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Supporting Information

Pore-Size Tuning of Hard Carbon to Optimize its Wettability for Efficient Na^+ Storage

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Supporting Information includes:

1. Supplementary Discussion

2. Supplementary Figures S1 to S10

3. Supplementary Tables S1 to S3

4. Supplementary Movies: Movies S1 to S2

5. Supplementary References

1. Supplementary Discussion

By adding TEOS with various mass ratios during polymerization, N-doped HMCNTs with smaller pore sizes (HMCNTs-2.3, 4.2, 5.1 and 6.1) were prepared. TPOS, which undergoes slower hydrolysis and condensation than TEOS, provides better control over silica core and primary particle formation. Specifically, the steric effect of TPOS leads to a slow hydrolysis process, which resulted in the open mesochannels, while the fast hydrolysis kinetics of TEOS leads to smaller mesochannels. [1] To further increase the pore size, we can modify the water-to-ethanol ratio during the polymerization process. During the synthesis process, an increase in the proportion of water in the solvent leads to a more uneven dispersion of silica in the solution system, resulting in the larger silica particles encapsulated in the shells of nanotubes, thereby forming larger pores after etching (i.e. HMCNTs-7.6 and 7.7).

2. Supplementary Figures

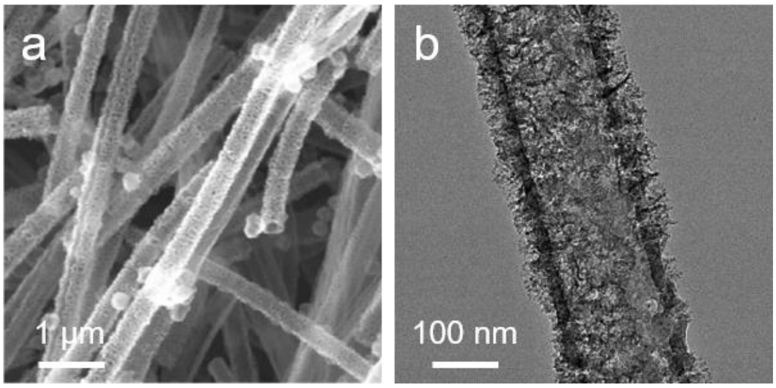

Figure S1 SEM and TEM images of HMCNTs-7.6.

