

Supporting Information for:

**Achieving High-Capacity Sodium Insertion of Coal-based Hard Carbon Anodes
via Closed-Pore Modification**

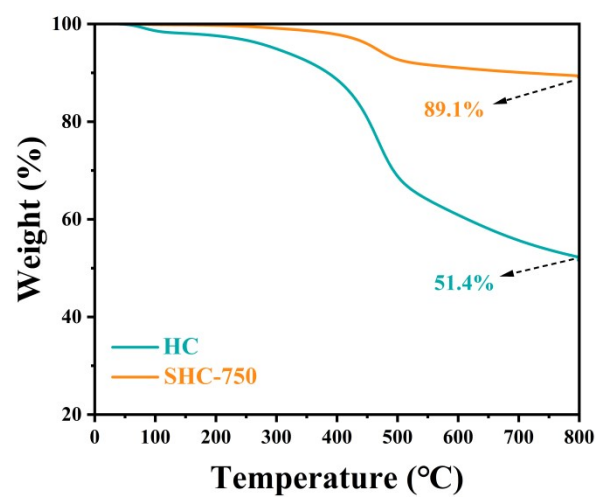


Figure S1 TG curves of HC and SHC-750

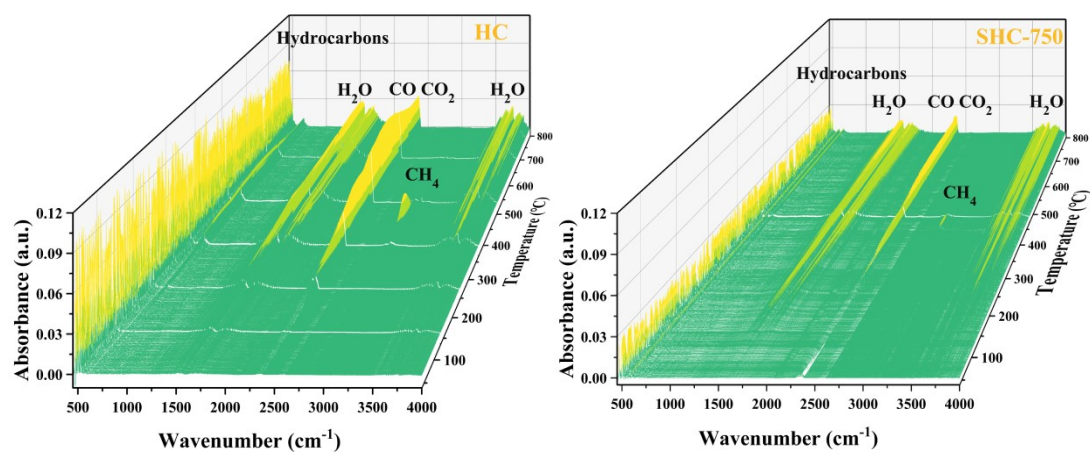


Figure S2 (a)HC, (b)SHC-750 的 TG-FTIR spectrum

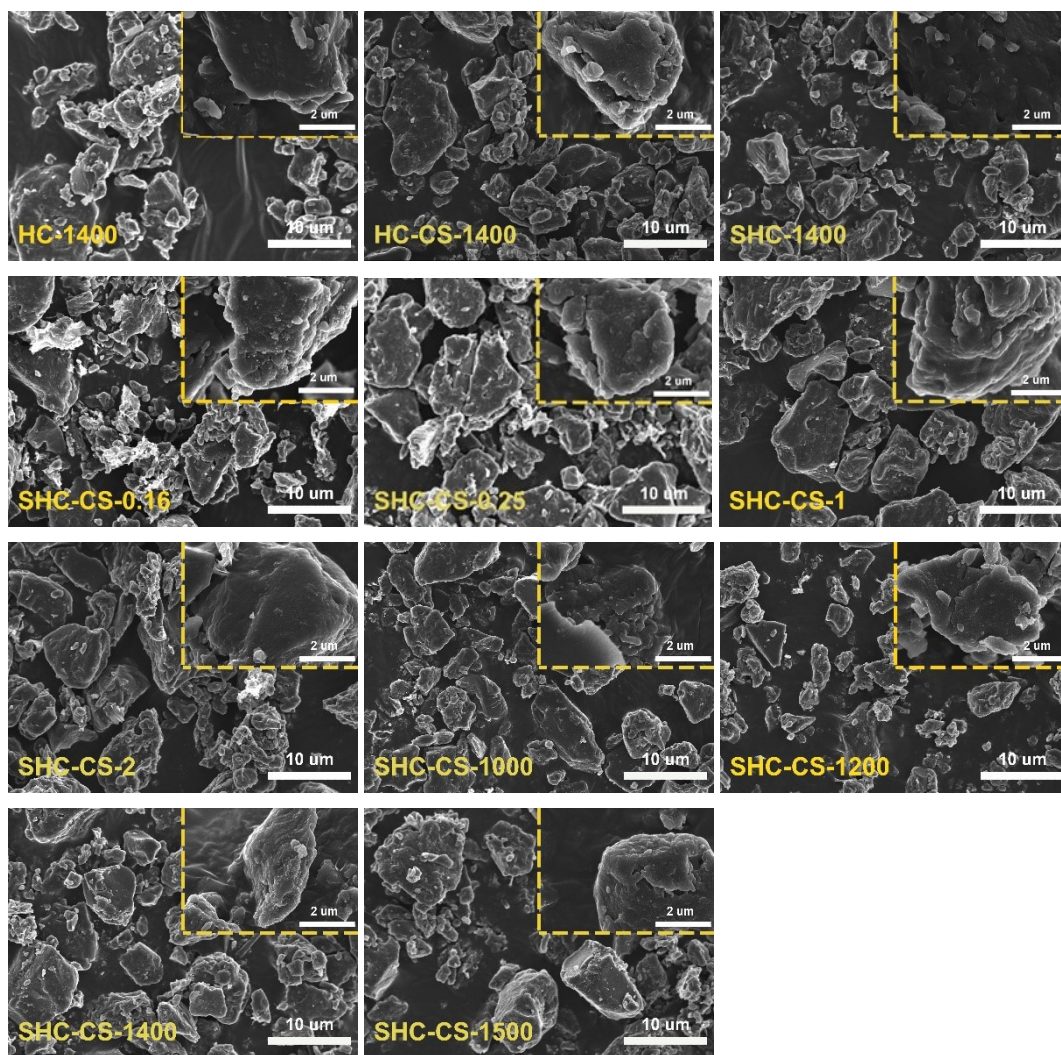


Figure S3 The SEM images of HC samples. SEM images of (a) HC-1400, (b) HC-CS-1400, (c) SHC-1400, (d) SHC-CS-0.16, (e) SHC-CS-0.25, (f) SHC-CS-1, (g) SHC-CS-2, (h) SHC-CS-1000, (i) SHC-CS-1200, (j) SHC-CS-1400 and (k) SHC-CS-1500 samples.

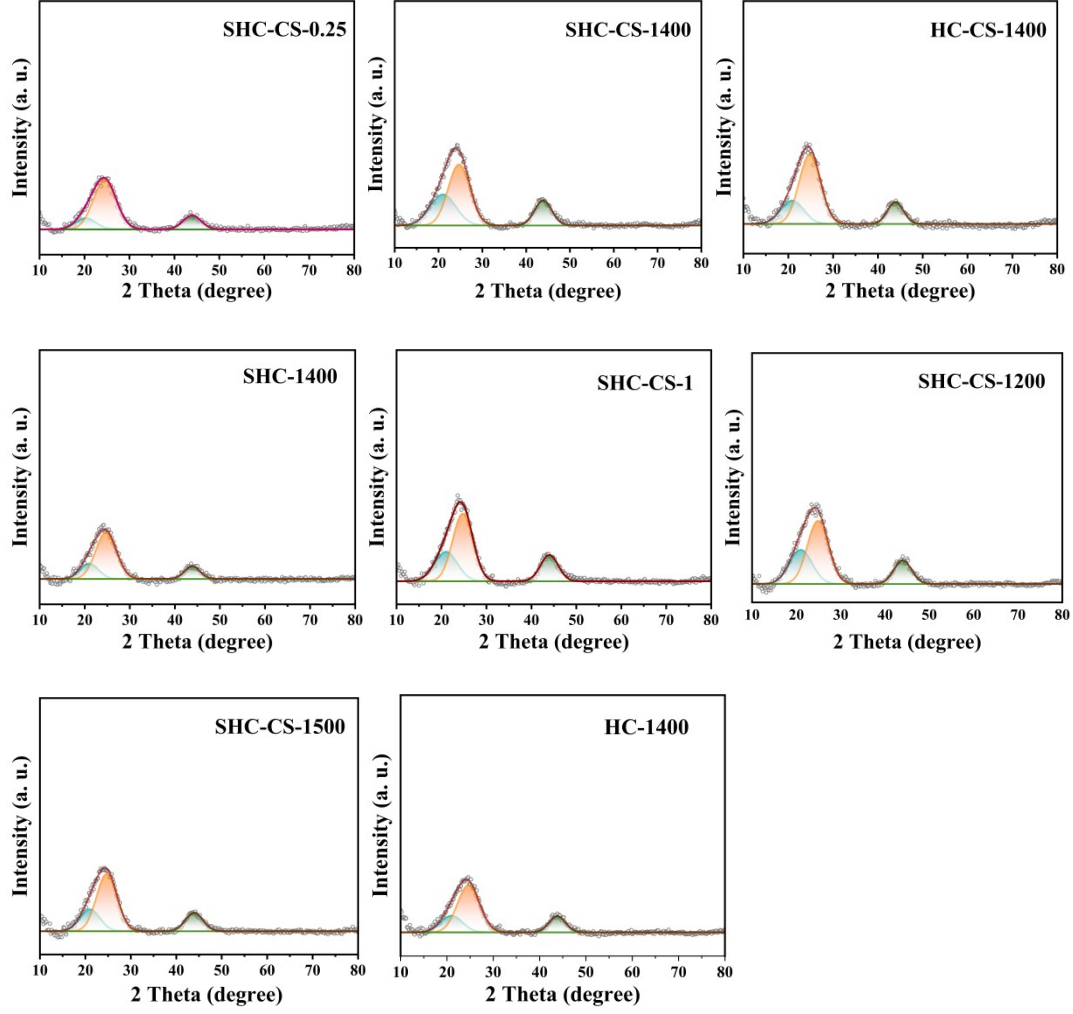


Figure S4 The fitting results of XRD patterns of (a) SHC-CS-0.25, (b) SHC-CS-1400, (c) HC-CS-1400, (d) SHC-1400, (e) SHC-CS-1, (f) SHC-CS-1200, (g) SHC-CS-1500 and (h) HC-1400 samples.

$$d = \frac{\lambda}{2 \times \sin(\theta_{002})}$$

Where λ is the wavelength of the X-rays (0.154178 nm), $2\theta_{002}$ is the peak position of (002) peak in the XRD pattern. $K_{Cu} = 0.15406$ nm.

$$L_a = 1.84\lambda / B_{100} \cos\theta_{100}$$

$$L_c = 0.89\lambda / B_{002} \cos\theta_{002}$$

Where λ is the wavelength of the X-rays (0.154178 nm), B_{100} and B_{002} are the full width at half maxima of the (100) and (002) peaks, $2\theta_{100}$ and $2\theta_{002}$ are the corresponding peak positions.

