Supporting information for:

Hard Carbon Micro-Nano Tubes Derived from Kapok Fiber as Anode Materials

for Sodium-Ion Batteries and the Sodium-Ion Storage Mechanism

Zhuo-Er Yu,^a Yingchun Lyu,^{*a} Yeting Wang,^a Shuyin Xu,^b Hongyu Cheng,^a Xiaoyang

Mu,^a Jiaqi Chu,^a Riming Chen,^a Yang Liu,^a and Bingkun Guo*^a

^a Materials Genome Institute, Shanghai University, Shanghai 200444, PR China

^b School of Physics Science and Technology, Inner Mongolia University, Hohhot

010021, PR China

Corresponding Author: yclyu@shu.edu.cn (Y. L.); guobingkun@shu.edu.cn (B. G.)

This file includes:

Experimental Section

Fig. S1-S13

Table S1-S3

Note S1-S4

Experimental Section

Materials synthesis

Hard carbon micro-nano tube samples were synthesized by direct pyrolysis methods. The initial Kapok fibers were treated with preliminary carbonation in a tube furnace at 800 °C for 3 h and further carbonized at 1200 °C and 1400 °C, respectively for 2 h under argon flow atmosphere. The subsequent coating of soft carbon was adopted to decrease the specific surface area by pyrolysis of toluene. The corresponding obtained samples are marked as 1200HCMNT and 1400HCMNT, respectively.

Materials characterizations

The X-ray diffraction (XRD) patterns of the samples were collected with a Bruker D2 X-ray diffractometer equipped with a Cu K α radiation source (λ_1 =1.54060 Å, λ_2 =1.54439 Å). The Raman spectra were collected using Renishaw inVia Basis Raman spectroscopy with a 632.08 nm helium-neon gas laser. The morphologies and the tube size of the samples were analyzed by Hitachi S4800 and SU5000 scanning electron microscope (SEM). The high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were recorded on JEM-2100F. The specific surface area was computed by the Brunauer-Emmett-Teller (BET) method using the adsorption branch of N₂ adsorption and desorption isotherms on a Quantachorme Autosorb-iQ3 automated gas sorption analyzer. The element composition analysis was measured by energy-dispersive X-ray spectroscopy (EDS) elemental mapping on Hitachi SU5000, and X-ray photoelectron spectroscopy (XPS) on ThermoFisher ESCALAB 250Xi. Electron paramagnetic resonance (EPR) spectroscopy of HCMNTs at different sodiation state were gathered on the Bruker EMXplus spectrometer system in X-band (9.5 GHz) at room temperature. And the microwave power and modulation amplitude were 0.2 mW and 4 G, respectively. The

low temperature DSC results were obtained by NETZSCH DSC 214 under sealed state in aluminium crucible.

Electrochemical measurements

The working electrodes were prepared of the active materials, and carboxymethylcellulose (CMC) binder solved in water with a ratio of 95:5. For EPR and thermal analysis technique polytetrafluoroethylene (PTFE) binder replaced CMC without current collector (active materials: PTFE is 90:10). The electrolyte was a solution of 1 M NaClO₄ or NaPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 w/w). A sodium sheet was used as reference electrode and glass fiber (Whatman GF/D) was chosen as separator. The galvanostatic discharge-charge properties were measured by a LANHE CT2001A battery test system in a voltage range of 0 - 2 V at 0.1 C (1 C = 300 mAh g^{-1}) rate at room temperature. The galvanostatic intermittent titration technique (GITT) tests were measured at 0.1 C for 0.5 h and relax time of 12 h with a cut-off voltage of 0 V. The rate performance was measured by Maccor 4200 at different rate. The cyclic voltammetry (CV) measurements were carried out on a Solartron 1470E Analytical electrochemical workstation at respective scan rates in voltage range of 0 - 2 V. The full cell was assembled with a Na₂MnFe(CN)₆ Prussian Blue (PB) as the cathode, has a weight ratio of 1.93 (PB : HCMNT). The preparation of PB cathode was gotten from literature ^[1]. The electrochemical performance was tested in voltage range of 1.5 - 3.7 V at 30 mA g⁻¹.



Fig. S1. SEM images of (a) 1400HCMNT after carbonization, (b and c) pristine silk-

cotton.



