

Optimization of Nonatitanate Electrodes for Sodium-Ion Batteries

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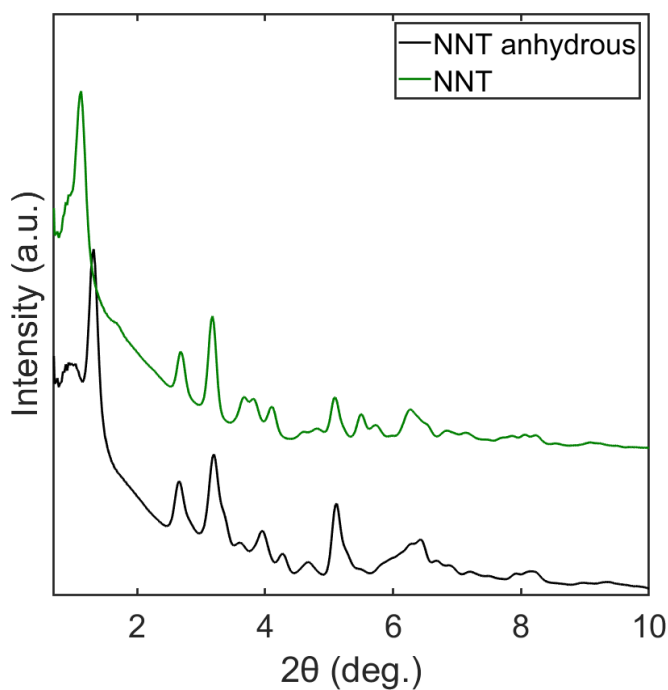


Fig. S1. XRD patterns of as prepared NNT and anhydrous NNT (annealed at 600 °C).

Table S1. Rietveld refinements of XRD patterns of as prepared NNT, anhydrous NNT, as prepared NNT-GO, and anhydrous NNT-GO.

Material	As prepared NNT	Anhydrous NNT	As prepared NNT-GO	Anhydrous NNT-GO
Formula	NaTi ₃ O ₆ OH·2H ₂ O	NaTi ₃ O ₆ OH	NaTi ₃ O ₆ OH·2H ₂ O	NaTi ₃ O ₆ OH
Space group	C/2m	C/2m	C/2m	C/2m
<i>a</i> (Å)	21.4(3)	20.8(4)	21.5(1)	21.5(7)
<i>b</i> (Å)	3.741(2)	3.793(5)	3.747(1)	3.767(4)
<i>c</i> (Å)	12.0(1)	10.6(1)	11.99(4)	11.1(2)
β (°)	135.8(2)	137.1(3)	135.96(9)	138.3 (5)
Cryst. Size (nm, eq.)	>200 nm	>200 nm	>200 nm	>200 nm
Cryst. Size (nm, ax.)	22(3)	15(2)	32(4)	8.0(7)
%R _{wp}	2.49	4.63	2.82	3.55

Table S2. Atomic positions of as prepared NNT determined by Rietveld refinement.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Wyckoff Site
Na	0.759(5)	0	0.896(8)	4i
Ti1	0.75463(2)	0	0.391(2)	4i
Ti2	0.584(3)	0.5	0.517(4)	4i
Ti3	0.564(2)	0	0.291(4)	4i
O1	0.741(6)	0	0.60(1)	4i
O2	0.629(8)	0	0.21(2)	4i
O3	0.660(7)	0.5	0.61(1)	4i
O4	0.599(8)	0.5	0.38(1)	4i
O5	0.565(4)	0.5	0.658(9)	4i
O6	0.528(6)	0	0.42(1)	4i
O-H	0.452(7)	0	0.11(1)	4i
O-H ₂	0.329(5)	0	0.080(9)	4i
O-H ₂	0.877(7)	0	0.88(1)	4i