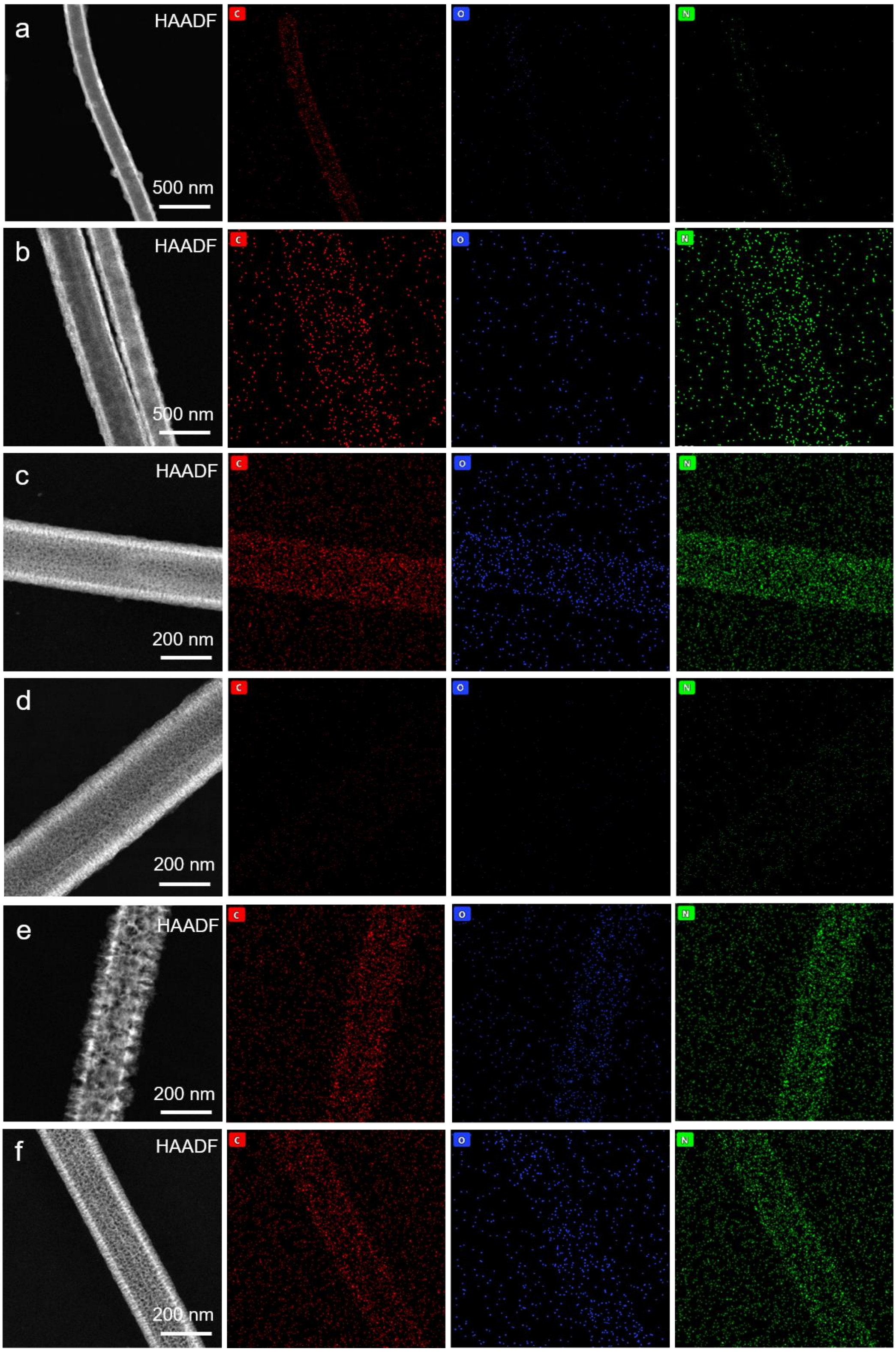

Figure S2 HADDF and EDS mapping images of hollow mesoporous carbon nanotubes. (a) HMCNTs-2.3; (b) HMCNTs-4.2; (c) HMCNTs-5.1; (d) HMCNTs-6.1; (e) HMCNTs-7.6; (f) HMCNTs-7.7.

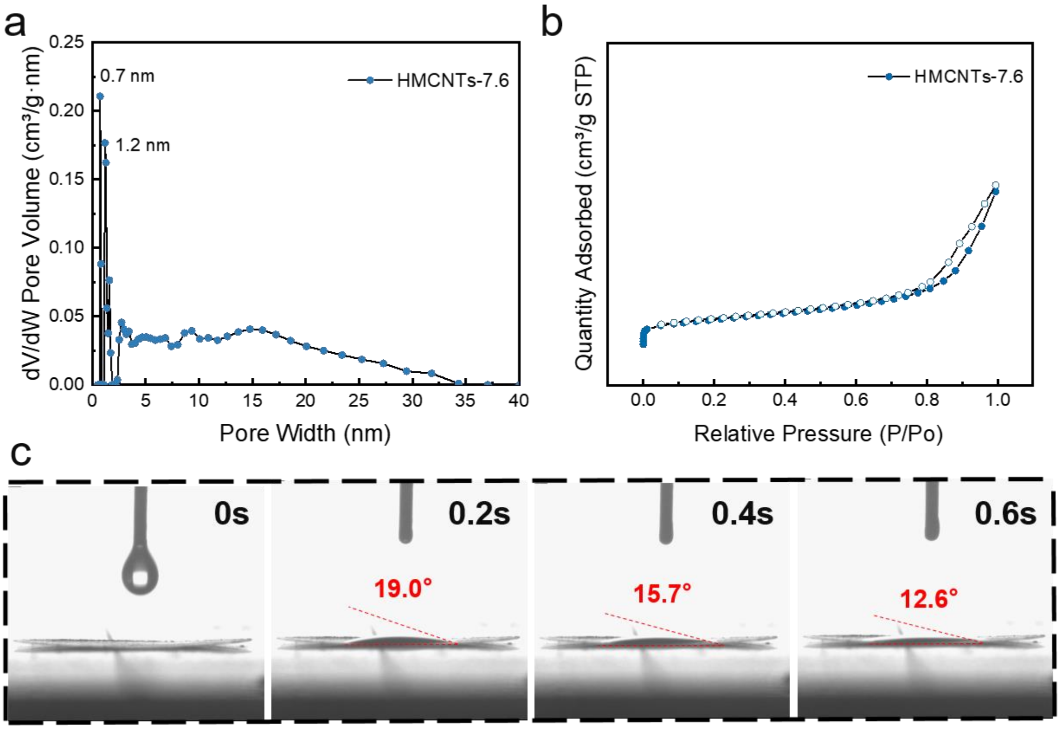

Figure S3 (a) Pore size distributions. (b) N_2 isothermal adsorption/desorption curves. (c) Dynamic contact angles between the electrolyte and HMNCTs-7.6 electrodes.

