Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

CNTs Cocoon on Sodium Manganate Nanotubes Forming Core/branch cathode coupled with helical carbon nanofibres anode for enhanced sodium ion Batteries

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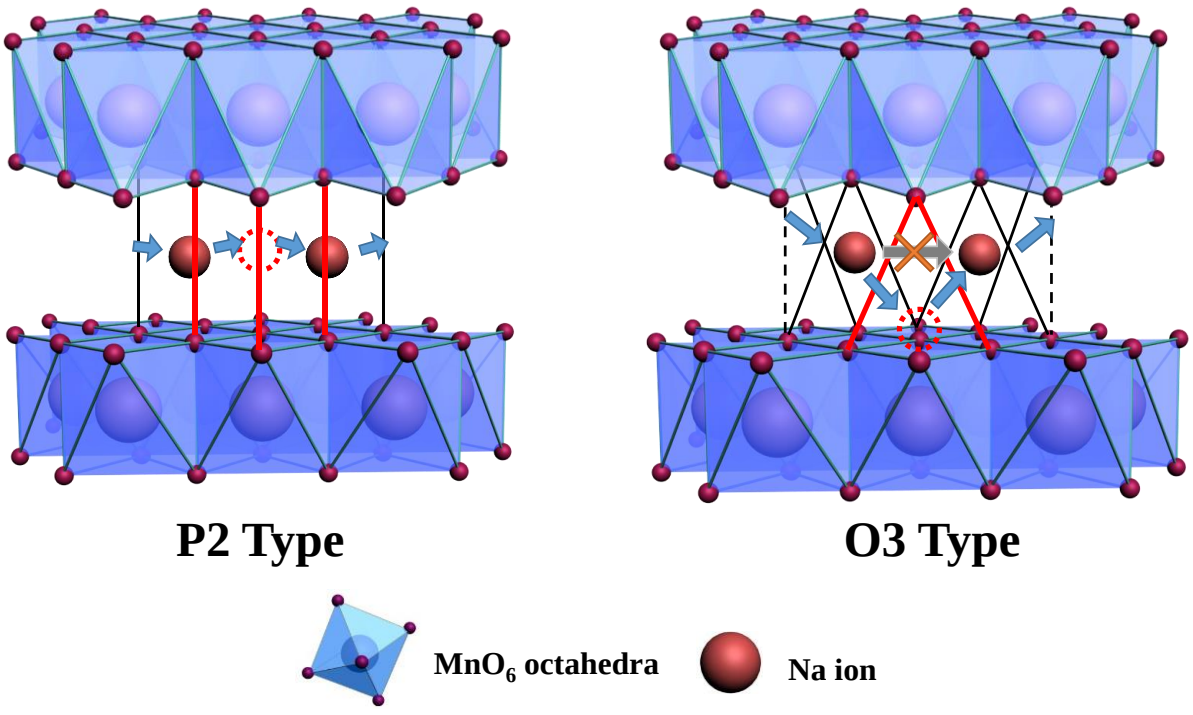

Figure S1. Schematic of the P2-type and O3-type layered sodium manganese oxides and the mobility path of sodium ions in the interlayers

