Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

A carbon-based material with hierarchical structure and intrinsic heteroatom for sodium-ion storage with ultrahigh rate and capacity

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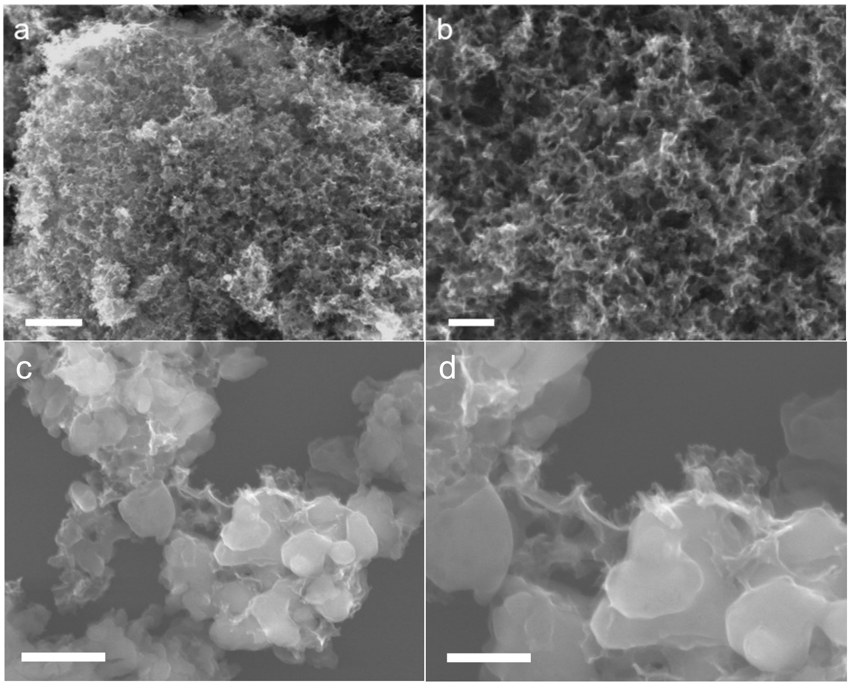

Figure S1. SEM images of HSIH-CMs (a, b) and HSIH-CMs@CaO (c, d). Scar bar: (a, c) 0.5 μm; (b, d) 0.2 μm.

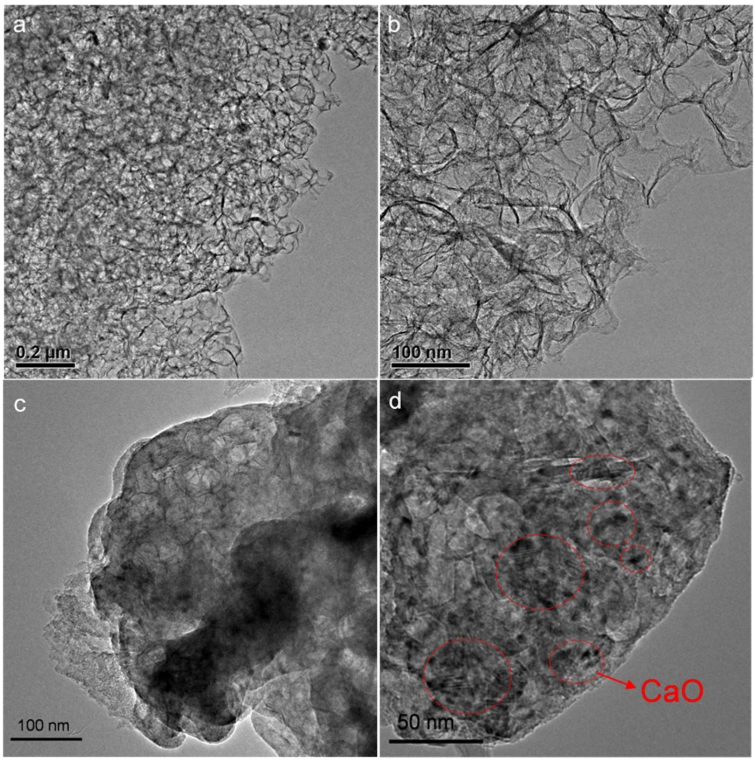

Figure S2. TEM images of HSIH-CMs (a, b) and HSIH-CMs@CaO (c, d).

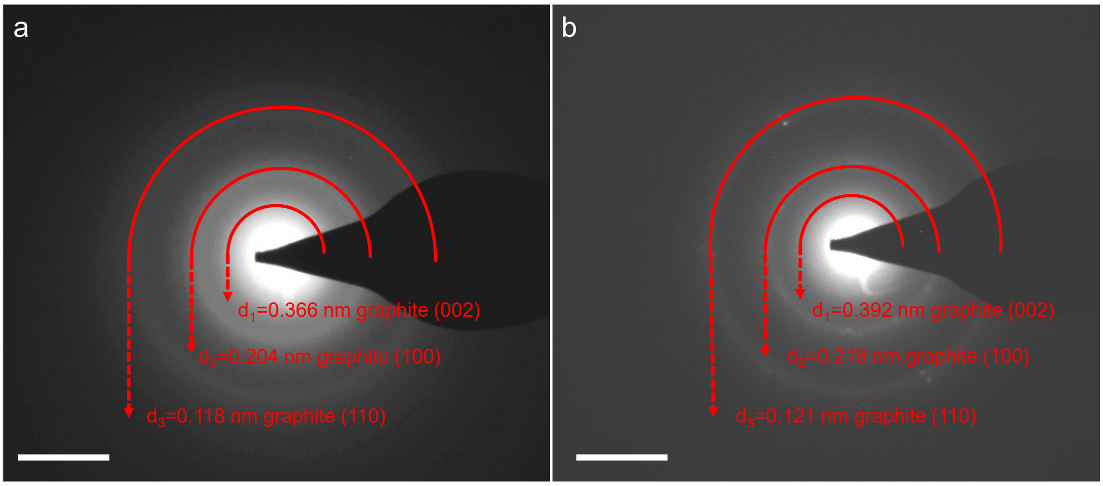

Figure S3. SAED patterns of the ordinary carbon (a) and HSIH-CMs (b) materials, respectively. Scar bar: (a) 5 1/nm; (b) 5 1/nm.

