Electronic Supplementary Information for

Capacitance-enhanced sodium-ion storage in nitrogen-rich hard carbon

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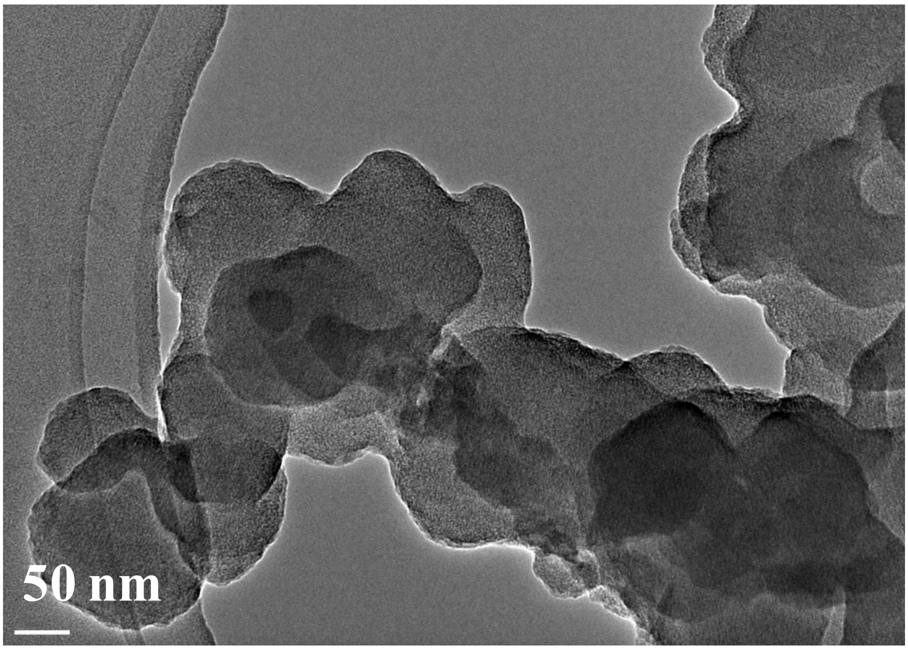

Figure S1. Transmission electron microscope image of HCS.

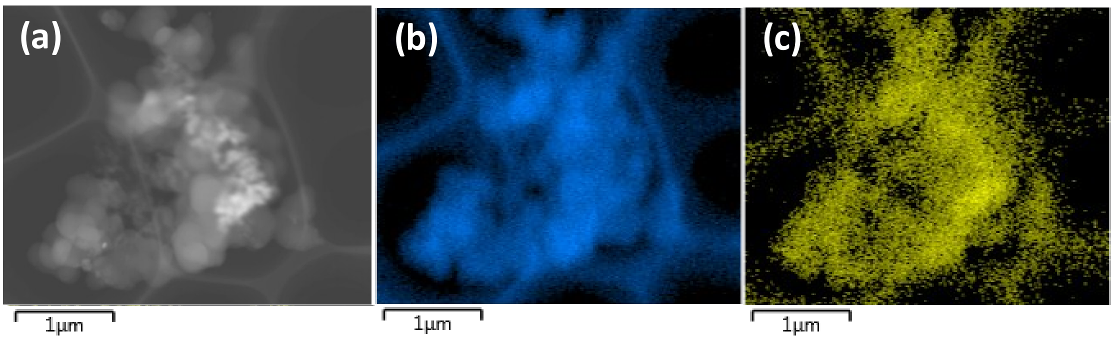

Figure S2. Energy dispersive X-ray mapping of HCS: (a) electron image, (b) carbon, and (c) oxygen.

