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Supplementary Information

Nb-doped titanium phosphate for sodium storage: electrochemical performance and structural insights

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Table S1. Lattice parameters obtained from Rietveld refinement of the XRD data of NTP, NTP-C, NNbTP and NNbTP-C powders and their electric conductivities

	NTP	**NTP-C**	**NNbTP**	**NNbTP-C**
Composition	$NaTi_2(PO_4)_3$	$NaTi_2(PO_4)_3$	$NaNb_{0.05}Ti_{1.95}(PO_4)_3$	$NaNb_{0.05}Ti_{1.95}(PO_4)_3$
Space group	$R\bar{3}c$	$R\bar{3}c$	$R\bar{3}c$	$R\bar{3}c$
Lattice parameters	a=8.4925 (5)Å b=8.4925 (5)Å c=21.8036 (5)Å V=1361.861(3)Å^3	a=8.4897 (5)Å b=8.4897 (5)Å c=21.8035 (5)Å V=1360.951 (3)Å^3	a=8.4932 (5)Å b=8.4932 (5)Å c=21.8042 (5)Å V=1362.123 (3)Å^3	a=8.4905 (5)Å b=8.4905 (5)Å c=21.8069 (5)Å V=1361.407 (3)Å^3
*R*p / %	5.84	5.10	7.45	5.64
*R*wp / %	6.48	5.21	8.61	5.81
χ^2	1.78	1.67	1.95	1.87
Electric conductivity / S cm^{-1}	7×10^{-6}	9×10^{-4}	3×10^{-5}	2×10^{-3}

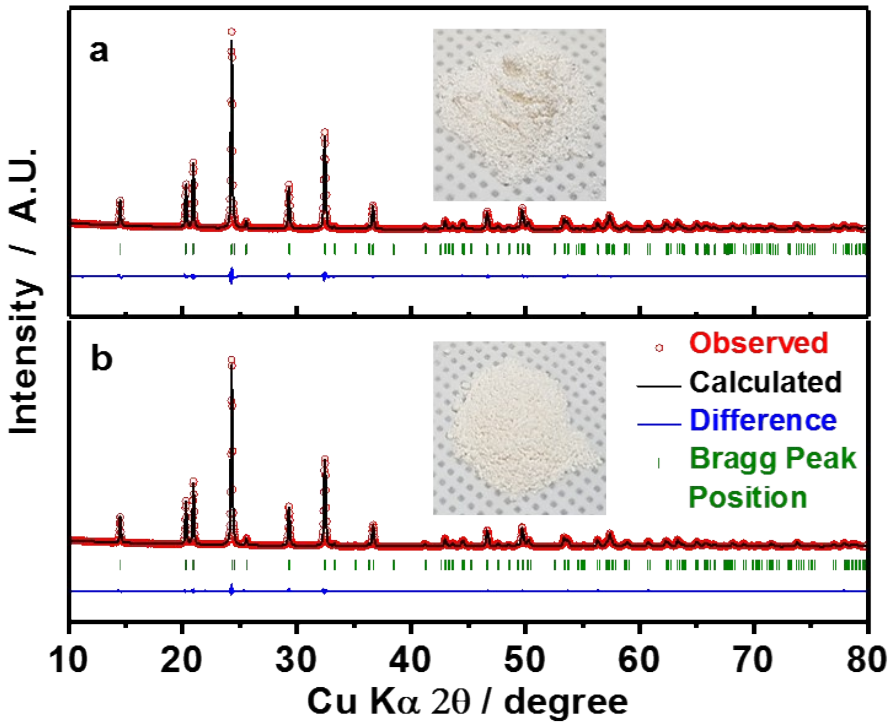

Figure S1. Rietveld refinement results of XRD data for (a) NTP and (b) NNbTP (inset: resulting digital images of powders)