Table S3. Atomic positions of anhydrous NNT determined by Rietveld refinement.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Wyckoff Site
Na	0.83(2)	0.25(5)	0.02(4)	8j
Ti1	0.7420(2)	0	0.393(6)	4i
Ti2	0.573(5)	0.5	0.56(1)	4i
Ti3	0.563(4)	0	0.293(7)	4i
O1	0.73(1)	0	0.55(3)	4i
O2	0.62(1)	0	0.22(3)	4i
O3	0.752(8)	0.5	0.69(2)	4i
O4	0.61(2)	0.5	0.22(3)	4i
O5	0.58(2)	0.5	0.72(3)	4i
O6	0.58(2)	0	0.52(5)	4i
O-H	0.34(4)	0.25(9)	0.07(5)	8j

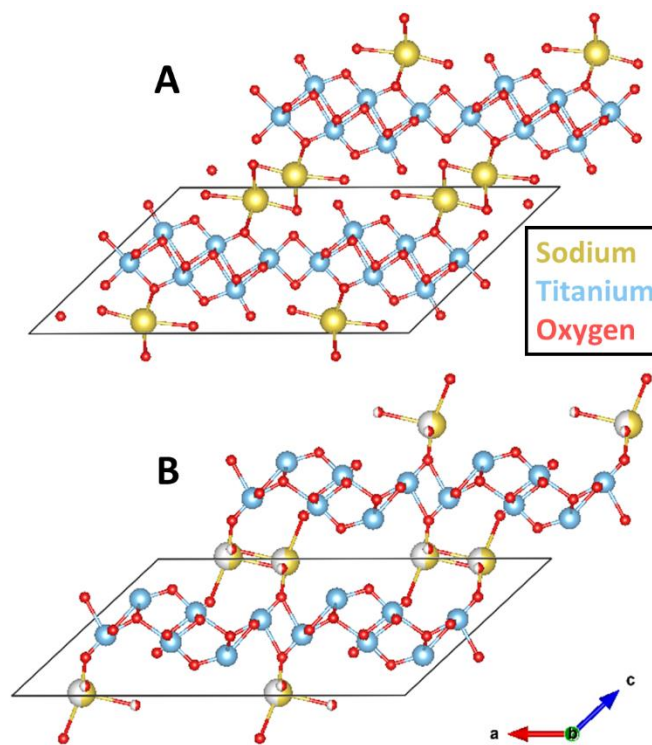


Fig. S2. Crystal structures of (a) NNT as prepared and (b) NNT annealed at 600 °C.

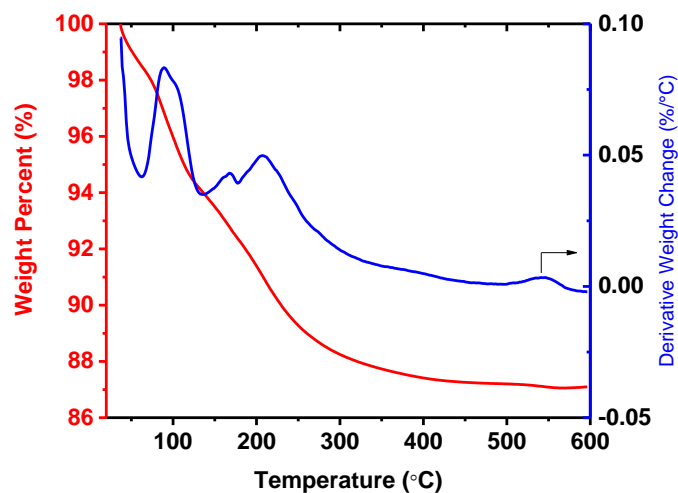


Fig. S3. Thermogravimetric analysis of as-prepared NNT under nitrogen using a heating rate of 5 °C/minute.

