Supplementary Information

Molecular self-assembly of a nanorod-like N-$Li_4Ti_5O_{12}$/TiO_2/C anode for superior lithium ion storage

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Contents:

Figure S1

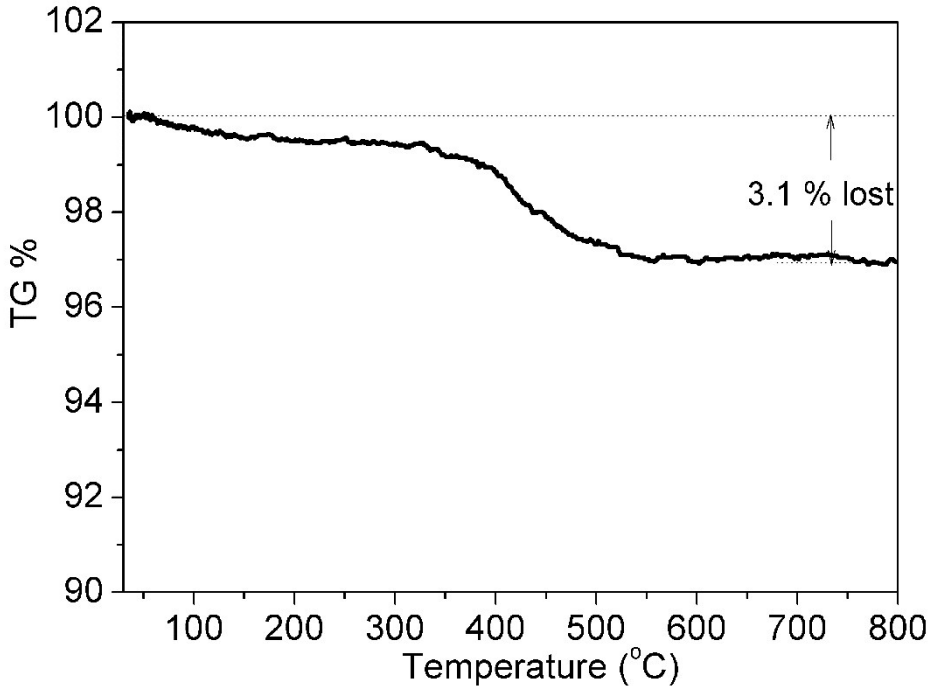

Figure S1 TGA curve for the NT-LTO/C composite in an air atmosphere with a heating rate of 10 ^{o}C min^{-1}.

Figure S2

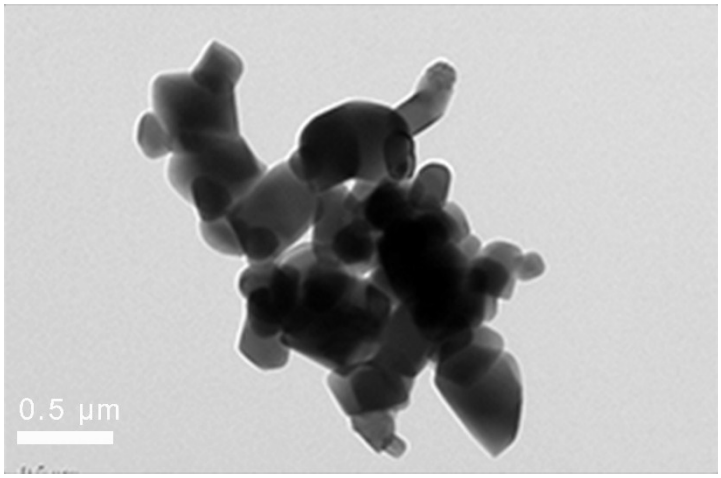

Figure S2 TEM photographs of pristine LTO with mechanical mixing of anatase-TiO_2 and LiOH as reactants after the calcination at 750 ^{o}C for 5 h in a N_2 atmosphere.

