Supplementary Material

Architectural design and phase engineering of N/B-codoped TiO₂(B)/anatase nanotube assemblies for high-rate and long-life lithium storage

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Fig. S1. TEM images of the products prepared for different ionothermal reaction time: (a) 6 h, (b) 12 h, and (c) 30 h. (d) Illustration of the time-dependent morphology evolution.
Fig. S2. (a) SEM image (inset shows the magnified SEM image), (b) XRD pattern, (c) TEM image, and (d) HRTEM image for the Na$_2$Ti$_3$O$_7$ (NTO) product.

Fig. S3. (a,b,c,d) SEM, TEM, HRTEM images and XRD pattern for the TiO$_2$ nanorod assemblies. (e,f,g,h) TEM, HRTEM images and XRD pattern for the TiO$_2$(B) nanobelts.
**Fig. S4.** Volume comparison of the TiO$_2$ nanotube assemblies and the TiO$_2$(B) nanobelts with the same mass.

**Fig. S5.** High resolution XPS spectra of TiO$_2$ nanorod assemblies: (a) B 1s; (b) N 1s; and (c) Ti 2p.
Fig. S6. CV curves of the TiO$_2$ nanotube assemblies at different scan rates.

Fig. S7. Capacity contribution varies upon the TiO$_2$ products from Region I to IV.
Fig. S8. Possible N/B doping sites in TiO$_2$(B). (a) O atoms substituted sites by nitrogen or boron; (b) interstitial sites for nitrogen doping.

**Supplementary Method: DFT calculation details**

Considering the majority of the phase composition in the product of TiO$_2$ nanotube assemblies is TiO$_2$(B) (~81%), only TiO$_2$(B) was taken into account in the first principle calculations. Nitrogen (~2 at.%) can be located in the lattice of TiO$_2$ interstitially or substitutionally and boron (~1 at.%) can be located in substitutionally combining our XPS results. The formation possibilities of three types of doping are investigated.

To discuss the N-doped TiO$_2$, we calculated interstitial and substitutional sites respectively. The possible substitutional and interstitial doping sites are shown in Figure S8a and b, respectively. The following formulas are used to calculate the N-doped formation energy, $E_f$, and listed in Table S1.

For O atoms substituted by nitrogen:

$$E_f = E_{doped-TiO_2} - E_{bulk-TiO_2} - \frac{1}{2} E_{N_2(g)} + \frac{1}{2} E_{O_2(g)}$$

For interstitial nitrogen doping:

$$E_f = E_{doped-TiO_2} - E_{bulk-TiO_2} - \frac{1}{2} E_{N_2(g)}$$

Here $E_{doped-TiO_2}$ is the total energy of N-doped TiO$_2$-B bulk, $E_{bulk-TiO_2}$ is the total energy of TiO$_2$(B) bulk, $E_{N_2(g)}$ is the energy of one N$_2$ molecular, and $E_{O_2(g)}$ is the energy of one O$_2$ molecular.

The formation energy shows that the S$_N$4 and I$_N$2 sites can be formed easier than the other sites. Thus, these two sites are chosen for N doping sites in the N-doped TiO$_2$. Figure 7c shows the relaxed structure of mixed N-doped TiO$_2$. Based on the above analysis, B doping sites in the N/B-codoped TiO$_2$(B) are calculated, and the
influences between defects are ignored. The codoped defects formation energy, $E_f$, is defined as follow and listed in Table S1.

$$E_f = E_{doped-TiO_2} - E_{bulk-TiO_2} - E_{N_2(g)} - E_{o-B} + \frac{1}{2} E_{O_2(g)}$$

Here $E_{o-B}$ refers to the energy of one boron atom in the TiO$_2$(B) bulk. The results show that site S$_B$4 is more stable. These structures shown in Figure 7a, c and e are employed to represent undoped TiO$_2$, N-doped TiO$_2$, N/B-codoped TiO$_2$ and their density of states (DOSs) are displayed in Figure 7b, d and f.

**Supplementary Table S1.** Defect formation energy of TiO$_2$(B).

<table>
<thead>
<tr>
<th>Sites</th>
<th>$S_N1$</th>
<th>$S_N2$</th>
<th>$S_N3$</th>
<th>$S_N4$</th>
<th>$I_N1$</th>
<th>$I_N2$</th>
<th>$I_N3$</th>
<th>$S_B1$</th>
<th>$S_B2$</th>
<th>$S_B3$</th>
<th>$S_B4$</th>
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<tr>
<td>$E_f$/eV</td>
<td>5.67</td>
<td>5.54</td>
<td>5.73</td>
<td>5.46</td>
<td>4.34</td>
<td>4.06</td>
<td>5.22</td>
<td>13.4</td>
<td>12.6</td>
<td>12.6</td>
<td>12.0</td>
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We should also note that the calculated band gap of pure TiO$_2$(B) is about 2.344 eV (see Figure 7b) while the experimental value is reported to be 3–3.2 eV. The underestimation always exists in the band gap calculations due to the well-known limitation of the DFT theory. However, our discussions about energy gap will not be affected because only the relative energy changes are to be concerned, and the trend of the energy gap is expected to be reasonable and reliable.$^{1,2}$

**Supplementary Table S2.** The diffusion coefficients ($D_{Li}$) of the three electrodes and the corresponding data.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$\delta$</th>
<th>$dE/dx$</th>
<th>$A$ (cm$^{-2}$)</th>
<th>$D_{Li}$</th>
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<tr>
<td>nanobelts</td>
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<td>1.69</td>
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<tr>
<td>nanotubes</td>
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<td>0.94</td>
<td>1.23</td>
<td>5.68 x 10$^{-14}$</td>
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<td>nanorods</td>
<td>97.92</td>
<td>0.85</td>
<td>0.46</td>
<td>8.72 x 10$^{-15}$</td>
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**Supplementary references**