Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting information

R Regulation of Microcrystalline and Pore Structures in Pitch-Based Hard Carbon via Liquid-Phase Crosslinking-Assisted Grain Boundary Etching to Enhance Sodium Storage Performance

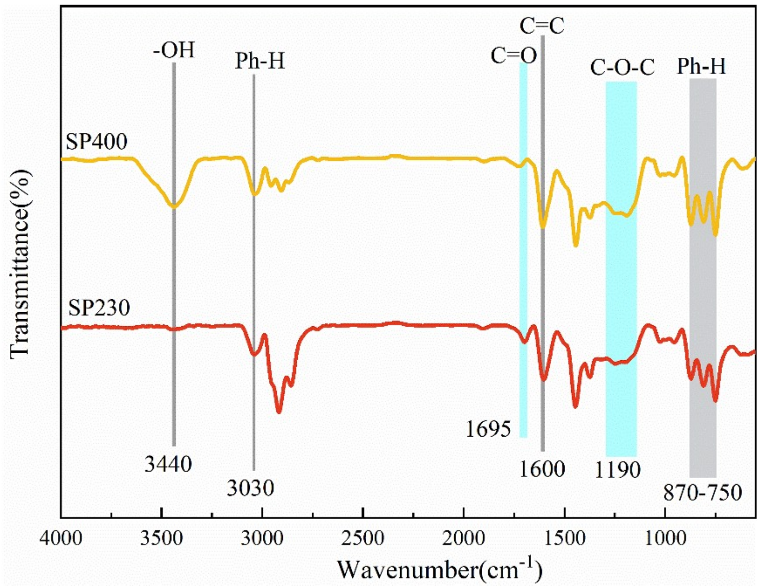

Figure S1. FTIR spectra of SP230 and SP400.

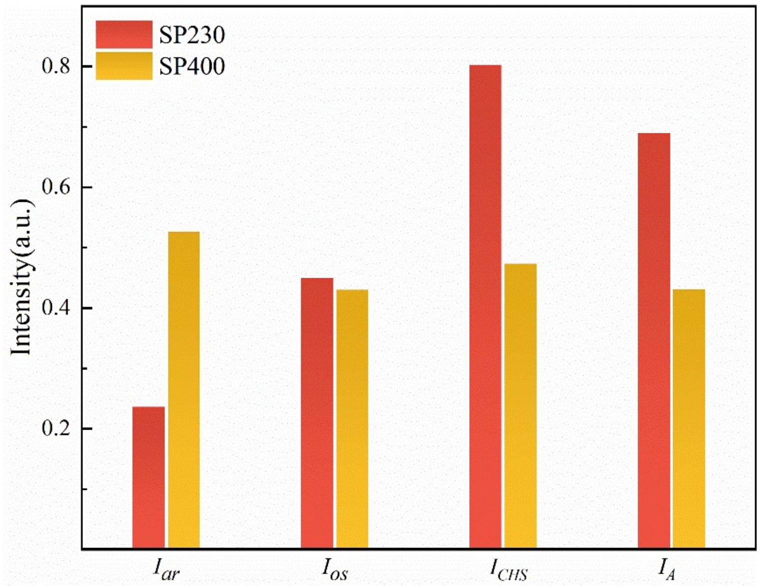

Figure S2. FTIR structural indices of SP230 and SP400.

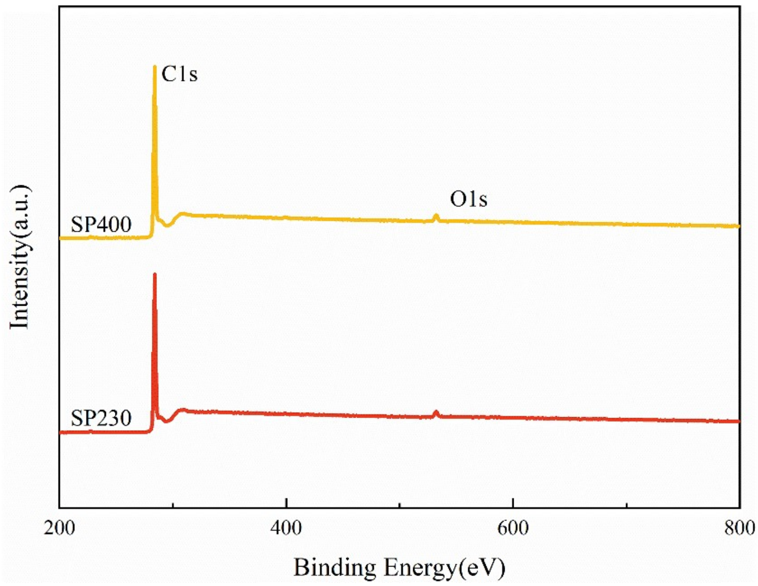

Figure S3 XPS spectra of SP230 and SP400.