Fig. S2. (a) SEM image of 1400HCMNT; EDS elemental mapping images of (b) carbon, (c) oxygen, (d) silicon, and (e) potassium in HCMNT; (f) XPS survey spectra of 1400HCMNT; (g) high-resolution XPS scan of the C1s spectra of the 1400HCMNT. Table S1. Physical parameters and electrochemical properties for HCMNTs.

| Sample | I_D/I_G | $\mathbf{S}_{\mathrm{BET}}$ | d ₀₀₂ | L _c | L _a | RC ^a | ICE ^b |
|-----------|-----------|-----------------------------|------------------|----------------|----------------|------------------------|------------------|
| | | $(m^2 g^{-1})$ | (nm) | (nm) | (nm) | (mAh g ⁻¹) | (%) |
| 1200HCMNT | 1.63 | 10.055 | 0.39 | 1.90 | 23.56 | 228.6 | 79 |
| 1400HCMNT | 1.71 | 9.162 | 0.38 | 1.89 | 22.49 | 292.5 | 80 |

^a The reversible capacity. ^b The initial Coulombic efficiency.

Table S2. EDS and XPS elemental ratio of 1400HCMNT.

| Measurement | C-K | O-K | Si-K | K-K |
|-------------|-------|-------|-------|-------|
| | (wt%) | (wt%) | (wt%) | (wt%) |
| XPS | 93.59 | 5.30 | 1.11 | _ |
| EDS | 91.41 | 8.33 | 0.04 | 0.22 |

Note S1

The electrochemical performance of HCMNT1400 were carried out in different electrolytes as shown in **Fig. S3**. The electrode in the NaClO₄ electrolyte shows a higher initial coulombic efficiency and reversible capacity, compared to that in the NaPF₆ electrolyte. Therefore, we choose NaClO₄ electrolyte for further electrochemical tests.



Fig. S3. (a) Galvanostatic charge–discharge and (b) cycle performance profiles of 1400HCMNT in different electrolyte system at 30 mA g^{-1} .



Fig. S4. CV curves at 0.1 mV s⁻¹ of (a) 1200HCMNT, (b) 1400HCMNT.



Fig. S5. (a) Tenth cycle galvanostatic charge-discharge profiles of HCMNTs at 30 mA

g⁻¹; (b) specific capacity of the slope region and plateau region for HCMNTs at different



carbonization temperature.



Fig. S6. (a) Discharge profiles at various currents of 1400HCMNT; (b) specific capacity of the slope region and plateau region for 1400HCMNT at different rate.

Fig. S7. Capacity retention of 1400HCMNT and hard carbon materials in literatures ^[2].

Note S2

 $Na_2MnFe(CN)_6$ materials are applied for the full cell performance. The full cell was assembled with a cathode electrode of $Na_2MnFe(CN)_6$, with a N/P ratio of 1 : 1.93. The half-cell charge-discharge test of $Na_2MnFe(CN)_6$ is shown in **Fig. S8a**. It shows an initial reversible capacity of 97.8 mAh g⁻¹ and a capacity retention of 76.6 mAh g⁻¹ after 20 cycles. The full cell delivers a first charge capacity of 155 mA h g⁻¹ at a current density of 30 mA g⁻¹ in voltage range of 1.5 - 3.7 V. However, the initial coulombic efficiency is reliable low. The full cell demonstrated a stable cycling performance after irreversible reaction (**Fig. S8c**). The performance of full cell needs to be further optimized.



Fig. S8. The charge-discharge curves of (a) $Na_2MnFe(CN)_6$ and (b) $Na_2MnFe(CN)_6/1400HCMNT$ full cell of selected cycle numbers. (c) cycling performance of full cell at 30 mA g⁻¹. Note that the calculation for the specific capacity of the full cell is based on the weight of $Na_2MnFe(CN)_6$.



Fig. S9. GITT profiles of (a) 1200HCMT and (b) 1400HCMNT.

Note S3

The stability of HCMNT anode materials were further proved by SEM and EDS mapping images before and after electrochemical process as shown in **Fig. S10**. Due to the as-prepared electrode slurry underwent strong grind, the electrode was a compound of micro-nano tubes and nano sheets. During the first cycle, the structure and morphology of the HCMNTs are retentive, as shown in **Fig. S10**. Signals of Na and Cl elements are observed in the EDS results of the discharged or charged samples, resulting from the formation of SEI.



Fig. S10. SEM and EDS mapping images of (a) initial 1400HCMNT electrode; 1400HCMNT electrode at (b) discharged to 0.1 V, (c) discharged to 0 V, and (d) charged state after stable cycles.