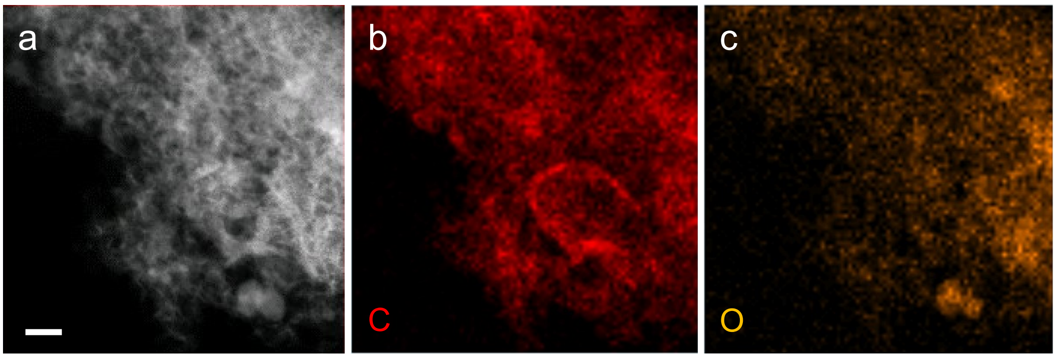

Figure S4. HAADF-STEM image (a) and corresponding EDX maps (b, c) of HSIH-CMs, scale bar: 100 nm.

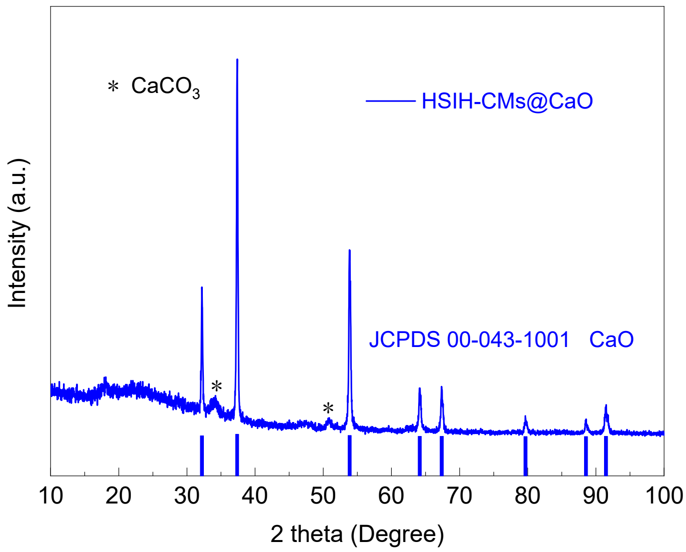

Figure S5. XRD pattern of the HSIH-CMs@CaO material.

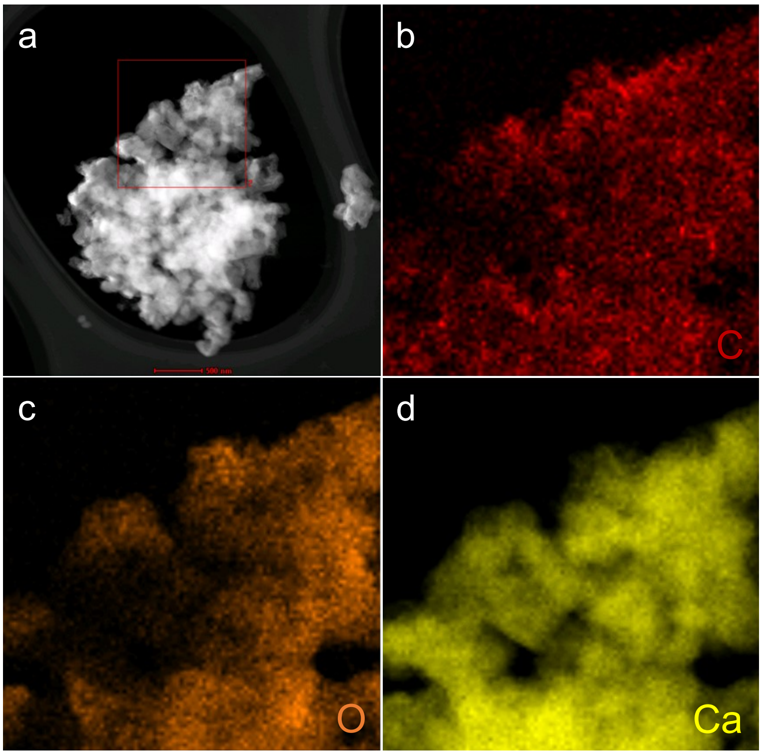

Figure S6. HAADF-STEM image (a) and corresponding EDX maps (b–d) of HSIH-CMs@CaO.

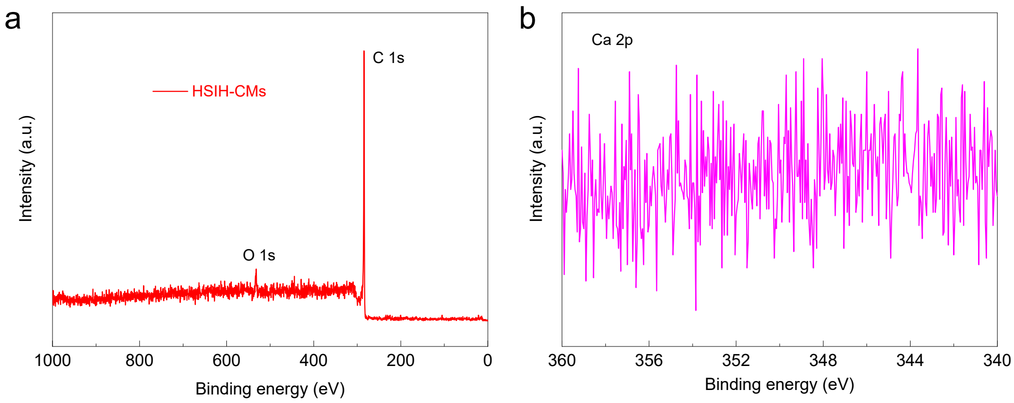

Figure S7. The XPS survey spectra (a) and Ca 2p spectra (b) of HSIH-CMs.