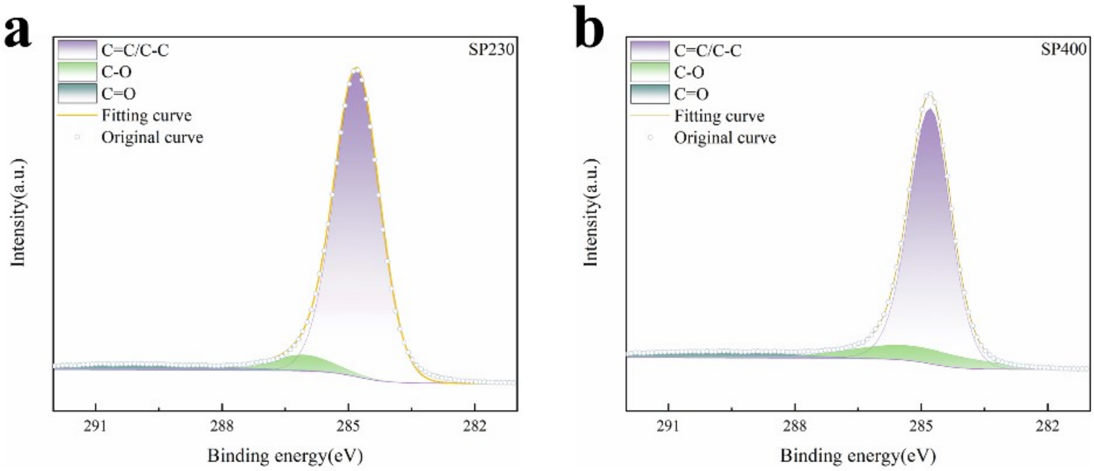

Figure S4. C1s XPS spectra of SP230 and SP400.

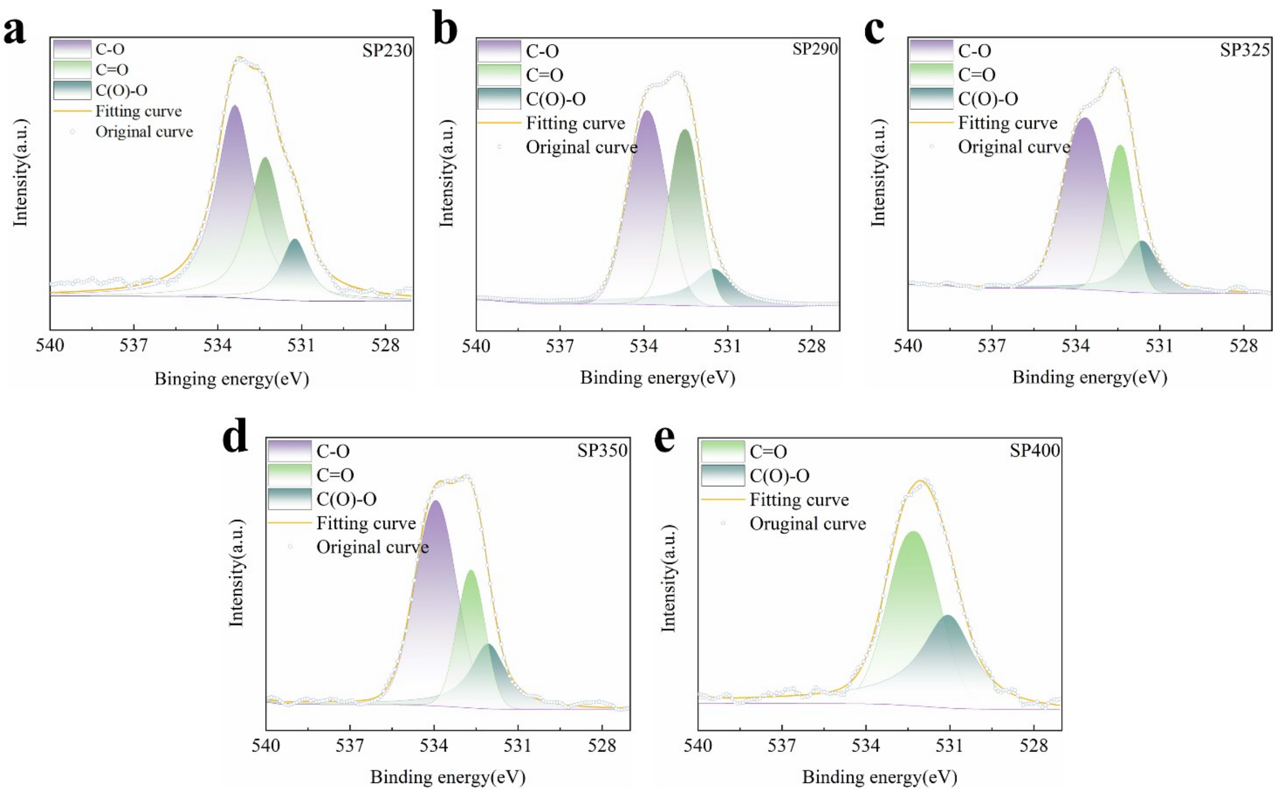

Figure S5. O1s XPS spectra of SP230 SP290, SP325, SP350 and SP400.

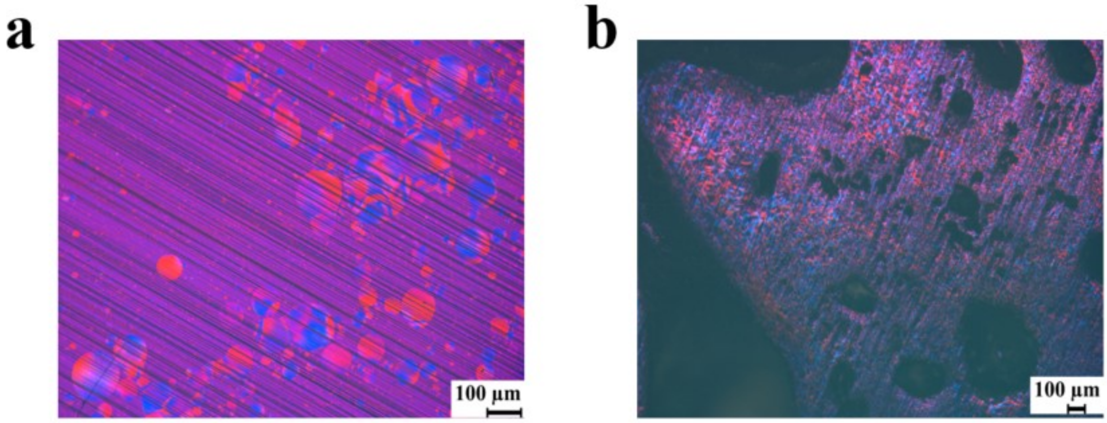

Figure S6. The optical microscopic images of HO and SP325 carbonization for 1 h.