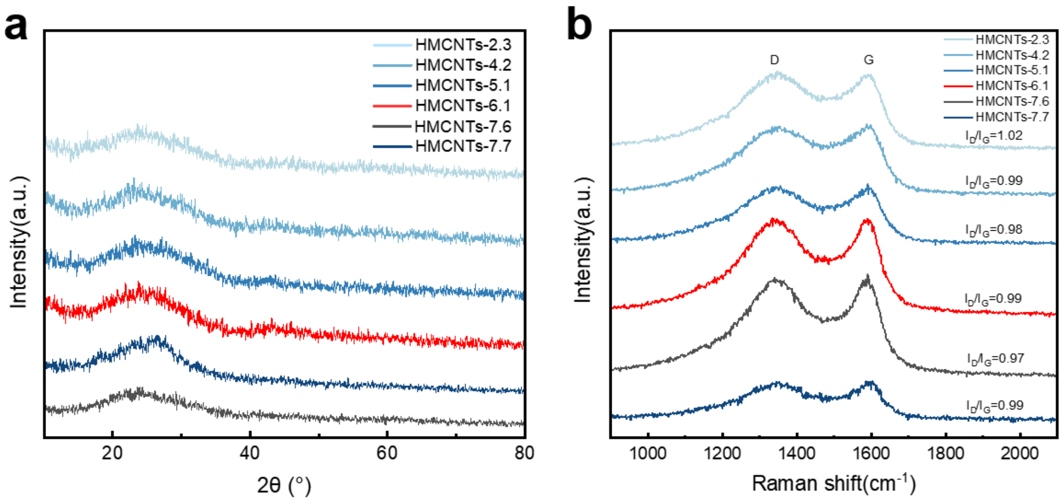

Figure S4 (a) XRD spectrum and (b) Raman spectrum of the series of HMCNTs.

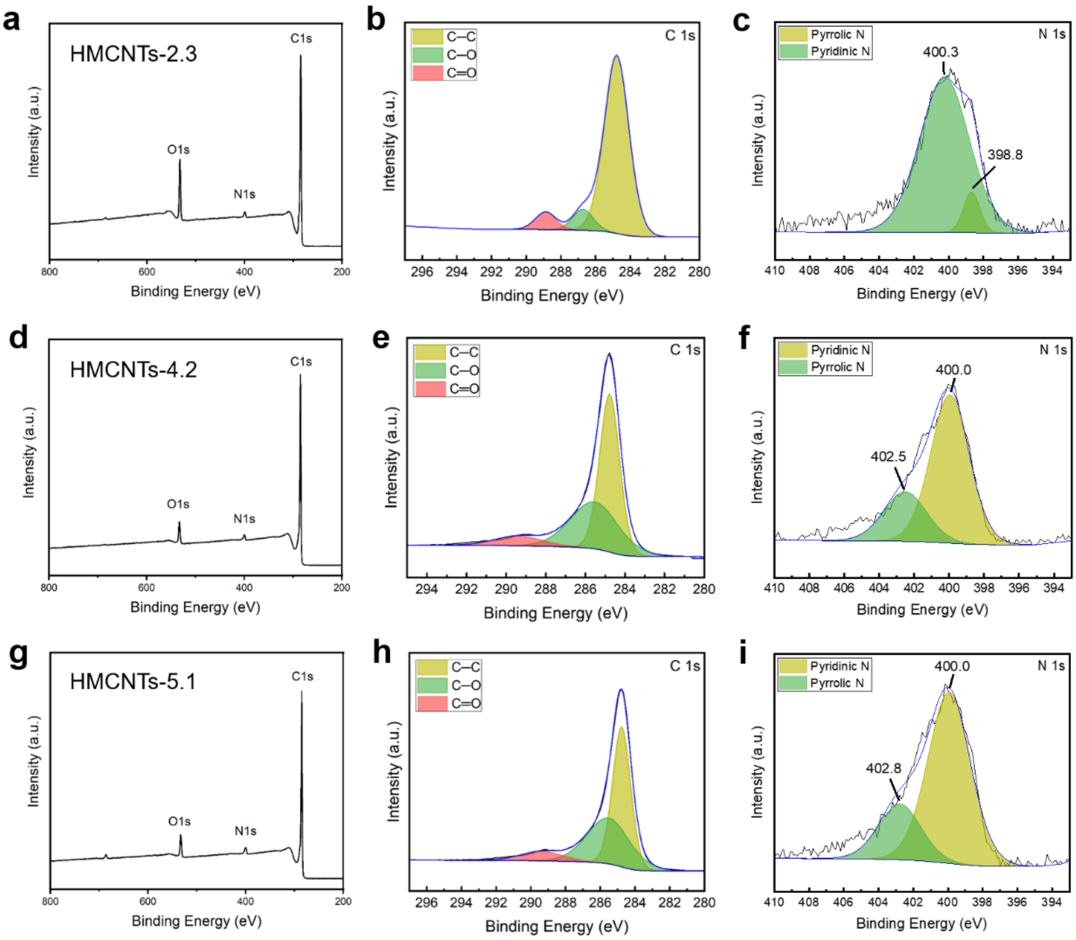

Figure S5 (a) XPS survey, (b) C 1s spectrum and (c) N 1s spectrum of HMCNTs-2.3. (d) XPS survey, (e) C 1s spectrum and (f) N 1s spectrum of HMCNTs-4.2. (g) XPS survey, (h) C 1s spectrum and (i) N 1s spectrum of HMCNTs-5.1.