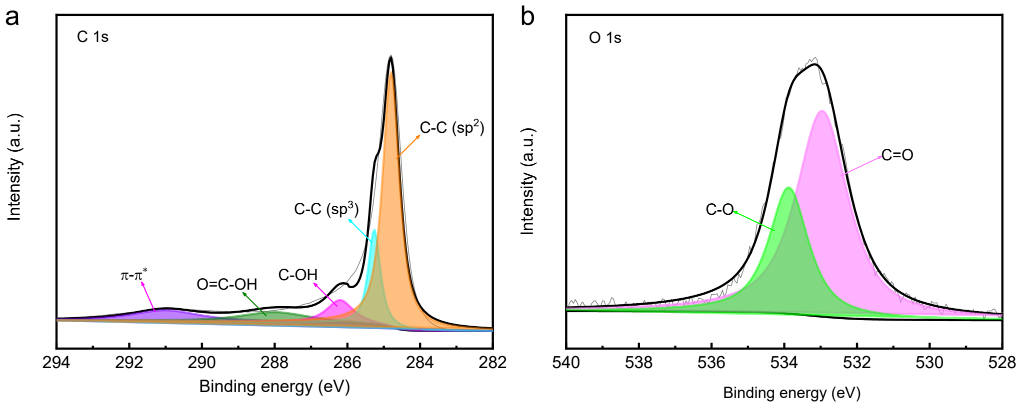

Figure S8. The XPS spectra for C 1s (a) and O 1s (b) of HSIH-CMs.

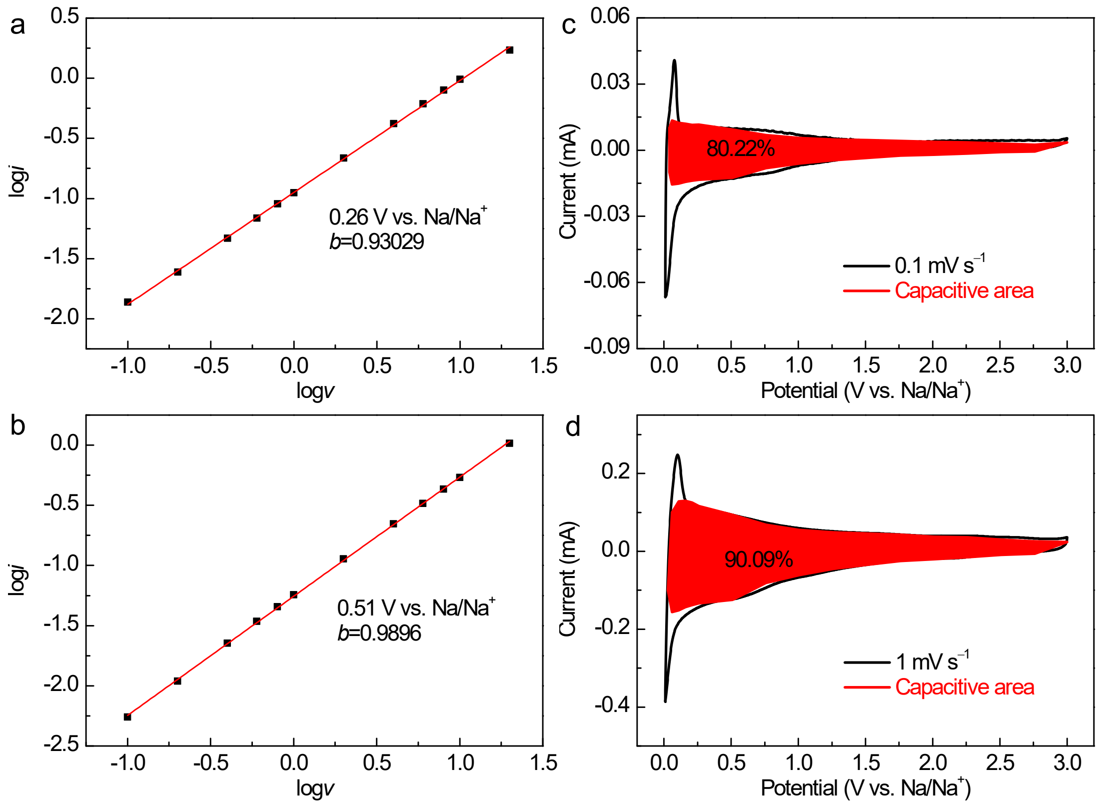

Figure S9. (a, b) *b* values of the HSIH-CMs anode at potentials of 0.26 V (a) and 0.51 V (b), respectively. (c, d) CV profiles of the HSIH-CMs with the capacitive contribution at scan rates of 0.1 mV s^{-1} (c) and 1 mV s^{-1} (d), respectively.

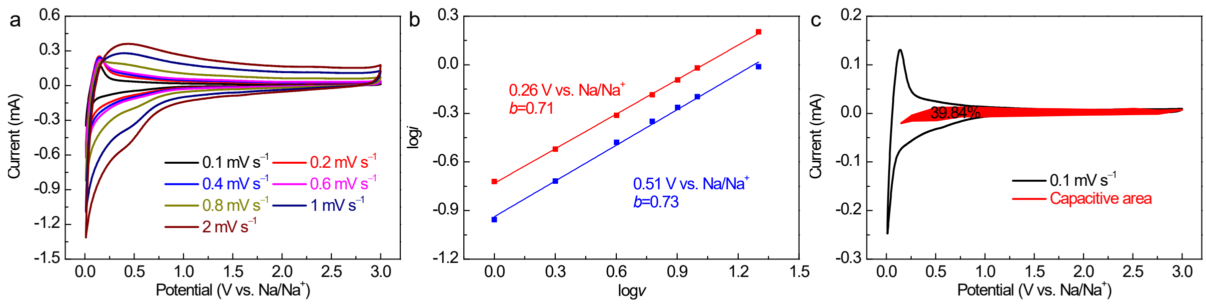

Figure S10. (a) CV curves of the ordinary carbon anode at various scan rates ranging from 0.1 to 2 mV s^{-1}. (b) *b* values of the ordinary carbon anode at potentials of 0.26 and 0.51 V. (c) CV profile of the ordinary carbon anode with the capacitive contribution at a scan rate of 0.1 mV s^{-1}.

