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Supporting Information

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Regulating the Interlayer Spacings of Hard Carbon Nanofibers Enables Enhanced Pore Filling Sodium Storage

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Keywords: Hard carbon, nanofiber, sodium storage mechanism, slope capacity, plateau capacity

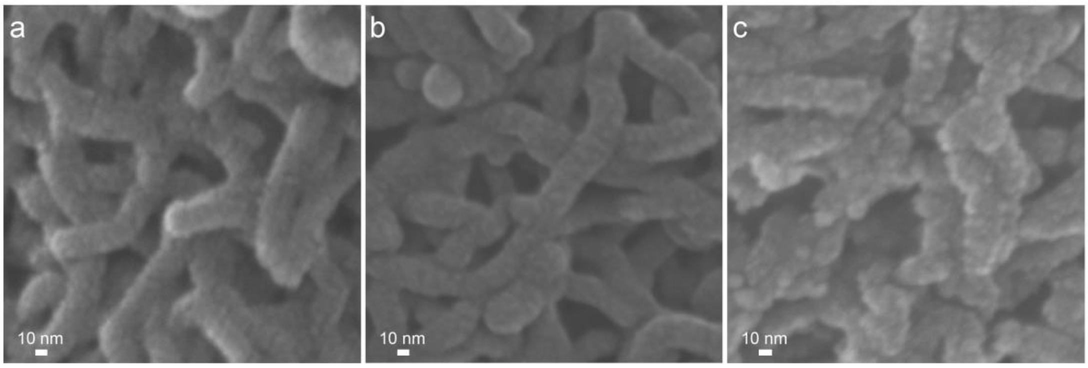

Figure S1. High-magnification SEM images of HCNF-1200 (a), HCNF-1400 (b) and HCNF-1600 (c).

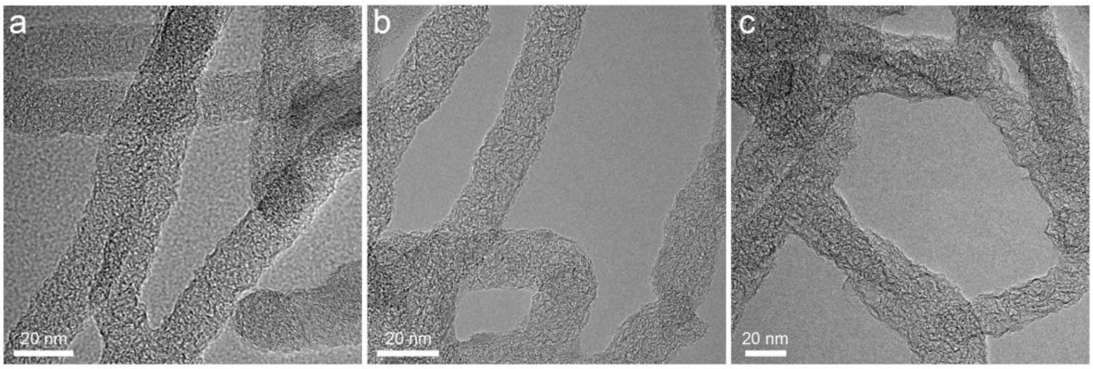

Figure S2. TEM images of HCNF-1200 (a), HCNF-1400 (b) and HCNF-1600 (c).

