

## Supporting Information

### **Flame-retardant polymer-enabled space-confined carbonization toward quasi-spherical hard carbon for high-rate sodium storage**

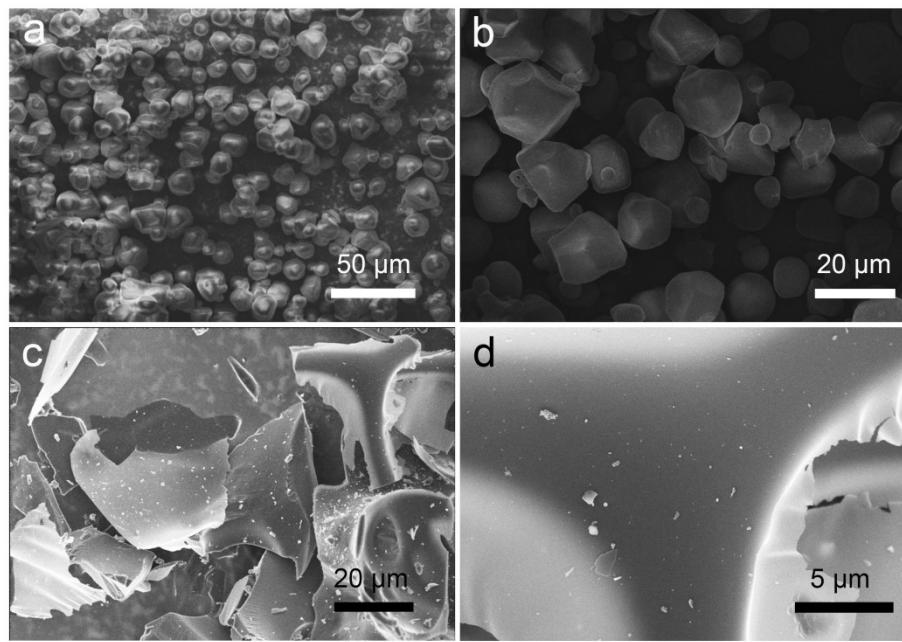
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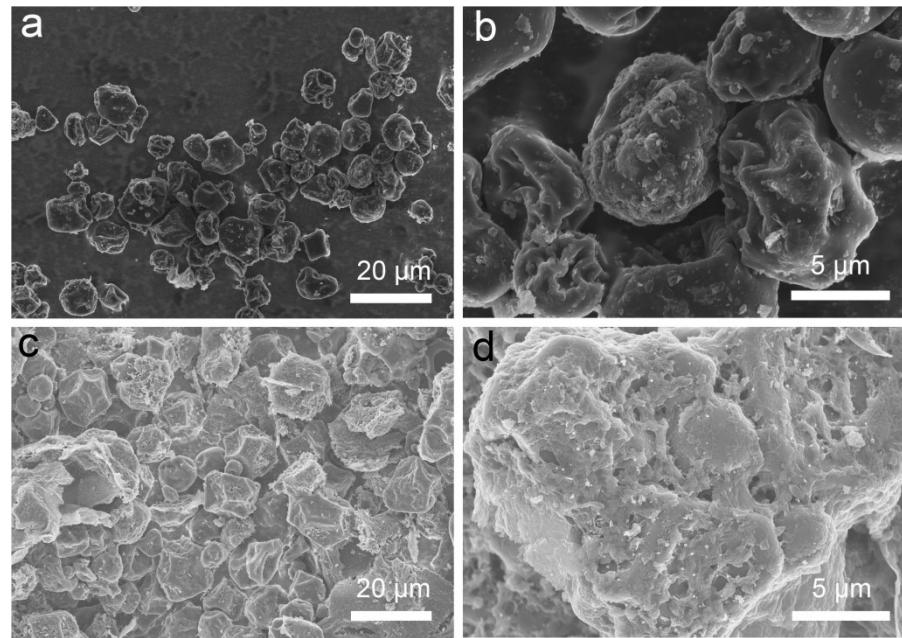