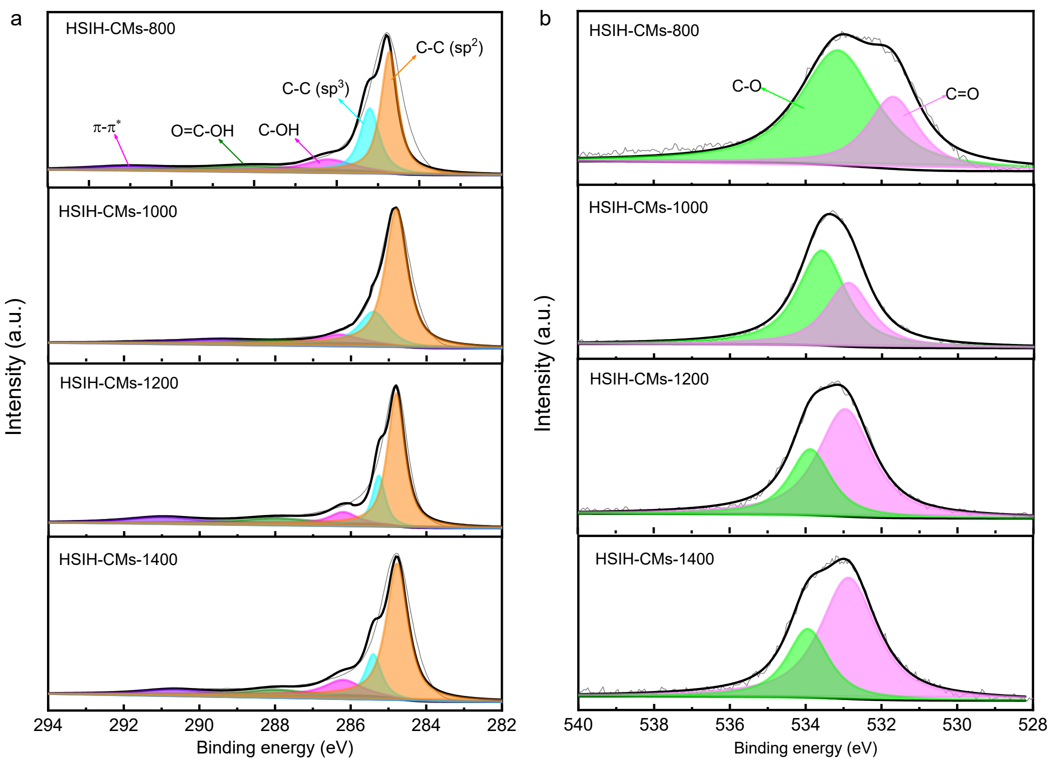

Figure S11. The XPS spectra for C 1s (a) and O 1s (b) of HSIH-CMs at different temperature.

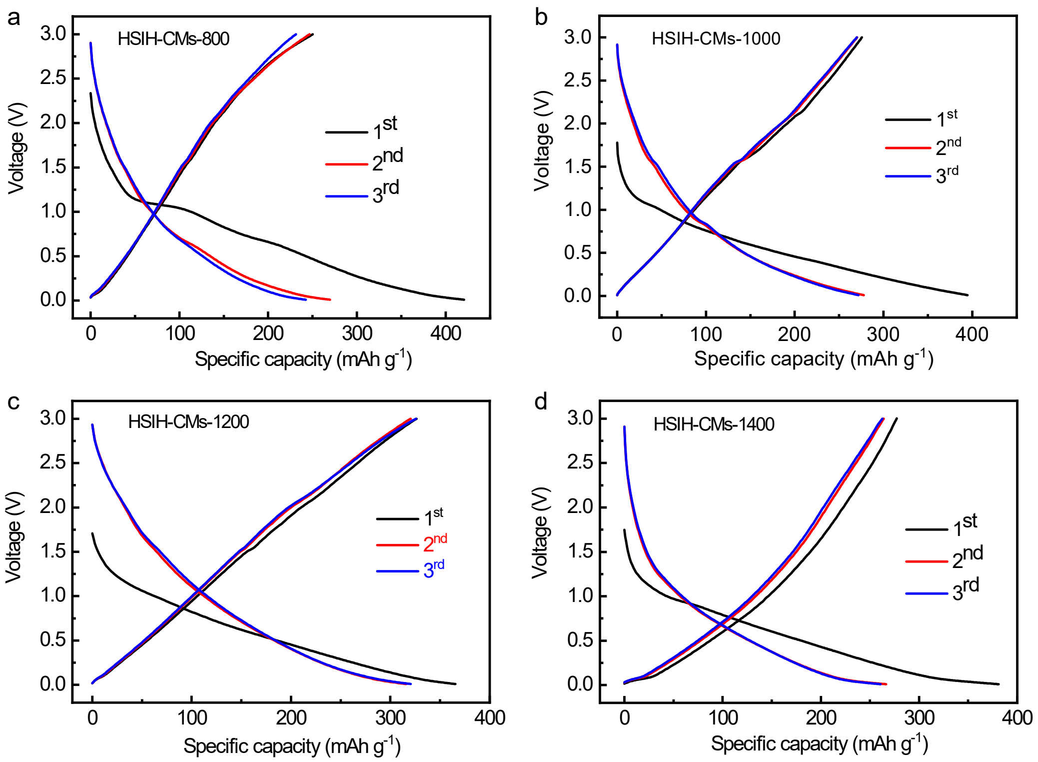

Figure S12. The first, second, and third galvanostatic discharge−charge profiles of (a) HSIH-CMs-800, (b) HSIH-CMs-1000, (c) HSIH-CMs-1200 and (d) HSIH-CMs-1400 anode at a current density of 100 mA g^{-1}.