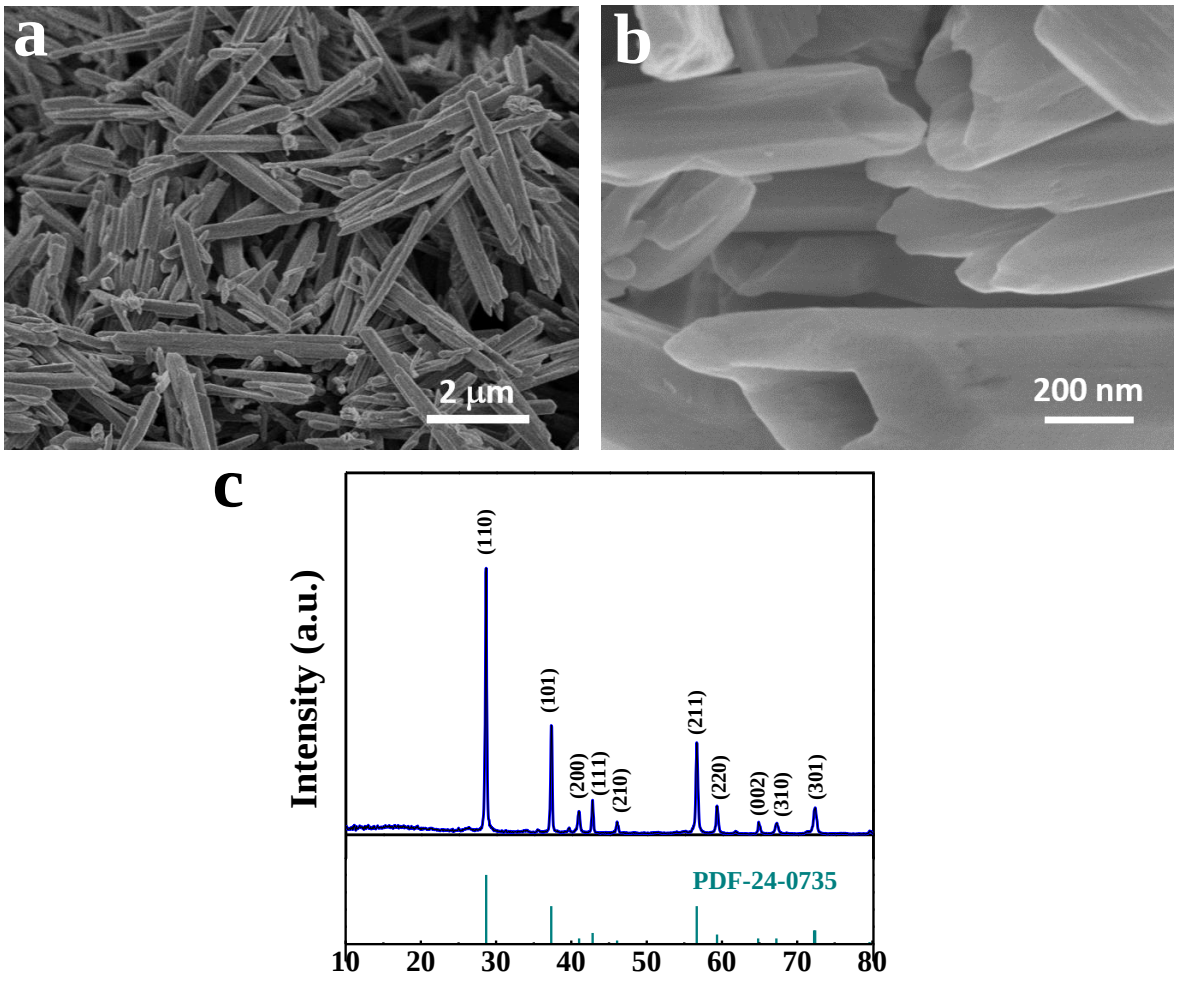

Figure S2. a,b) SEM images of as-prepared-MnO_2; c) XRD pattern of as-prepared β-MnO_2.

