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

Supporting Information for

Ultra-Micropores of Hard Carbons for Ultrafast Na-ion Storage

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Supporting Figures

Fig. S1 Macroscopic morphology of CS, NP, and NP5.

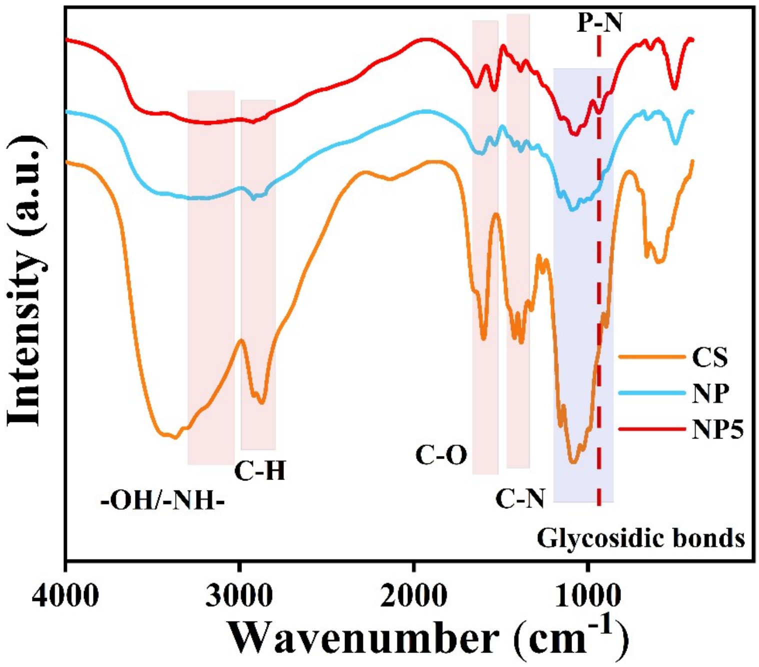

Fig. S2 FT-IR of CS, NP, and NP5.

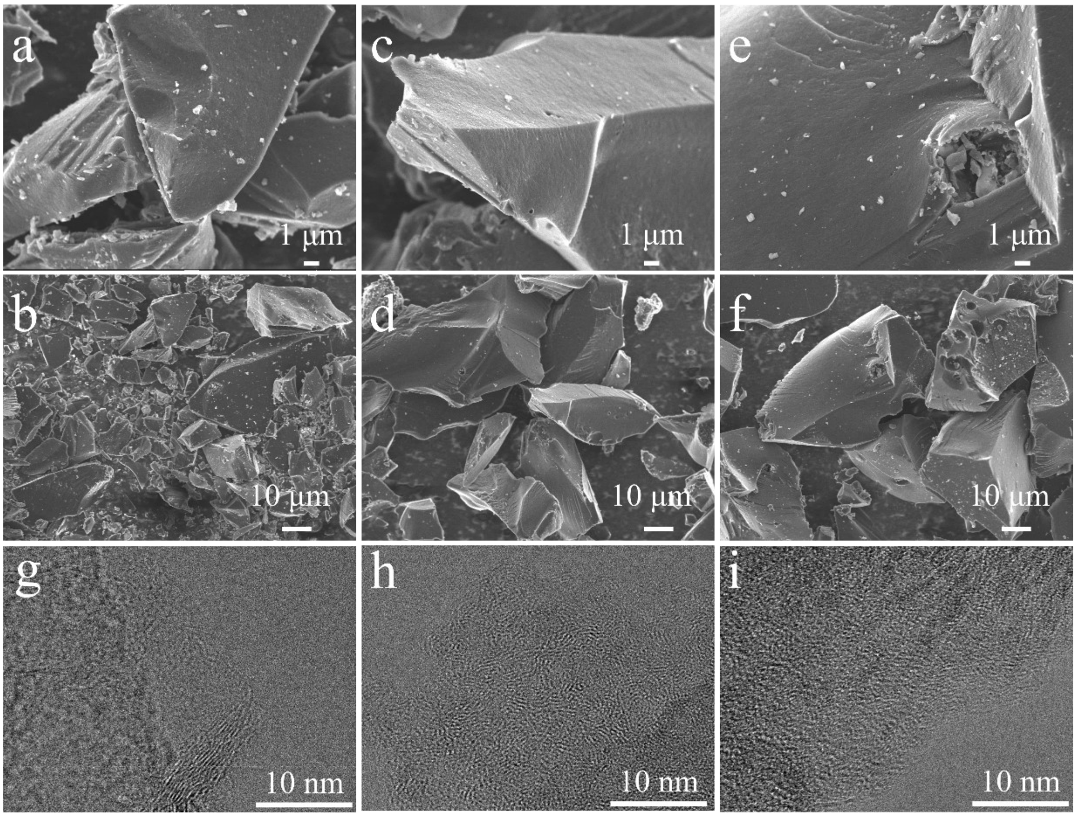

Fig. S3 SEM images of NP1 (a-b), NP3 (c-d) and NP7 (e-f), TEM images of CS, NP and NP5.