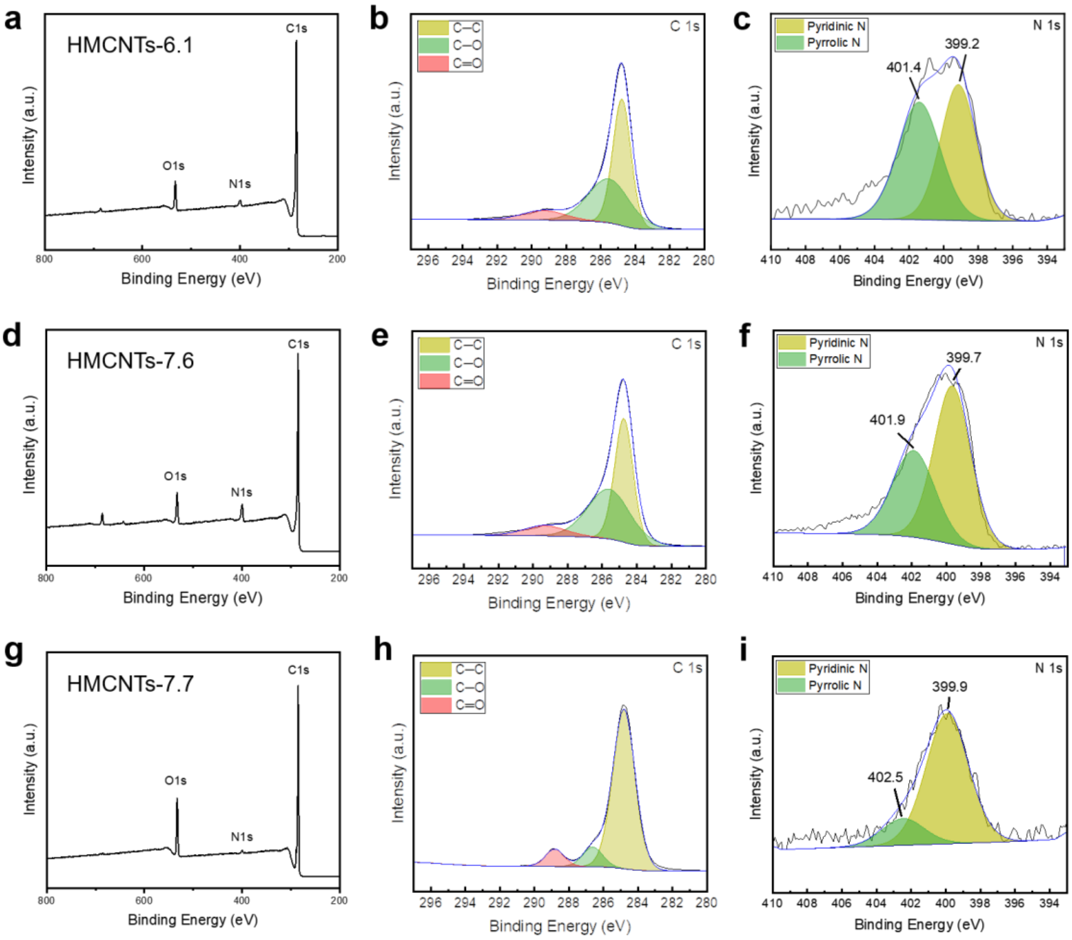

Figure S6 (a) XPS survey, (b) C 1s spectrum and (c) N 1s spectrum of HMCNTs-6.1. (d) XPS survey, (e) C 1s spectrum and (f) N 1s spectrum of HMCNTs-7.6. (g) XPS survey, (h) C 1s spectrum and (i) N 1s spectrum of HMCNTs-7.7.