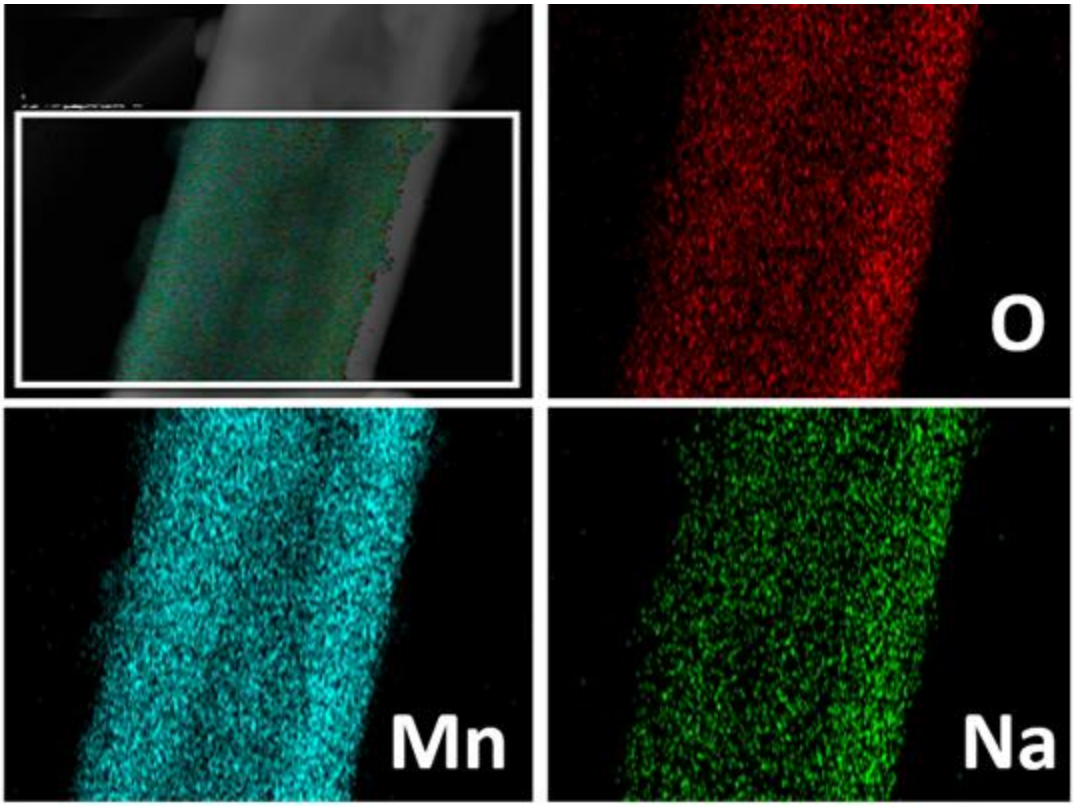

Figure S3. Element mapping images of O, Mn and Na.

Table S1. Na:Mn stoichiometric ratio of the as-prepared NMO analyzed by ICP-AES.

Element	Na	Mn
Molar ratio	0.7	1

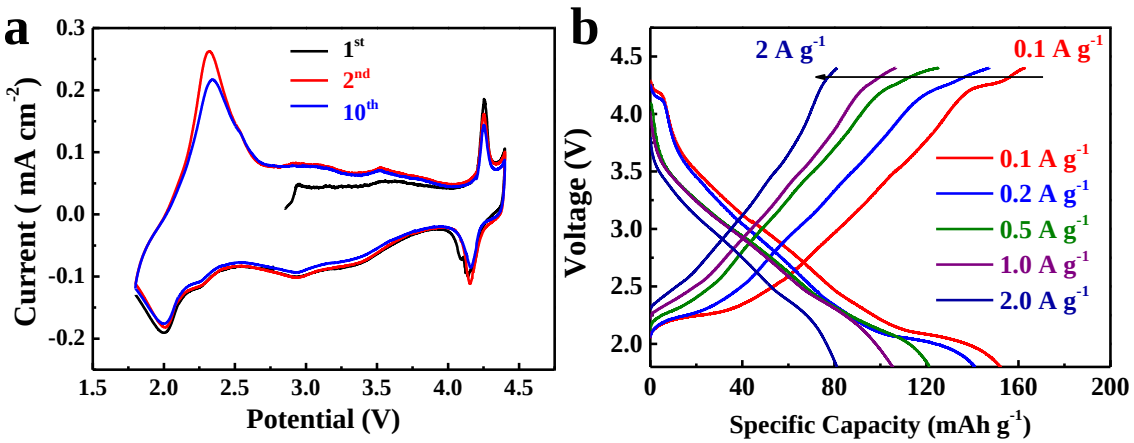

Figure S4. a) CV curves of NMO at a scan rate of 0.1 mVs^{-1} of the 1st, 2nd and 10th cycle between 1.8 and 4.4 V. b) Discharge/charge voltage profiles at the various current densities from 0.1 A g^{-1} to 2 A g^{-1} at the 2th cycle.

Table S2: Literature overview: Sodium storage capacities for different sodium manganese oxide materials.

Type of NMO	Current Density/ A g-1	Capacity/ mAh g^{-1}	Cycling performance	Potential Window /V	Reference
$Na_4Mn_9O_{18}$	0.12	128	77% after 1000 cycles	1.5 - 4.1	[1]
	1.2	94			
	2.4	82			
$Na_{0.7}MnO_2$	0.04	163	93.7% after 10 cycles	2 - 4.5	[2]
	0.08	150			
	0.18	125			
$Na_{0.67}MnO_2$	0.01	174	83% after 60 cycles	2 – 4.3	[3]
	0.05	120			
	0.25	88			
$Na_{0.71}MnO_2{\cdot}0.25H_2O$	0.01	149.5	87% after 100 cycles	1.8 – 3.7	[4]
	0.02	135.3			
	0.4	89.7			
$Na_{0.6}MnO_2$	Not reported	156	36% after 10 cycles	2.0 – 3.8	[5]
$Na_{0.7}MnO_{2.05}$	0.1	162.3	88% after 100 cycles at 0.1 A g^{-1}	1.8 – 4.4	This work
	0.5	133.9			
	2.0	101.9			