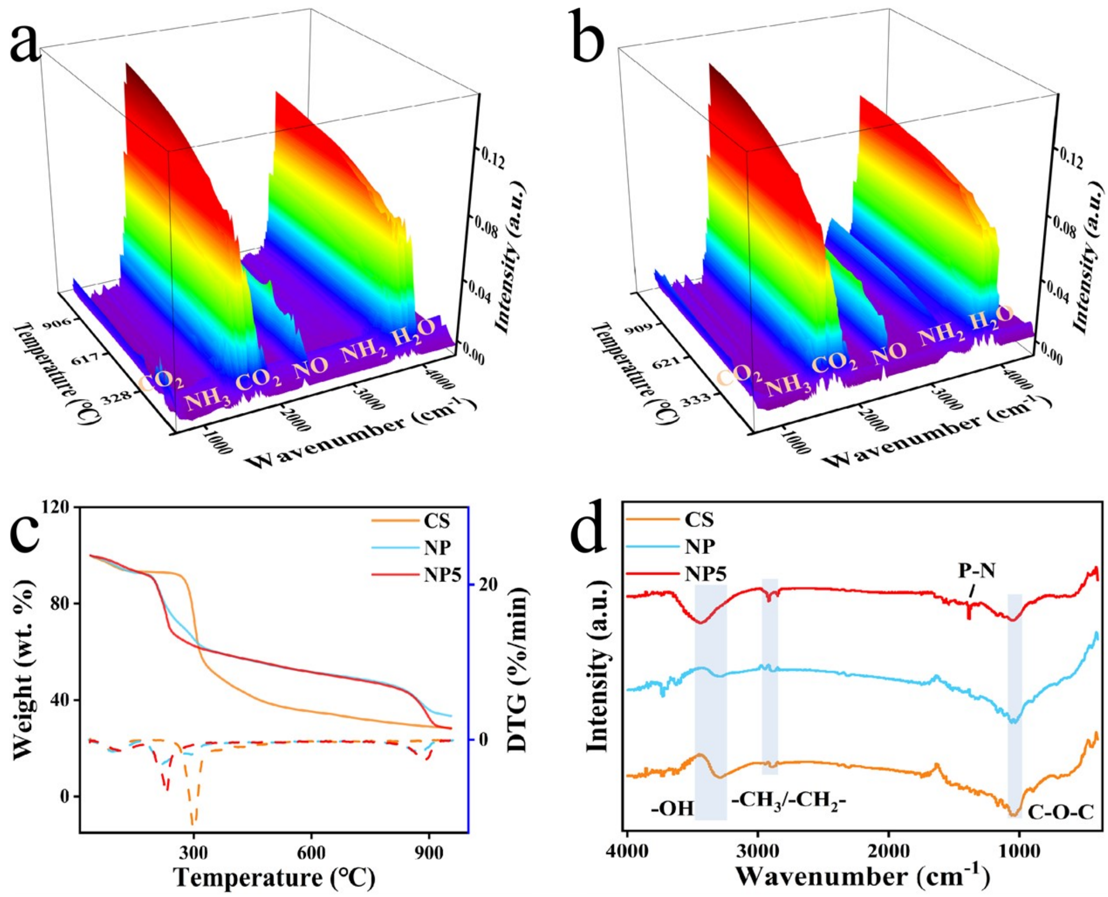

Fig. S4 The In-situ TG-IR curves of the two samples (a) CS, (b) NP. The TGA curves of the three samples CS (c). The FTIR curves of the three samples (d).

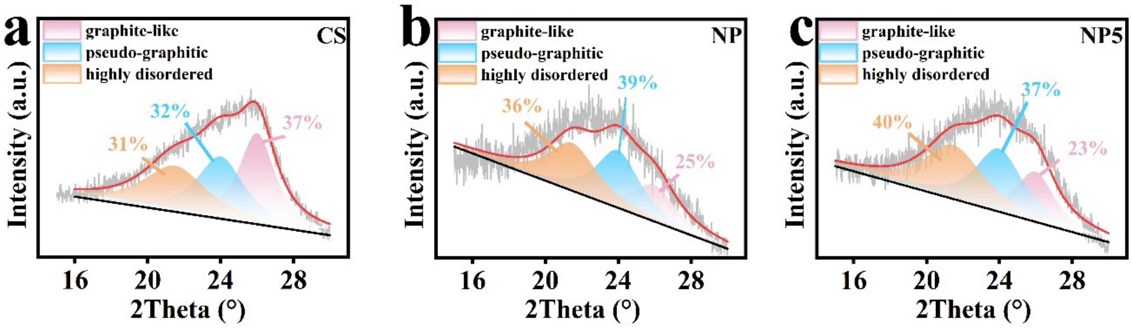

Fig. S5 Evolution of microstructures examined by the deconvolution of (002) XRD planes: (a) CS, (b) NP, (c) NP5.