Figure S6.

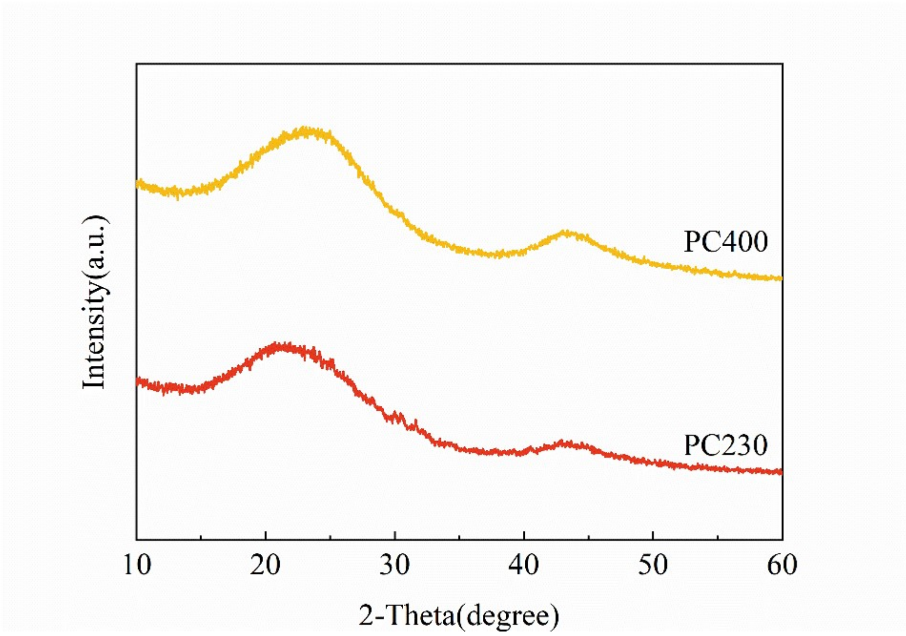

Figure S7. XRD spectra of PC230 and PC400.

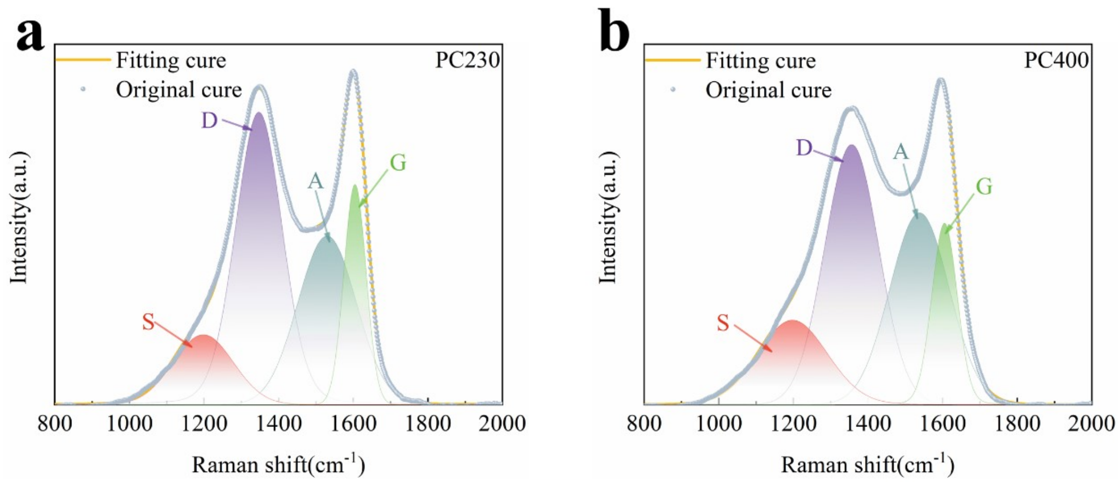

Figure S8. Raman spectra and fitted curves of PC230 and PC400.