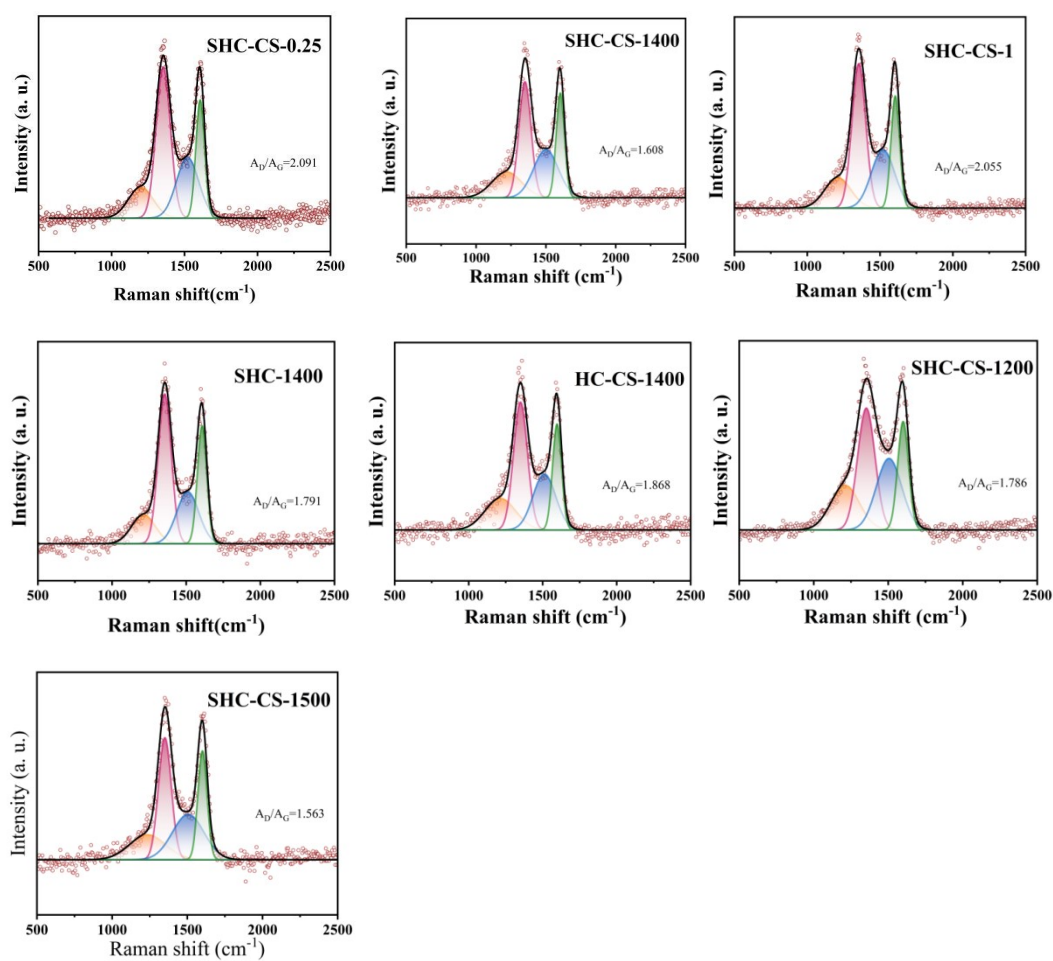


Figure S5 The fitting results of Raman spectra of (a) SHC-CS-0.25, (b) SHC-CS-1400, (c) SHC-CS-1, (d) SHC-1400, (e) HC-CS-1400, (f) SHC-CS-1200, and (g) SHC-CS-1500 samples.

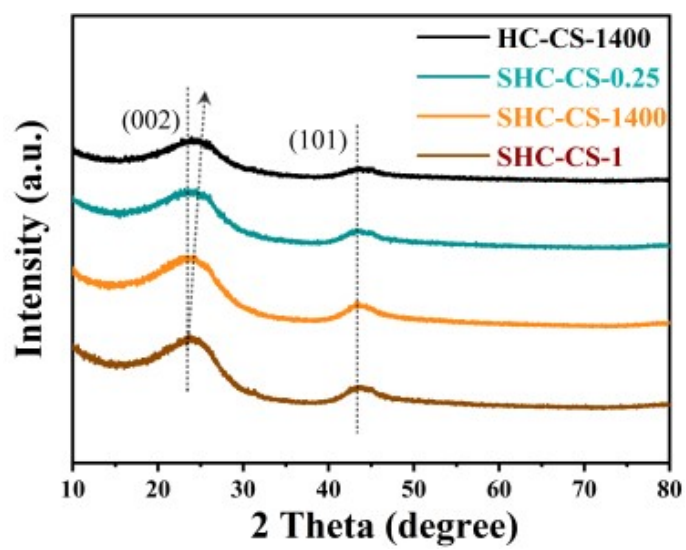


Figure S6 XRD patterns of HC samples with different CS ratios.