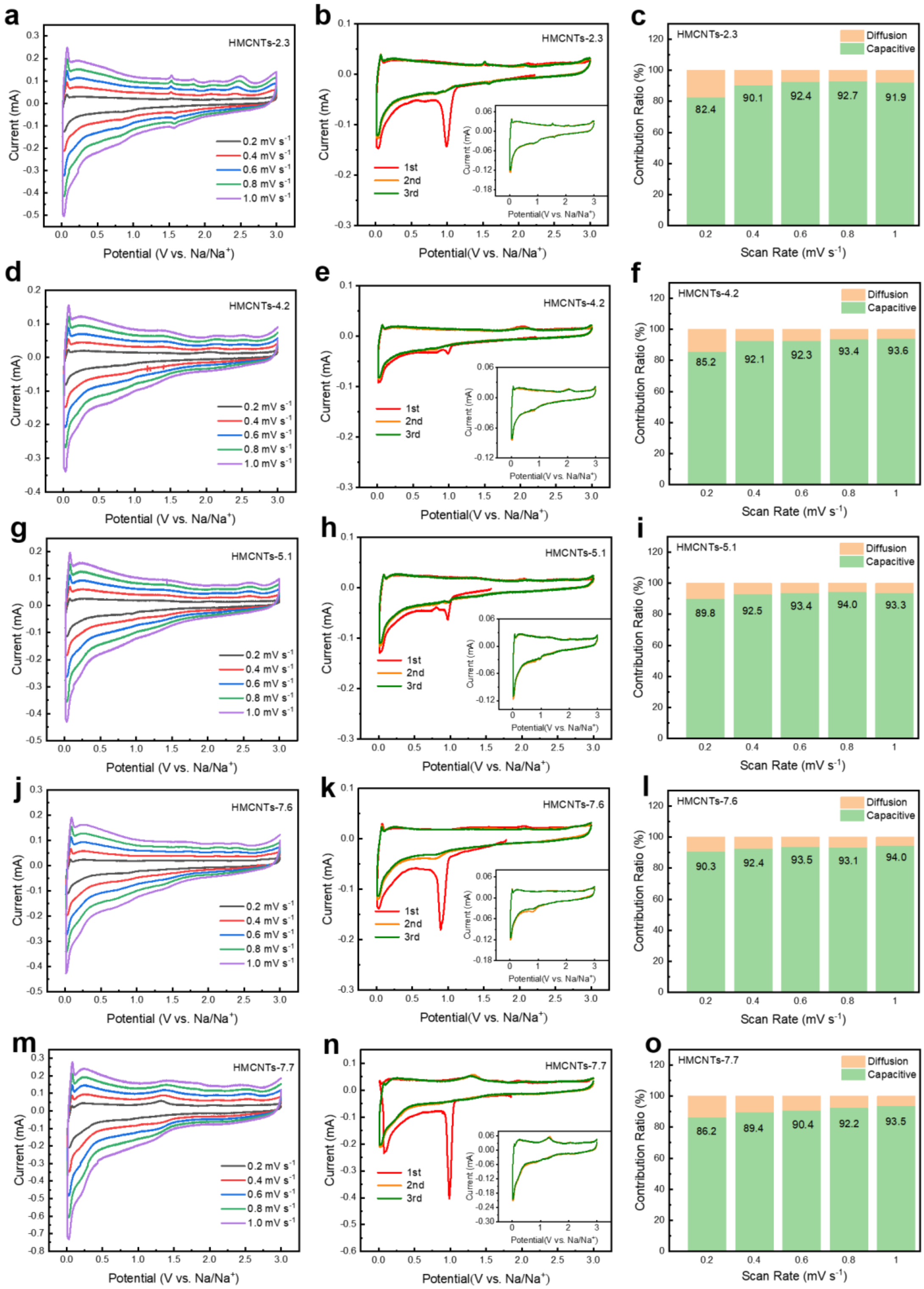

Figure S7 CV curves of HMCNs-2.3 at (a) different scan rates and (b) the first three cycles at 0.2 mV s^{-1}. (c) Capacitive contribution of HMCNs-2.3. CV curves of HMCNs-4.2 at (d) different scan rates and (e) 0.2 mV s^{-1}. (f) Capacitive contribution of HMCNs-4.2. CV curves of HMCNs-5.1 at (g) different scan rates and (h) 0.2 mV s^{-1}. (i) Capacitive contribution of HMCNs-5.1. CV curves of HMCNs-7.6 at (j) different scan rates and (k) 0.2 mV s^{-1}. (l) Capacitive contribution of HMCNs-7.6. CV curves of HMCNs-7.7 at (m) different scan rates and (n) 0.2 mV s^{-1}. (o) capacitive contribution of HMCNs-7.7.