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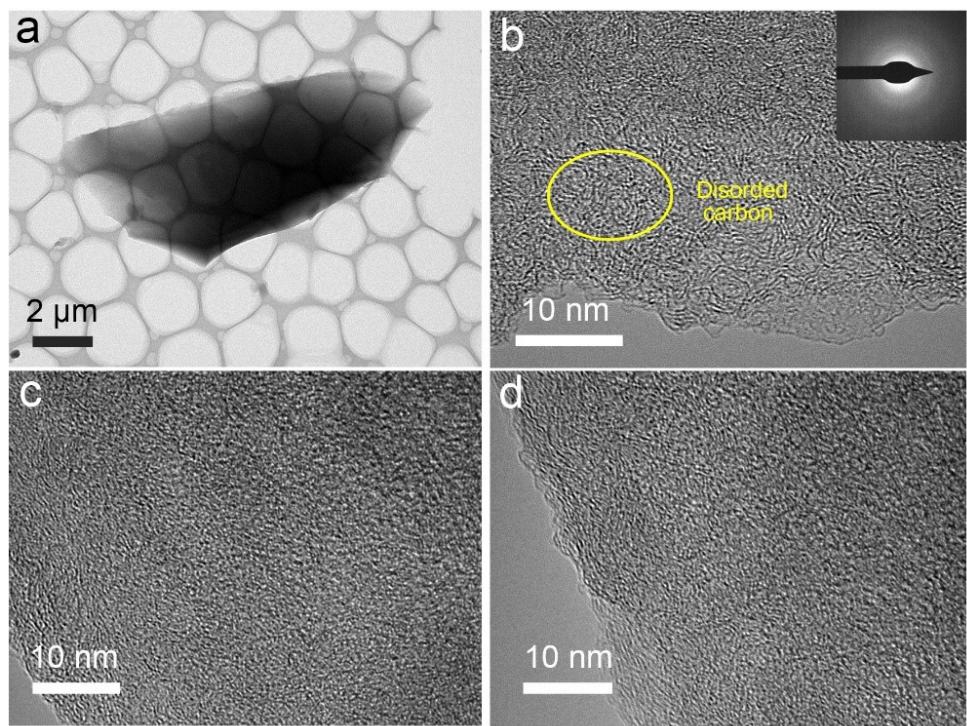
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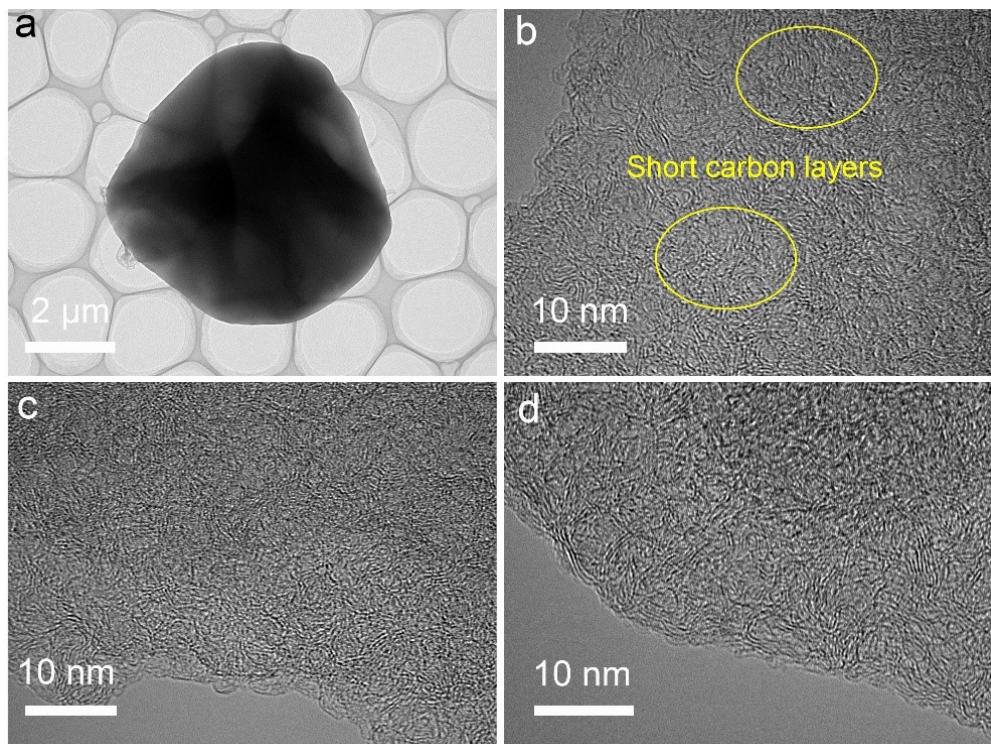
**Figure S1.** SEM images of (a, b) and (c, d) HC.