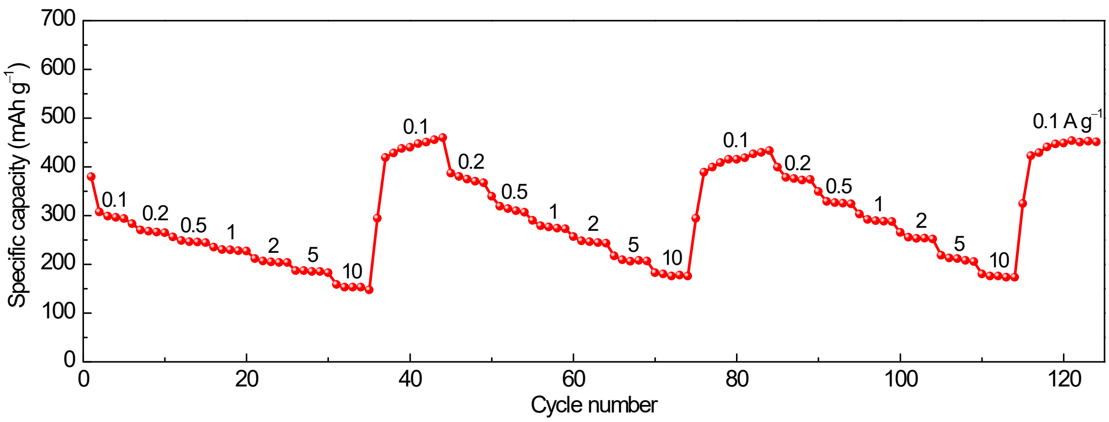

Figure S13. Rate capability of the HSIH-CMs anode at different current densities ranging from 0.1 to 10 A g^{-1}.

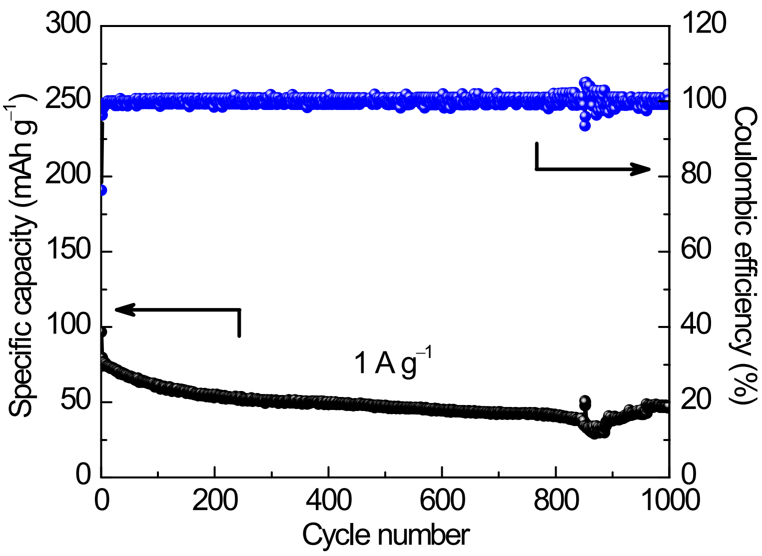

Figure S14. Cycling performance and corresponding Coulombic efficiency of the ordinary carbon anode at a current density of 1 A g^{-1}.

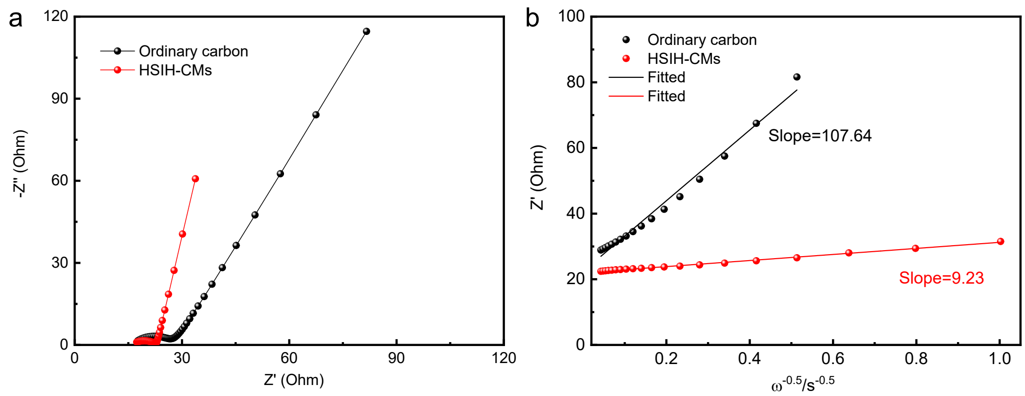

Figure S15. (a) Nyquist plots of the HSIH-CMs and ordinary carbon anodes after 100 cycles. (b) The Z'~$\omega^{-1/2}$ plots of the HSIH-CMs and ordinary carbon anodes after 100 cycles at the low-frequency region, respectively.

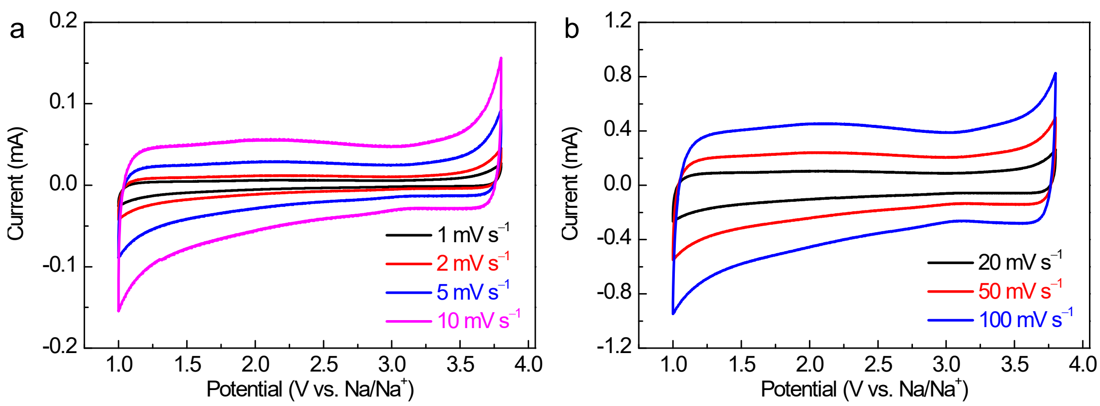

Figure S16. (a, b) CV curves of the ordinary carbon cathode at different scan rates ranging from 1 to 10 mV s^{-1} (a) and 20 to 100 mV s^{-1} (b), respectively, in a potential window of 1−3.8 V.