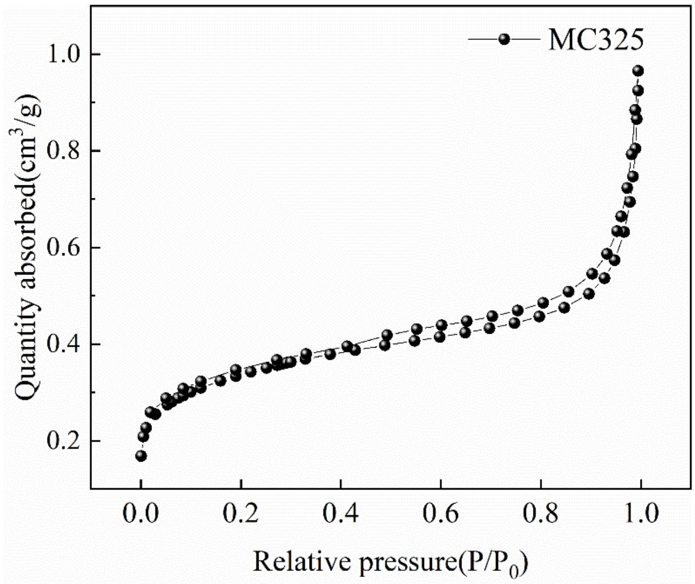

Figure S9. The N2 adsorption-desorption isotherms of MC325

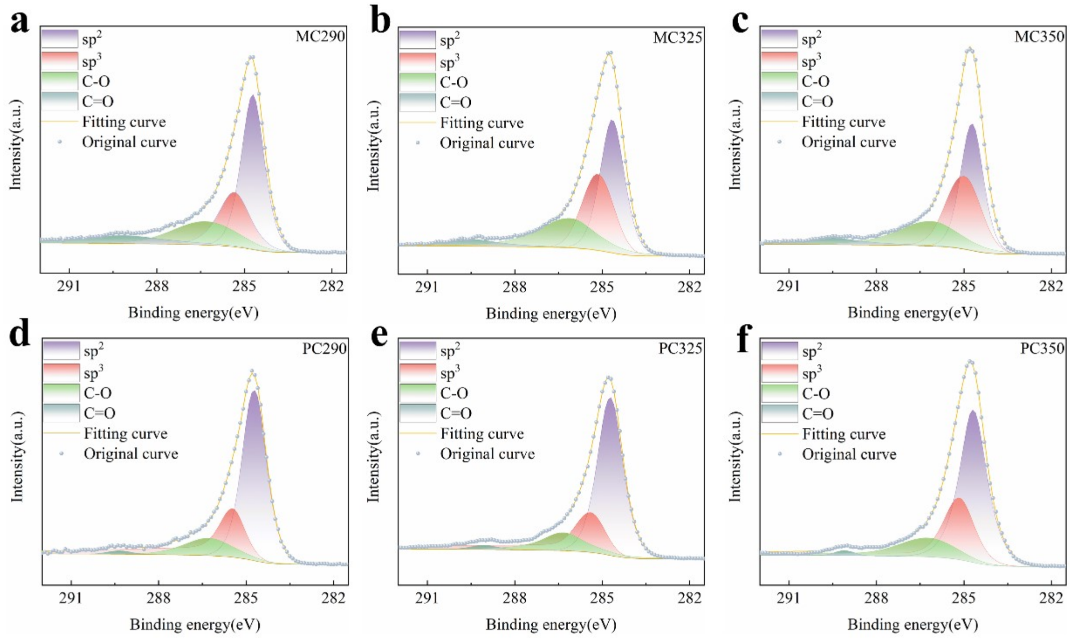

Figure S10. (a-c) C1s XPS spectra of MC290, MC325 and MC350. (d-f) C1s XPS spectra ofPC290, PC325 and PC350.

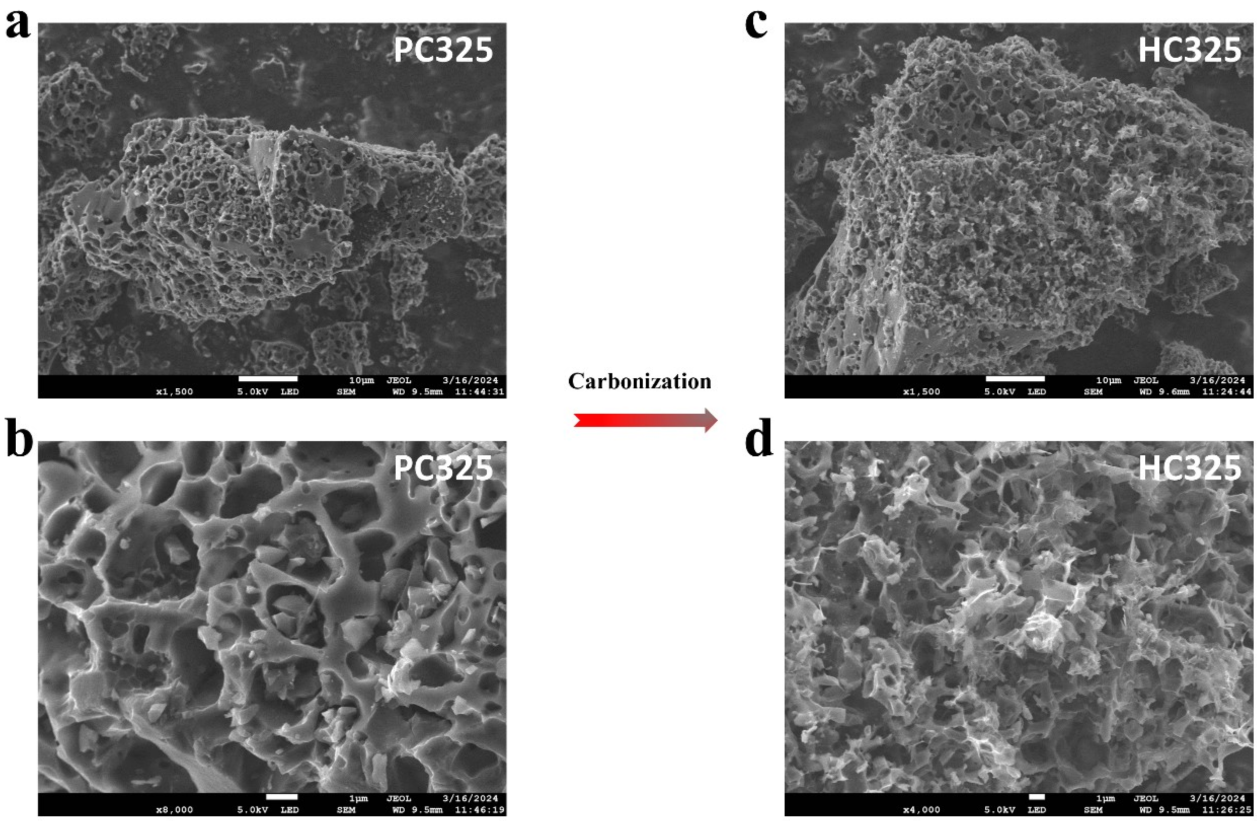

Figure S11. SEM images of PC325 and HC325.