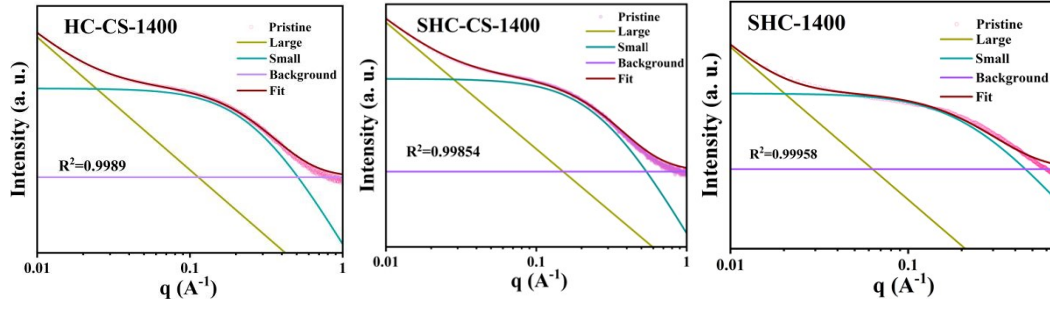


Figure S7 Fitted SXAS patterns of HC samples.

The scattered intensity from a medium containing nanopores together with macropores can be represented by the function:

$$I(q) = \frac{A}{q^a} + \frac{Ba_1^4}{(1 + a_1^2 q^2)^2} + D$$

Where q is the wavevector, A and B are proportional to the total surface areas of the large and small pores, and D is a constant background term. the radius of a spherical pore equivalent to Debye's length, is $R = a_1\sqrt{10}$

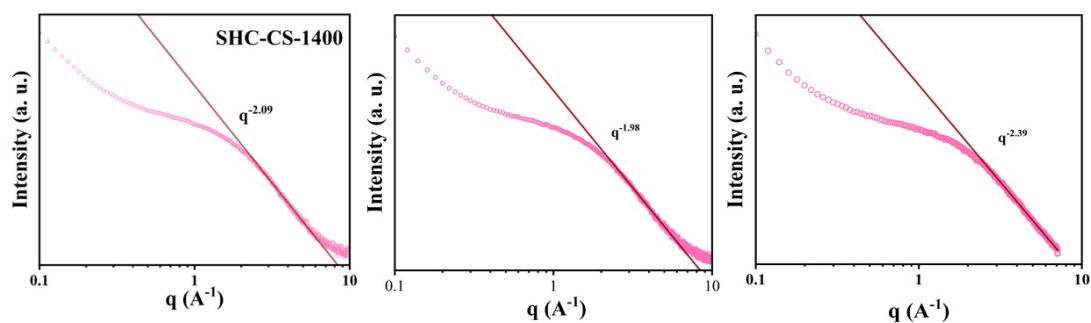


Figure S8 Porod fitted SXAS patterns of HC samples.

A power law fit in this region of the scattering curve, $I(q) = A \cdot q^{-n}$ ($q = 3 \sim 6 \text{ nm}^{-1}$), is applied to access pore surface and surface roughness. A is the Pollard constant proportional to the inner surface and n is the power exponent. The n is related to the surface roughness of the nanopore. A larger value indicates a smoother surface.

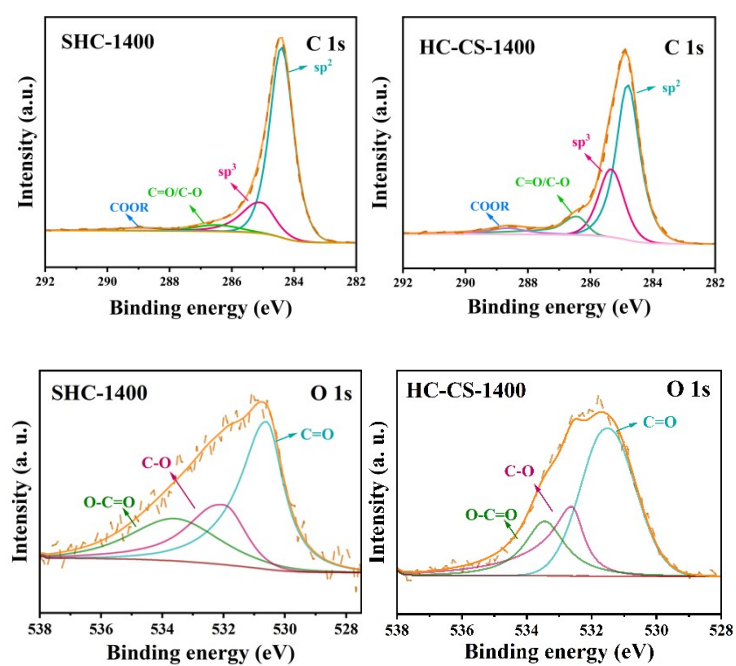


Figure S9 The high-resolution C 1s XPS spectra of (a) SHC-1400, (b) HC-CS-1400; The high-resolution O 1s XPS spectra of (c) SHC-1400 (d) HC-CS-1400.

