Electronic Supplementary Information (ESI)

Understanding the effects of cellulose polymorphism on the hard carbon for sodium-ion batteries

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S1 Experimental

S1.1 Preparation of precursor

Cellulose II was prepared by immersing 1 g microcrystalline cellulose (MCC) in 50 mL 18.5 wt% NaOH solution at room temperature for 1.5 h, and then washing with deionized water until neutral. Cellulose III was obtained by soaking MCC in ethylenediamine (EDA) (Aladdin, >99%) (1 g : 20 ml) at room temperature for 24 h, and then washing with methanol (Aladdin, >99.5%) to remove EDA completely. Excess methanol was removed by volatilization with a vacuum dryer.

S1.2 Preparation of HC-1, HC-2, and HC-3

Cellulose I, cellulose II, and cellulose III were calcined at 1300 °C (the heating rate was 2 °C min⁻¹) for 3 h in argon atmosphere to prepare HC-1, HC-2, and HC-3, respectively.

S2 Material characterization

X-ray diffraction (XRD, PANalytical, Empyrean 2) was implemented to identify the crystalline characteristics of precursors and hard carbon samples. The defect structures of HCs were characterized by Raman spectroscopy (Raman, LabRAM, JY-HR 80). The surface and morphology of cellulose and HCs were characterized by scanning electron microscopy (SEM, JEOL, JSM-7610FPlus) and transmission electron microscopy (TEM, JEOL, JEM-F200). X-ray photoelectron spectroscopy (XPS) was tested with Thermo Kalpha under a monochromatic AlKa source (Mono AlKa) with an energy of 1486.6 eV. Small angle X-ray scattering (SAXS) was performed with Xenocs Xeuss2.0 with a Cu K α light source to study the obturator structure of carbon materials. True density test was performed on the AccuPyc II 1340 with helium as the working gas. Specific surface area and pore size were analyzed using JW-BK200 (JWGB SCI.& TECH).

S3 Electrochemical characterization

Carbon anodes were prepared by mixing the HCs, Super P, carboxymethyl cellulose, and polymeric styrene-butadiene rubber with deionized water at a mass ratio of 92 : 3 : 1.5 : 3.5, followed by casting the slurry onto copper foil and vacuum-drying overnight at 80 °C.

CR2016 coin-type cells were used for electrochemical testing of HCs. Sodium metal was used as the counter electrode, 1.0 M NaPF₆ in diglyme as the electrolyte, and glass fiber as the separator. Half-cell assembly was performed in an argon-filled glove box (MIKROUNA) with water and oxygen concentrations below 1 ppm.

Charge–discharge testing and galvanostatic intermittent titration technique (GITT) were conducted on the Neware BTS Battery Test System. Charge and discharge cycles were carried out at different current densities between 0.001 and 2 V. GITT parameters were set to a 0.5 h current pulse duration at 20 mA g^{-1} and a 2 h stagnation time. Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) tests were performed using CHI660e Electrochemical Workstation.

Allomorph	Crystal system	Chain	a(nm)	b(nm)	c(nm)	γ (°)	Reference
		arrangement					
Cellulose I_{β}	Two chain	Parallel	0.778	0.820	0.104	96.55	1
	monoclinic						
Cellulose II	Two chain	Antiparallel	0.810	0.903	0.103	117.10	2
	monoclinic						
Cellulose III _I	Two chain	Parallel	0.445	0.785	0.103	105.10	3
	monoclinic						

Table S1. Lattice parameters of cellulose.

For simplicity, in this paper, cellulose I and III uniformly refer to cellulose I_{β} and III_I, respectively. All cellulose models are constructed based on published atomic coordinates and unit cell dimensions. ^{1,2,4}



Fig. S1 XRD patterns of (a) cellulose I, (b) cellulose II, and (c) cellulose III.



Fig. S2 (a) N₂ adsorption-desorption isotherms and (b) S_{BET} of cellulose.

All cellulose polymorphs exhibit type III N₂ adsorption/desorption isotherms (Fig. S2a), implying similar surface structure. Furthermore, the Brunauer–Emmett–Teller surface areas (S_{BET}) are determined to be 2.41, 2.31, and 3.64 m² g⁻¹ for cellulose I, cellulose II, and cellulose III, respectively (Fig. S2b).



Fig. S3 SEM images of (a-c) cellulose I, (d-f) cellulose II, and (g-i) cellulose III.



Fig. S4 SEM images of (a-c) HC-1, (d-f) HC-2, and (g-i) HC-3.

Sample	<i>d</i> ₀₀₂ (nm)	$L_{\rm c}({\rm nm})$	La(nm)	$I_{\rm D1}/I_{\rm G}$
HC-1	0.384	1.168	4.725	2.50
HC-2	0.378	1.224	5.543	2.26
HC-3	0.386	1.181	4.641	2.87

Table S2. Structure parameters of HCs.

Bragg's law:

 $2d\sin\theta = \mathbf{n}\cdot\lambda$

S-1

where:

d—Interplanar spacing (nm);

 θ — The Angle between the incident X-ray and the crystal plane;

n— Periodic multiple of wavelength (integer, n=1 here);

 λ — The wavelength of X ray (λ = 0.154 nm here).