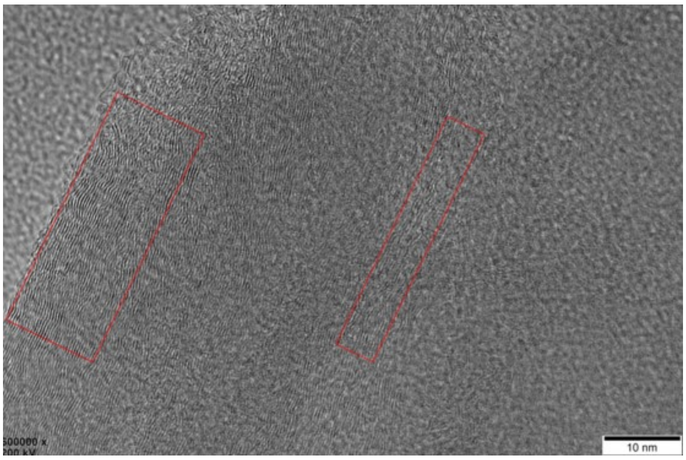

Figure S12. HRTEM images of CMC325

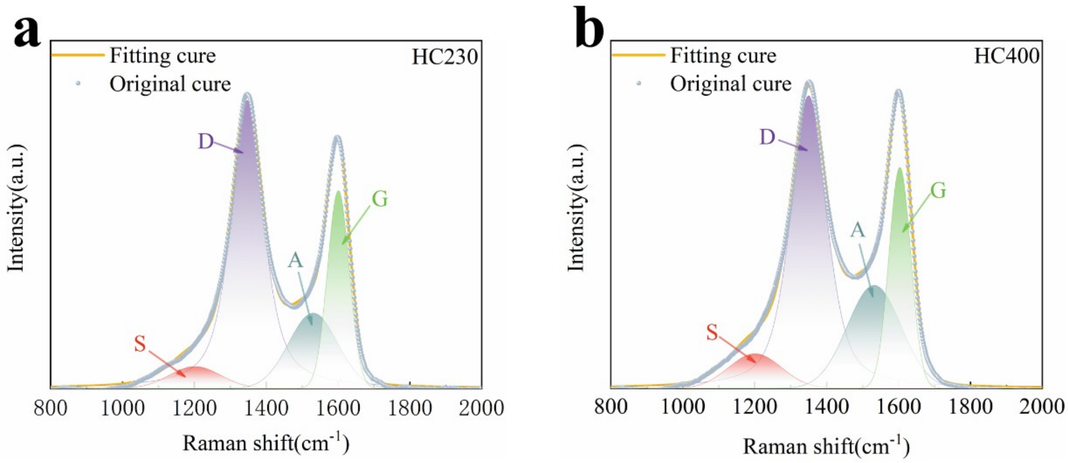

Figure S13. Raman spectra and fitted curves of HC230 and HC400.

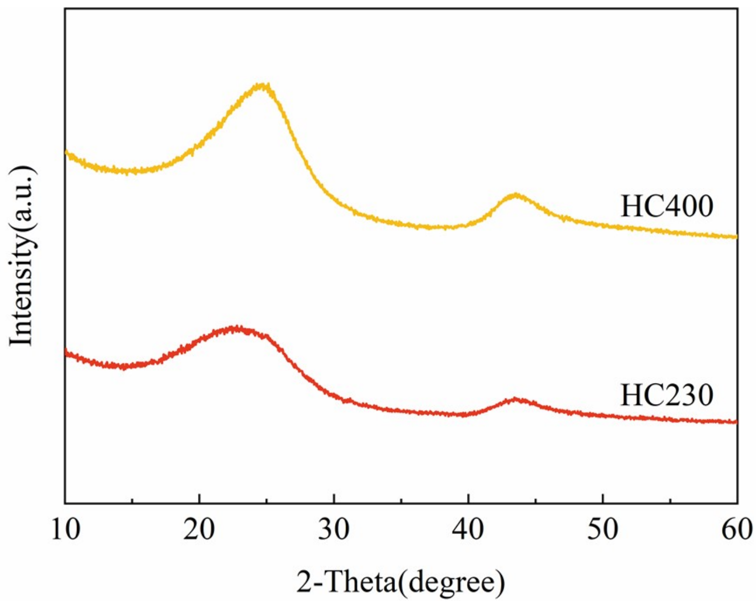

Figure S14. XRD spectra of HC230 and HC400.

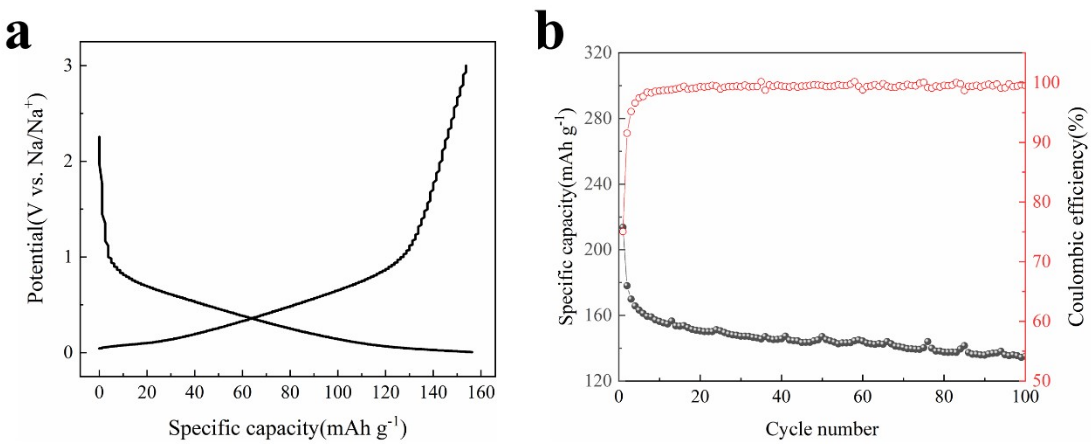

Figure S15. Electrochemical properties of CMC325. (a) GCD curves at 100 mA g^{-1}. (b) Cycling performance of CMC325.