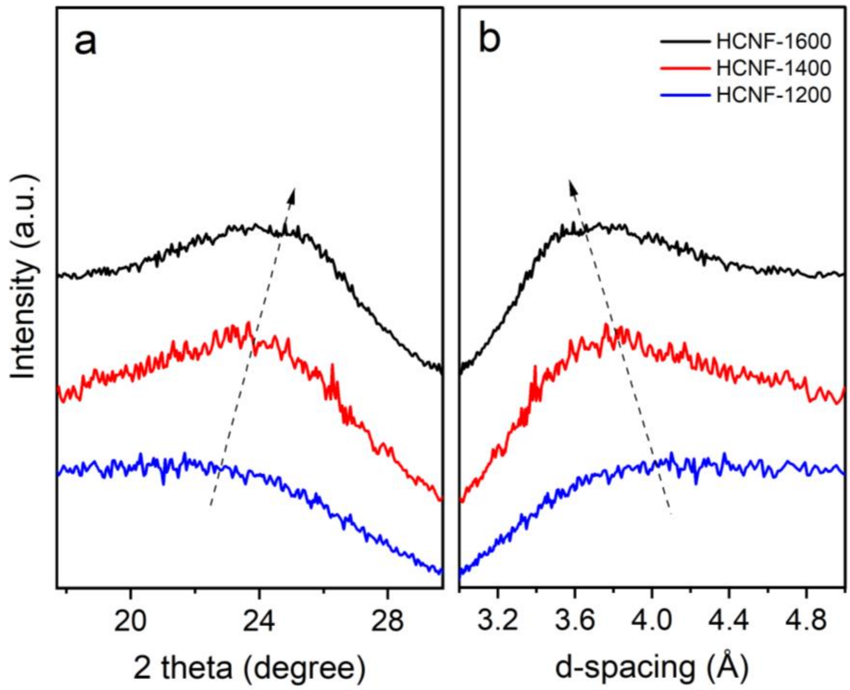

Figure S3. (a) The enlarged XRD patterns showing the (002) diffraction of the samples. (b) The interlayer spacings of HCNFs calculated from the XRD patterns.

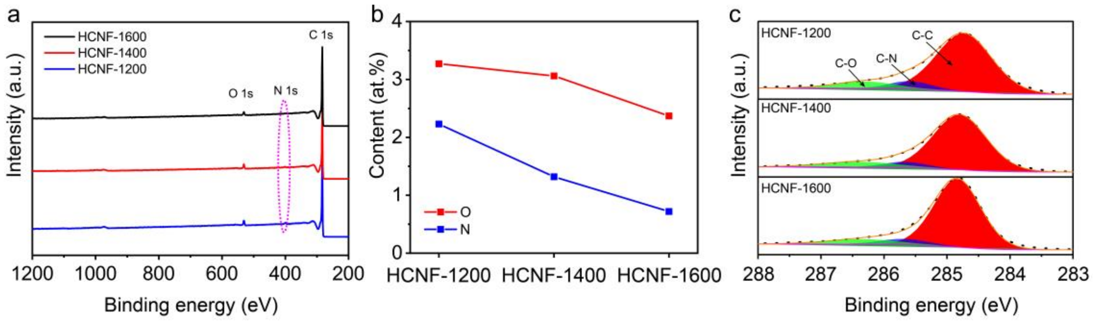

Figure S4. (a) XPS survey spectra of the HCNFs. (b) O and N contents of the HCNFs obtained at different carbonization temperatures. (c) C 1s XPS spectra of the HCNFs.

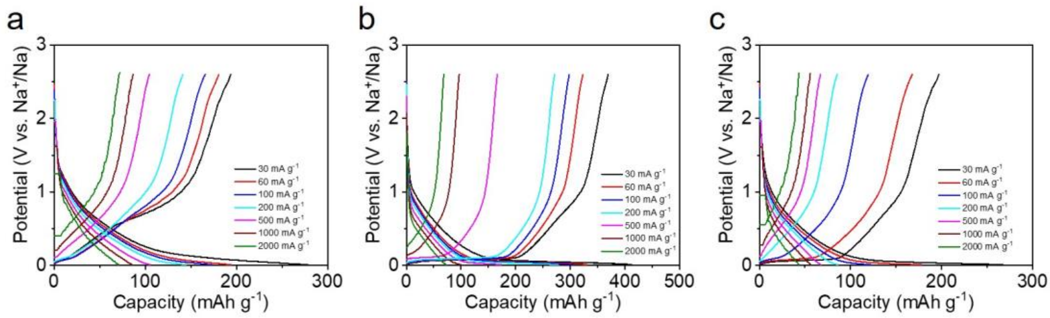

Figure S5. Representative charge/discharge profiles of (a) HCNF-1200, (b) HCNF-1400, (c) HCNF-1600 at different current densities.