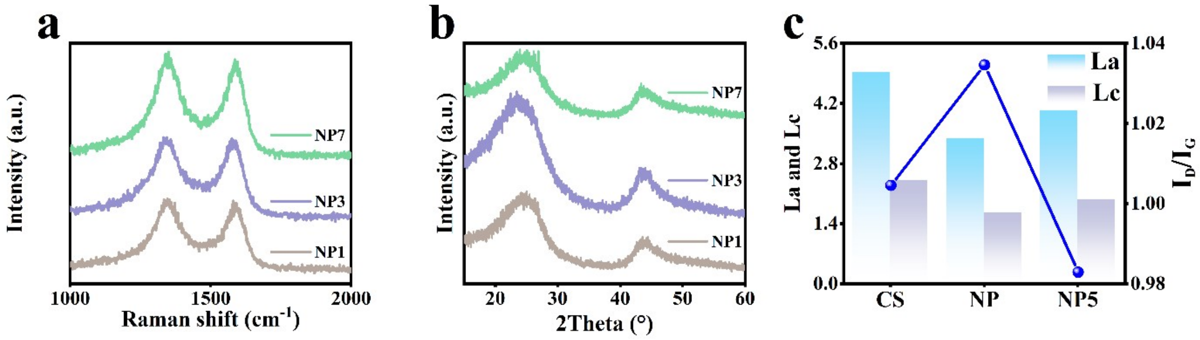

Fig. S6 Raman images of NP1, NP3 and NP7 (a). XRD images of NP1, NP3 and NP7 (b). The values of the I_D/I_G and La, Lc (c).

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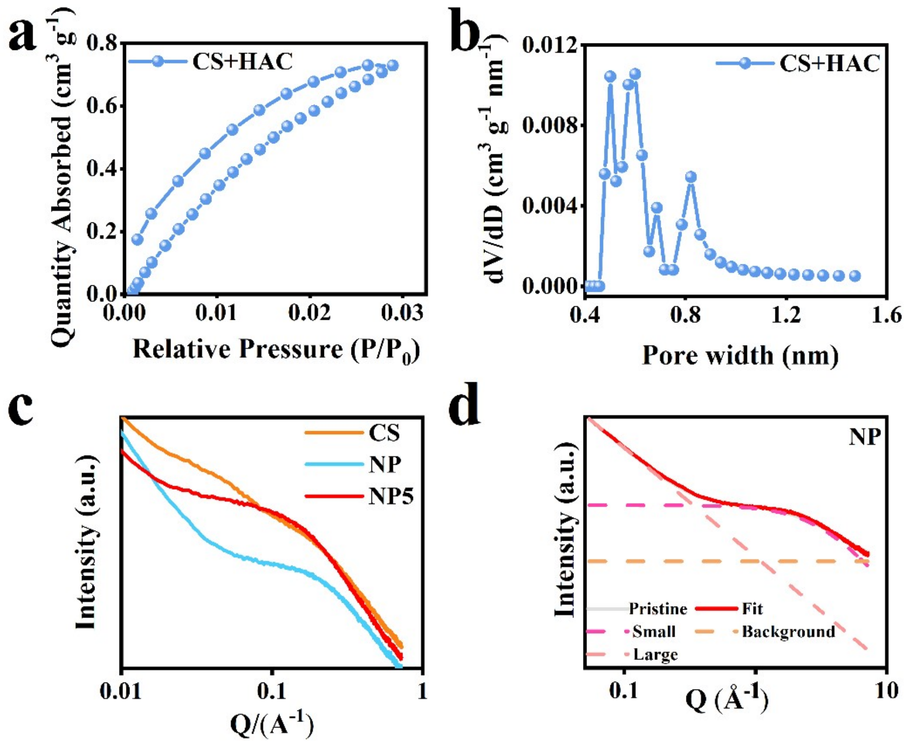

Fig. S7 CO_2 adsorption-desorption isotherms of CS+HAC (a). Pore size distribution of CS+HAC (b). SAXS patterns of CS, NP and NP5 (c). Fitted SAXS patterns of NP (d).

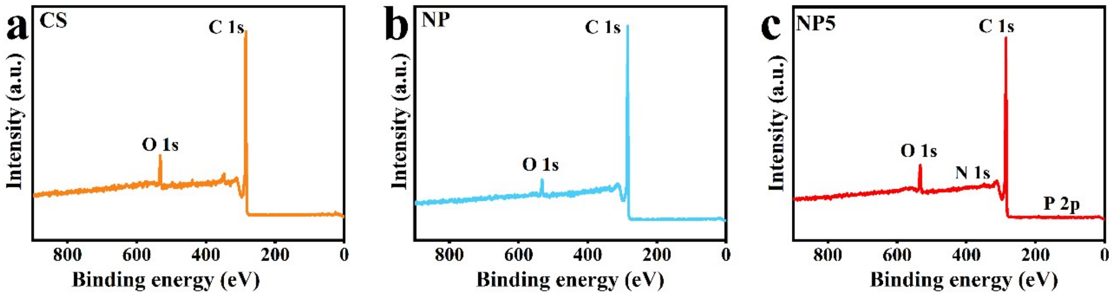

Fig. S8 XPS survey spectra of samples: (a) CS, (b) NP and (c) NP5.