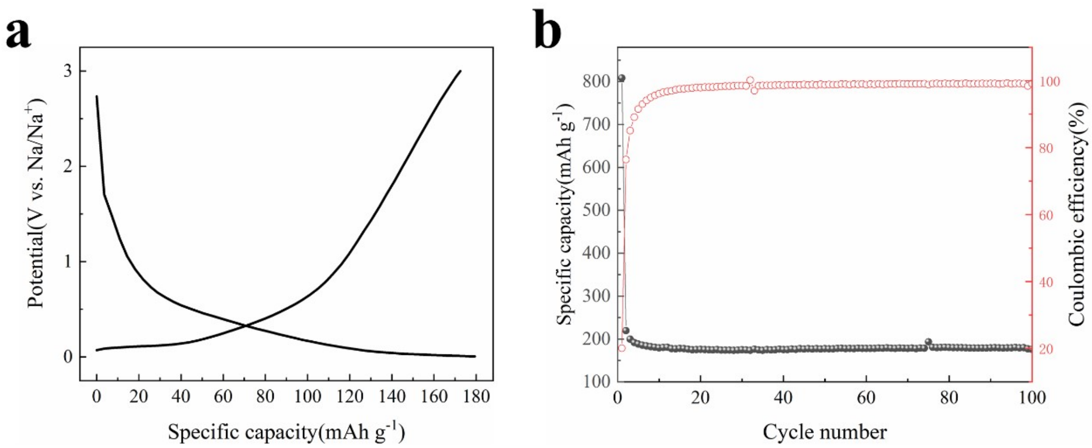

Figure S16. Electrochemical properties of CPNC. (a) GCD curves at 100 mA g^{-1}. (b) Cycling performance of CPNC.

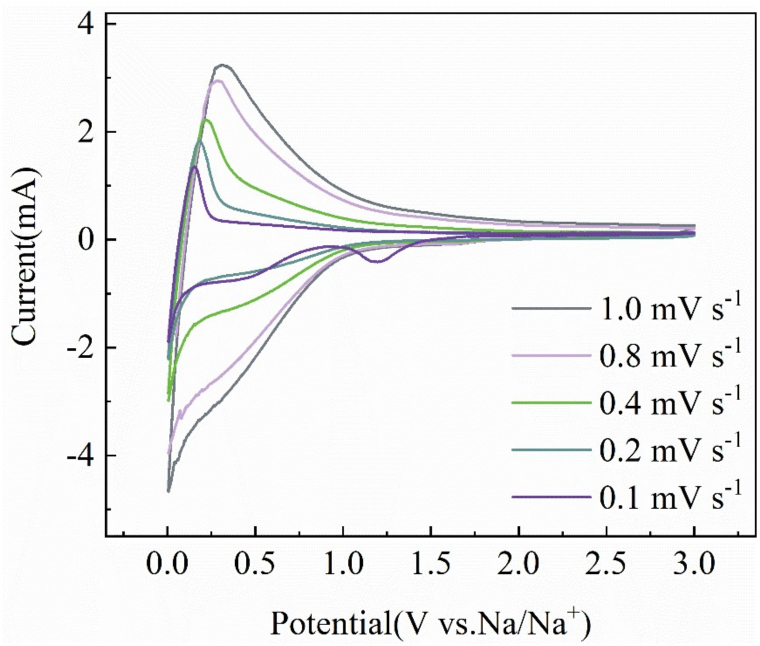

Figure S17. CV curve at different scan rates of HC325.

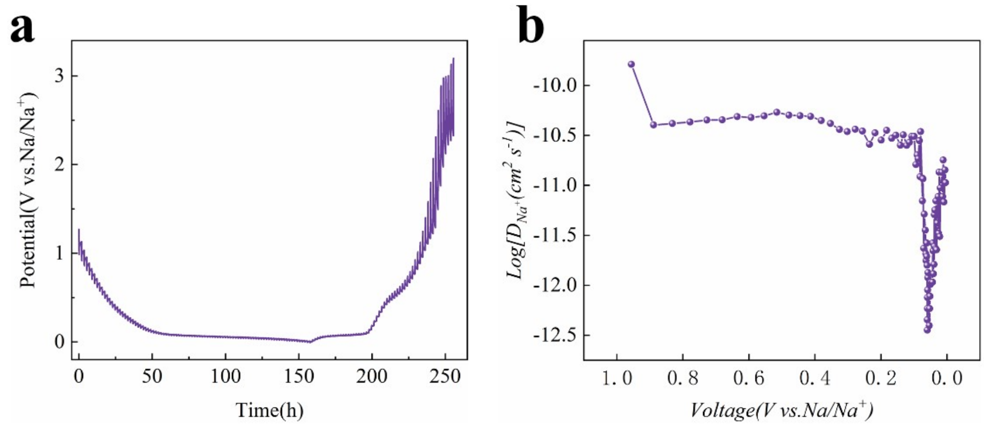

Figure S18. GITT curves.of HC325.