Figure S3

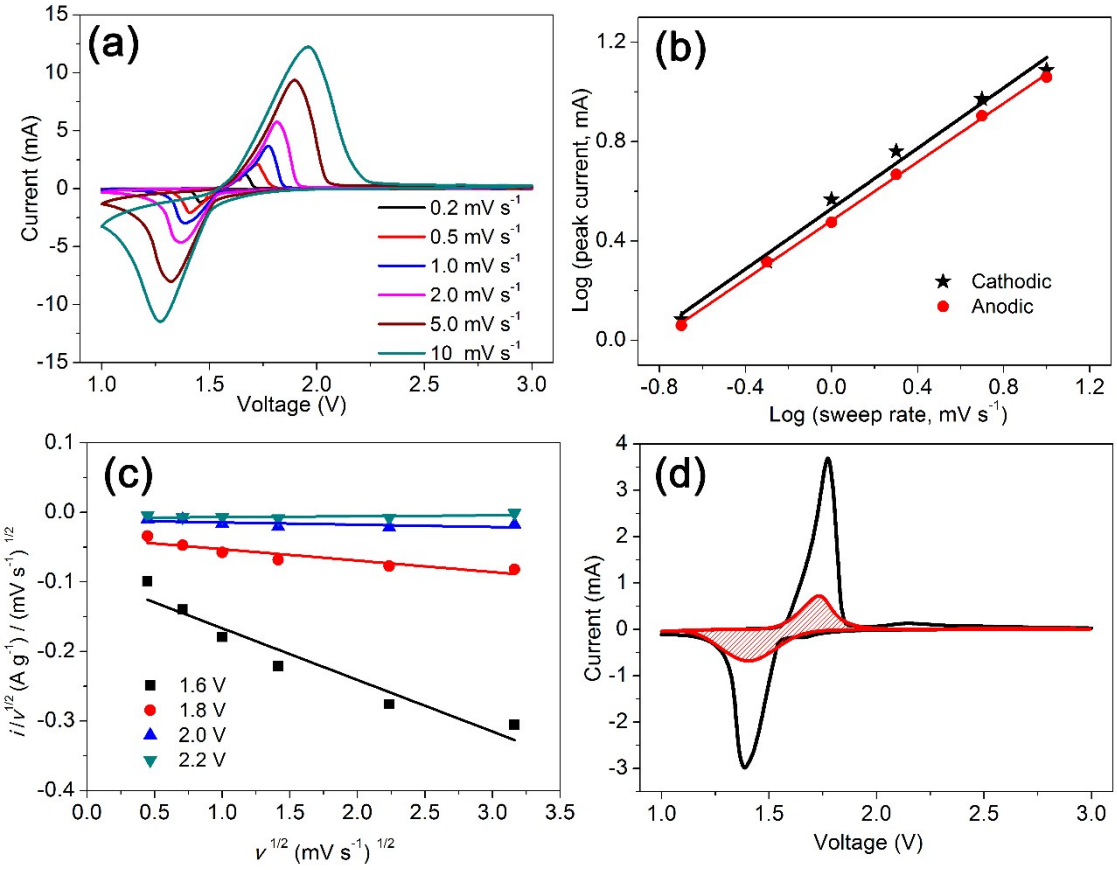

Figure S3. (a) CV curves from 0.2 to 10 mV s^{-1}; (b) analysis of *b*-value for anodic and cathodic peak currents; (c) The plots of $v^{1/2}$ vs $i/v^{1/2}$ used for calculating constants k_1 and k_2 at different potentials; (d) capacitive (red) and diffusion currents contributed to charge storage of NT-LTO/C at a scan rate of 1 mV s^{-1}.

To investigate the pseudocapacitance performance of the NT-LTO/C electrode, the ion diffusion and charge storage kinetics of NT-LTO/C electrode are inverstigated by CV at various scan rates from 0.2 to 10 mV s^{-1} (**Figure S3a**). **Equation S1** describes the kinetic mechanism by the dependence of the current (i) on the scan rate (v).[1]

$$i = av^b \qquad \text{(Eq. S1)}$$

where, b value is an adjustable parameter, which represents the slope of the log(v)–log(i) plots. Typically, the slope of 0.5 (b=0.5) signifies a diffusion-controlled process, and the slope of 1 (b=1) suggests a capacitive-controlled behavior (also named surface Faradic redox reaction).[2] As displayed in **Figure S3b**, the cathodic and anodic b values of NT-LTO/C anode in LIBs are 0.61 and 0.59 respectively, demonstrating that the ion storage mechanism of NT-LTO/C anode tends to both diffusion-controlled and capacitive-controlled processes. Moreover, the contribution ratios of diffusion-controlled processe and capacitive-controlled process are quantitatively separated through the method by Dunn and co-workers:[3]

$$i = k_1 v + k_2 v^{1/2} \qquad \text{(Eq. S2)}$$

In **Equation S2**, $k_1 v$ and $k_2 v^{1/2}$ represent the surface capacitive and diffusion-controlled process, respectively.[4,5] The current at a fixed potential (i) can be expressed as a combination of $k_1 v$ and $k_2 v^{1/2}$. By plotting $i/v^{1/2}$ versus $v^{1/2}$ (**Figure S3c**), one can determine k_1 and k_2 from the slope and the y-axis intercept point of a straight line, respectively. Comparing the shaded area ($k_1 v$) in **Figure S3d**, it can be found that ~30.5 % of the total charge in the NT-LTO/C electrode is surface capacitive (red region) at a scan rate of 1 mV s^{-1}. This result suggests that the NT-LTO/C electrode is dominated by pseudocapacitive nature during the charge/discharge process.