Fig. S11. First cycle galvanostatic charge–discharge profiles of 1400HCMNT. Insert shows the Na deposition potential at -0.023 V with an obvious turning point.

Note S4

Further characterizations have been carried out to understand the intercalation mechanism of graphitic layers. As show in Fig. S12a-b, the HRTEM images of the HCMNTs discharged to 0 V show no prominent increase of the d₀₀₂ compared with the pristine samples. The Raman results also do not reveal obvious change of the relative integrated intensity I_D/I_G ratios (shown in Fig. S12c, S13a, Table. S3, and S4) even after discharged to 0 V. These results confirm that there is no obvious sodium-ion intercalation reaction during the sodiation process. However, the TEM and XRD results of as-synthesized HCMNTs (Fig. 1) reveal that interlayer spacing of graphite sheet layers reduces with increasing of carbonization temperature. Those results further confirm that sodium-ion intercalation into graphite layers does not dominate the sodiation process. Therefore, it is expected that the slope part and the plateau are related to Na⁺ adsorption on the defect sites and sodium clusters formation, respectively. For comparison, the EPR spectra measurement of the 1200HCMNT electrode after discharging (Fig. S13b) was also collected. Due to the lower capacity of plateau region, the signal of metallic sodium was weaker than the results of 1400HCMNT.



10 / 12

Fig. S12. HR-TEM images of (a) 1200HCMT and (b) 1400HCMNT at discharged state;



(c) Ex-situ Raman spectroscopy of 1400HCMNT.

Fig. S13. (a)Ex-situ Raman spectroscopy, and (b) EPR spectra of 1200HCMNT for

before and after electrochemical test.

 Table S3. Physical parameters for 1400HCMNT and 1200HCMNT before and after

 electrochemical test.

| sample | I_D/I_G |
|-----------------------------|-----------|
| 1400HCMNT Initial electrode | 2.05 |
| 1400HCMNT discharge to 0.1V | 2.08 |
| 1400HCMNT discharge to 0V | 2.07 |
| 1200HCMNT Initial electrode | 1.79 |
| 1200HCMNT discharge to 0.1V | 1.77 |
| 1200HCMNT discharge to 0V | 1.80 |

References

- J. Song, L. Wang, Y. Lu, J. Liu, B. Guo, P. Xiao, J. J. Lee, X. Q. Yang, G. Henkelman, J. B. Goodenough, *J. Am. Chem. Soc.*, 2015, 137, 2658.
- [2] a) Y. Zhu, M. Chen, Q. Li, C. Yuan, C. Wang, *Carbon* 2017, 123, 727; b) P.
 Zheng, T. Liu, S. Guo, *Sci. Rep.*, 2016, 6, 35620; c) Q. Jiang, Z. Zhang, S. Yin,
 Z. Guo, S. Wang, C. Feng, *Appl. Surf. Sci.*, 2016, 379, 73; d) Y. Cao, L. Xiao,
 M. L. Sushko, W. Wang, B. Schwenzer, J. Xiao, Z. Nie, L. V. Saraf, Z. Yang,
 J. Liu, *Nano Lett.*, 2012, 12, 3783; e) Y. Li, L. Mu, Y.-S. Hu, H. Li, L. Chen,

X. Huang, *Energy Storage Mater.*, **2016**, 2, 139; f) Y. Zheng, Y. Wang, Y. Lu, Y.-S. Hu, J. Li, *Nano Energy*, **2017**, 39, 489; g) Z. Jian, Z. Xing, C. Bommier, Z. Li, X. Ji, *Adv. Energy Mater.*, **2016**, 6, 1501874; h) J. Xiang, W. Lv, C. Mu, J. Zhao, B. Wang, *J. Alloy. Compd.*, **2017**, 701, 870; i) K.-l. Hong, L. Qie, R. Zeng, Z.-q. Yi, W. Zhang, D. Wang, W. Yin, C. Wu, Q.-j. Fan, W.-x. Zhang, Y.-h. Huang, *J. Mater. Chem. A*, **2014**, 2, 12733; j) Y. Li, Y.-S. Hu, M.-M. Titirici, L. Chen, X. Huang, *Adv. Energy Mater.*, **2016**, 6, 1600659.

[3] S. Li, J. Qiu, C. Lai, M. Ling, H. Zhao, S. Zhang, *Nano Energy*, 2015, 12, 224.