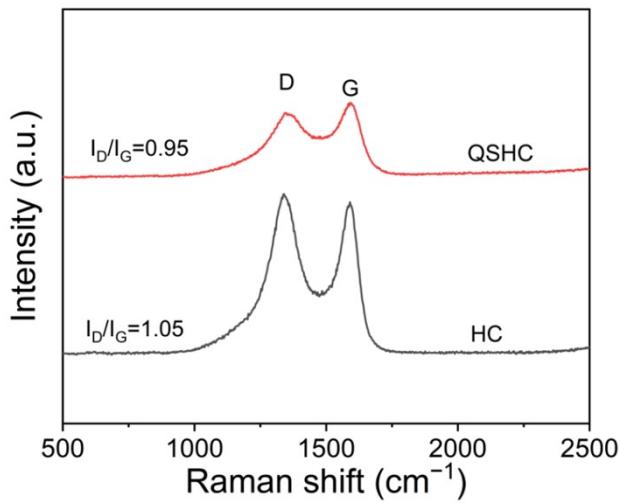
**Figure S2.** SEM images of QSHC prepared with the starch-to-PPD-PP mass ratio of (a, b) 10:1 and (c, d) 1:1.



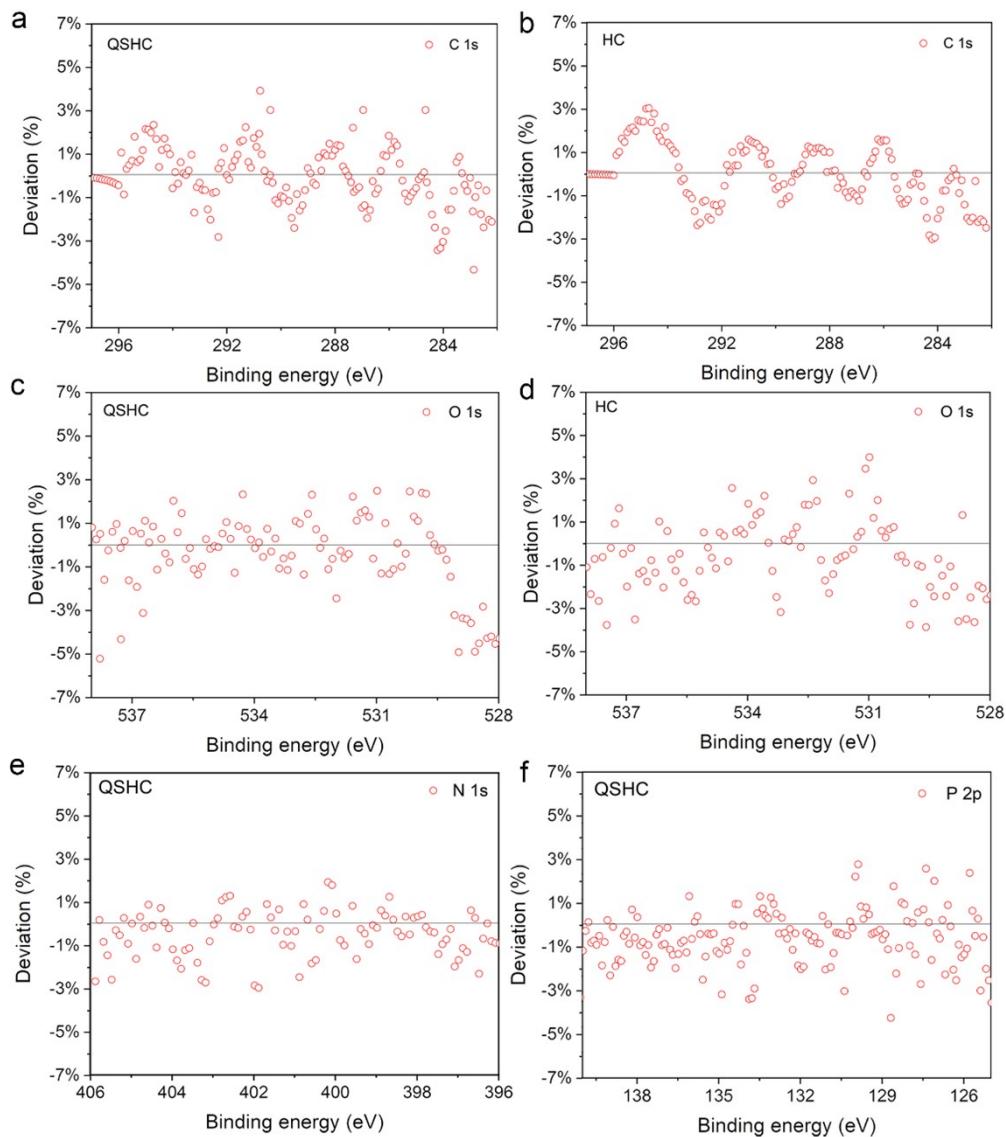
**Figure S3.** (a) TEM and (b-d) HRTEM images of HC.