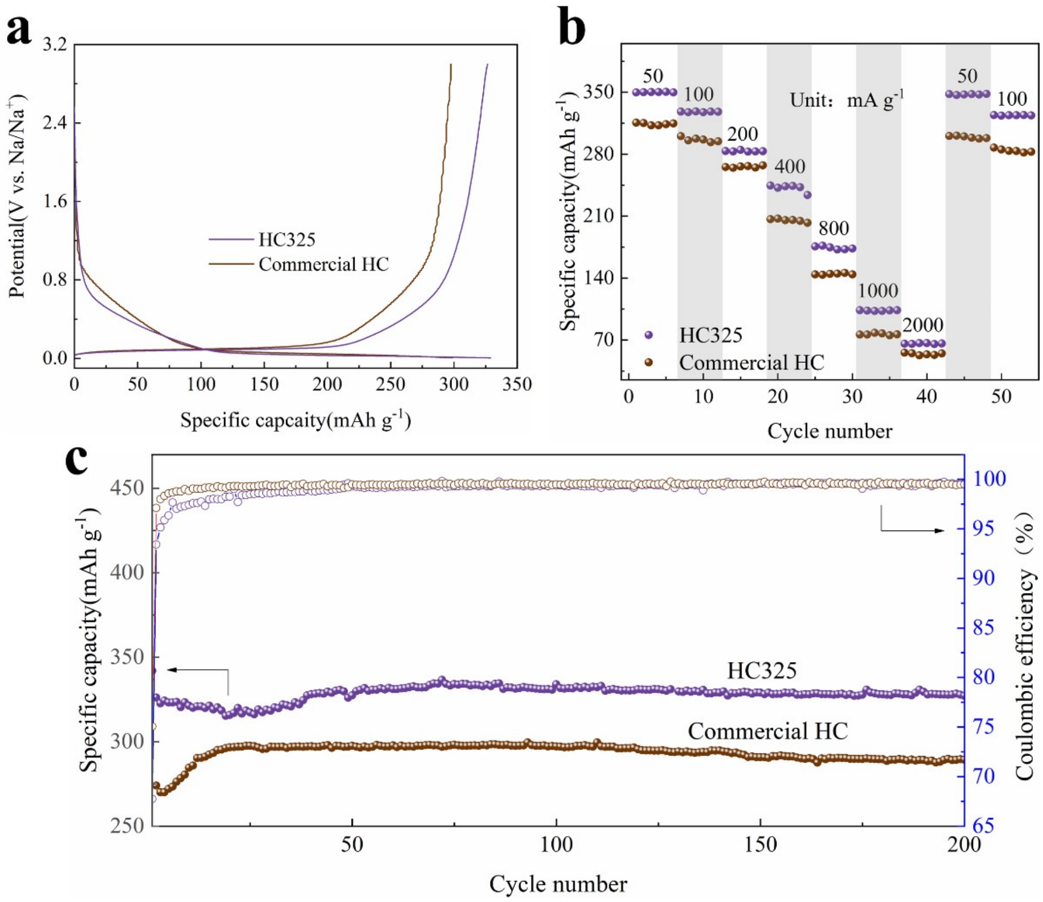

Figure S19. Electrochemical properties of Hard carbon. (a) GCD curves at 100 mA g−1. (b) Rate performance of HC325 and Commercial HC. (c) Cycling performance of HC325 and Commercial HC.

Table S1. Basic properties of HO.

Basic properties		HO
Density (20℃)/(g/cm^3)		1.18
Elemental composition	*C /wt%*	90.11
	H /wt%	9.14
	S /wt%	0.58
	N /wt%	0.17
	O /wt%	0
	C/H	0.97
SARA Four components	Saturates */wt%*	13.77
	Aromatics */wt%*	73.78
	Resins */wt%*	11.25
	Asphaltenes */wt%*	1.21

Table S2. Elemental analysis of cross-linked pitch.

Sample	*C/wt%*	*H/wt%*	*S/wt%*	*N/wt%*	*O/wt%*
SP230	89.21	8.01	0.64	0.11	2.03
SP290	87.89	7.32	0.66	0.09	4.04
SP325	87.52	6.64	0.54	0.09	5.21
SP350	86.96	6.39	0.51	0.08	6.06
SP400	91.22	6.02	0.49	0.09	2.18

Table S3. FTIR structural indices of cross-linked pitch

Sample	*Iar*	*Ios*	I_{CH}	I_A
HO	0.1681	0.4491	0.8319	0.7802
SP230	0.2368	0.4495	0.8032	0.6897
SP290	0.2545	0.4425	0.7955	0.7221
SP325	0.2833	0.4403	0.7167	0.6591
SP350	0.3433	0.4393	0.6567	0.6209
SP400	0.5265	0.4305	0.4735	0.4313

Iar: the fraction of aromatic carbon without alkyl substituents, indicating the degree of condensation of sample, defined by the formula: $Iar = Abs_{3050}/(Abs_{3050}+Abs_{2920})$.

Ios: the fraction of aromatic rings with ortho-substituents (i.e. four neighboring hydrogen atoms) compared to all aromatic rings with at least one hydrogen atom, which responds to the relative size and degree of condensation of aromatic molecules, defined by the formula: $Ios = Abs_{750}/(Abs_{750}+Abs_{814}+Abs_{840}+Abs_{880})$.