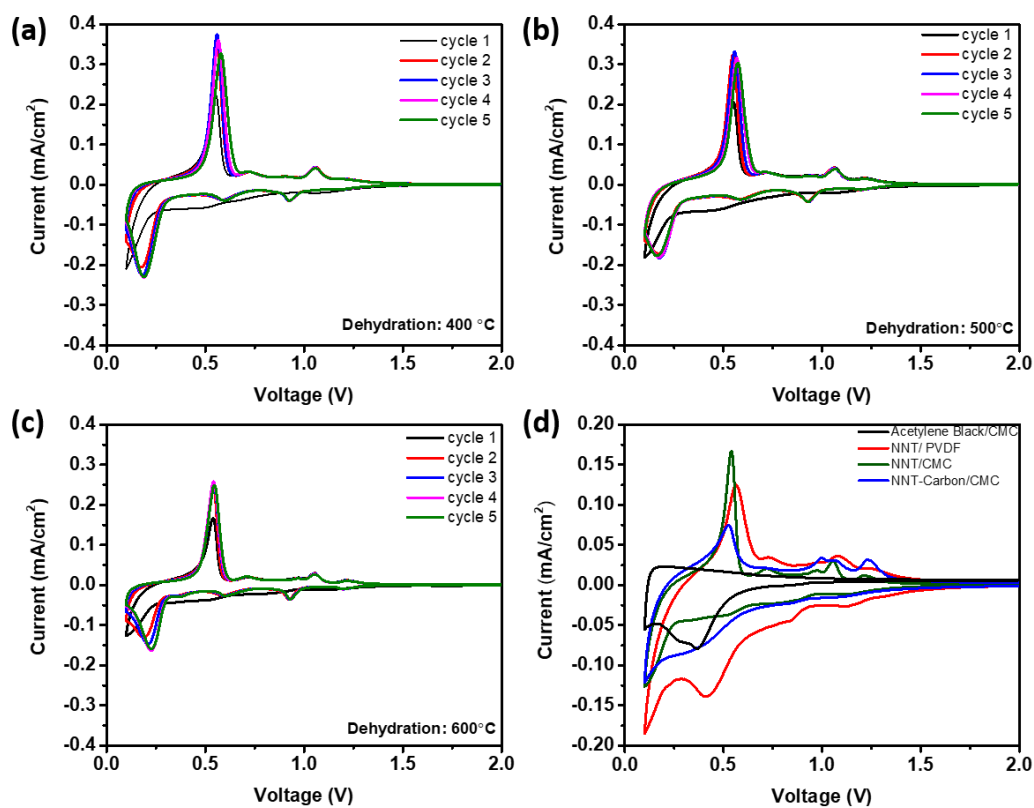


Fig. S4. (a-c) CV curves of half cells containing the dehydrated NNT samples heated to the indicated temperatures using CMC binder in the electrodes, at a scan rate of 0.5 mV/s. (d) First CV curves of half-cells containing NNT electrodes made with PVDF or CMC binders, and C-

coated NNT electrodes with CMC binder. Also shown is a CV curve of a blank electrode made with acetylene black.

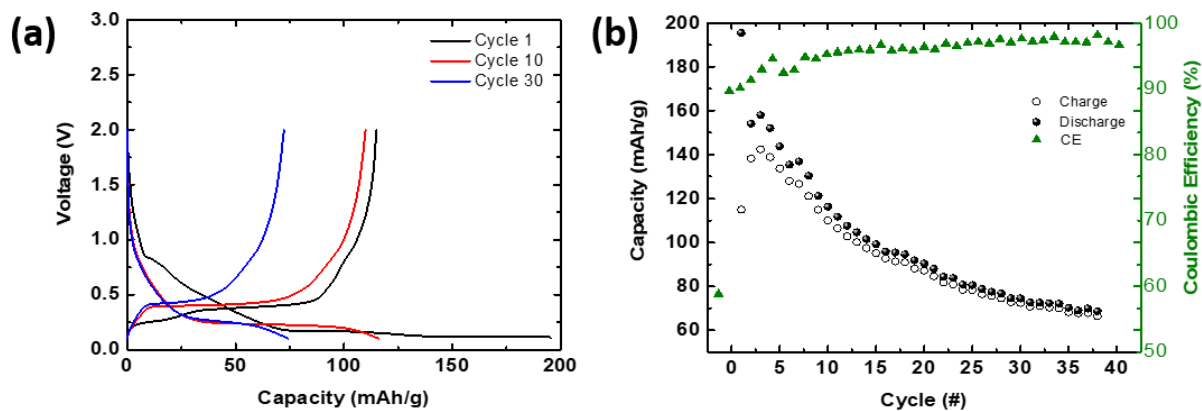


Fig. S5. The potential versus specific capacity profile for a half-cell containing carbon-coated NNT dehydrated at 800 °C cycled between 1.5 and 0.1 V at 0.15 mA cm⁻² (15 mA g⁻¹) (a), specific discharge and charge capacities and Coulombic efficiencies as a function of cycle number (b).

