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Supporting Information

Melamine-assisted Synthesis of Fe₃N Featuring Highly Reversible Crystalline-Phase Transformation for Ultrastable Sodium Ion Storage

Xiangdong Ma^a, Xunhui Xiong^{a,*}, Jinquan Zeng^b, Pinjuan Zou^a, Zhang Lin^a, and Meilin Liu^c

^aGuangzhou Key Laboratory of Surface Chemistry of Energy Materials, New Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou, 510006, P. R. China

^bDepartment of Materials Science and Engineering, Sun - Yat Sen University, Guangzhou, 510275 Guangdong, P. R. China

^cSchool of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta 30332-0245, GA, United States

* Corresponding authors

E-mail: <u>esxxiong@scut.edu.cn</u>



Fig. S1 (a) FTIR spectrum, (c) XPS survey spectrum and (d) high-resolution N 1s XPS spectrum of MA sponge and the precursor; (b) EDS mapping of the precursor.



Fig. S2 Digital photos of the precursors before (a) and after (b) extensive sonication in deionized water.



Fig. S3 XRD patterns of the 3DNCF.



Fig. S4 SEM images of the 3DNCF.



Fig. S5 SEM (a-b), TEM (c-d) images and (e) XPS survey spectrum and high-resolution elemental (f) C 1s, (g) N 1s and (h) Fe 2p spectra of $Fe_3N/3DNCF$ composite without adding glucose.



Fig. S6 *Ex situ* TEM images of Fe₃N@C/3DNCF anode for the first cycle at a discharged state of a) 0.55 V and b) 0.01 V, and at a charged state of c) 1.0 V and d) 3.0 V.



Fig. S7 (a) The galvanostatic charge and discharge voltage profile at 0.1 A g⁻¹, (b) cycle performances of 3DNCF at 1 A g⁻¹.

Table S1. ICP result of the Fe $_3N@C/3DNCF$ and Fe $_3N/3DNCF$ composites

| Material | Analyte | Conc.Units | Fe (wt. %) | Fe ₃ N (wt. %) |
|---------------------------|---------|------------|------------|---------------------------|
| Fe ₃ N@C/3DNCF | Fe | 1.4 mg/L | 25.38 | 27.5 |
| Fe ₃ N/3DNCF | Fe | 1.35 mg/L | 24.37 | 26.4 |

| | Materials | Synthesis approach | Capacity Retention | Reference |
|---------|--------------------------------|--|---|---|
| Ref. S2 | G-VNQD-500 | Hydrothermal and annealing at NH ₃ atmosphere | $280 \text{ mA h } \text{g}^{-1} \text{ after}$ $800 \text{ cycles at } 240$ mA g^{-1} | Adv. Energy Mater. 2016, 6(6): 1502067 |
| Ref. S4 | Fe ₃ N@C | Electrospinning and two step annealing | 280 mA h g^{-1} after 300 cycles at 400 mA g^{-1} | Adv. Mater. 2018, 1800525 |
| Ref. S6 | Mo ₂ N | Hydrothermal and annealing at NH ₃ atmosphere | 180 mA h g^{-1} after 300 cycles at 500 mA g^{-1} | Energy Storage Materials, 2019, doi: 10.1016/j.ensm.2019 .04.007 |
| Ref. S1 | VNQD@NC HSs | Hydrothermal and annealing at NH ₃ atmosphere | $306 \text{ mAh } \text{g}^{-1} \text{ after}$ 1400 cycles at 1000 mA g ⁻¹ | J. Mater. Chem. A, 2019, 7(15): 9289- 9296 |
| Ref. S3 | Sn ₃ N ₄ | two step ammonolysis process and annealing at NH ₃ atmosphere | 152 mA h g ⁻¹ after 50 cycles at 200 mA g ⁻¹ | J. Mater. Chem. A, 2016, 4, 5081 |
| Ref. S5 | Ni ₃ N | Solution-based method and annealing at NH ₃ atmosphere | 80 mA h g ⁻¹ after 20 cycles at 423 mA g ⁻¹ | J. Mater. Chem. A, 2013, 1, 6441–6445 |
| | Fe ₃ N@C/3DNCF | Solution-based method and one step annealing | 375 mA h g^{-1} after 2000 cycles at 1000 mA g ⁻¹ | Our work |

Table S2 Comparison of synthesis approach and cycling performance of Fe₃N@C/3DNCF with previously reported metal nitrides anodes for SIBs.



Fig. S8 The rate performance of (a) $Fe_3N@C/3DNCF$ and (b) $Fe_3N/3DNCF$.



Fig. S9 Recorded electrochemical impedance spectra of $Fe_3N@C/3DNCF$ and $Fe_3N/3DNCF$. The inset is the corresponding equivalent circuit.



Fig. S10 SEM images of Na₃V₂(PO₄)₃@C composites.



Fig. S11 (a) Typical XRD and (b) charge-discharge profiles of the $Na_3V_2(PO_4)_3@C$ at 0.1 A g⁻¹.



Fig. S12 The SEM and TEM images of Fe₃N@C/3DNCF after 2000 cycles.



Fig. S13 High-resolution XPS spectra of $Fe_3N@C/3DNCF$ after 2000 cycles. (a) Survey XPS spectra. High-resolution XPS spectra: (b) C 1s; (c) N 1s and (d) Fe 2p spectrum of $Fe_3N@C/3DNCF$.