I_{CH}*: fraction of aromatic carbons that are substituted by alkyl side chains or methylene groups, indicating the number of alkyl side chains, defined by the formula:* $I_{CH} = Abs_{2920}/(Abs_{3050}+Abs_{2920})$

I_A*: the fraction of alkyl groups that are linked to non-aromatic carbon atoms (instead of aromatic carbon atoms) and itcan reflect the length of the alkyl side chain, which is defined by the formula:* $I_A=Abs_{2960}/(Abs_{3050}+Abs_{2960})$.

Table S4. XPS compositional analysis, fitted parameters of the C 1s, and O 1s spectra of cross-linked pitch.

Binding Energy (eV)	*C1s*			*O1s*		
	284.8	*286.3*	*289.4*	*531.8*	*532.6*	*533.8*
	C-C/C=C	*C-O*	*C=O*	*C(O)-O*	*C=O*	*C-O*
SP230	87.61	6.04	6.46			
SP290	68.85	27.23	3.92	16.97	35.77	47.26
SP325	75.9	18.93	5.17	17.53	28.06	54.41
SP350	78.6	15.17	6.24	21.13	24.85	54.02
SP400	74.21	18.35	7.43	33.58	59.41	7.01

Table S5. Structure parameters of PC

Sample	L_C / nm	d_{002} / nm	N	L_a / nm	I_D/I_G	I_A/I_G	L_a (Raman) / nm	$S_{BET}(N_2)$ / m²/g	V_{total} / cm³/g
PC230	1.458	0.413	4.528	6.06	2.93	2.02	6.55	518.57	0.221
PC290	1.270	0.415	4.056	5.28	3.14	2.27	6.12	534.82	0.220
PC325	0.948	0.417	3.272	5.01	3.28	2.31	5.86	739.07	0.299
PC350	0.930	0.418	3.222	4.78	3.39	2.23	5.68	554.33	0.230
PC400	0.926	0.391	3.368	5.17	2.96	1.06	6.49	528.44	0.223
MC325	1.536	0.358	5.291	5.81	2.22	1.88	8.66	9.787	0.006

Table S6. Structure parameters of HC

Sample	L_C / nm	d_{002} / nm	N	L_a / nm	I_D/I_G	I_A/I_G	L_a (Raman) / nm
HC230	1.329	0.379	4.451	7.12	2.38	0.72	8.07
HC290	1.205	0.381	4.162	5.37	2.52	0.81	7.63
HC325	1.094	0.380	3.879	5.12	2.59	0.98	7.42
HC350	1.089	0.380	3.866	4.87	2.69	1.12	7.14
HC400	1.388	0.361	4.854	5.83	2.48	1.15	7.73

Table S7. Specific surface area and pore volume of HC.

Sample	$S_{BET}(N_2)$ / $m^2\ g^{-1}$	V_{total} / $cm^3\ g^{-1}$	S_{SAXS} / $m^2\ g^{-1}$	True density	V_{Closed}
HC230	12.47	0.014	-	1.8472	0.0989
HC290	42.23	0.030	691.9	1.5948	0.1846
HC325	71.84	0.042	783.6	1.5372	0.2081
HC350	122.28	0.059	640.5	1.6473	0.1646
HC400	5.79	0.008	-	2.0131	0.0543

Table S8. Structure parameters of carbon materials.

Sample	L_C / nm	d_{002} / nm	N	L_a / nm	I_D/I_G	I_A/I_G	L_a (Raman) / nm

NC	1.657	0.349	5.748	7.28	1.77	1.26	10.87
PNC	1.416	0.358	4.955	5.76	2.17	1.60	8.85
CNC	3.651	0.345	11.531	23.53	1.07	0.67	17.97
MC290	1.541	0.355	5.341	6.06	2.05	1.75	9.34
MC325	1.536	0.358	5.291	5.81	2.22	1.88	8.66
MC350	1.392	0.362	4.845	4.58	2.35	1.95	8.18
CMC325	3.092	0.347	9.911	17.64	1.24	1.01	15.53

Table S9. XPS compositional analysis, fitted parameters of the C1s spectra of Carbon materials.

Binding Energy (eV)	*C1s*			
	284.5	*285.3*	*286.3*	*289.4*
	C=C(sp²)	*C-C(sp³)*	*C-O*	*C=O*
MC290	47.02	23.89	19.74	9.35
MC325	41.72	29.76	23.01	5.44
MC350	38.87	33.28	21.21	6.64
PC290	57.43	29.93	11.69	1.03
PC325	58.37	26.94	13.13	1.56
PC350	46.86	25.66	14.84	0.97

Table S10. Electrochemical properties of Hard Carbon derived from fossil feedstocks

Materials	Specific capacity	Plateau capacity	Current density	ICE	Ref.

Heavy Oil	**328 mAh/g**	**223.2 mAh/g**	**0.1A/g**	**67%**	**This work**
Pitch	300.6 mAh/g	-	0.1C	88.6%	[1]
Pitch and Lignin	254 mAh/g	163.8 mAh/g	0.03A/g	82%	[2]
Coal and Pitch	312.2 mAh/g	185.7 mAh/g	0.03A/g	85.3%	[3]
Pitch	300.83 mAh/g	132.2 mAh/g	0.02A/g	82.82%	[4]
Pitch and Resin	349.9 mAh/g	-	0.05A/g	60.9%	[5]
Coal tar pitch	276.8 mAh/g	-	0.25C	67.5%	[6]
Polystyrene	279.3 mAh/g	136.2 mAh/g	0.2C	70.2%	[7]
Coal	293 mAh/g	-	0.03A/g	84%	[8]
Coal	303.1 mAh/g	163.5 mAh/g	0.05A/g	64.8%	[9]
Pitch	313.83 mAh/g	-	0.1C	86.14	[10]

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