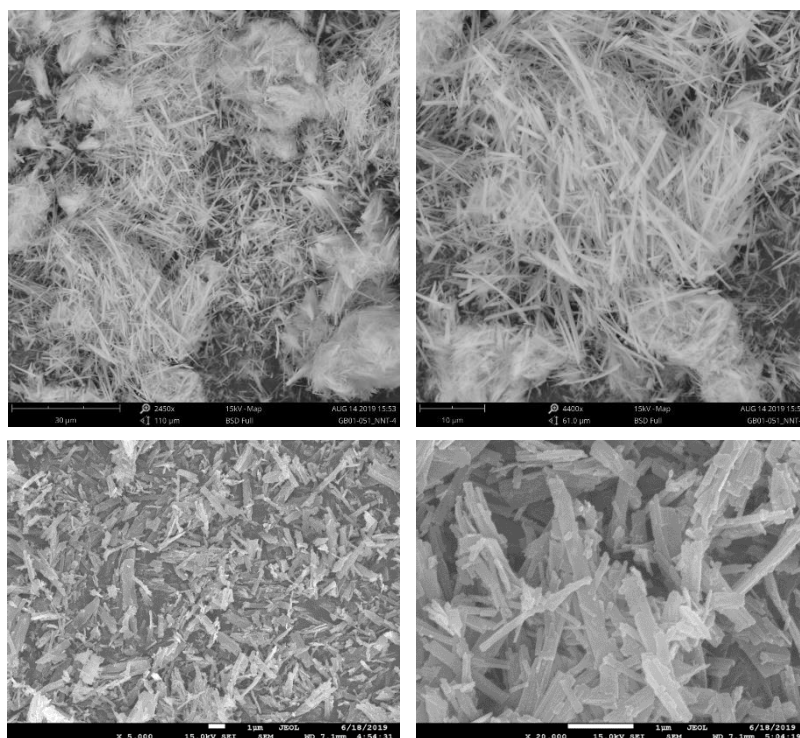


Fig. S6. SEM images of the as-prepared (top) and carbon coated (bottom) NNT samples.

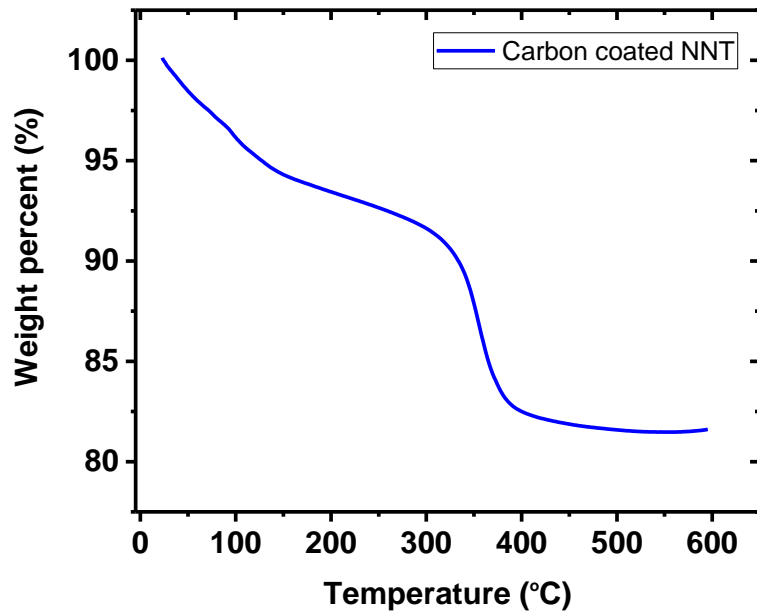


Fig. S7. Thermogravimetric analysis of carbon-coated NNT in air using a heating rate of 5 °C/minute.