Figure S4

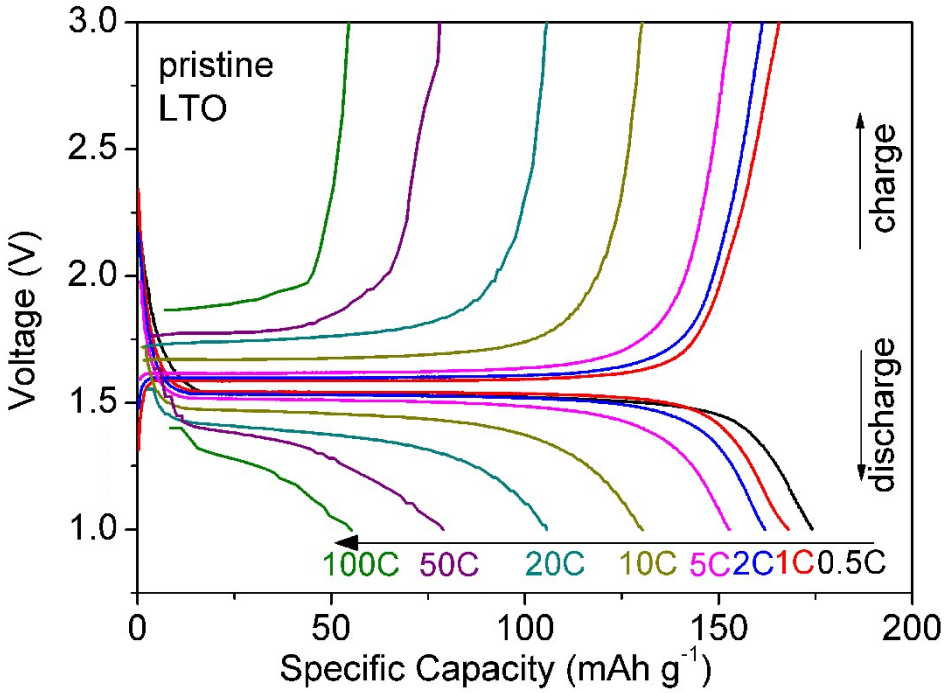

Figure S4 The discharge and charge profiles for the pristine LTO electrode at various rates from 0.5 C to 100 C.

Figure S5

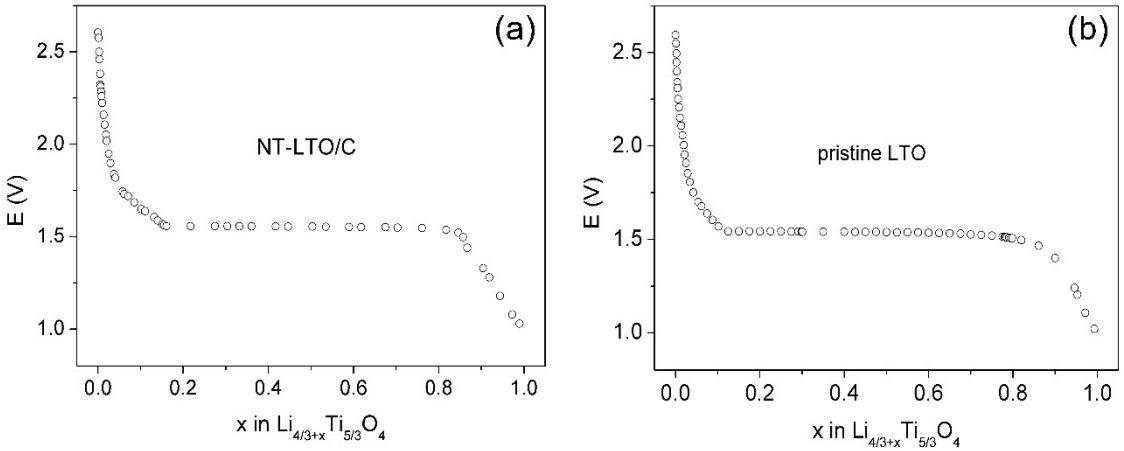

Figure S5 The relationship of the voltage vs. x in NT-LTO/C and LTO electrodes.