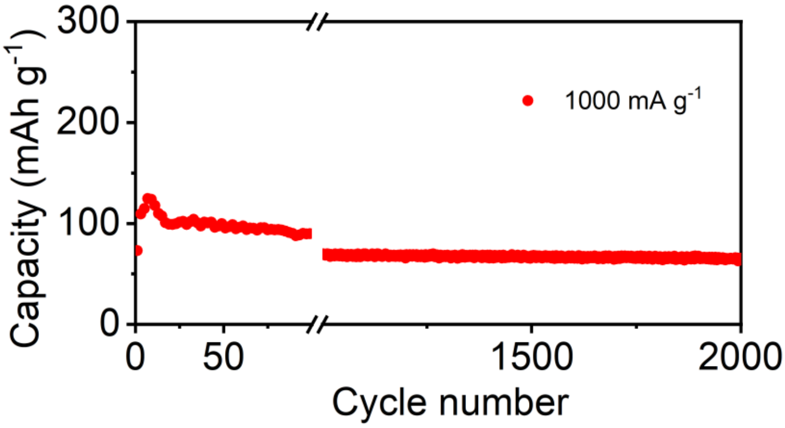

Figure S6. Long-term cyclic performance of HCNF-1400 at 1000 mA g^{-1}.

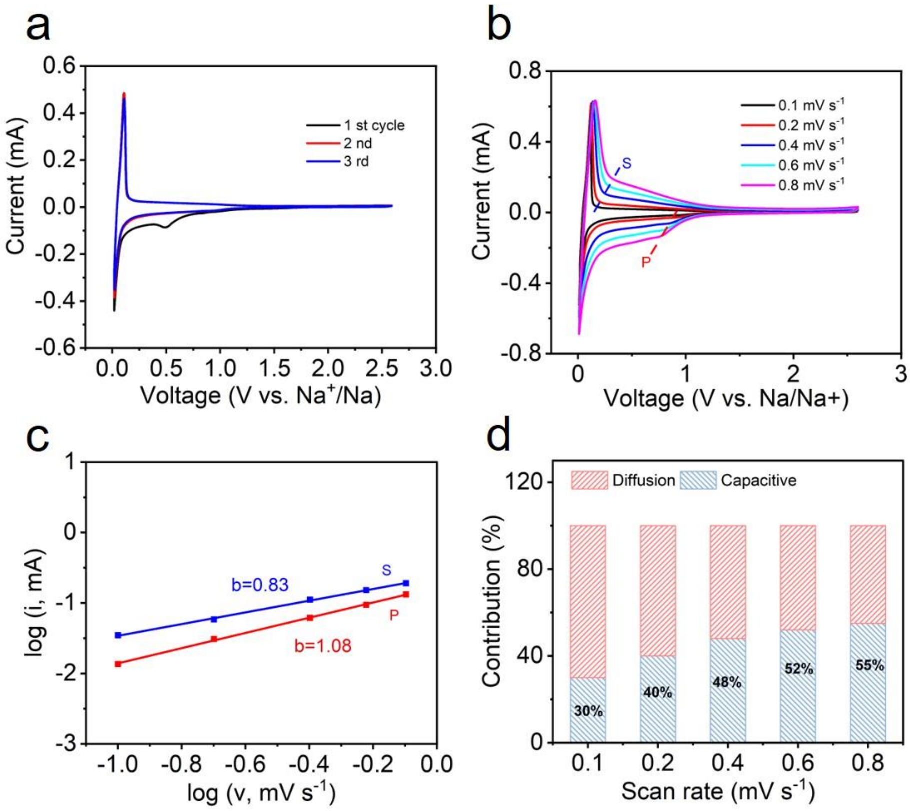

Figure S7. The first three CV curves at the scan rate of 0.1 mV s^{-1} (a) and CV curves at different scan rates (b) of HCNF-1400. (c) Plots of log(i) versus log(v) and the corresponding linear fitting. (d) Normalized contribution ratio of capacitive contribution of HCNF-1400 at different scan rates.

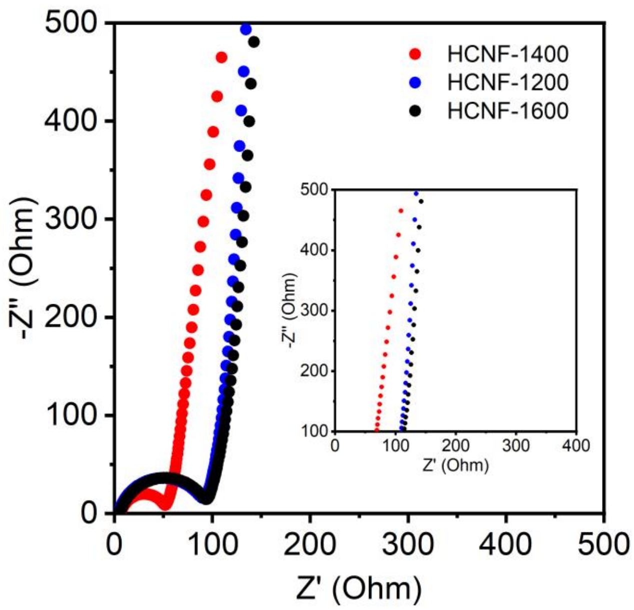

Figure S8. EIS of the HCNFs.