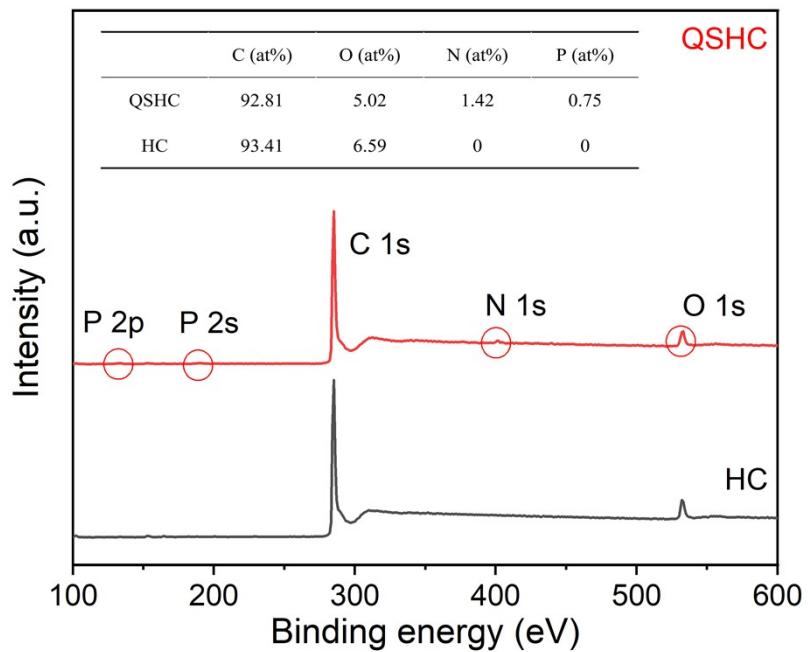
**Figure S4.** (a) TEM and (b-d) HRTEM images of QSHC.