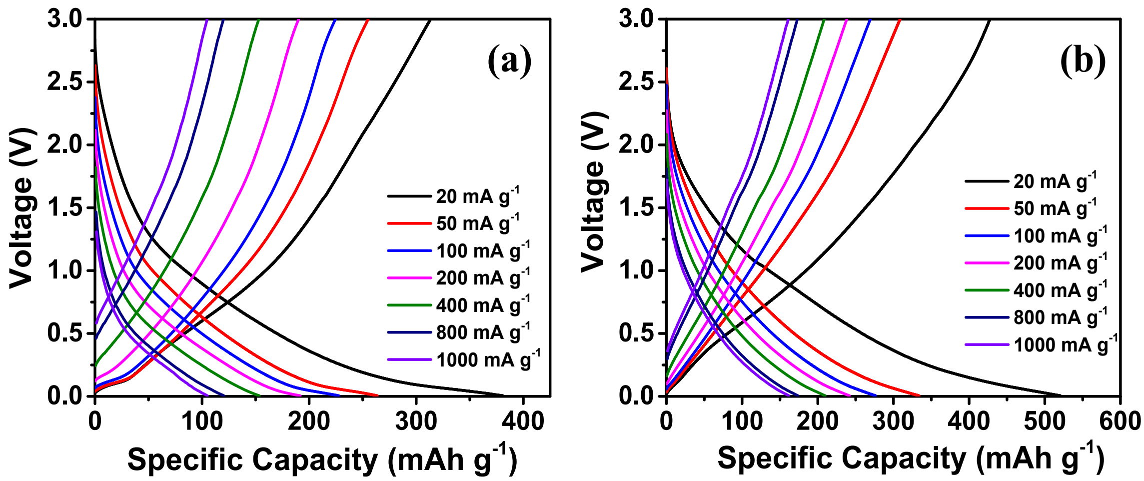

Figure S3. Charge-discharge curves at different rates for (a) HCS and (b) *N*-HCS tested against sodium.

Table S1. Physical and chemical properties of HCS and *N*-HCS

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Elemental composition (at. %)	d-spacing	I_D/I_G ratio
HCS	82	0.04	C (69.81), O (30.19)	0.37 nm	0.75
N-HCS	16	0.03	C (72.77), N (9.06), O (18.17)	0.39 nm	0.86

Table S2. Kinetic parameters obtained from equivalent circuit fittings of the experimental data for samples HCS and *N*-HCS before and after 5 cycles.

Sample	R_{el} (Ω)	R_{ct} (Ω)
HCS (before cycling)	14.46	100.5
HCS (after 5 cycles)	10.04	131.3
N-HCS (before cycling)	12.30	20.78
N-HCS (after 5 cycles)	13.40	27.96

Table S3. A comparison of the N-rich carbon with those reported in the literature for sodium-ion batteries

Material	Synthesis method	Potential Range (V)	Electrolyte*	Capacity (mA h g^{-1})	Cycling stability	Rate capability	Remarks	Theoretical studies performed	Ref.
N-HCS	Hydrothermal synthesis followed by pyrolysis	0.005 – 3	$NaClO_4$ in EC, PC and FEC	520 at 20 mA g^{-1}	~204 mAhg^{-1} obtained after 1000 cycles at 1 A g^{-1}	333 mA h g^{-1} at 0.05 A g^{-1} 277 mA h g^{-1} at 1 A g^{-1}	Highly stable cycling performance.	Yes	This work
Nitrogen rich porous carbon	Pyrolysis in Ar atmosphere	0.01 - 3	$NaPF_6$ in EC and DC	335 at 100 mA g^{-1}	~130 mA h g^{-1} at 5 A g^{-1} after 1000 cycles was obtained.	256 mA h g^{-1} at 0.2 A g^{-1} 213 mA h g^{-1} at 1 A g^{-1}	A sloping profile was observable during charge-discharge	No	[1]
Nitrogen-rich bamboo-like carbon	Pyrolysis in Ar atmosphere	0.01 - 3	$NaClO_4$ in EC and DC	270 at 50 mA g^{-1}	Lower than 120 mA h g^{-1} at 0.5 A g^{-1} after 160 cycles was obtained.	167 mA h g^{-1} at 0.1 A g^{-1} 138 mA h g^{-1} at 0.2 A g^{-1}	Hollow structure and nitrogen content was credited to the performance	No	[2]
Nitrogen-doped carbon/graphene hybrid	Pyrolysis in N_2 atmosphere between 700-800 °C	0.01 - 3	$NaClO_4$ in EC and DC	303 at 50 mA g^{-1}	~270 mA h g^{-1} at 50 mA g^{-1} after 200 cycles was obtained.	207 mA h g^{-1} at 1 A g^{-1} 177 mA h g^{-1} at 2 A g^{-1}	Large interlayer spacing and high content of nitrogen provide good performance	No	[3]
Nitrogen-rich	Pyrolysis in N_2	0.01 - 3	$NaClO_4$ in	338 at 30	~252 mA h g-	86 mA h g^{-1}	Amorphous	No	[4]