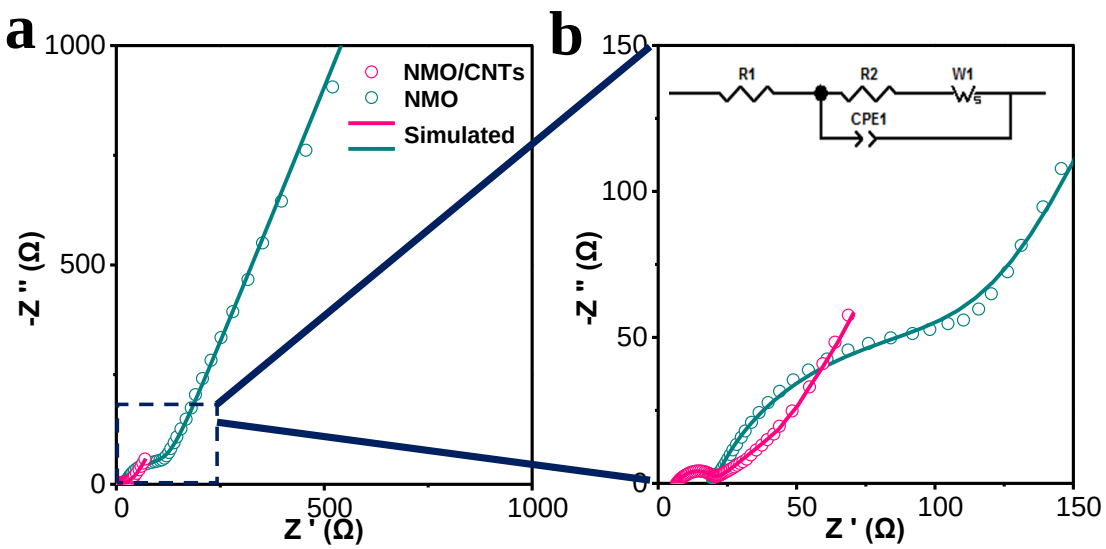

Figure S5. a) Nyquist plots of NMO and NOMO/CNTs at potential of 4.3 V after 5th cycle. b) Enlarged Nyquist plots of the marked area in (a).

Table S3: Literature overview: sodium storage capacities for different carbon-based materials.

Type of carbon	Temp./ °C	Capacity/ mAh g^{-1}	Rate/ Current density	Potential Window /V	Reference
Templated carbon	RT	130	C/5	0.01-1.6	[6]
Carbon black	RT	121	C/75	Not reported	[7]
Biomass-derived carbon	RT	122	0.1 A g^{-1}	0.001-2.8	[8]
Carbon black	RT	120	0.1 A g^{-1}	0.15-2.0	[9]
Sphere carbon	RT	105	0.075 A g^{-1}	0.1-2.0	[10]
HCNFs	RT	136.1	0.1 A g^{-1}	0.01-1.5	This work

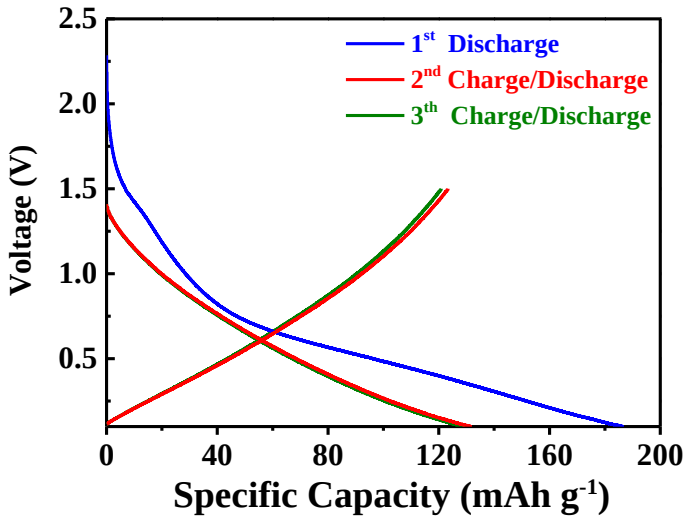

Figure S6. Discharge/charge voltage profiles of HCNFs electrode at 0.1 A g−1 at the 1st cycle, 2nd cycle and 3rd cycle.