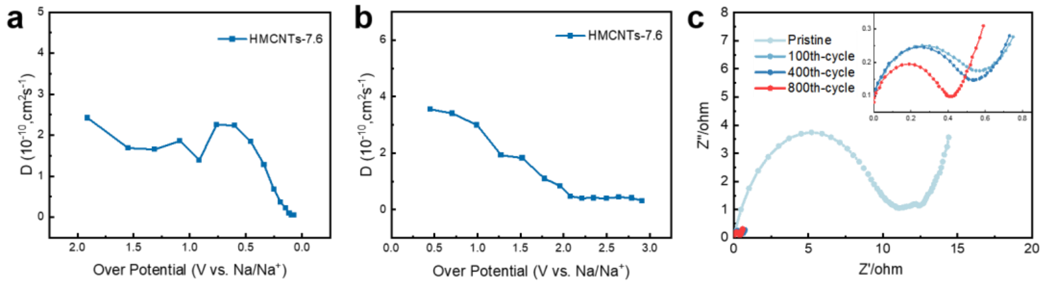

Figure S8 D_{Na+} of HMCNTs-7.6 in the (a) charge and (b) discharge processes. (c) Nyquist fitting plots of HMCNTs-7.6.

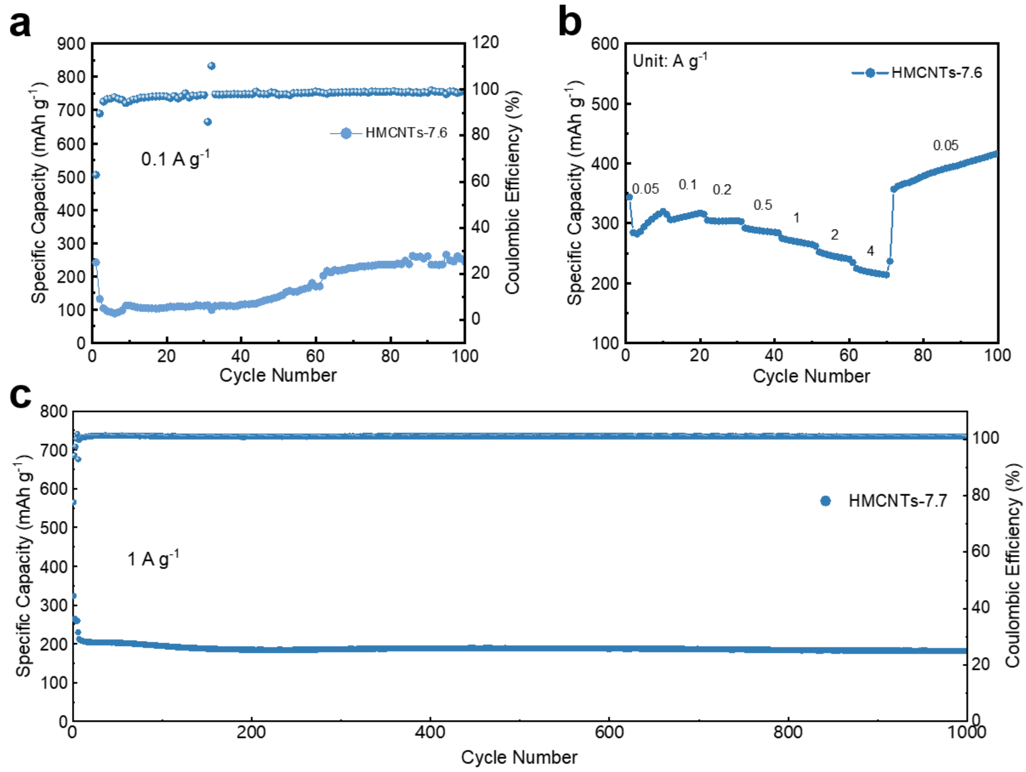

Figure S9 (a) Cycling performance at 0.1 A g^{-1} of HMCNTs-7.6. (b) Rate performance of HMCNTs-7.6. (c) Cycling performance at 1 A g^{-1} of HMCNTs-7.6.