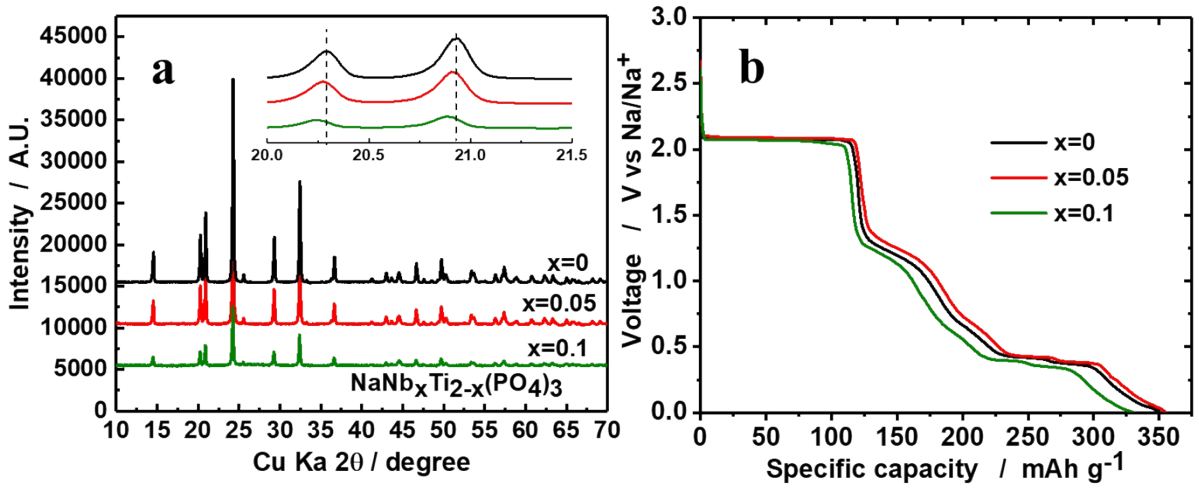

Figure S2. (a) XRD patterns of a corresponding $NaNb_xTi_{2-x}(PO_4)_3$ (x=0; 0.05; 0.1) materials (inset: magnified XRD patterns) (b) Discharge profiles of $NaNb_xTi_{2-x}(PO_4)_3$ of first cycle.

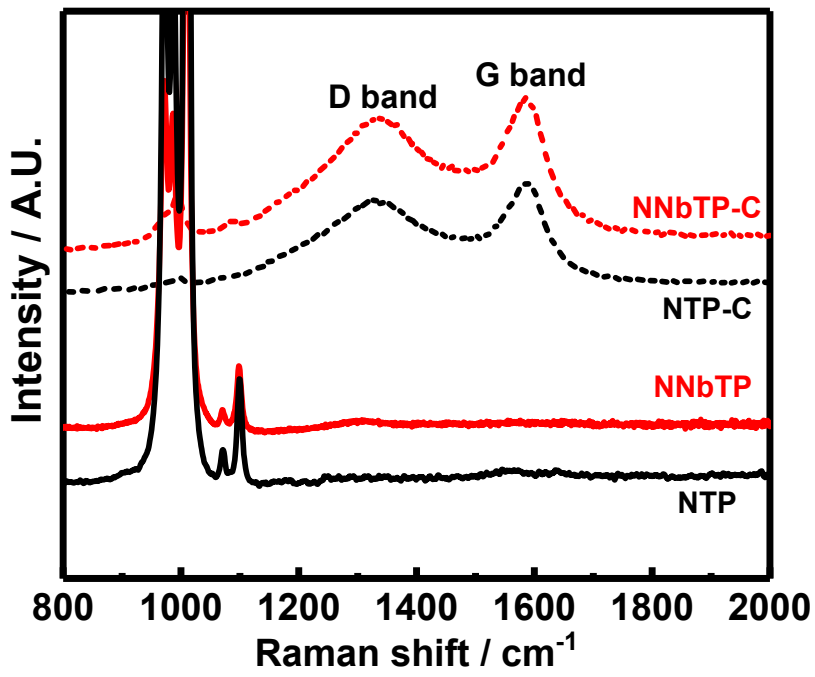

Figure S3. Raman spectra of NTP, NTP-C, NNbTP and NNbTP-C

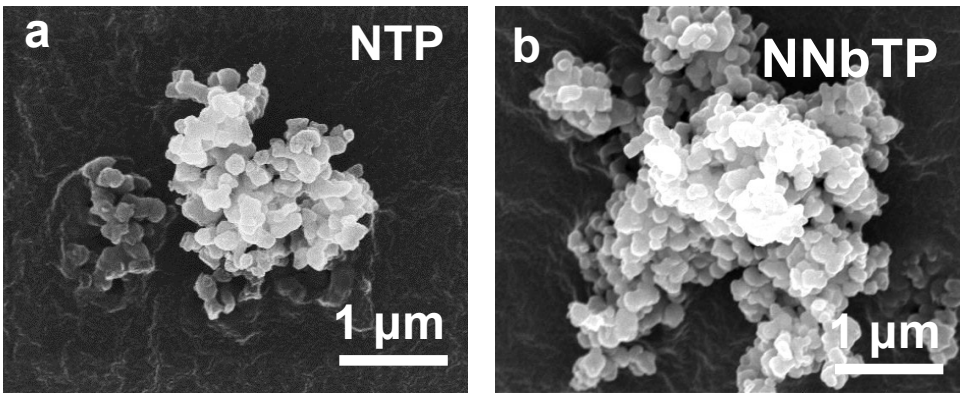

Figure S4. SEM image of (a) NTP, (b) NNbTP

Table S2. Lattice parameters obtained from Rietveld refinement of the XRD data of electrodes NTP-C, NNbTP-C after first discharge to 1.5 V; 0.01V and after first charge to 1.5 V; 3 V