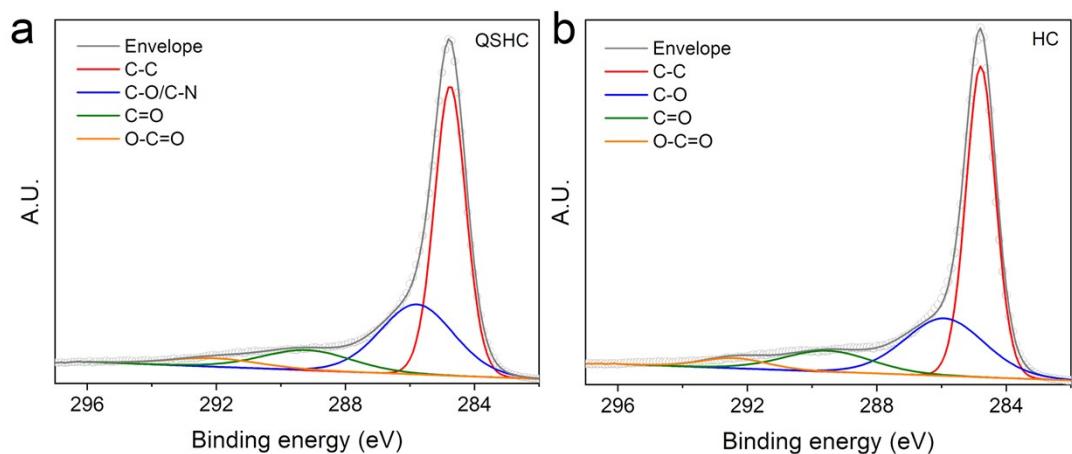
**Figure S5.** Raman spectra of QSHC and HC.



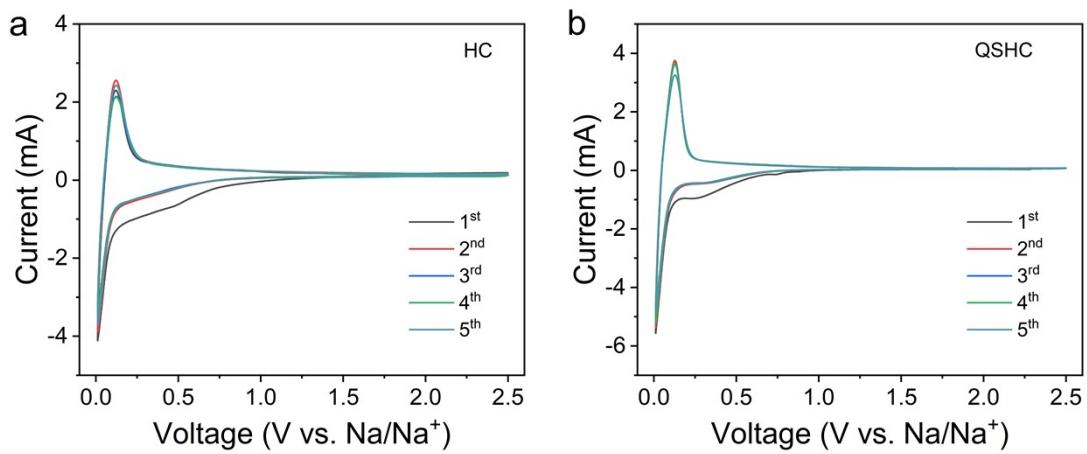
**Figure S6.** Residual plots of the fitted XPS spectra of (a, b) C 1s, (c, d) O 1s, (e) N 1s, and (f) P 2p, which belong to (a, c, e, f) QSHC and (b, d) HC samples.



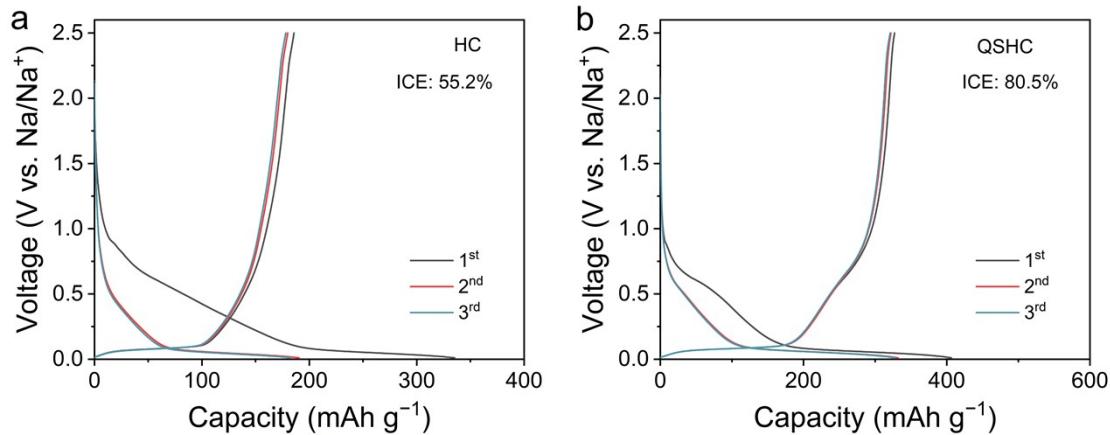
**Figure S7.** XPS survey spectra of QSHC and HC associated with their atomic contents.