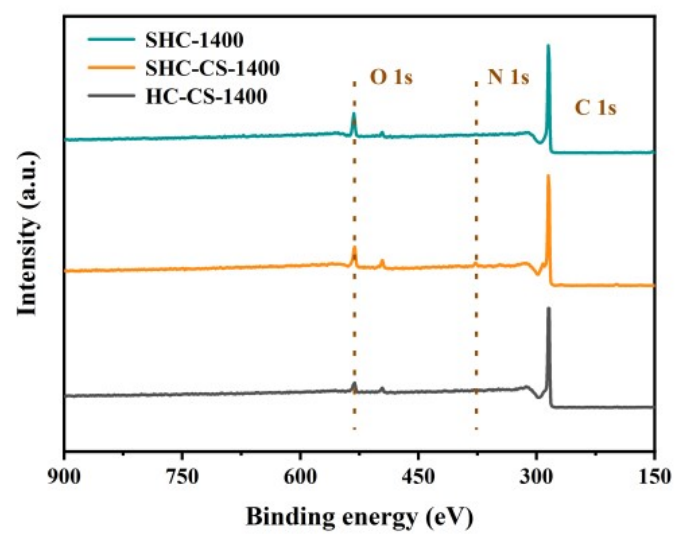


Figure S10 XPS full spectrum of HC samples: SHC-1400, SHC-CS-1400, HC-CS-1400.

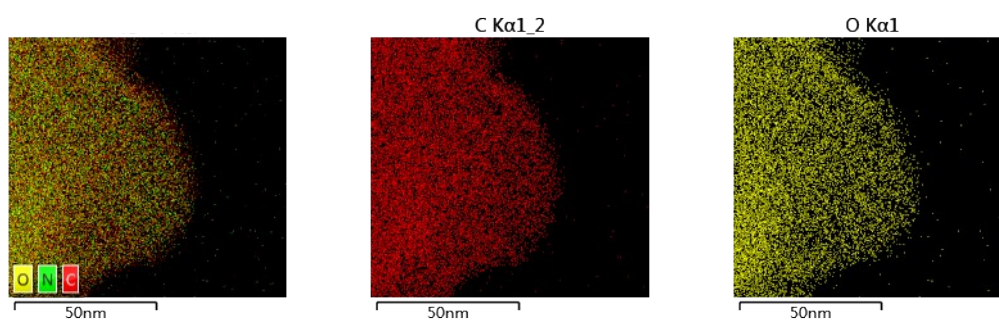


Figure S11 EDS of SHC-CS-1400

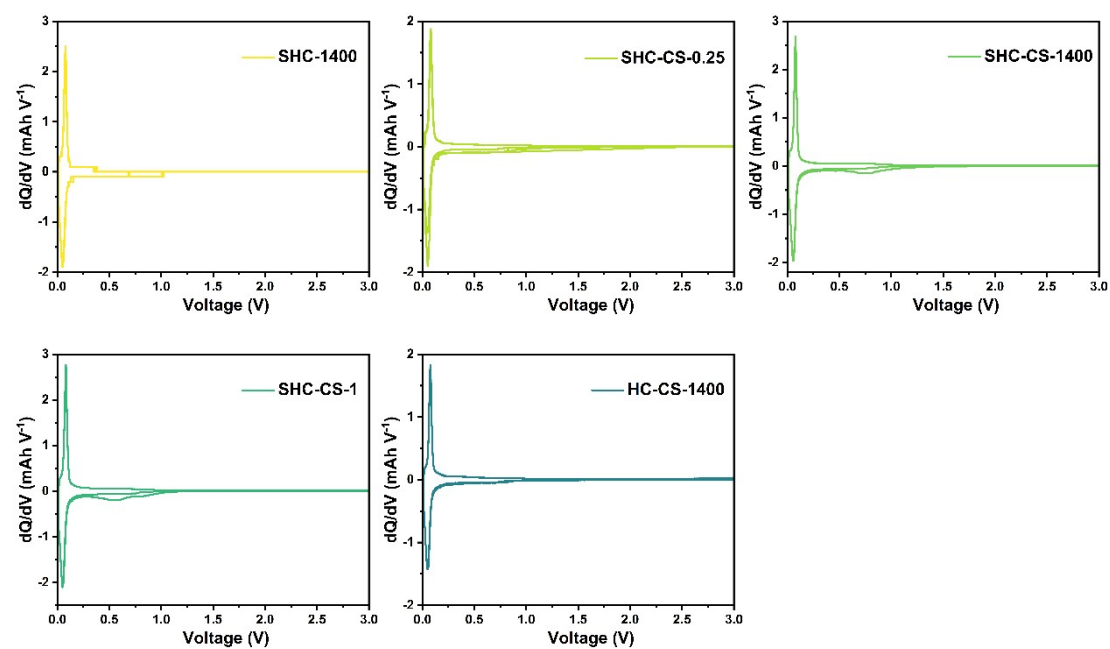


Figure S12 The dQ/dV curves of HC samples.

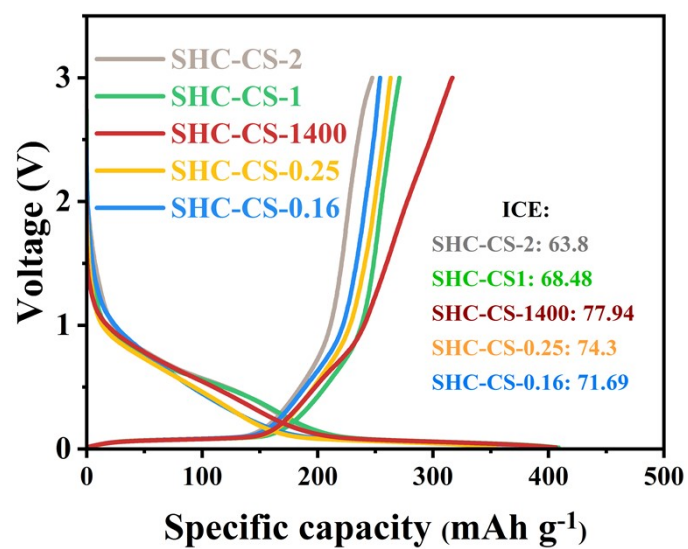


Figure S13 GCD curves of SHC-CS-2, SHC-CS-1, SHC-CS-1400, SHC-CS-0.25, SHC-CS-0.16.