Figure S6

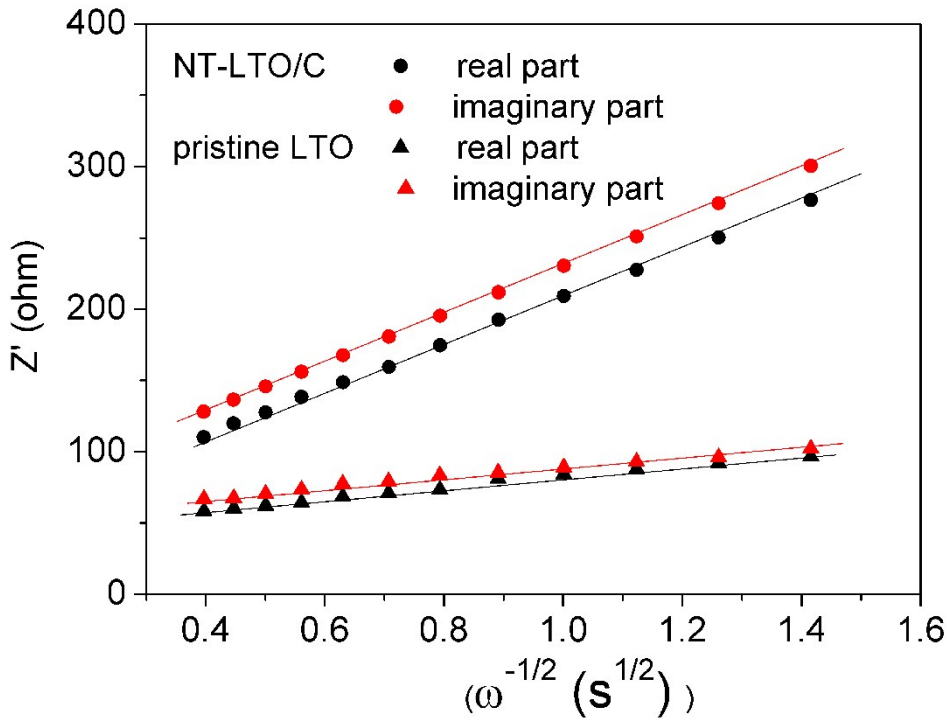

Figure S6 Real and imaginary parts of the complex impedance vs. $\omega^{-1/2}$ for the NT-LTO/C and LTO electrodes.

Figure S7

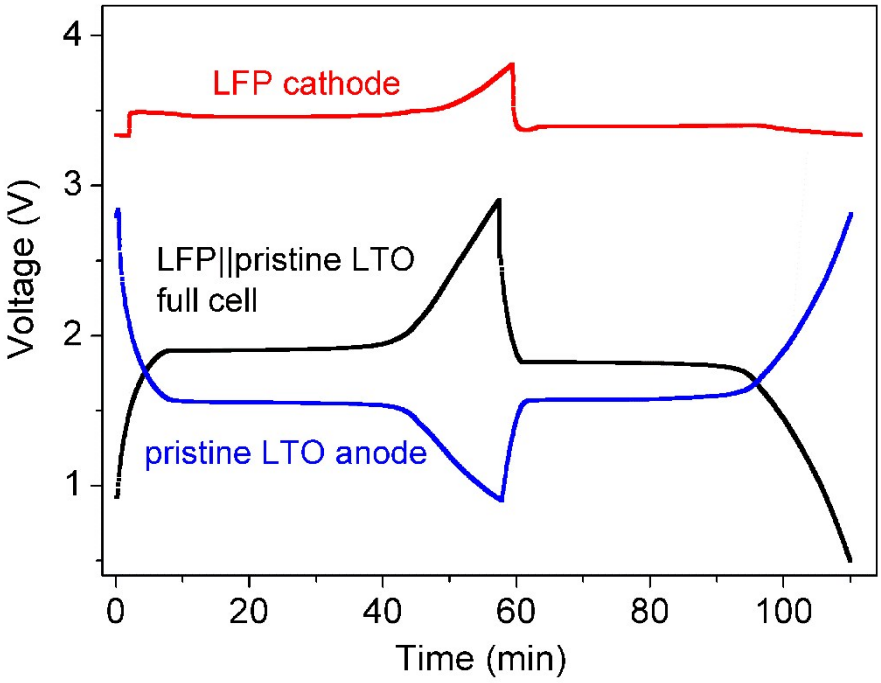

Figure S7 The corresponding cathode and anode curves during the charge/discharge process of the LFP||pristine LTO cell.