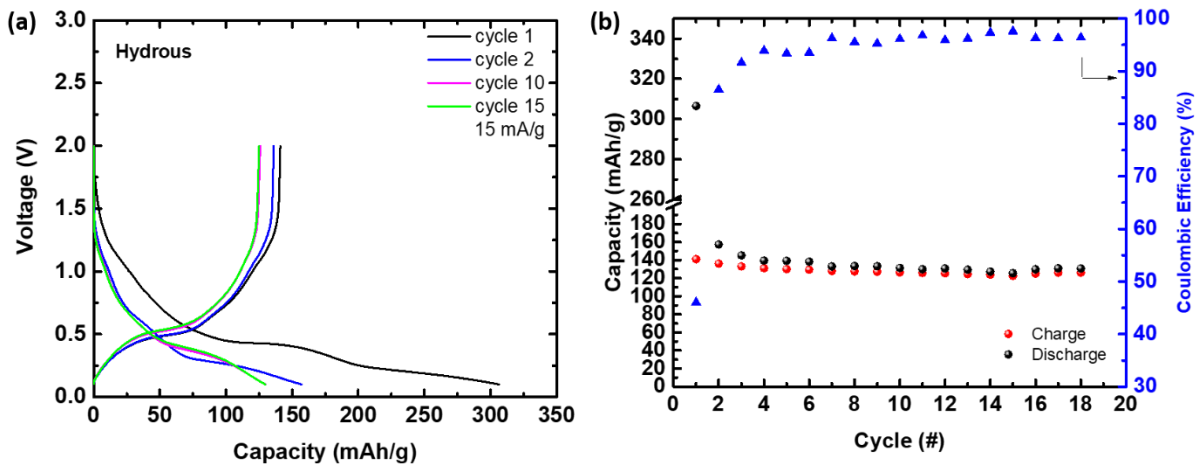


Fig. S8. The potential versus specific capacity profiles for the hydrous NNT samples in Na half-cells using CMC binder without C-coating (a) specific discharge and charge capacities and Coulombic efficiency as a function of cycle number (b). The cell cycled between 2.0 and 0.1 V at 0.15 mA cm^{-2} (15 mA g^{-1}).

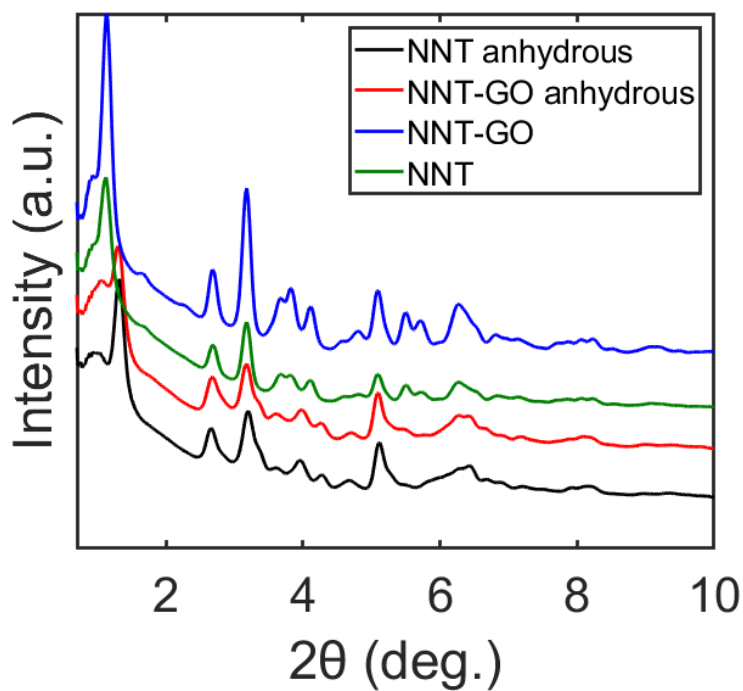


Fig. S9. Synchrotron XRD patterns of as prepared NNT and anhydrous NNT (annealed at 600 °C) with and without graphene (GO) wrapping.