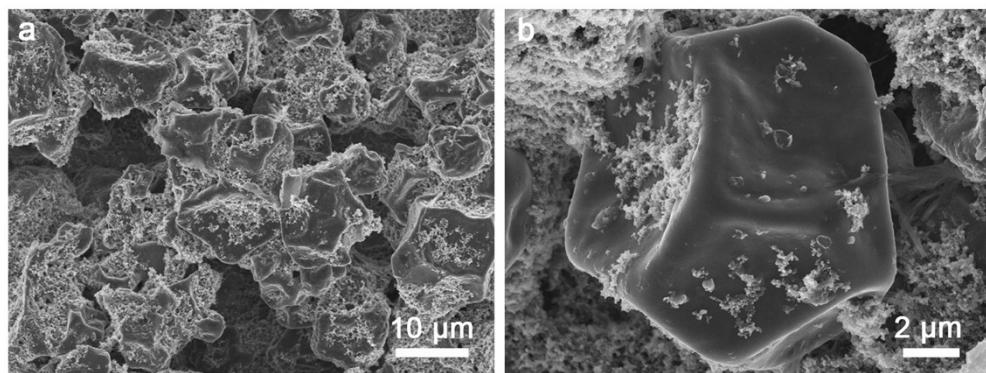
**Figure S8.** High-resolution C 1s XPS spectra of (a) QSHC and (b) HC.



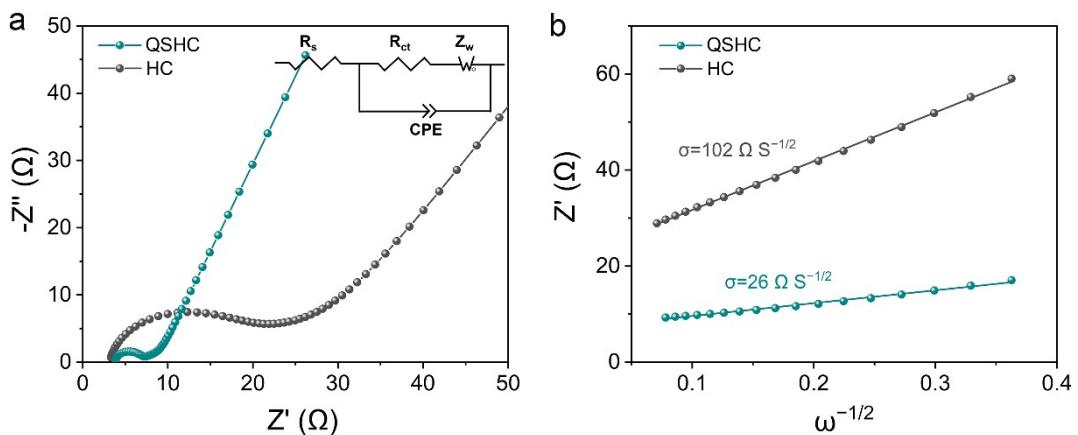
**Figure S9.** CV profiles of (a) HC and (b) QSHC from 1st to 5th cycles.



**Figure S10.** GCD curves of (a) HC and (b) QSHC for the initial 3 cycles.



**Figure S11.** (a, b) SEM images of QSHC electrode after 100 cycles at  $1 \text{ A g}^{-1}$ .



**Figure S12.** (a) EIS curves of QSHC and HC-based coin cells. (b) Linear fitting relationship between  $Z'$  and  $\omega^{-1/2}$  for QSHC and HC electrodes.