Table S1 Refined structural parameters of $Li_4Ti_5O_{12}$ obtained from the two phase Rietveld refinement using X-ray powder diffraction data at room temperature. The symbols, g and U, represent the occupation and isotropic thermal parameters, respectively. The profile factor is R_p, the weighted profile factor is R_{wp}.

$Li_4Ti_5O_{12}$ (phase No. 1)						
Atom	site	x	Y	z	g	U
Li	8a	0.0000	0.0000	0.0000	1.000	0.0000
Li	16c	0.6250	0.6250	0.6250	0.1667	0.0000
Ti	16c	0.6250	0.6250	0.6250	0.8333	0.0000
O	32e	0.3890	0.3890	0.3890	1.0000	0.0000
a=8.357 Å b=8.357 Å c=8.357 Å α=β=γ=90°						
TiO_2 (phase No. 2)						
Atom	site	x	y	z	g	U
Ti	4a	0.0000	0.7500	0.1250	1.0000	0.0000
O	8e	0.0000	0.7500	0.3333	1.0000	0.0000
a=3.785 Å b=3.785 Å c=9.514 Å α=β=γ=90°						

R-factors and weight fraction
R_{wp} = 9.77% R_p = 7.26% S = 1.5914
$Li_4Ti_5O_{12}$: 95.48 % TiO_2 : 4.52 %

Table S2 Ratio analysis of the peaks in the XPS spectrum of the NT-LTO/C composite

	Ratios (% at.)				
	Li	Ti	O	C	N
NT-LTO/C	11.3	36.6	38.7	11.0	2.4

Table S3 Ti2p composition from XPS

	Ti^{4+}2p1/2	Ti^{3+}2p1/2	Ti^{4+}2p3/2	Ti^{3+}2p3/2
Binding Energy (eV)	464.3	463.1	458.4	457.2
Ratios (% at.)	14.41	14.57	47.96	23.06

Table S4 N1s composition from XPS

peaks	N4	N3	N2	N1	TiN
Nitrogen atom components	High-oxidation states-N	Protonated-N	Pyrrolic-N	Pyridinic-N	TiN
Binding Energy (eV)	401.3	400.3	399.5	398.81	397.5
Ratios (atomic %)	12.2	33.4	12.5	5.0	36.9

Table S5 Values of *A*, *dE/dx* and the diffusion coefficient *D* of NT-LTO/C and LTO electrodes at a discharge voltage of 2.0 V.

Electrodes	*A*	*dE/dx*	*D* (cm^2 s^{-1})
C-LTO	28.22	15.957	3.01×10^{-12}
LTO	163.22	7.422	1.94×10^{-14}

The chemical diffusion coefficients of Li^+ inside NT-LTO/C and LTO electrodes can be estimated from the impedance results. The following expression for Z_w was derived by solving Fick's law:[6]

$$Z_w = A\omega^{-1/2} - jA\omega^{-1/2} \quad \text{(Eq. S3)}$$

$$A = \frac{V_M (dE/dx)}{\sqrt{2} z F D^{1/2} a} \quad \text{(Eq. S4)}$$

where, ω is the frequency, $j = \sqrt{-1}$, and the pre-exponential factor *A* is a constant that contains a concentration independent chemical diffusion coefficient, as shown in **Equation S4**. V_M is the molar volume of LTO (45.73 cm^3 mol^{-1}), *dE*/*dx* values are the slope of the NT-LTO/C and LTO electrode potential curves vs. x in **Figure S5**, *z* is the charge transfer number (z=1 in the lithium intercalation reaction), *a* is the electroactive surface area of the electrode, which is

1.13 cm^2 in our testing electrode, F is the Faraday constant, and *D* is the diffusion coefficient. **Figure S6** displays the dependence of the impedances on the frequencies of the NT-LTO/C and LTO electrodes. Both the real and imaginary parts of the impedance were found to be parallel to each other, and proportional to $\omega^{-1/2}$. Based on the slope of the plot, the value of *A* was obtained. Since *A* is inversely proportional to the chemical diffusion coefficient, *D*, as demonstrated in **Equation S4**, the larger A, the slower the diffusion rate of Li^+ in the solid matrix of the electrode should be. **Table S5** lists the values of the *dE*/*dx*, *A* and *D* of NT-LTO/C and LTO electrodes. The chemical diffusion coefficients of the NT-LTO/C and LTO electrodes are 3.01×10^{-12} cm^2 s^{-1} and 1.94×10^{-14} cm^2 s^{-1}, respectively.

References

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