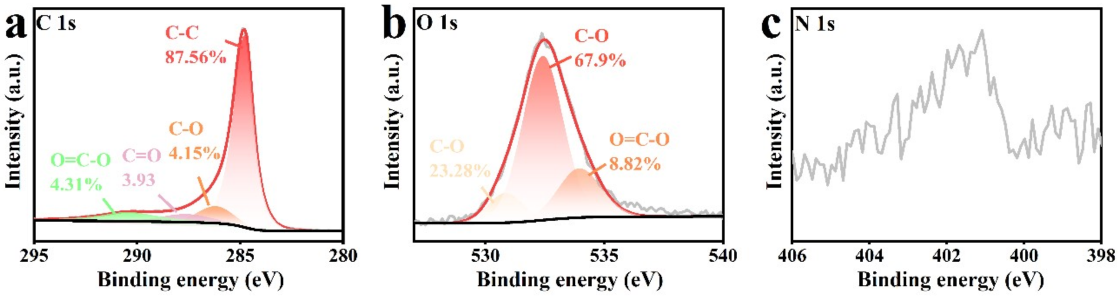

Fig. S9 XPS spectra of CS: (a) C 1s, (b) O 1s and (c) N 1s.

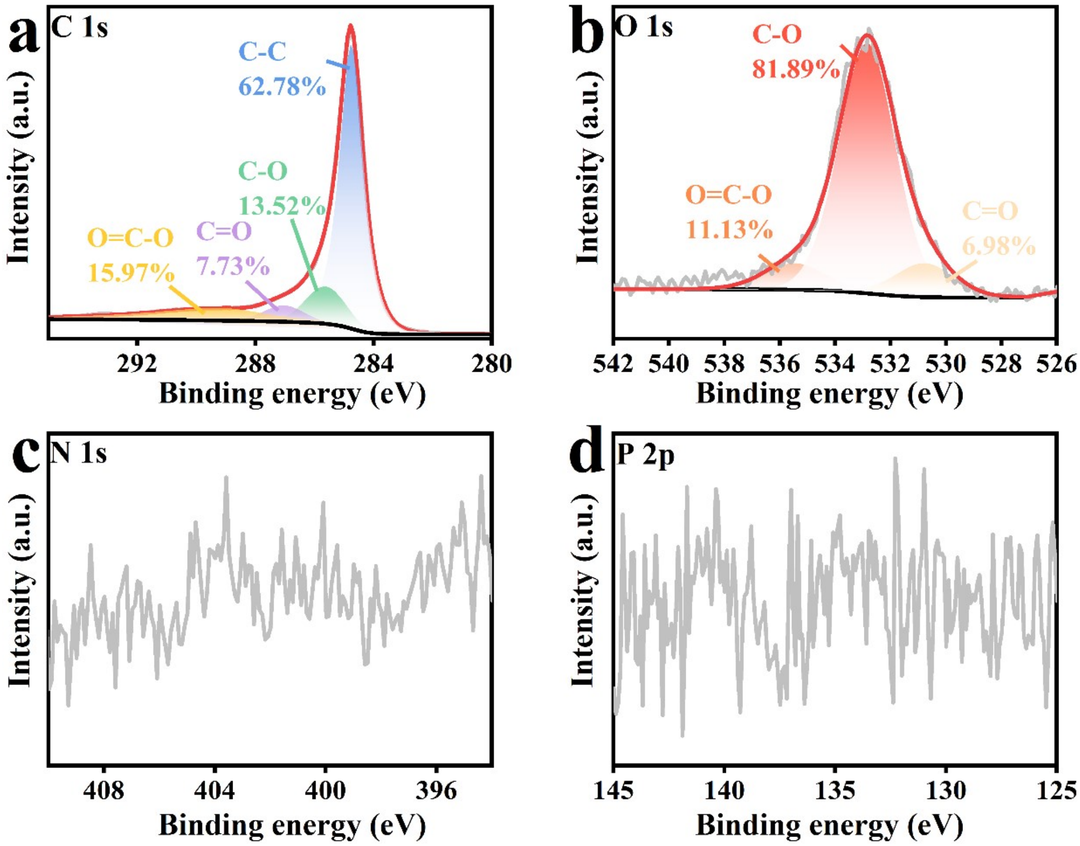

Fig. S10 XPS spectra of NP: (a) C 1s, (b) O 1s, (c) N 1s and (d) P 2p.

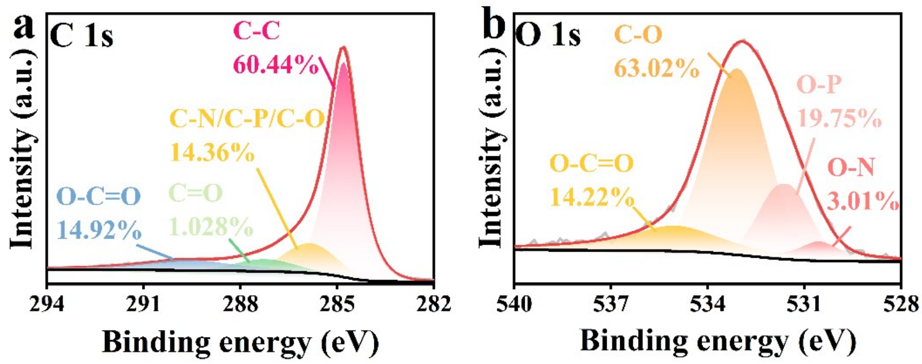

Fig. S11 XPS spectra of NP5: a) C 1s, b) O 1s.