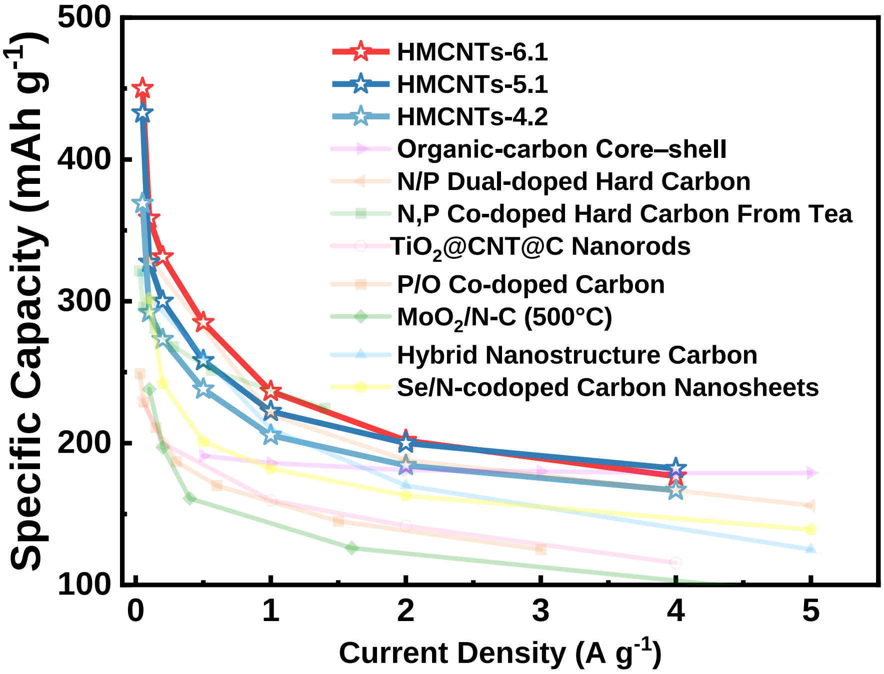

Figure S10 Performance comparison with the carbonaceous SIB anodes in recent reports.

3. Supplementary Tables

Table S1 BET test results of all the HMCNTs samples

Material	Specific Surface Area (m^2 g^{-1})	Pore Volume (cm^3 g^{-1})
HMCNTs-2.3	710.6876	0.409852
HMCNTs-4.2	924.8423	0.961903
HMCNTs-5.1	683.2594	0.873429
HMCNTs-6.1	1303.7746	2.002073
HMCNTs-7.6	504.5282	0.955496
HMCNTs-7.7	827.1601	1.592770

Table S2 Element content ratios of all the the HMCNTs samples

Material	Element Content (at.%)		
	C	N	O
HMCNTs-2.3	85.21	2.50	12.29
HMCNTs-4.2	90.94	3.05	6.01
HMCNTs-5.1	90.22	3.64	6.14
HMCNTs-6.1	90.48	2.95	6.57
HMCNTs-7.6	84.73	1.74	13.53
HMCNTs-7.7	86.09	7.01	6.90

Table S3 Electrical performance comparison among different carbonaceous anodes for SIBs

Material	Initial CE	Rate Performance	Cycling performance	Ref.
AHC1100	/	200 mA h g^{-1} at 0.025 A g^{-1} 175 mA h g^{-1} at 0.05A g^{-1} 160 mA h g^{-1} at 0.1 A g^{-1} 140 mA h g^{-1} at 0.2 A g^{-1}	200 mA h g^{-1} at 0.025A g^{-1} after 20 cycles	[2]
PTCDI-DAQ@C	nearly 100 %	186 mA h g^{-1} at 1A g^{-1} 181 mA h g^{-1} at 2 A g^{-1} 180 mA h g^{-1} at 3 A g^{-1} 179 mA h g^{-1} at 4 A g^{-1} 179 mA h g^{-1} at 5 A g^{-1} 164 mA h g^{-1} at 10 A g^{-1}	173 mA h g^{-1} at 0.1 A g^{-1} after 2500 cycles 131 mA h g^{-1} at 3 A g^{-1} after 1000 cycles	[3]
CFAC/NIB-600	27%	156.3 mA h g^{-1} at 0.1A g^{-1} 30.1 mA h g^{-1} at 4 A g^{-1}	142.6 mA h g^{-1} at 0.1 A g^{-1} after 200 cycles	[4]
NPDC	/	330 mA h g^{-1} at 0.1A g^{-1} 220 mA h g^{-1} at 1 A g^{-1} 188 mA h g^{-1} at 2 A g^{-1} 156 mA h g^{-1} at 5 A g^{-1}	280 mA h g^{-1} at 2.0 A g^{-1} after 2000 cycles 122 mA h g^{-1} at 5.0 A g^{-1} for 28000 cycles	[5]
Tea-1100-NP	90%	321.6 mA h g^{-1} at 0.028 A g^{-1} 295.8 mA h g^{-1} at 0.056 A g^{-1} 281.0 mA h g^{-1} at 0.14 A g^{-1} 268.0 mA h g^{-1} at 0.28 A g^{-1} 251.5 mA h g^{-1} at 0.56 A g^{-1} 224.5 mA h g^{-1} at 1.4 A g^{-1}	77.2 mA h g^{-1} at 5.0 A g^{-1} after 300 cycles	[6]
TiO_2@CNT@C	/	230 mA h g^{-1} at 0.05 A g^{-1} 200 mA h g^{-1} at 0.2 A g^{-1} 159.6 mA h g^{-1} at 1 A g^{-1} 141.6 mA h g^{-1} at 2 A g^{-1} 115.5 mA h $g-^{-1}$ at 4 A g^{-1}	153 mA h g^{-1} at 1.0 A g^{-1} after 1000 cycles	[7]
HCNP-1150	/	275 mA h $g-^{1}$ at 0.025 A g^{1} 266 mA h g^{1} at 0.05 A g^{1} 236 mA h g^{1} at 0.125 A g^{1} 181 mA h g^{1} at 0.25A g^{1} 72 mA h g^{1} at 1.25 A g^{1} 45 mA h g^{1} at 2.5 A g^{1}	260 mA h g^{-1} at 0.05A g^{-1} after 200 cycles	[8]
PO-SC-S	80%	249 mA h g^{-1} at 0.03 A g^{-1} 229 mA h g^{-1} at 0.06 A g^{-1} 211 mA h g^{-1} at 0.15 A g^{-1} 187 mA h g^{-1} at 0.3 A g^{-1} 170 mA h g^{-1} at 0.6 A g^{-1} 145 mA h g^{-1} at 1.5 A g^{-1} 125 mA h g^{-1} at 3 A g^{-1}	/	[9]