Discharge 1.5 V	**NTP-C**	**NNbTP - C**
Composition	$Na_3Ti_2(PO_4)_3$	$Na_{2.95}Nb_{0.05}Ti_{1.95}(PO_4)_3$
Space group	P-1	P-1
Lattice parameters	a= 8.8408 (5)Å b= 8.8550 (5)Å c= 21.6733 (5)Å α=89.8904 ^{0} β=90.0035 ^{0} γ=59.9959 ^{0} V= 1469.329 (3)Å^3	a= 8.8560 (5)Å b= 8.8616 (5)Å c= 21.6335 (5)Å α= 89.8933 ^{0} β= 89.9790 ^{0} γ= 60.0580 ^{0} V= 1471.207 (3)Å^3
*R*p / %	14.0	19.2
*R*wp / %	12.2	17.7
χ^2	2.12	2.23

Discharge 0.01 V	**NTP-C**	**NNbTP - C**
Composition	$Na_4Ti_2(PO_4)_3$	$Na_{3.925}Nb_{0.05}Ti_{1.95}(PO_4)_3$
Space group	$R\bar{3}c$	$R\bar{3}c$
Lattice parameters	a= 9.0506 (5)Å b= 9.0506 (5)Å c= 21.3905 (5)Å V= 1517.409 (3)Å^3	a= 9.0536 (5)Å b= 9.0536 (5)Å c= 21.3972 (5)Å V= 1518.904 (3)Å^3
*R*p / %	14.4	16.4
*R*wp / %	18.4	19.6
χ^2	2.34	2.13

Charge 1.5 V	**NTP-C**	**NNbTP - C**
Composition	$Na_3Ti_2(PO_4)_3$	$Na_{2.95}Nb_{0.05}Ti_{1.95}(PO_4)_3$
Space group	P-1	P-1
Lattice parameters	a= 8.8430 (5)Å b= 8.8534 (5)Å c= 21.6340 (5)Å α=89.8734^0 β=89.9554 ^{0} γ=60.0380 ^{0} V= 1468.333 (3)Å^3	a= 8.8585 (5)Å b= 8.8644 (5)Å c= 21.6337 (5)Å α= 89.8771 ^{0} β= 89.9700 ^{0} γ= 59.9650 ^{0} V= 1470.691 (3)Å^3
*R*p / %	20.6	19.7
*R*wp / %	17.6	16.7
χ^2	2.15	2.07

Charge 3 V	**NTP-C**	**NNbTP - C**
Composition	$NaTi_2(PO_4)_3$	$NaNb_{0.05}Ti_{1.95}(PO_4)_3$
Space group	$R\bar{3}c$	$R\bar{3}c$
Lattice parameters	a= 8.4851 (5)Å b=8.4851 (5)Å c= 21.7878 (5)Å V=1358.480 (3)Å^3	a=8.4886 (5)Å b=8.4886 (5)Å c=21.7864 (5)Å V=1359.527 (3)Å^3
*R*p / %	12.2	11.6
*R*wp / %	12.0	9.88
χ^2	1.76	2.08