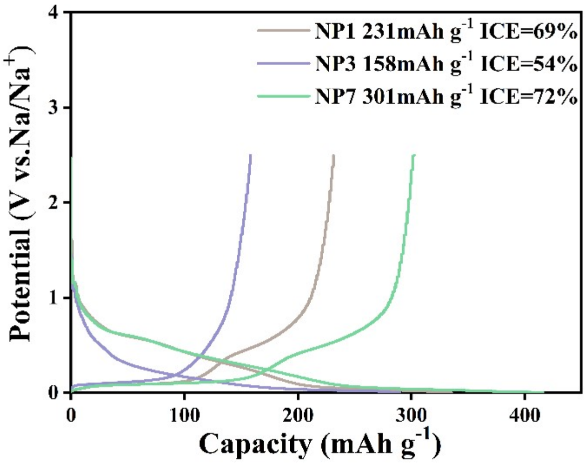

Fig. S12 First Charge/discharge curves for NP1, NP3 and NP7 at 0.02 A g^{-1}.

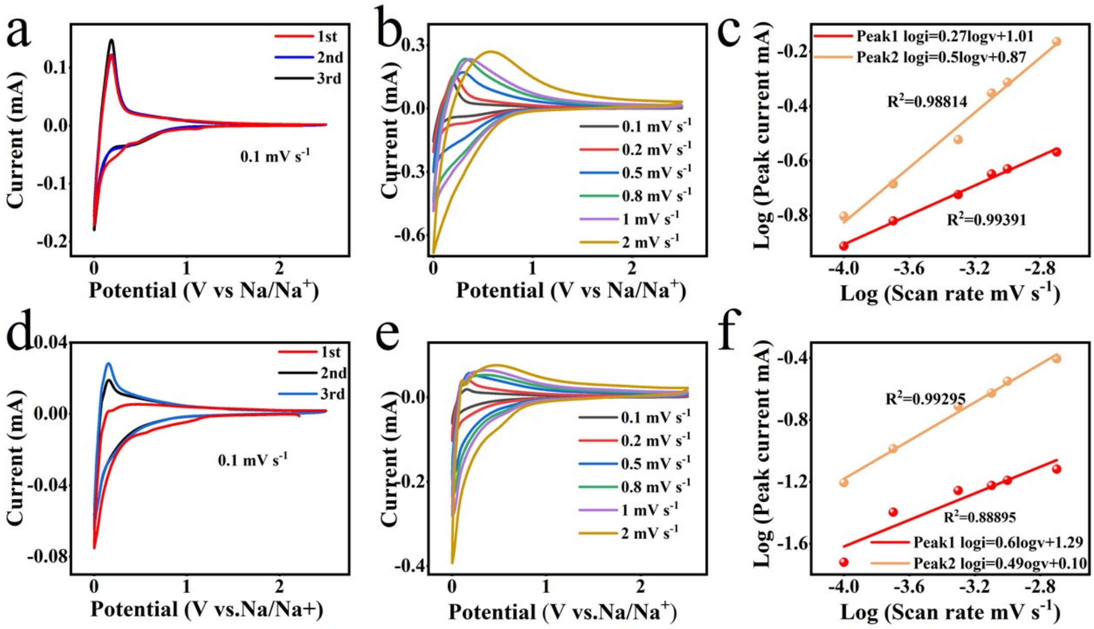

Fig. S13 the CV curves at 0.1 m V s^{-1} for CS (a) and NP (d), CV curves for CS (b) and NP (e), b-value derived from the currents of anodic and cathodic peaks at various scan rates for CS (c) and NP (f).

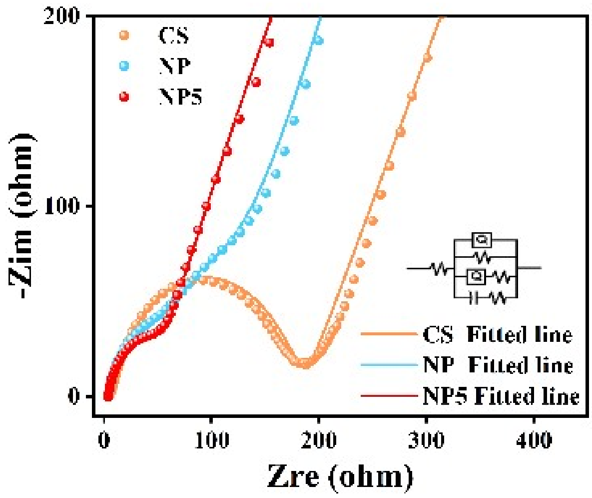

Fig. S14 Nyquist plots.