MoO2/N-C (500°C)	/	238 mA h g^{-1} at 0.1 A g^{-1} 197 mA h g^{-1} at 0.2 A g^{-1} 161 mA h g^{-1} at 0.4 A g^{-1} 126 mA h g^{-1} at 1.6 A g^{-1} 80 mA h g^{-1} at 6.4 A g^{-1}	134 mA h g^{-1} at 0.8 A g^{-1} after 200 cycles 115 mA h g^{-1} at 5 A g^{-1} after 5000 cycles	[10]
N/Se-CNs	/	302 mA h g^{-1} at 0.1 A g^{-1} 242 mA h g^{-1} at 0.2 A g^{-1} 201 mA h g^{-1} at 0.5 A g^{-1} 182 mA h g^{-1} at 1 A g^{-1} 163 mA h g^{-1} at 2 A g^{-1} 139 mA h g^{-1} at 5 A g^{-1}	218 mA h g^{-1} at 0.1A g^{-1} after 100 cycles 115 mA h g^{-1} at 5 A g^{-1} after 2000 cycles	[11]
HNC600	/	320 mA h g^{-1} at 0.1 A g^{-1} 303 mA h g^{-1} at 0.2 A g^{-1} 261 mA h g^{-1} at 0.4 A g^{-1} 170 mA h g^{-1} at 1.6 A g^{-1} 125 mA h g^{-1} at 6.4 A g^{-1}	120 mA h g^{-1} at 1 A g^{-1} after 2000 cycles	[12]
HMCNTs-6.1	**75%**	**450.0 mA h g^{-1} at 0.05 A g^{-1}** **358.5 mA h g^{-1} at 0.1 A g^{-1}** **331.3 mA h g^{-1} at 0.2 A g^{-1}** **284.9 mA h g^{-1} at 0.5 A g^{-1}** **236.4 mA h g^{-1} at 1.0 A g^{-1}** **201.8 mA h g^{-1} at 2.0 A g^{-1}** **176.6 mA h g^{-1} at 4.0 A g^{-1}**	**200 mA h g^{-1} at 1.0 A g^{-1}** **after 1000 cycles**	**This Work**
HMCNTs-5.1	**88%**	**432.7 mA h g^{-1} at 0.05 A g^{-1}** **327.4 mA h g^{-1} at 0.1 A g^{-1}** **300.0 mA h g^{-1} at 0.2 A g^{-1}** **258.1 mA h g^{-1} at 0.5 A g^{-1}** **222.3 mA h g^{-1} at 1.0 A g^{-1}** **200.0 mA h g^{-1} at 2.0 A g^{-1}** **182.0 mA h g^{-1} at 4.0 A g^{-1}**	**198 mA h g^{-1} at 1.0 A g^{-1}** **after 1000 cycles**	**This Work**
HMCNTs-4.2	**65%**	**369.0 mA h g^{-1} at 0.05 A g^{-1}** **292.0 mA h g^{-1} at 0.1 A g^{-1}** **273.2 mA h g^{-1} at 0.2 A g^{-1}** **237.9 mA h g^{-1} at 0.5 A g^{-1}** **205.5 mA h g^{-1} at 1.0 A g^{-1}** **184.2 mA h g^{-1} at 2.0 A g^{-1}** **166.7 mA h g^{-1} at 4.0 A g^{-1}**	**155 mA h g^{-1} at 1.0 A g^{-1}** **after 1000 cycles**	**This Work**

4. Supplementary Movies

Movies S1

In-situ TEM observation of the sodiation behavior of a single HMCNT-2.3. (Displayed with 10× speed)

Movies S2

In-situ TEM observation of the sodiation and plating behavior of a single HMCNT-6.1. (Displayed with 20× speed)

5. Supplementary References

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