mesoporous carbon	atmosphere at 700 °C		EC and DC	mA g^{-1}	^{1} at 50 mA g^{-1} after 100 cycles was obtained.	at 1 A g^{-1} 48.9 mA h g^{-1} at 2 A g^{-1}	crystallites with a porous structure and large interlayer spacing provide good stability.		
N-doped porous carbon	KOH activation followed by Pyrolysis in N_2 atmosphere	0.01 – 2.5	NaTFSI in EC and DC	274 at 25 mA g^{-1}	Good cycling stability for 100 cycles was observed with 88% capacity retention	58 mA h g^{-1} at 2 A g^{-1} 37 mA h g^{-1} at 4 A g^{-1}	Carbons derived from garlic peel waste.	No	[5]
Nitrogen doped holey carbon nano-sheets	KOH activation followed by Pyrolysis in N_2 atmosphere	0.01 - 3	$NaPF_6$ in EC and DMC	323 at 100 mA g^{-1}	~80 mA h g^{-1} at 1 A g^{-1} after 400 cycles was obtained.	194 mA h g^{-1} at 0.2 A g^{-1} 139 mA h g^{-1} at 0.5 A g^{-1}	Unique porous structure and nitrogen doping endow superior electrochemical performance	No	[6]
Nitrogen-doped carbon nanofiber films	Heating in vacuum followed by carbonising in Ar atmosphere	0.01 - 3	$NaClO_4$ in EC, DC and FEC	377 at 100 mA g^{-1}	~210 mA h g^{-1} at 5 A g^{-1} after 7000 cycles was obtained.	315 mA h g^{-1} at 0.5 A g^{-1} 154 mA h g^{-1} at 15 A g^{-1}	A free standing electrode	No	[7]
Nitrogen-doped carbon	Pyrolysis in N_2 atmosphere at	0.01 - 2	$NaPF_6$ in EC, DC and	150 at 200 mA	~134 mA h g^{-1} at 0.2 A g^{-1}	139 mA h g^{-1} at 0.5 A g^{-1}	Material prepared from polypyrrole	No	[8]

nanofibers	600 °C		PC	g^{-1}	after 200 cycles was obtained.	132 mA h g^{-1} at 1 A g^{-1}	nanofiber		
Nitrogen-doped carbon microspheres	Hydrothermal synthesis followed by thermal treatment	0.005 – 3	$NaClO_4$ in EC and PC	336 at 50 mA g^{-1}	~104 mA h g^{-1} at 10 A g^{-1} after 12500 cycles was obtained.	148 mA h g^{-1} at 5 A g^{-1} 132 mA h g^{-1} at 1 A g^{-1}	Highly stable cycling performance	No	[9]
Nitrogen-doped carbon sheets	Hydrothermal treatment followed by pyrolysis	0.01 – 2	$NaClO_4$ in EC, DMC and FEC	315 at 0.15 C	~247 mA h g^{-1} at 0.3 C after 50 cycles was obtained.	ca.100 mA h g^{-1} at 3 C 32.3 mA h g^{-1} at 30 C	High capacity and long cycle life batteries obtained	No	[10]

*PC = propylene carbonate, FEC = fluoroethylene carbonate, DMC = dimethyl carbonate, EC = ethylene carbonate, DC = diethyl carbonate.

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