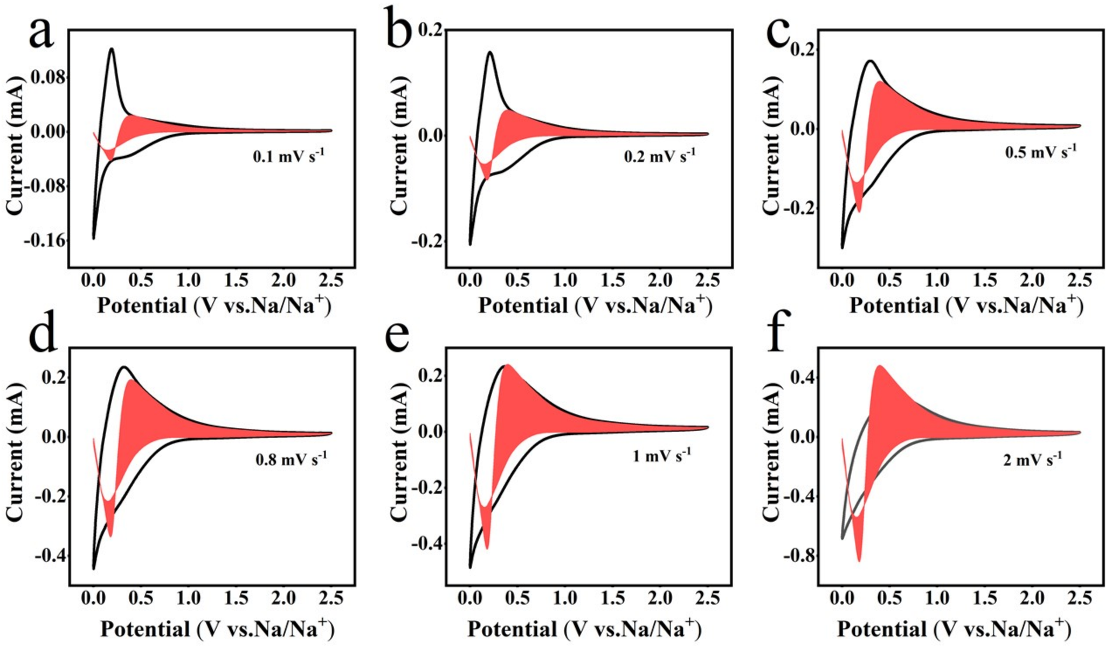

Fig. S15 The capacitive contribution for CS at 0.1-2 mV s^{-1}.

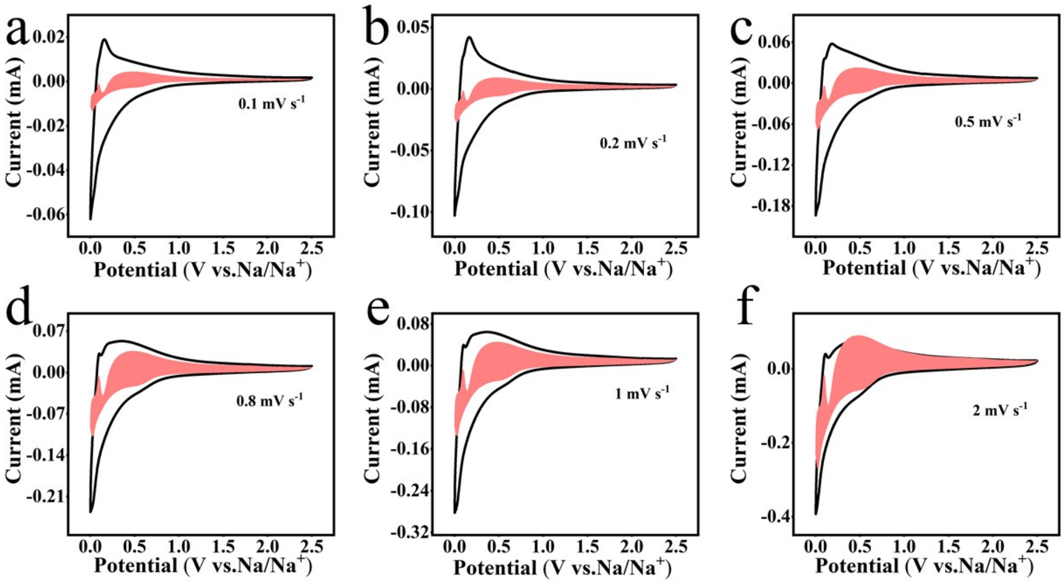

Fig. S16 The capacitive contribution for NP at 0.1-2 mV s^{-1}.