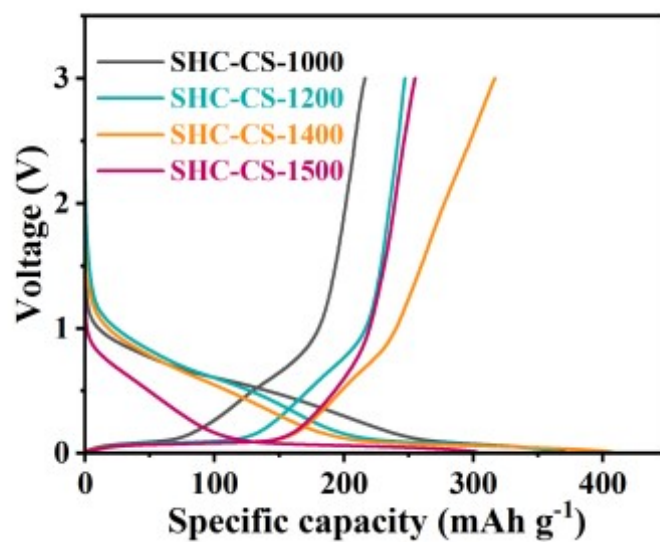


Figure S14 GCD curves of samples treated at different temperatures

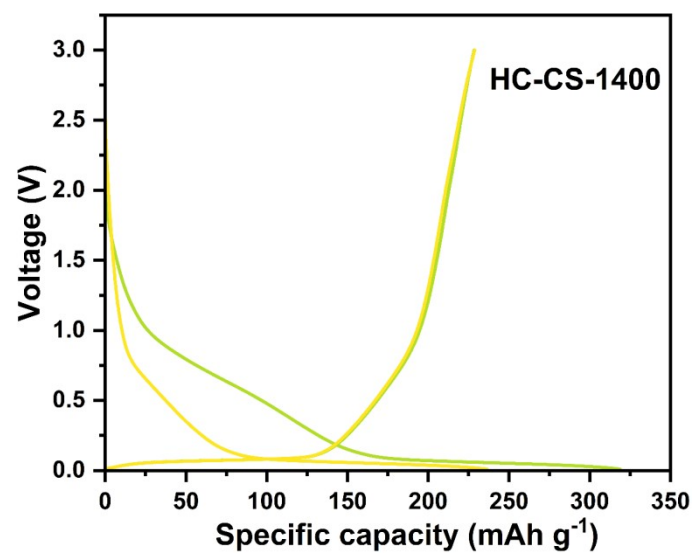


Figure S15 GCD curves of HC-CS-1400.

