confirms the existence of $g-C_3N_4$ in the intermediate. As shown in Fig. S1b, the peak at 810 cm⁻¹ is related to the triazine breathing vibration. All of the peaks in the $1200-1700$ cm⁻¹ region are derived from typical C-N heterocyclic stretches of the triazine (C_6N_7) ring[2]. Absorbance ranging from 3000 to 3400 cm^{-1} is associated with the N-H and O-H groups, suggesting the formation of g-C₃N₄ at 550 °C.

Fig. S2 TGA curve of DCDA in N² from room temperature to 1000 ℃.

Fig. S2 shows the TGA curve of DCDA in N² atmosphere from room temperature to 1000 ℃. It can be seen that DCDA suffers severe mass loss before 720 °C. With increasing the calcination temperature, DCDA gradually transformed to melamine, tris-s-triazine, and $g-C_3N_4$ in the range of 210-640 °C. Then, $g-C_3N_4$ undergoes thorough decomposition until 720 °C[3].

Fig. S3 SEM image of $PDA@SiO_2$ (a), NCN/NHCS-700 (b), and NCN/NHCS-900 (c).

Fig. S4 XPS spectra of NCN/NHCS-Ts.

Sample	$C(wt\%)$	$N(wt\%)$	$O(wt\%)$
NCN/NHCS-700	63.3	32.1	4.6
NCN/NHCS-800	72.1	23.2	47
NCN/NHCS-900	84.6	9.6	5.8

Table S1 The content (wt%) of C, N, and O elements in NCN/NHCS-Ts.

Fig. S5 Relationship between the specific capacitance and the current densities from $1-80$ A g^{-1} for NCN/NHCS-800.

performances in time electrone configurations.				
Materials	V	Electrolytes	Capacitance	
N-doped mesoporous carbon sheets [4]	$-1 - 0$	6 M KOH	232 F g^{-1} at 0.5 A g^{-1}	
Porous N-doped carbon [5]	$-1 - 0$	6 M KOH	350.8 F g^{-1} at 1 A g^{-1}	
N-rich graphene-like carbon sheets [6]	$-1 - 0$	6 M KOH	261 F g^{-1} at 1 A g^{-1}	
Super-hierarchical porous carbons [7]	$-1 - 0$	6 M KOH	420 F g^{-1} at 0.5 A g^{-1}	
N-doped hollow carbon nanospheres [8]	$0 - 0.8$	$1 M H_2SO_4$	240 F g^{-1} at 1 A g^{-1}	
N-doped mesoporous carbon spheres [9]	$-1 - 0$	6 M KOH	288 F g^{-1} at 0.1 A g^{-1}	
N-doped carbon polyhedrons/sheets [10]	$-0.2 - 0.8$	$1 M H_2SO_4$	495.0 F g^{-1} at 0.1 A g^{-1}	
N-doped hollow carbon spheres [11]	$-1 - 0$	6 M KOH	436.5 F g^{-1} at 0.5 A g^{-1}	
this work	$-1.0 - 0$	6 M KOH	425 F g^{-1} at 1 A g^{-1}	

Table S2 Summary of the recently reported N-doped carbon materials and their electrochemical performances in three-electrode configurations.

Fig. S6 (a) CV curve of carbon paper current collector at a scan rate of 5 mV s⁻¹, (b) CV curves of carbon paper current collector compared with NCN/NHCS-800 at a scan rate of 5 mV s^{-1} .

Fig. S7 Cycling performance of NCN/NHCS-800-SC at the current density of 10 A g^{-1} in two-electrode system.

References

[1] X.H. Li, S. Kurasch, U. Kaiser, M. Antonietti, Synthesis of Monolayer-Patched Graphene from Glucose, Angew. Chem.-Int. Edit. 51(38) (2012) 9689-9692.

[2] W. Xing, W. Tu, Z. Han, Y. Hu, Q. Meng, G. Chen, Template-induced high-crystalline g-C₃N₄ nanosheets for enhanced photocatalytic H₂ evolution, ACS Energy Letters 3(3) (2018) 514-519.

[3] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.O. Muller, R. Schlogl, J.M. Carlsson, Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts, Journal of Materials Chemistry 18(41) (2008) 4893-4908.

[4] Y.N. Hou, Z.B. Zhao, Z.F. Yu, S. Zhang, S.F. Li, J. Yang, H. Zhang, C. Liu, Z.Y. Wang, J.S. Qiu, Microporous MOFs Engaged in the Formation of Nitrogen-Doped Mesoporous Carbon Nanosheets for High-Rate Supercapacitors, Chem.-Eur. J. 24(11) (2018) 2681-2686.

[5] K.X. Zou, Y.F. Deng, J.P. Chen, Y.Q. Qian, Y.W. Yang, Y.W. Li, G.H. Chen, Hierarchically porous nitrogen-doped carbon derived from the activation of agriculture waste by potassium hydroxide and urea for high-performance supercapacitors, Journal of Power Sources 378 (2018) 579-588.

[6] W. Yang, L.Q. Hou, X.W. Xu, Z.H. Li, X.L. Ma, F. Yang, Y.F. Li, Carbon nitride template-directed fabrication of nitrogen-rich porous graphene-like carbon for high performance supercapacitors, Carbon 130 (2018) 325-332.

[7] L. Peng, Y.R. Liang, H.W. Dong, H. Hu, X. Zhao, Y.J. Cai, Y. Xiao, Y.L. Liu, M.T. Zheng, Super-hierarchical porous carbons derived from mixed biomass wastes by a stepwise removal strategy for high-performance supercapacitors, Journal of Power Sources 377 (2018) 151-160.

[8] C. Liu, J. Wang, J. Li, M. Zeng, R. Luo, J. Shen, X. Sun, W. Han, L. Wang, Synthesis of N-doped hollow-structured mesoporous carbon nanospheres for high-performance supercapacitors, ACS applied materials & interfaces 8(11) (2016) 7194-7204.

[9] J.G. Wang, H.Z. Liu, H.H. Sun, W. Hua, H.W. Wang, X.R. Liu, B.Q. Wei, One-pot synthesis of nitrogen-doped ordered mesoporous carbon spheres for high-rate and long-cycle life supercapacitors, Carbon 127 (2018) 85-92.

[10] L.R. Kong, Q.R. Chen, X.P. Shen, Z.Y. Xu, C. Xu, Z.Y. Ji, J. Zhu, MOF derived nitrogen-doped carbon polyhedrons decorated on graphitic carbon nitride sheets with enhanced electrochemical capacitive energy storage performance, Electrochimica Acta 265 (2018) 651-661.

[11] J. Du, L. Liu, Y. Yu, Z. Hu, Y. Zhang, B. Liu, A. Chen, Tuning Confined Nanospace for Preparation of N‐doped Hollow Carbon Spheres for High Performance Supercapacitors, ChemSusChem 12(1) (2019) 303-309.