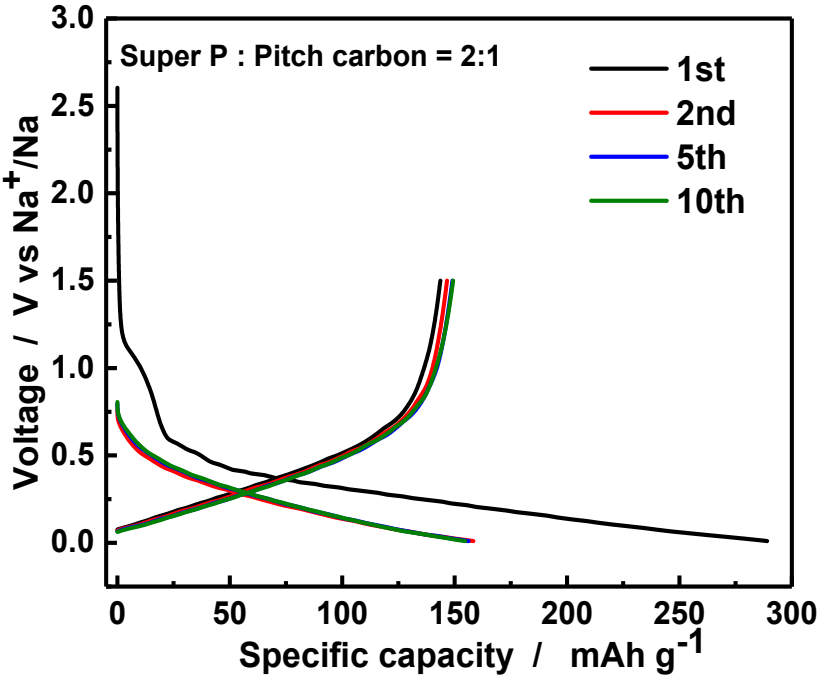

Figure S5. Charge/discharge profiles of *Super P : pitch carbon* (2:1) in the voltage range 0.01-1.5V

For electrode fabrication, a conducting agent Super P, pitch carbon and polyvinylidene fluoride (PVDF) were mixed at a weight ratio of 6:3:1 in *N*-methyl-2-pyrrolidone (NMP) to form a homogenous slurry. The electrode was prepared with the same conductive additive ratio as in NTP-C and NNbTP-C electrodes (Super P:pitch carbon =2:1)

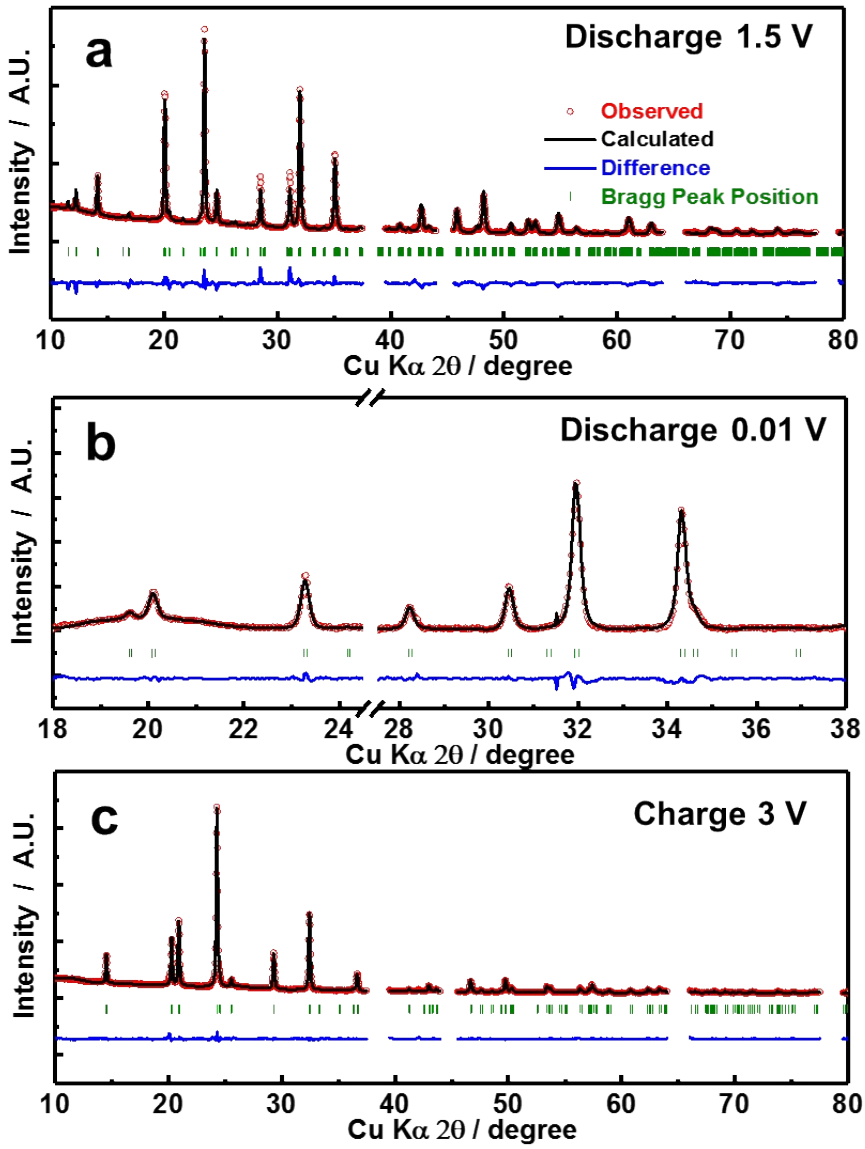

Figure S6. Rietveld refinement results of XRD data for NTP-C electrodes (a) upon discharge to 1.5 V (b) upon discharge to 0.01 V (c) upon charge to 3 V