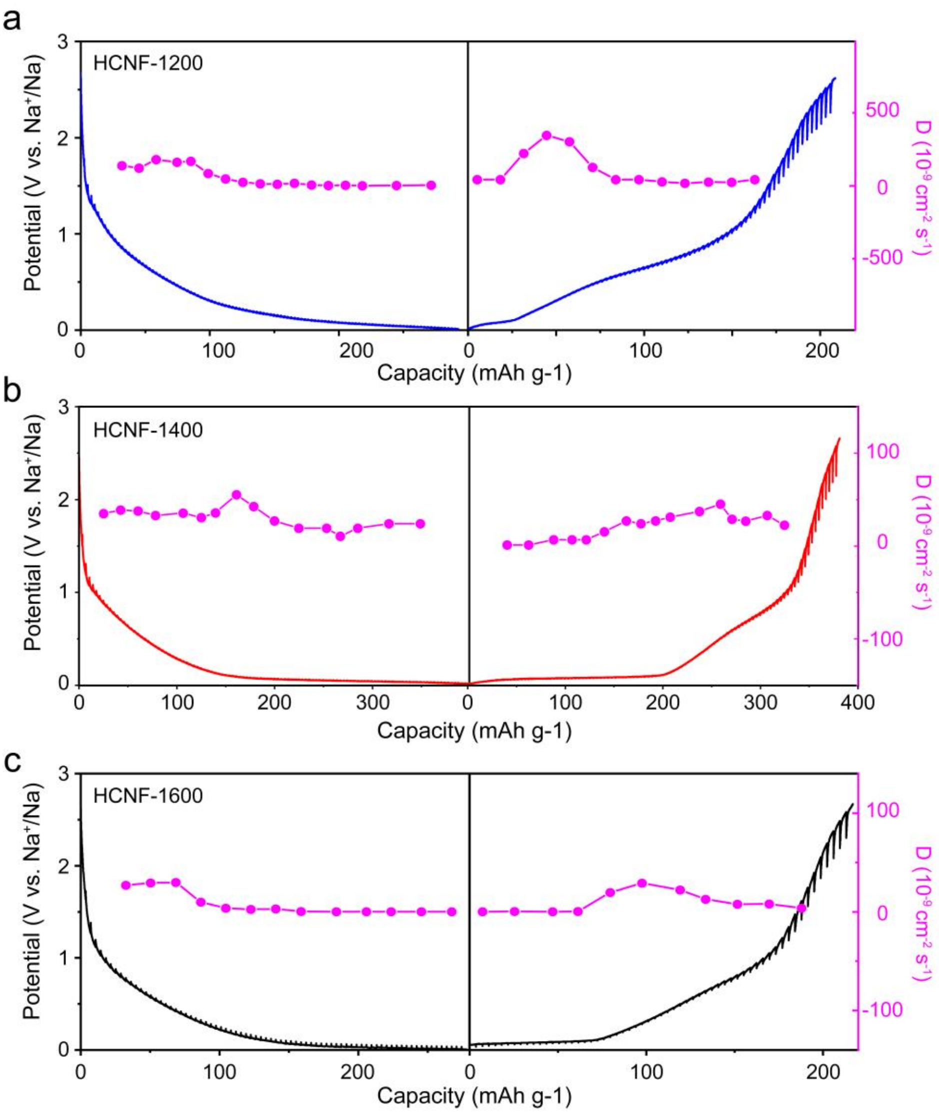

Figure S9. The GITT tests for HCNF-1200 (a), HCNF-1400 (b), HCNF-1600 (c).