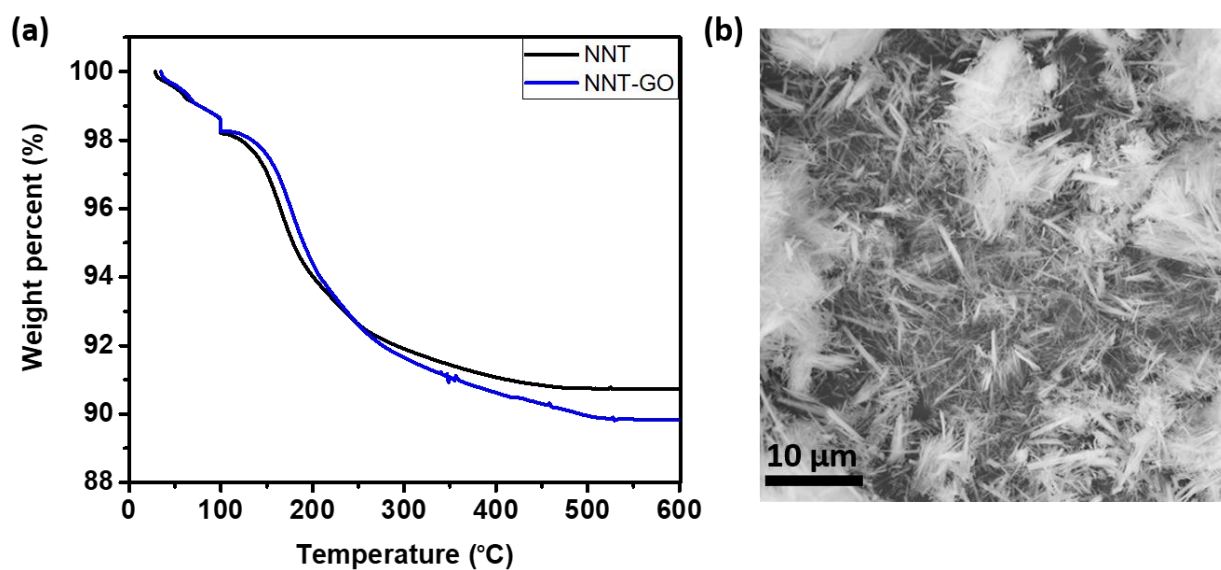


Fig. S10. (a) Thermogravimetric analysis of NNT-GO in air using a heating rate of 5 °C/min. (b) SEM micrograph of NNT-GO sample.

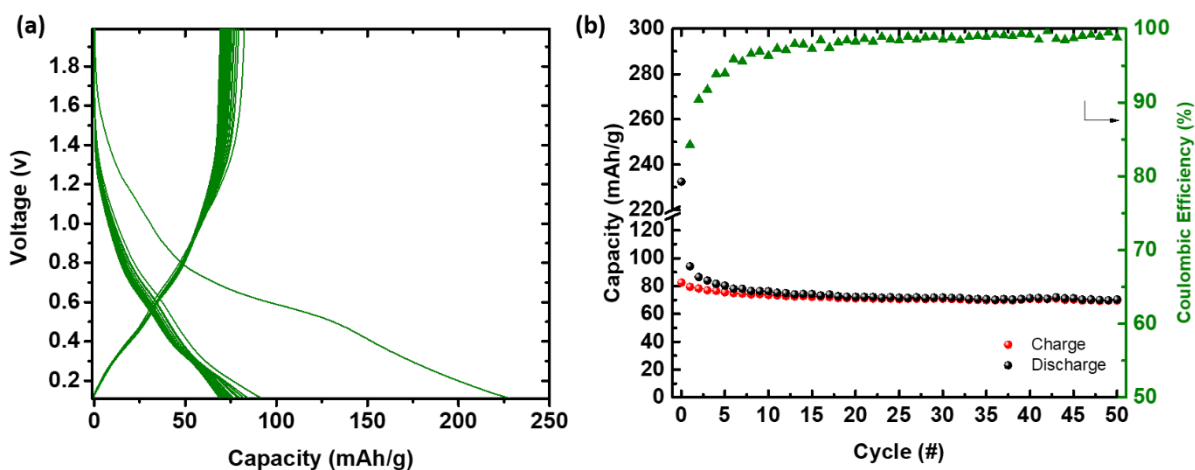


Fig. S11. The potential versus specific capacity profile for half-cells containing the graphene-wrapped NNT samples dehydrated at 500 °C in Na half-cells cycled between 2.0 and 0.1 V at 0.15 mA cm⁻² (15 mA g⁻¹) using PVDF binder (a), specific discharge and charge capacities and Coulombic efficiency as a function of cycle number (b).