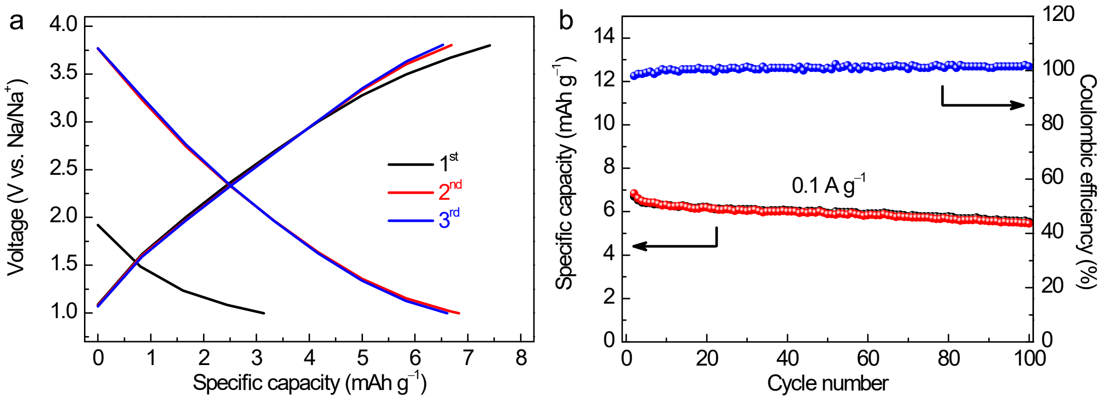

Figure S17. (a) The 1st, 2nd and 3rd galvanostatic charge-discharge curves of the ordinary carbon cathode at a current density of 0.1 A g^{-1}. (b) Cycling performance and the corresponding Coulombic efficiency of the ordinary carbon cathode at current density of 0.1 A g^{-1}.

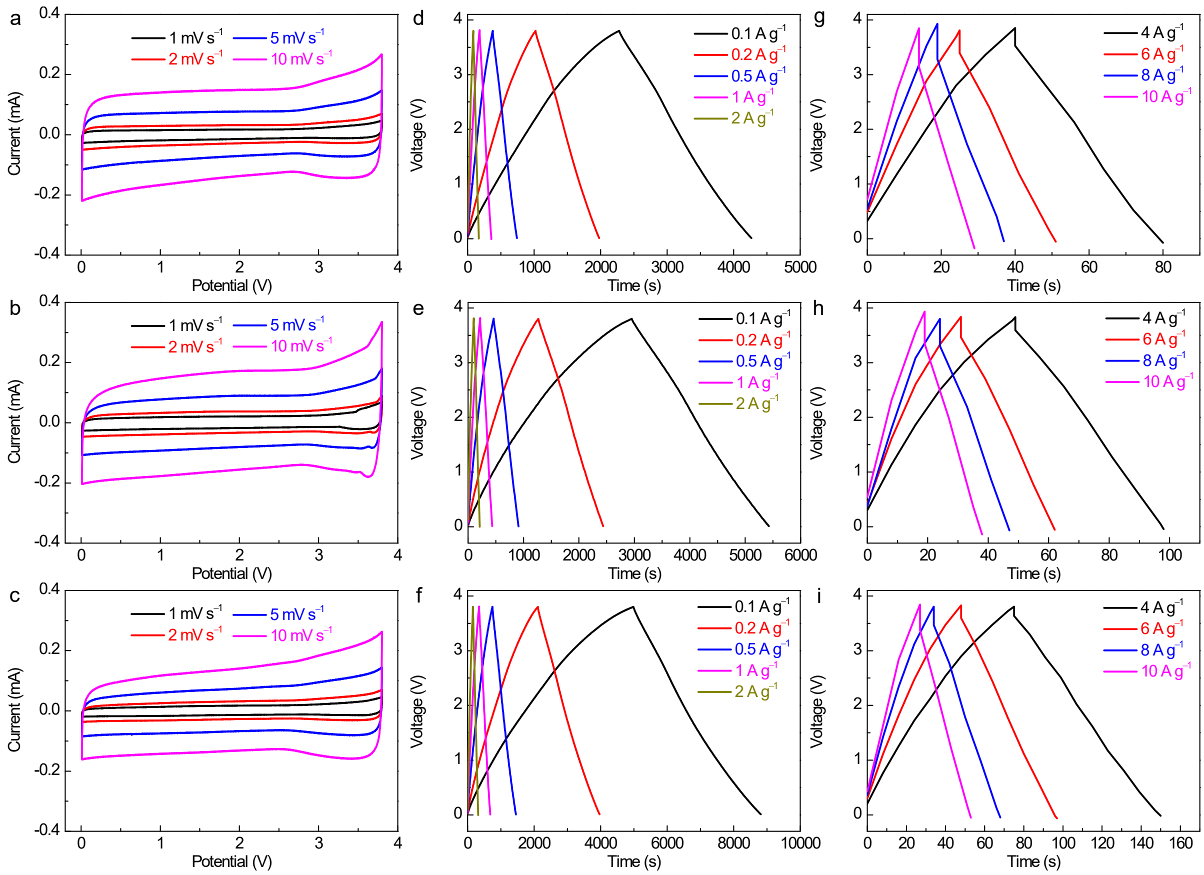

Figure S18. CV curves of the HSIH-CMs//HSIH-CMs SIC devices with different anode/cathode mass ratios: (a) 1:1, (b) 1:2, (c) 1:4. Galvanostatic charge-discharge curves of HSIH-CMs//HSIH-CMs SIC devices with different anode/cathode mass ratios of 1:1 (d, g), 1:2 (e, h), and 1:4 (f, i) at various current densities ranging from 0.1 to 10 A g^{-1}.

Table S1. Comparison of the electrochemical performance of our HSIH-CMs anode with recent reported carbon-based anodes for sodium-ion batteries/capacitors.