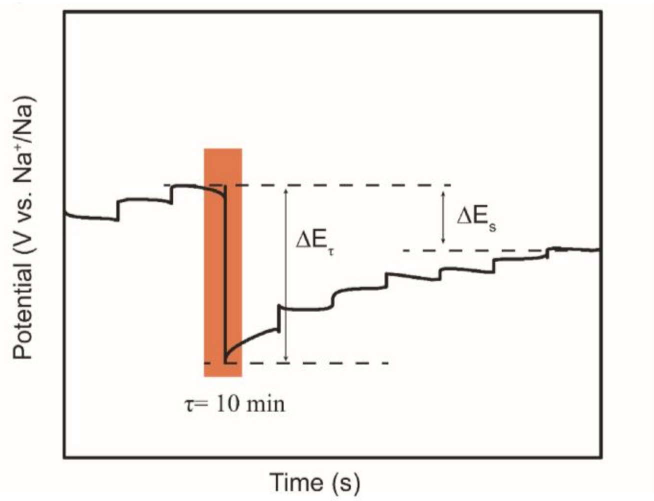

Figure S10. The schematic of the calculation of diffusion coefficient using the GITT test.

The D_{Na+} values can be calculated based on the following equation：

$$D_{Na^+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \quad \left(\tau \ll \frac{L^2}{D_{Na^+}}\right) \qquad \text{S1}$$

Where τ is the pulse duration, m_B and M_B are the active mass and molar mass of carbon, V_M is the molar volume, and S is the active surface area of the HCNF-1400 electrode. L is the average radius of the material particles. ΔE_s and ΔE_t can be obtained from the GITT curves.

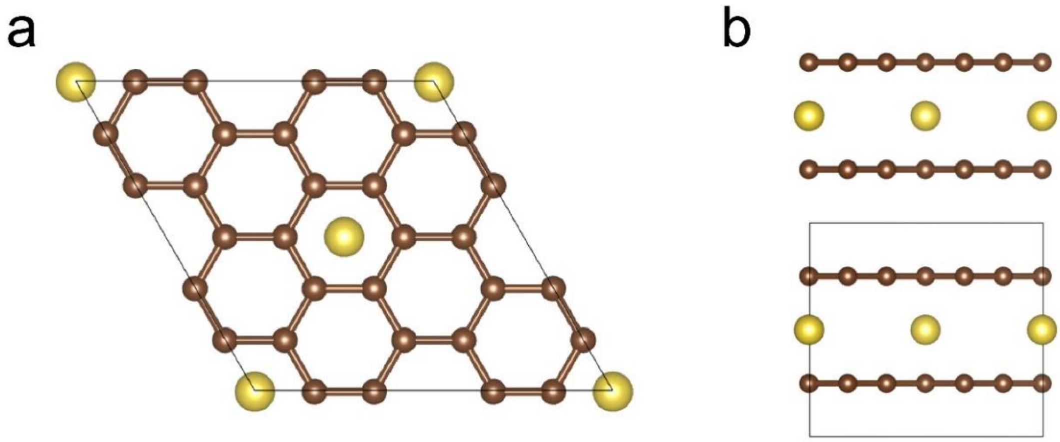

Figure S11. Top view (a) and side view (b) of the model structure used in the DFT calculations, corresponding to graphene layers with AA stacking. The atom ratio of Na to C is 1:24.

Table S1. The calculated energy cost of Na inserted into carbon (eV)

Distance (Å)	E(total)	E(graphite)	E(Na)	ΔE(cost)
3.4	-439.927732	-441.479409	-0.130422	0.906261
3.7	-442.823188	-442.170910	-0.130422	-0.195716
4.0	-444.345261	-442.372457	-0.130422	-0.855979
4.5	-445.286951	-442.422366	-0.130422	-1.301870

Table S2. Comparison of the sodium storage performances of HCNF-1400 with various hard carbon materials.

Hard carbon material	Specific capacity/mAh g^{-1} (Current density/mA g^{-1})	References
Microporous spherical carbon	223 (20) 67 (1000)	1
Cotton derived microtubes	315 (30) 180 (300)	2
pitch and lignin derived carbon	254 (30) 162 (300)	3
Phenol-formaldehyde Resin derived carbon	410 (30) ~50 (600)	4
cellulose-derived hard carbon	322 (50) 90 (1000)	5
Hollow carbon nanofibers	326 (20) 85 (1600)	6
rod-like ordered mesoporous carbons	~230 (50) 120 (1000)	7
Hard carbon nanofibers	**388 (30)** **271 (200)** **167 (500)**	**This work**

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