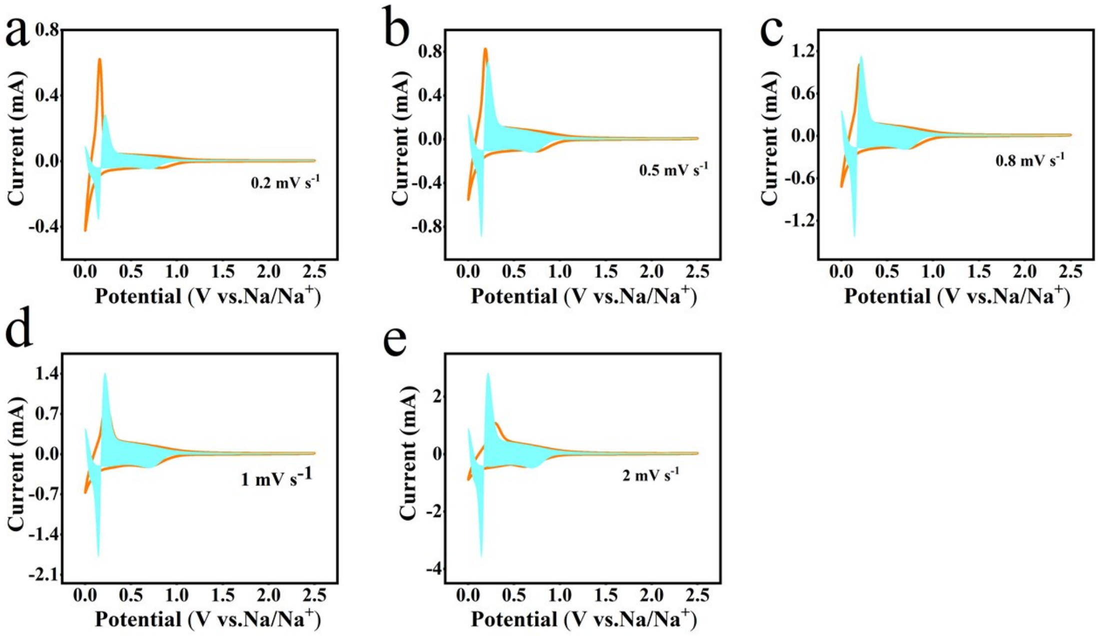

Fig. S17 The capacitive contribution for NP5 at 0.2-2 mV s^{-1}.

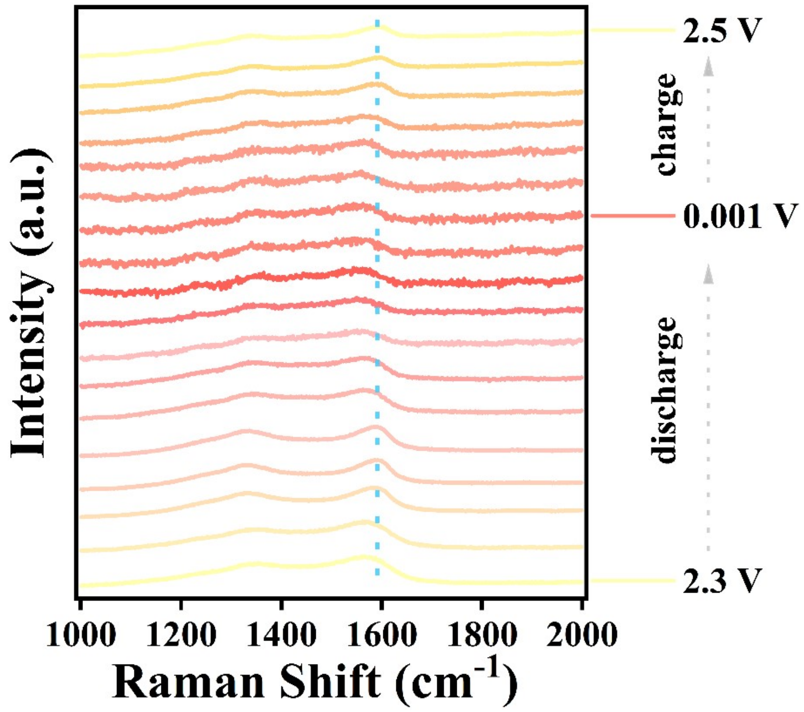

Fig. S18 The in-situ Raman spectra.

Supporting Tables

Table S1 Physical parameters of different hard carbons from the XRD spectra.

		CS	NP	NP5
Area (%)	Highly disordered	31	36	40
	Pseudo-graphitic	32	39	37
	Graphite-like	37	25	23

Table S2 Physical parameters of different hard carbons.

	La (nm)	Lc (nm)	d002 (nm)	I_D/I_G
CS	4.94	2.42	0.35	0.98
NP	3.39	1.66	0.37	1.03
NP1	3.72	1.82	0.36	1.01
NP3	3.19	1.56	0.37	1.00
NP5	4.04	1.98	0.39	1.00
NP7	2.91	1.42	0.36	0.93

Table S3 Pore structural parameters of CS, NP and NP5.

	Specific Surface Area (N_2) (m^2/g)	Pore Volume (N_2) (cm^3/g)	Specific Surface Area (CO_2) (m^2/g)	Pore Volume (CO_2) (cm^3/g)
CS	12.568	0.012	11.475	0.004
NP	16.289	0.017	76.751	0.028
NP5	423.602	0.187	578.291	0.194

Table S4 CS, NP and NP5 in 0.4-0.8 nm pore volume.

	Pore Volume (N_2) (cm^3/g)	Pore Volume (CO_2) (cm^3/g)
CS	0	0.002
NP	0	0.017
NP5	0.092	0.136

Table S5 Percentage composition after peak split fitted XPS.