**Table S1.** Nitrogen sorption results of HC and QSHC.

	Adsorption volume ( $\text{cm}^3 \text{ STP g}^{-1}$ )	Specific surface area ( $\text{m}^2 \text{ g}^{-1}$ )	Total pore volume ( $\text{cm}^3 \text{ g}^{-1}$ )	Average pore size (nm)
HC	86.146	343	0.177	4.703
QSHC	30.567	111	0.077	9.727

**Table S2.** Fitting parameters, references, and RSS of the XPS spectra.

Background type	Peak shape	RSS (Residual Sum of Squares)	References
C 1s		QSHC: 472.35 HC: 397.22	<i>J. Mater. Chem. A</i> 2014, 2, 12924
O 1s	Shirley	QSHC: 113.53 HC: 141.18	<i>Adv. Funct. Mater.</i> 2021, 31, 2104137
N 1s	LG30	QSHC: 6.64	<i>Adv. Mater.</i> 2023, 35, 2211461
P 2p		QSHC: 4.27	<i>Adv. Funct. Mater.</i> 2025, 35, 2426075

**Table S3.** Performance comparison of QSHC with previously reported HC anodes for sodium storage.

Sample	Rate	Plateau capacity contribution (%)	Cycling	ICE (%)	Ref.
<b>QSHC</b>	<b>180 mAh g<sup>-1</sup> at 1A g<sup>-1</sup></b>	<b>71.1</b>	<b>171 mAh g<sup>-1</sup> at 1A g<sup>-1</sup> (2000 cycles)</b>	<b>80.5</b>	<b>This work</b>
HC300-1000	60 mAh g <sup>-1</sup> at 1 A g <sup>-1</sup>	55.4	~250 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> (100 cycles)	82.5	<i>Energy Storage Mater.</i> 2022, 51, 620
PCLC	106.1 mAh g <sup>-1</sup> at 1 A g <sup>-1</sup>	59.4	246.8 mAh g <sup>-1</sup> at 0.3 A g <sup>-1</sup> (1000 cycles)	88.4	<i>Energy Storage Mater.</i> 2023, 56, 532
HCG	106 mAh g <sup>-1</sup> at 1 A g <sup>-1</sup>	25	198 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> (200 cycles)	80.1	<i>Chem. Eng. J.</i> 2022, 432, 133257
SSHC	198.5 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>	-	158 mAh g <sup>-1</sup> at 3A g <sup>-1</sup> (1000 cycles)	-	<i>J. Mater. Chem. A</i> 2020, 8, 14993
CS@2%PP	92 mAh g <sup>-1</sup> at 0.5 A g <sup>-1</sup>	73.3	272 mAh g <sup>-1</sup> at 0.025 A g <sup>-1</sup> (50 cycles)	81	<i>Energy Technol.</i> 2019, 7, 1900779
HC-SC	122 mAh g <sup>-1</sup> at 1 A g <sup>-1</sup>	-	241 mAh g <sup>-1</sup> at 0.05 A g <sup>-1</sup> (100 cycles)	92.7	<i>Mater. Lett.</i> 2023, 330, 133368
BHCS-1200	198.5 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>	~60	180 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> (1000 cycles)	65.4	<i>J. Mater. Chem. A</i> 2022, 10, 17225

**Table S4.** Fitted parameters using the Nyquist equivalent circuit model.

	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )
QSHC	3.205	2.736
HC	3.838	13.012

**Table S5.** Power and energy density of QSHC//NCPFC full cell at different current densities.

	Current density (A g <sup>-1</sup> )				
	0.1	0.2	0.5	1.0	2.0
Power (W)	56.5	112.1	298.2	541.1	938.3
Power density (W kg <sup>-1</sup> )	424.6	842.7	2241.6	4066.9	7052.5
Energy (Wh)	45.3	43.5	40.2	36.0	31.9
Energy density (Wh kg <sup>-1</sup> )	340.4	327.1	302.2	270.4	239.7
Mass loading of active materials			$M_p: 4.0 \text{ mg cm}^{-2}; A_p: 1.54 \text{ cm}^2$		
			$M_n: 1.2 \text{ mg cm}^{-2}; A_n: 1.13 \text{ cm}^2$		