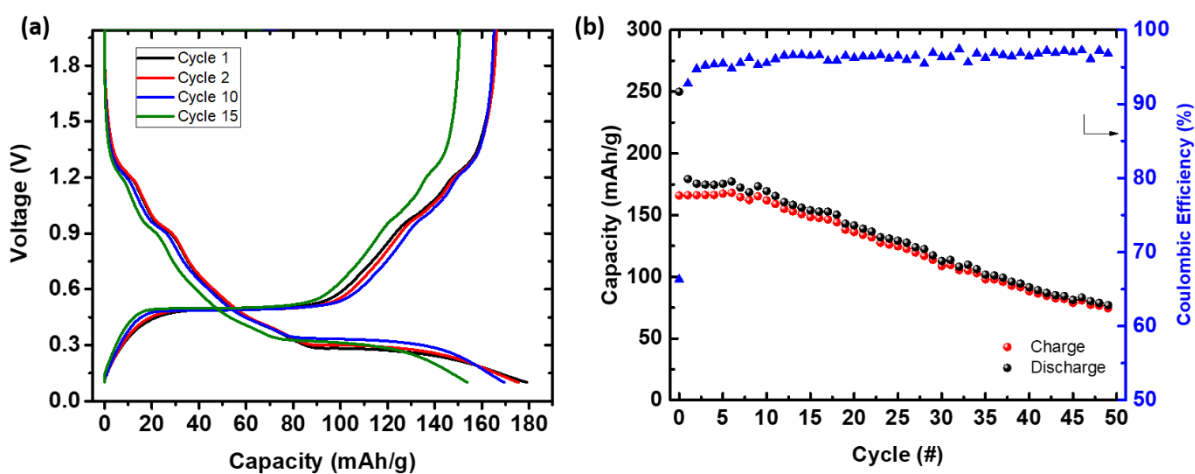


Fig. S12. The potential versus specific capacity profile for cells containing the graphene-wrapped NNT samples dehydrated at 500 °C in Na half-cells cycled between 2.0 and 0.1 V at 0.15 mA cm⁻² (15 mA g⁻¹) using CMC binder (a), specific discharge and charge capacities and Coulombic efficiency as a function of cycle number (b).

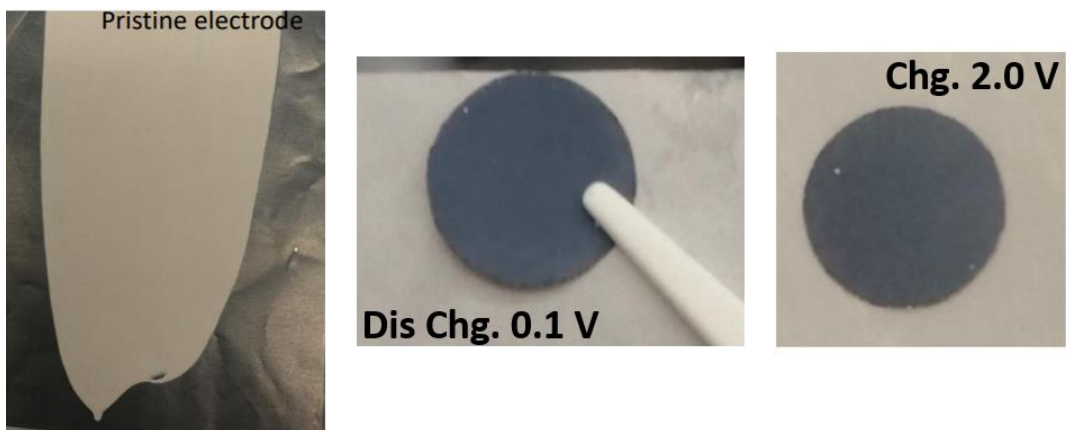


Fig. S13. Optical images of carbon-free pristine and cycled electrodes in different states of charge and discharge.