Materials	Initial Coulombic efficiency	Cycling stability (A/B/n)	Rate capability (C/D)	Ref.
3D MmCF	89.3%	256/1/1000	190/5	This work
		167/5/10000	158/10	
Commercially available hard carbon	78%	225/0.025/100	/	*Adv. Funct. Mater*. **2011**, *21*, 3859.
NSHC	~77%	289/0.02 /100	95/0.5	*Electrochim. Acta*, **2015**, *161*, 23.
Apple biowaste derived hard carbon	61%	85/1/1000	112/2	*ChemElectroChem*, **2016**, *3*, 292.
RSS	~80%	143/0.1/200	32/5	*J. Alloys Compd*. **2017**, *695*, 632.
NDC	50%	305/ 0.1 /150	157/1.0	*Energy Fuels*, **2017**, *1*, 1090.
Argan-X	83.9%	282/0.025/70	/	*J. Mater. Chem. A* **2017**, *5*, 9917.
FP-MP 5:2 1000	80%	191/0.15/100	282/0.03	*Adv. Funct. Mater.* **2019**, *29*, 1901072.
MSC	45%	103/0.5/3000	62/5	*J. Mater. Chem. A* **2016**, *4*, 6472.
EG	~49.53%	150 /0.1/2000	91/0.2	*Nat. Commun*. **2014**, *5*, 4033.
Natural graphite	~52%	127/0.1/300	~78/10	*Adv. Funct. Mater*. **2015**, *25*, 534.
GICs	~93%	110/0.2/6000	102/10	*J. Power Sources* **2015**, *293*, 626.
Graphite	90%	110/0.0327/100	~112/0.22	*Adv. Energy Mater*. **2018**, *8*, 1702724.
Few-layered graphene	~58%	~115/12/8000	125/10	*Nano Lett.* **2015**, *16*, 543.
NS-GNS	50.86%	260/1/10000	141/5	*Energy Storage Mater.* **2018**, *13*, 134.
S-SG	55.6%	~250/2/1000	217/3.2	*Adv. Sci.* **2018**, *5*, 1700880.
BPPG	67.8%	298/0.1/300	70/5	*ACS Nano* **2014**, *8*, 7115.
Wood fibre derived carbon	72%	196/0.1/200	/	*ACS Appl. Mater. Interfaces*, **2015**, *7*,

				23291.
HCC	86%	275/ 0.06/100	211/0.6	*J. Mater. Chem. A* **2016**, *4*, 13046.
HTPC-H	60%	253/0.02/1000	103/0.2	*Sci. Rep.* **2016**, *6*, 26246.
ANPGs	34.9%	155/0.05/200	~45/5	*ChemSusChem*, **2013**, *6*, 56.
G@HPC	41.8%	134.2/0.2/200	100/5	*Adv. Energy Mater.* **2014**, *4*, 1301584.
N–GF	42.6%	594.0/0.5/150	137.7/5	*Adv. Mater*. **2015**, *27*, 2042.
ACFs	46%	243/0.05/100	101/5	*Nanoscale* **2014**, *6*, 1384.
DC-S	63.2%	271/1/1000	211/2	*Energy Environ. Sci.* **2015**, *8*, 2916.
Expanded 3D graphene	74%	425/ 0.1/100	148/10	*Adv. Energy Mater.* **2018**, *8*, 1800353.
N-HC	79.5%	255.9/0.5/3000	150/2	*Nano Energy* **2019**, *56*, 828.
N-FLG	83.5%	210/0.5/2000	113.8/10 56.6/40	*Adv. Mater*. **2019**, *31*, 1901261.
NACF	48.01%	105/1/8000	126/1	*Nano Energy* **2018**, *45*, 220.
pTTPN	69.5%	74/10/2000	95/5	*J. Mater. Chem. A,* **2019**, *7*, 6363.
N-GCNs	/	174/0.1/200	63/5	*Adv. Funct. Mater.* **2018**, *28*, 1706294.
NPGA	~43%	195/1/1000 132/5/2000	218/1 189/3	*Carbon* **2018**, *139*, 1117.
NSC	47.7%	260/0.5/1000	172/10	*Energy Storage Mater.* **2018**, *11*, 274.
CNTs@N,O-CNFs	25.4%	225.8/0.05/300	98.2/2	*RSC Adv.* **2020**, *10*, 7780.
PNCs-C600	27.2%	161/1/5000	136.3/10	*Chem. Eng. J.* **2021**, *415*, 129012.
NHC-5	57.45%	~120/2/1000	280/0.5	*Chem. Eng. J.* ***2021**, 420, 129647.*
NS-GHNS	36%	~150/5/10000	112/20	*Energy Storage Mater.* **2020**, *25*, 702.
PCNS	29%	180/7/10000	105/10	*J. Power Sources* **2020**, *475*, 228679.

[a]A/B/n means the capacity (A, mA h g^{-1}) remained after n cycles at a certain current density (B, A g^{-1}).

[b]C/D means the capacity (C, mA h g^{-1}) remained at a certain current density (D, A g^{-1}).

Table S2. Comparison of the electrochemical performance of our HSIH-CMs cathode with recent reported carbon-based cathodes for sodium-ion capacitors.

Materials	Reversible specific capacity (A/B)	Cycling stability (C/D/n)	Rate capability (E/F)	Ref.
3D MmCF	119/0.1	100/5/10000	91/10	This work
ZDPC	151.7/0.1	~87/1/2000	96.1/10	*Adv. Funct. Mater*. **2018,** *28*, 1800757.
NPHC	~250/1	100/2 /1000	68/5	*Adv. Energy Mater.* **2018**, *8*, 1800140.
3DFAC	71.3/1	55/5/2000	59/5	*Adv. Energy Mater.* **2018**, *8*, 1702409.
OCG	105/0.1	~91/1/3000	32/5	*Energy Storage Mater.* **2018**, *11*, 8.
NS-GHNS	~52/0.2	~32/ 5 /150	19/20	*Energy Storage Mater.* **2020**, *25*, 702.
GDPC	152/0.05	~55/5/10000	~67/10	*J. Mater. Chem. A* **2017**, *5*, 9917.
STC-16	70/0.1	/	/	*Adv. Funct. Mater*. **2019,** *29*, 1902858.
PSNC	72/0.1	/	40/12.8	*Nano Energy* **2016**, *23*, 129.
GNS	~50/0.25	~36/1/1500	~32/5	*Adv. Energy Mater.* **2017**, *7*, 1602654.
CS-800-6	67.5/0.1	~45/2/2000	40.7/5	*J. Power Sources* **2018**, *379*, 33.
NHPAC	110/0.1	/	30/2	*J. Mater. Chem. A* **2019**, *7*, 13540.
N-OMC	105.6/0.5	~90/1/6500	58.8/10	*J. Mater. Chem. A,* **2021**, *9*, 3360.
OPDN-CTF-A	127/0.1	~38.25/10/10000	45/10	*J. Energy Chem.* **2021***, 55*, 304.
A-CNFs-4	82.5/0.05	67/0.5/1000	66/2	*RSC Adv.* **2020**, *10*, 7780.