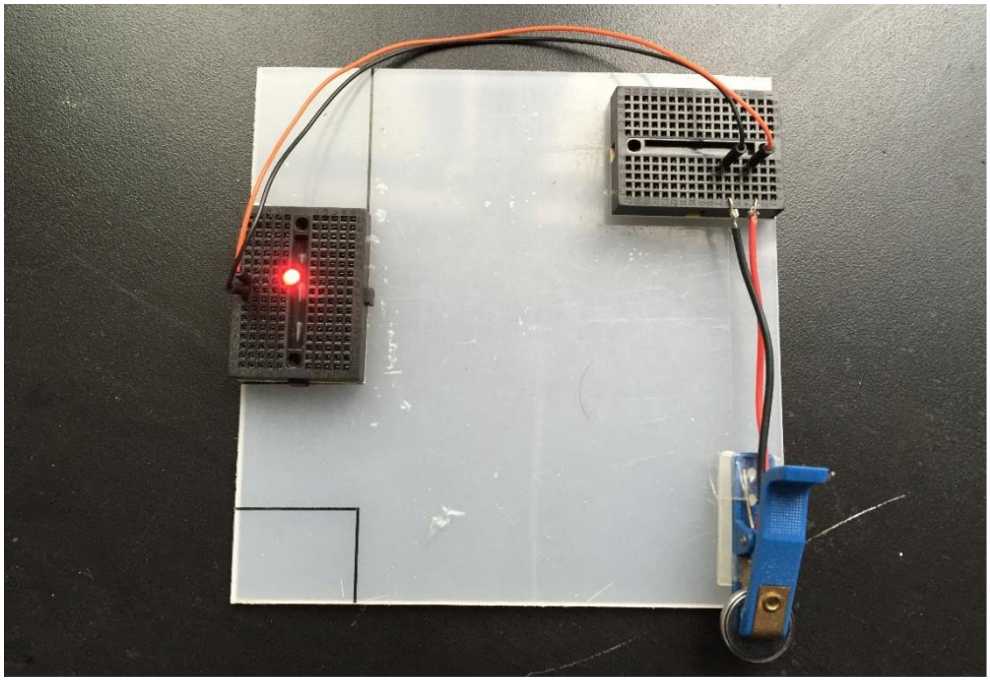

Figure S7. Optical image showing a LED (2.0 V) powered by NMO/CNTs//HCNFs SIB full cell.

[1] Y. Cao, L. Xiao, W. Wang, D. Choi, Z. Nie, J. Yu, L. V. Saraf, Z. Yang, J. Liu, Advanced materials **2011**, 23, 3155.

[2] D. Su, C. Wang, H. J. Ahn, G. Wang, Chemistry **2013**, 19, 10884.

[3] M. Xu, Y. Niu, Y. Li, S. Bao, C. M. Li, RSC Advances **2014**, 4, 30340.

[4] K. W. Nam, S. Kim, E. Yang, Y. Jung, E. Levi, D. Aurbach, J. W. Choi, Chemistry of Materials **2015**, 27, 3721.

[5] A. Caballero, L. Hernan, J. Morales, L. Sanchez, J. S. Pena, M. Aranda, Journal of Materials Chemistry **2002**, 12, 1142.

[6] S. Wenzel, T. Hara, J. Janek, P. Adelhelm, Energy & Environmental Science **2011**, 4, 3342.

[7] R. Alcántara, J. M. Jiménez-Mateos, P. Lavela, J. L. Tirado, Electrochemistry Communications **2001**, 3, 639.

[8] P. Wang, B. Qiao, Y. Du, Y. Li, X. Zhou, Z. Dai, J. Bao, The Journal of Physical Chemistry C **2015**, 119, 21336.

[9] W. Luo, C. Bommier, Z. Jian, X. Li, R. Carter, S. Vail, Y. Lu, J.-J. Lee, X. Ji, ACS applied materials & interfaces **2015**, 7, 2626.

[10] V. G. Pol, E. Lee, D. Zhou, F. Dogan, J. M. Calderon-Moreno, C. S. Johnson, Electrochimica Acta **2014**, 127, 61.