		CS	NP	NP5
C 1s	C-C	87.59	62.78	60.44
	C-O (C-N, C-P)	4.15	13.52	14.36
	C=O	3.93	7.73	1.028
	O=C-O	4.31	15.97	14.92
O 1s	C=O	23.28	6.98	
	C-O	67.9	81.89	63.02
	O=C-O	8.82	11.13	14.22
	O-N			3.01
	O-P			19.75
N 1s	N-O			8.59
	N-Q			31.63
	N-P			30.49
	N-5			9.83
	N-6			19.46
P 2p	O-P			33.17
	N-P			33.66
	C-P			33.17

Table S6 Na-ion storage performance of NP-X hard carbons.

	Capacity	ICE	plateau capacity	slope capacity
CS	181 mAh/g	56%	49 mAh/g	108 mAh/g
NP	222 mAh/g	44%	99 mAh/g	107 mAh/g
NP1	231 mAh/g	69%	81 mAh/g	150 mAh/g
NP3	158 mAh/g	54%	30 mAh/g	128 mAh/g
NP5	386 mAh/g	73%	173 mAh/g	213 mAh/g
NP7	301 mAh/g	72%	96 mAh/g	205 mAh/g

Table S7 Comparison of the slope capacities and plateau capacities of hard carbons.

	Capacity	Slope capacity	Plateau capacity	Journals
1	302 mAh g^{-1}	152 mAh g^{-1}	101 mAh g^{-1}	Small[1]
2	346 mAh g^{-1}	117 mAh g^{-1}	108 mAh g^{-1}	Nano Micro Lett.[2]
3	323 mAh g^{-1}	135 mAh g^{-1}	232 mAh g^{-1}	Energy Storage Mater [3]
4	417 mAh g^{-1}	100 mAh g^{-1}	317 mAh g^{-1}	Energy Storage Mater [4]
5	279 mAh g^{-1}	156 mAh g^{-1}	123 mAh g^{-1}	Carbon[5]
6	361 mAh g^{-1}	129 mAh g^{-1}	171 mAh g^{-1}	Chem. Eng. J. [6]
8	326 mAh g^{-1}	262 mAh g^{-1}	64 mAh g^{-1}	Adv. Mater.[7]
9	386 mAh g^{-1}	173 mAh g^{-1}	213 mAh g^{-1}	This work

Table S8 Comparison of the physical properties and Na-ion storage performance of hard carbon anodes.

Name	SSA (m^2/g)	Capacity ($mAh\ g^{-1}$)	Rate Capability ($mAh\ g^{-1}$)	ICE (%)	Cycle Life	Journals
L6-1300	2.51	305 @0.1C	174 @ 5C	85	87.5% retention over 500 cycles, 237 $mAh\ g^{-1}$@1C	Small[1]
ACGC900	19.4	346 @30 $mA\ g^{-1}$	192 @ 1 $A\ g^{-1}$	80	90% retention over 200 cycles, 252 $mAh\ g^{-1}$@50 $mA\ g^{-1}$	Nano Micro Lett.[2]
PCBC125	76.19	330 @20 $mA\ g^{-1}$	182 @ 1 $A\ g^{-1}$	89	96% retention over 300 cycles, 252 $mAh\ g^{-1}$@100 $mA\ g^{-1}$	Energy Storage Mater[3]
VHC-1200	227.57	260 @100 $mA\ g^{-1}$	206 @ 1 $A\ g^{-1}$	72	82% retention over 1000 cycles, 200 $mAh\ g^{-1}$@500 $mA\ g^{-1}$	Carbon[5]
HHC	7	279 @20 $mA\ g^{-1}$	132 @ 1 $A\ g^{-1}$	70	85% retention over 500 cycles, 162 $mAh\ g^{-1}$@1 $A\ g^{-1}$	Carbon Energy[8]
HC-DB-6	82	350 @20 $mA\ g^{-1}$	83 @ 1 $A\ g^{-1}$	86	96% retention over 100 cycles, 270 $mAh\ g^{-1}$@100 $mA\ g^{-1}$	Adv. Mater.[9]
NP5	578.291	386 @20 $mA\ g^{-1}$	151 @ 1 $A\ g^{-1}$	73	85% retention over 2000 cycles, 180 $mAh\ g^{-1}$@1 $A\ g^{-1}$	This work

Table S9 Electrode parameters and diffusion coefficient for CS, NP and NP5 anode.

Samples	R_s (Ω)	R_{ct} (Ω)
CS	5.568	178.9
NP	4.317	137.8
NP5	4.204	98.35

Table S10 Percentage of capacitive contribution at different sweep speeds.

	0.1 mV s^{-1}	0.2 mV s^{-1}	0.5 mV s^{-1}	0.8 mV s^{-1}	1 mV s^{-1}	2 mV s^{-1}
CS	27.08	32.55	44.63	48.46	54.55	80.61
NP	30.32	31.73	40.32	52.84	55.32	81.22
NP5	33.53	41.13	52.40	56.57	62.73	74.24

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