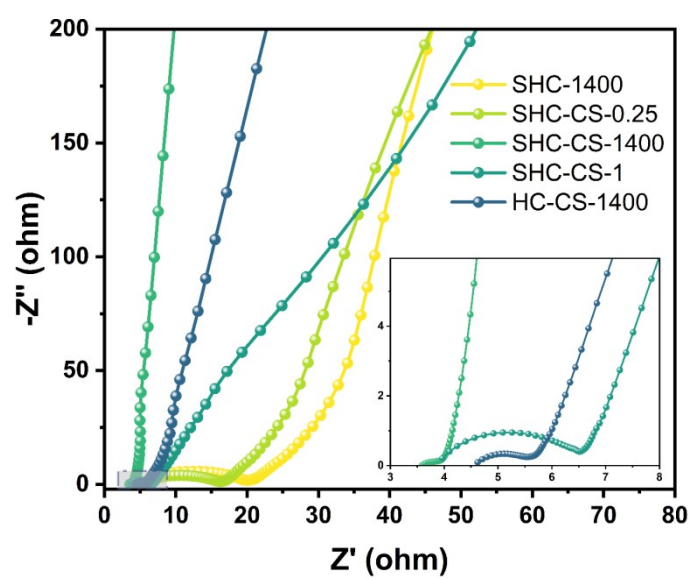


Figure S16 EIS results of HC electrodes at initial open-circuit voltage

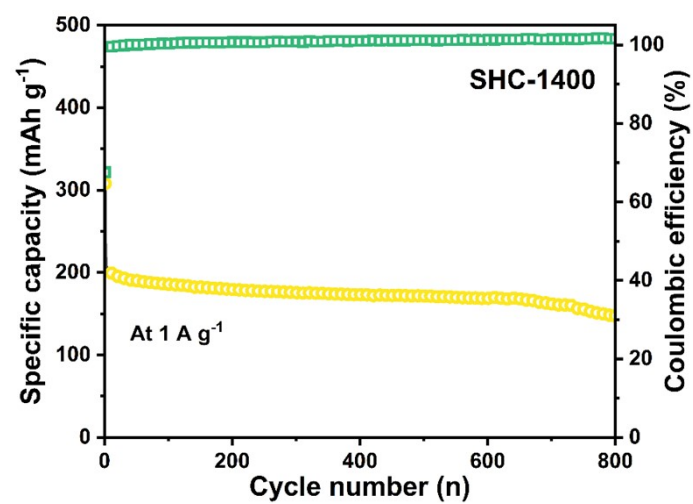


Figure S17 Cycling performance of SHC-1400 at 1A g⁻¹ current density

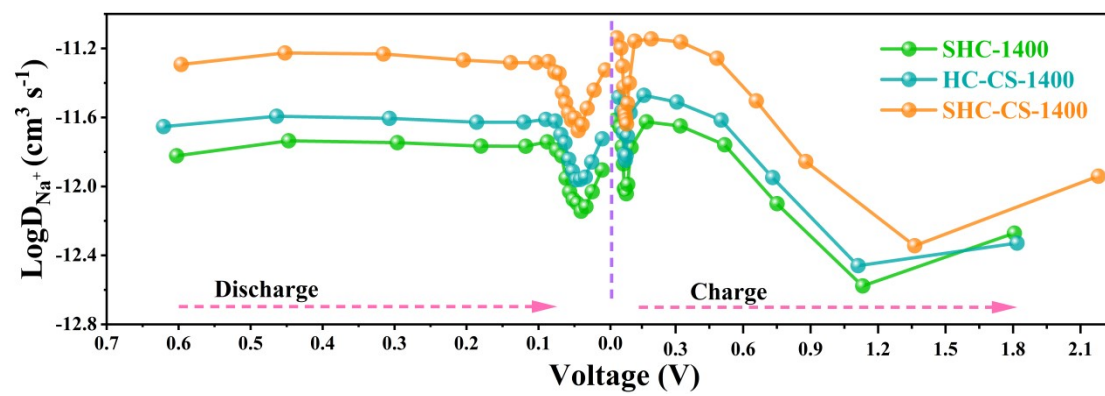


Figure S18 GITT curves of SHC-1400, HC-CS-1400 and SHC-CS-1400

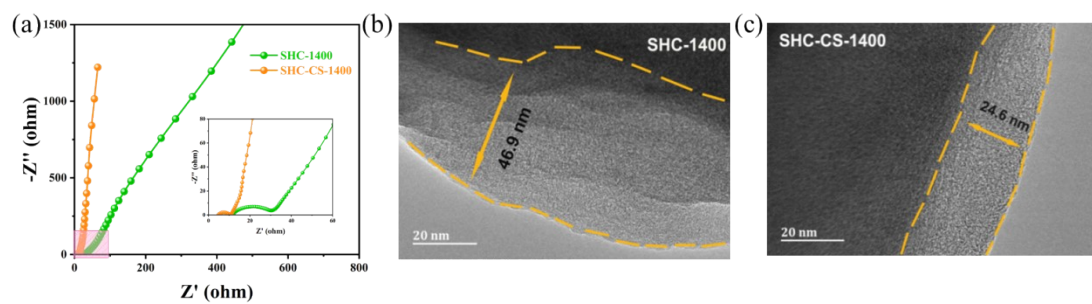


Figure S19 (a) EIS curves for the SHC-1400 and SHC-CS-1400 anode after cycling, HRTEM images of the SEI from (b) SHC-1400 and (c) SHC-CS-1400 anodes



Figure S20 Optical photographs of (a) HC-CS-1400, (b) SHC-1400 and (c) SHC-CS-1400 electrodes immersed in an ethanol solution containing phenolphthalein at different discharge stages

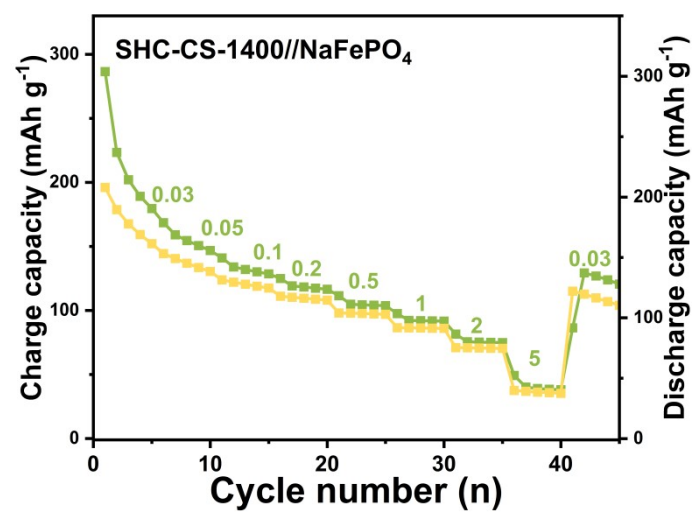


Figure S21 The rate capability of SHC-CS-1400//NaFePO₄.