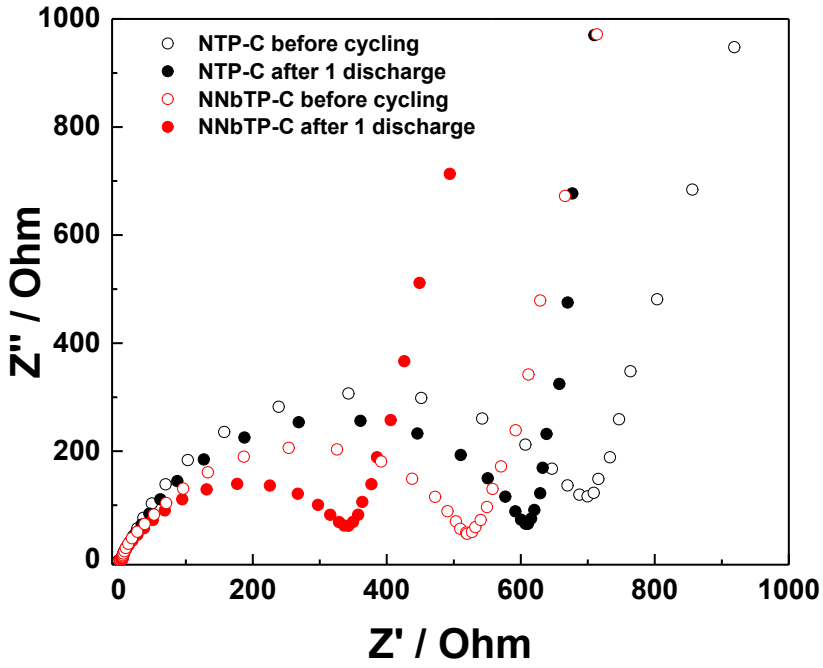

Figure S7. AC impedance spectra of NTP-C and NNbTP-C before cycling and after first discharge

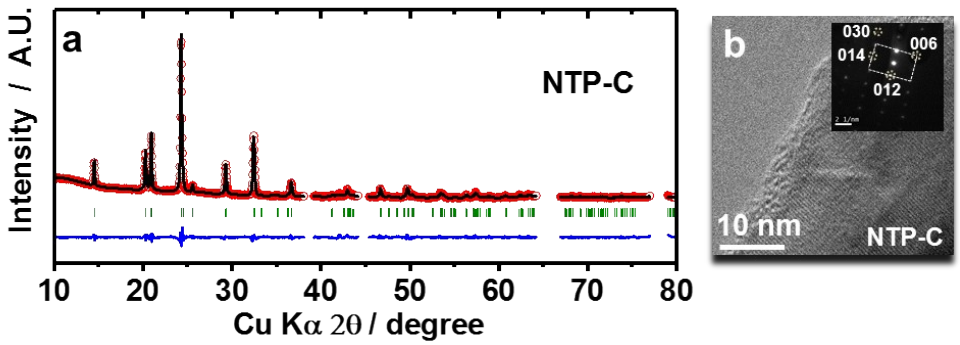

Figure S8. (a) Rietveld refinement results of XRD data for NTP-C electrodes after 1000 cycles charged to 3 V; (b) TEM image and corresponding SAED pattern of NTP-C along the [100] zone axis

Table S3. Lattice parameters obtained from Rietveld refinement of the XRD data of electrodes NTP-C, NNbTP-C after 1000 cycles

After 1000 cycles	**NTP-C**	**NNbTP - C**
Composition	$NaTi_2(PO_4)_3$	$NaNb_{0.05}Ti_{1.95}(PO_4)_3$
Space group	$R\bar{3}c$	$R\bar{3}c$
Lattice parameters	a= 8.4865 (5)Å b= 8.4865 (5)Å c= 21.7890 (5)Å V= 1359.002 (3)Å^3	a= 8.4901 (5)Å b= 8.4901 (5)Å c= 21.7898 (5)Å V= 1360.218 (3)Å^3
*R*p / %	19.3	16.6
*R*wp / %	15.1	15.4
χ^2	2.35	2.25