Supplementary Information

Molecular self-assembly of a nanorod-like N-Li$_4$Ti$_5$O$_{12}$/TiO$_2$/C anode for superior lithium ion storage

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Figure S1

Figure S1 TGA curve for the NT-LTO/C composite in an air atmosphere with a heating rate of 10 °C min⁻¹.
Figure S2 TEM photographs of pristine LTO with mechanical mixing of anatase-TiO$_2$ and LiOH as reactants after the calcination at 750 °C for 5 h in a N$_2$ atmosphere.
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 investigated 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 \((v)\).\(^1\)

\[ i = av^b \quad \text{(Eq. S1)} \]
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). 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 processes and capacitive-controlled process are quantitatively separated through the method by Dunn and co-workers:3

\[ i = k_1v + k_2v^{1/2} \]  
(Eq. S2)

In Equation S2, \( k_1v \) and \( k_2v^{1/2} \) 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 \( k_1v \) and \( k_2v^{1/2} \). 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 \( (k_1v) \) 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 The discharge and charge profiles for the pristine LTO electrode at various rates from 0.5 C to 100 C.
Figure S5

(a) NT-LTO/C

(b) pristine LTO

Figure S5 The relationship of the voltage vs. x in NT-LTO/C and LTO electrodes.
Figure S6 Real and imaginary parts of the complex impedance vs. $\omega^{-1/2}$ for the NT-LTO/C and LTO electrodes.
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$_4$Ti$_5$O$_{12}$ 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 $R_{wp}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>g</th>
<th>U</th>
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<tbody>
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<td>0.1667</td>
<td>0.0000</td>
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<td>0.6250</td>
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<tr>
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<td>1.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

$a=8.357$ Å  $b=8.357$ Å  $c=8.357$ Å  $\alpha=\beta=\gamma=90^\circ$

<table>
<thead>
<tr>
<th>Atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>g</th>
<th>U</th>
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<td>0.7500</td>
<td>0.3333</td>
<td>1.0000</td>
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$a=3.785$ Å  $b=3.785$ Å  $c=9.514$ Å  $\alpha=\beta=\gamma=90^\circ$

**R-factors and weight fraction**

$R_{wp} = 9.77\%$  $R_p = 7.26\%$  $S = 1.5914$

Li$_4$Ti$_5$O$_{12}$ : 95.48%  TiO$_2$ : 4.52%
Table S2 Ratio analysis of the peaks in the XPS spectrum of the NT-LTO/C composite

<table>
<thead>
<tr>
<th>Ratios (% at.)</th>
<th>Li</th>
<th>Ti</th>
<th>O</th>
<th>C</th>
<th>N</th>
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</thead>
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<tr>
<td>NT-LTO/C</td>
<td>11.3</td>
<td>36.6</td>
<td>38.7</td>
<td>11.0</td>
<td>2.4</td>
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<tr>
<td>Binding Energy (eV)</td>
<td>Ti(^{4+})2p(^{1/2})</td>
<td>Ti(^{3+})2p(^{1/2})</td>
<td>Ti(^{4+})2p(^{3/2})</td>
<td>Ti(^{3+})2p(^{3/2})</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td></td>
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<tr>
<td>Ratios (% at.)</td>
<td>14.41</td>
<td>14.57</td>
<td>47.96</td>
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Table S4 N1s composition from XPS

<table>
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<th>Peaks</th>
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<th>N3</th>
<th>N2</th>
<th>N1</th>
<th>TiN</th>
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<td>Protonated-N</td>
<td>Pyrrolic-N</td>
<td>Pyridinic-N</td>
<td>TiN</td>
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<td>400.3</td>
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<td>397.5</td>
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<tr>
<td>Ratios (atomic %)</td>
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<td>33.4</td>
<td>12.5</td>
<td>5.0</td>
<td>36.9</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>$A$</th>
<th>$dE/dx$</th>
<th>$D$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-LTO</td>
<td>28.22</td>
<td>15.957</td>
<td>3.01×10$^{-12}$</td>
</tr>
<tr>
<td>LTO</td>
<td>163.22</td>
<td>7.422</td>
<td>1.94×10$^{-14}$</td>
</tr>
</tbody>
</table>

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:

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

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

where, $\omega$ 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 cm² 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 \( \frac{dE}{dx} \), \( A \) and \( D \) of NT-LTO/C and LTO electrodes. The chemical diffusion coefficients of the NT-LTO/C and LTO electrodes are \( 3.01 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1} \) and \( 1.94 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1} \), respectively.

**References**