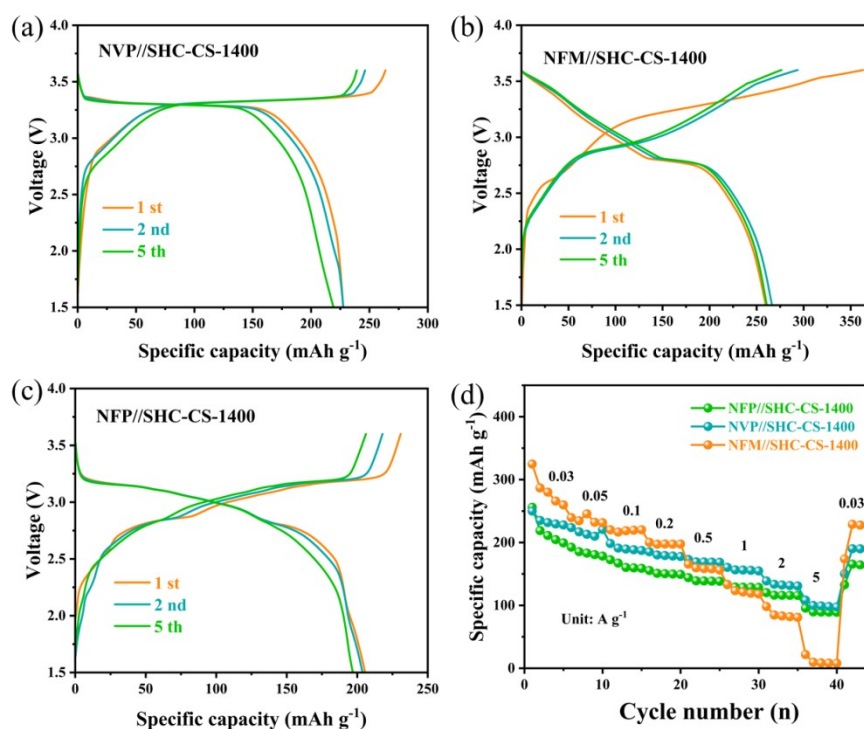


Figure S22 (a) 1st, 2nd, and 5th turn GCD curves of (a) NVP//SHC-CS-1400, (b) NFM//SHC-CS-1400, and (c) NFP//SHC-CS-1400; and (d) rate capability of the full battery

Table S1 Physicochemical properties of HC samples

sample	$2\theta_{002}$	d_{002}	R	$2\theta_{100}$	B_{100}	L_a	B_{002}	L_c	I_D/I_G	A_D/A_G
SHC-1400	23.88	0.372	/	43.47	3.640	4.807	5.728	1.403	1.202	1.791
SHC-CS-0.25	23.98	0.371	2.027	43.34	3.923	4.458	5.909	1.360	1.191	2.091
SHC-CS-1400	23.51	0.378	2.049	43.46	3.944	4.436	6.355	1.264	1.132	1.608
SHC-CS-1	23.77	0.374	2.129	43.79	3.986	4.395	5.853	1.373	1.103	2.055
HC-CS-1400	24.54	0.362	/	43.72	3.827	4.576	6.027	1.335	0.997	1.868
HC-1400	24.09	0.369	/	43.23	3.587	4.874	5.848	1.375	/	/
SHC-CS-1200	23.62	0.376	2.125	43.99	4.081	4.296	6.370	1.261	1.234	1.786
SHC-CS-1500	24.10	0.369	2.042	43.27	3.861	4.529	5.670	1.418	1.169	1.563

Table S2 Porosity information of HC samples

sample	$SSA_{BET, N_2}/m^2 g^{-1}$	$V_{N_2, <300 nm}/cm^3 g^{-1}$	True density /g mL ⁻¹	$V_{closed pore}$	$D_{closed pore}/nm$	n
SHC-1400	1.8102	0.005635	1.916	0.07951	1.489	2.390
SHC-CS-1400	0.8770	0.006036	1.827	0.1050	1.219	2.093
HC-CS-1400	1.849	0.004025	1.736	0.1334	1.193	1.980

Table S3 Electrochemical data of samples treated at different temperatures

Samples	Charge-specific Capacity (mA h g ⁻¹)	Discharge-specific Capacity (mA h g ⁻¹)	Initial Coulombic Efficiency (%)
SHC-CS-1000	216.30	370.82	58.33
SHC-CS-1200	232.05	340.11	68.49
SHC-CS-1400	316.75	406.38	77.94
SHC-CS-1500	255.04	302.52	84.31

Table S4 Comparison of electrochemical performance of SHC-CS-1400 anode with other coal-based anode materials for sodium ion storage reported in previous literatures

Number	Current density (mA/g)	ICE (%)	Specific capacity (mAh/g)	Current density (mA/g)	Specific capacity (mAh/g)	Material	Reference
1	0.03	77.8	316	5	203.	Coal	This work
2	0.05	85.3	312.2	1	106.1	Coal	1
3	0.02	79.5	291	0.4	~50	Subbituminous coal	2
4	0.02	64	200	1	58.2	Coal	3
5	0.02	82.82	300.83	5	140	Coal tar pitch	4
6	0.05	80	278.2	1	207.3	Anthracite coal	5
7	0.037	82.3	308.4	0.6	95	Coal	6
8	0.03	82.9	356	1	100	Lignite coal	7
9	0.02	66	330	5	164	Coal pitch	8
10	0.05	74.2	282	2	130	Anthracite	9
11	0.037	67.5	276.8	0.6	87	Coal tar pitches	10
12	0.02	48.1	284.4	1	61.1	Subbituminous coal	11
13	0.1	55.87	212.3	5	94	Coal	12
14	0.03	74.8	274.2	2	~50	Bituminous coal	13

Table S5 Comparison of the fast-charging performance of SHC-CS-1400 with other HC materials previously reported in the literature for sodium-ion storage

Number	name	Current density (A/g)	Specific capacity (mAh/g)	Material	Reference
1	BC/R-HC	5	~135	resin	14
2	C—S/C= S	5	254	polydopamine	15
3	RHC	8	109	bamboo powder	16
4	HC-DB	5	~100	bamboo	17
5	HHC	2	83	polystyrene	18
6	M-1500	2	190	wood	19
7	PO-SC-S	3	125	petroleum residue	20
8	CMAC	0.6	70	polypropylene	21
9	HCMP-CO ₂	0.8	171	starch	22
10	TDT	5	215	TDT	23
11	PCHC-10	0.6	103	resin	24
12	SHC-CS-1400	5	203	coal	This work

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