[a]A/B means the reversible capacity (A, mA h g^{-1}) obtained at a certain current density (B, A g^{-1}).

[b]C/D/n means the capacity (C, mA h g^{-1}) remained after n cycles at a certain current density (D, A g^{-1}).

[c]E/F means the capacity (E, mA h g^{-1}) remained at a certain current density (F, A g^{-1}).

Table S3. Comparison of the electrochemical performance of our optimal HSIH-CMs//HSIH−CMs device with other previously reported sodium−ion capacitors.

System	Voltage range (V)	Energy density (Wh kg^{-1})	Power density (kW kg^{-1})	Cycling life (A/n/B)	Ref.
3D MmCF//3D MmCF	0.01−3.8	224	0.18	91%/10000/2	This work
		128	17.16		
PSC//NTO@CNT	0−3	58.5	0.3	75%/4000/0.4	*J. Mater. Chem. A,* **2015**, *3*, 21277.
		71.6	3		
Na_2Ti_3O7//rGO film	1−3	55	0.2	80%/2500/0.5	*Adv. Funct. Mater.* **2016**, *26*, 3703.
		21.7	3		
Nb_2O_5 nanosheets//PSC	1−3	43.2	0.16	80%/3000/1.3	*Chem. Mater.* **2016**, 28, 5753.
		24	5.76		
$Na_2Ti_3O_7$//AC	0.5−3.5	111.2	0.8	86%/3000/3.2	*Nano Lett.* **2016**, *16*, 5938.
		33.2	11.2		
$Na_2Ti_2O_4(OH)_2$//porous carbon	1−4	65	0.5	93%/3000/1	*J. Power Sources* **2017**, *353*, 85.
		21	5		
Sb_2O_3//carbon fibers	1.5−4.3	117	0.58	90%/3500/1	*J. Mater. Chem. A* **2017**, *5*, 9169.
		65	5.8		
TiO_2/C//ZDPC	1−4	142.7	0.25	90%/10000/1	*Adv. Funct. Mater.* **2018**, *28*, 1800757.
		61.8	25		
$MoSe_2$/G//AC	0.5−3	82	0.063	81%/5000/5	*Nano Energy* **2018**, *47*, 224.
		43	6.688		
Gr-Nb_2O_5//AC	1−4.3	112.9	0.08	97%/1500/1	*Adv. Mater.* **2018**, *30*, 1800963.
		62.2	5.33		
3D-IO-FeS-QDs@NC//AC	0.5−3.4	151.8	0.145	91%/5000/1	*J. Mater. Chem. A* **2019**, *7*, 1138.
		72.2	9.28		
3DFC//3DFAC	0−4	111	0.2	75.6/15000/2	*Adv. Energy Mater.* **2018**, *8*, 1702409.
		67	20		
OCG// OCG	0.5−3.5	121.3	0.3	87%/2500/0.5	*Energy Storage Mater.* **2018**, *11*, 8.
		51.2	8		
Q-LT//rGO/AC	1.5−4.5	124	0.3	88%/5000/5	*Nano Energy* **2019**, *59*, 17.
		33	6		
$Na_3V_2O_2(PO_4)_2F$@PEDOT//AC	1−4.2	158	0.23	85%/1000/1	*J. Mater. Chem. A* **2019**, *7*, 1030.
		25	7		
$V_2O_5 \cdot nH_2O$//MCMB	0.1−4	96	0.059	95%/800/1	*Small* **2019**, *15*, 1900379.
		37.5	14		
HAT-CNF-850//STC-16	0.5−4	95	0.19	90%/1000/1	*Adv. Funct. Mater.*

		18	13		**2019**, *29*, 1902858.
OMC//N-OMC	0–4	107	0.145	73%/1800/1	*J. Mater. Chem. A,* **2021**, *9*, 3360.
3D-CoO-NrGO//AC	1–4	153	0.041	81%/5000/1	*ACS Appl. Mater. Interfaces* **2021**, *13*, 27999.
		31	6.357		
FeVO UNSs// NVOPF/rGO	0–3.3	126	0.091	68%/9000/1.2	*Nanomicro Lett.* **2021**, *13*, 1.
		20	5.2		
TiO_2-800s@PBC//AC	1–4	91	0.165	71%/5000/2	*J. Power Sources* **2021**, *493*, 229678.
		43.4	13		
V_2O_3@MCNFs//AC	1–4	96	0.25	80.9/10000/1	*ACS Appl. Mater. Interfaces* **2021**, *13*, 10001.
		76.8	7.68		

[a]A/n/B means the capacity retention percentage (A) after n cycles at a certain current density (B, A g^{-1}).

Table S4. The XPS spectra analysis result of HSIH-CMs at different temperature.

Sample	at.% of O	at.% of C=O	at.% of C–O
HSIH-CMs-800	5.77	1.71	4.06
HSIH-CMs-1000	4.44	1.73	2.71
HSIH-CMs-1200	3.14	2.14	1.00
HSIH-CMs-1400	3.02	2.12	0.90

Table S5. The electrochemical performance of HSIH-CMs samples

Sample	ICE (%)	Charge capacity of 1^{st} (mAh g^{-1})	Discharge capacity of 1^{st} (mAh g^{-1})
HSIH-CMs-800	59.46	250.14	420.66
HSIH-CMs-1000	69.88	275.77	394.65
HSIH-CMs-1200	89.30	326.29	365.37
HSIH-CMs-1400	72.77	277.30	381.06