Scherrer Formula:

$$L_a \& L_c = \frac{\mathbf{K} \cdot \lambda}{\beta \cdot \cos \theta}$$
 S-2

where:

$$L_a \& L_c$$
 — The lateral size (L_a) and thickness (L_c) (nm);

K— Scheller constant (K=1.84 for $L_a \& K$ =0.89 for L_c);

 λ — The wavelength of X ray (λ = 0.154 nm here);

 β — The half-height width of (1 0 0) peak (for L_a) or (0 0 2) peak (for L_c);

 θ —The reflection angle of (1 0 0) peak (for L_a) or (0 0 2) peak (for L_c).



Fig. S5 Raman spectra of (a) HC-1, (b) HC-2, and (c) HC-3.



Fig. S6 XPS curves of HCs.

Table S3. Ca	arbon and oxyge	n contents of	HCs in XPS.
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	HC-1	HC-2	HC-3
C(atomic%)	96.93	95.53	97.80
O(atomic%)	3.07	4.47	2.20

Table S3 shows that HC-2 has the lowest oxygen content, while HC-3 exhibits the highest oxygen content. The complex hydrogen bond network of cellulose II increases the binding energy of oxygen atoms, making their release more difficult. In contrast, the greater sheet distance in cellulose III provides more space for the escape of oxygen atoms.

	HC-1	HC-2	HC-3
sp ² C(atomic%)	66.52	65.60	63.80
sp ³ C(atomic%)	13.83	12.22	15.18
C-O(atomic%)	3.51	5.41	4.63
C=O(atomic%)	6.11	6.79	5.21
COOR(atomic%)	10.03	9.98	11.18

Table S4. Ratio of each peak in C 1s of HCs.



Fig. S7 Deconvoluted O 1s spectra of (a) HC-1, (b) HC-2, and (c) HC-3.

	HC-1	HC-2	HC-3
C=O (atomic%)	23.18	15.72	8.08
C-OH/C-O-C (atomic%)	32.60	34.79	36.68
O=C-O (atomic%)	44.22	49.49	55.24

Table S5. Ratio of each peak in O 1s of HCs.



Fig. S8 Fitted SAXS patterns of (a) HC-1, (b) HC-2, and (c) HC-3.

The SAXS spectra for all HCs show a broad hump, which is derived from the scattering of closed pores and nanometer-sized voids between carbon planes.⁵ Moreover, the SAXS spectra are fitted by Matlab software, as presented in Fig. S9. The fitted model is as follows:⁶

$$I(Q) = \frac{A}{Q^a} + \frac{B \cdot b^4}{(1 + b^2 Q^2)^2} + C$$
 S-3

where:

I(Q) — scattered intensity as a function of Q;

Q — scattering vector;

A — scale factor for the surface scattering at low Q;

B — scale factor for the pore scattering, and proportional to the surface area of pores;

b — size factor related to the radius of spherical pore;

C — height of the flat background.

All SAXS spectra can be fitted into two parts, corresponding to the scattering of the particle surface (in the lowest Q -value region) and the scattering of closed pore structure (in the middle Q -value region). The average pore sizes of HCs are obtained from the b value (R = $2 \times b \times \sqrt{10}$). From the fitting results, the average pore sizes of all materials are similar, but the B value of HC-1 (2.39×10⁻³) is greater than that of HC-2 (1.97×10⁻³) and HC-3 (1.56×10⁻³).



Fig. S9 Charge/discharge profiles of (a) HC-1, (b) HC-2, and (c) HC-3.



Fig. S10 Cycling performance of HCs.



Fig. S11 CV curves of (a) HC-1, (b) HC-2, and (c) HC-3 at 0.4 mV s⁻¹.



Fig. S12 CV curves of (a) HC-1, (b) HC-2, and (c) HC-3 at 0.2-1.0 mV s⁻¹.

	$R_{s}\left(\Omega ight)$	$R_{ m ct}\left(\Omega ight)$	Equivalent circuit diagrams
HC-1	7.45	1.74	Rs CPE
HC-2	7.52	20.52	Rs CPE Rct W
HC-3	10.16	3.71	Rs CPE Rct W

Table S6. The fitted circuit diagram and the corresponding values of the EIS

In the equivalent circuit diagrams, R_s represents the solution resistance; CPE is the constant phase element associated with the double-layer capacitance; R_{ct} denotes the charge transfer resistance of the electrode; and W_0 is the Warburg impedance corresponding to solid-state diffusion. Obviously, the R_{ct} in HC-2 electrode is higher than other samples, verifying that large graphite microcrystals are detrimental to the interfacial charge transfer kinetics.



Fig. S13 GITT curves of HCs.

The Na^+ diffusion coefficients (D(Na^+)) can be calculated using the following formular:⁷

$$D = \frac{4}{\pi\tau} \left(\frac{m_B V_m}{M_B S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)$$

where m_B is the mass of the electrode active material (1.827mg for HC-1 and HC-2, 1.840mg for HC-3); M_B is the molar mass of the material (12 g mol⁻¹); V_m is the molar volume of the electrode active material (5.58, 5.50, and 5.48 cm³ mol⁻¹ for HC-1, HC-2, and HC-3); *S* is the geometric area of the electrode sheet (1.13 cm²); τ is the current pulse time (1800 s); ΔE_{τ} and ΔE_s are obtained from the GITT curves.

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