Supplementary Information

A 3D porous architecture composed of TiO\textsubscript{2} nanotubes connected with a carbon nanofiber matrix for fast energy storage

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Fig. S1. XRD pattern of ST-TiO$_2$/C.
Fig. S2. Raman spectra of ST-TiO$_2$/C and 3D-TiO$_2$/C.

In both Raman spectra, two broad peaks were observed at approximately 1345 cm$^{-1}$ and 1603 cm$^{-1}$, indicating the successful formation of the carbon matrix. The former peak is named the D band, corresponding to the in-plane vibrations of disordered carbon, whereas the latter peak is referred to as the G band, indicating the E$_{2g}$ mode of graphite. The ratios of the D band to the G band ($I_D/I_G$) were 1.94 and 1.96 for ST-TiO$_2$/C and 3D-TiO$_2$/C, respectively. The similarities between these values indicated that there was no obvious change in the graphitization degree of the carbon after the hydrothermal treatment.
Fig. S3. Thermogravimetric analysis (TGA) of 3D-TiO$_2$/C. The weight loss below 100 °C is most likely caused by the evaporation of the absorbed moisture contents, which is common for materials with a large surface area. The carbon content was calculated based on the weight at 100 °C because the weight of the film electrode was determined after being dried under vacuum at 100 °C, (94.7 wt.%-75.1 wt.%)/94.7 wt.%=20.7 wt.%.
**Fig. S4.** FE-SEM image of the cross-section of the 3D-TiO$_2$/C film.
Fig. S5. (a) XPS survey spectrum and (b, c) XPS spectra of Ti 2p\textsubscript{3/2-1/2} and C 1s of 3D-TiO\textsubscript{2}/C; (d, e) XPS spectra of Ti 2p\textsubscript{3/2-1/2} and C 1s in ST-TiO\textsubscript{2}/C.

The X-ray photoelectron spectroscopy (XPS) analysis of the 3D-TiO\textsubscript{2}/C sample was conducted from 0 to 1000 eV (Fig. S5a). Ti, O and C elements were detected. The high resolution spectrum of Ti 2p in 3D-TiO\textsubscript{2}/C is shown in Fig. S5b. The presence of two unique
peaks at 459.0 eV (Ti 2p_{3/2}) and 464.7 eV (Ti 2p_{1/2}) corresponded to a +4 formal oxidation state for the Ti atoms in an octahedral environment. However, the starting raw material for the hydrothermal reaction, ST-TiO_2/C, showed additional peaks at lower binding energies (457.6-462.1 eV) due to the presence of a +3 formal oxidation state for the Ti atoms after the heat treatment under the reducing H_2/Ar atmosphere at high temperature (Fig. S5d). The disappearance of the +3 valence state in the 3D-TiO_2/C sample may be due to the oxidation reaction with dissolved oxygen during the hydrothermal treatment. In comparison with ST-TiO_2/C, the C 1s peak of 3D-TiO_2/C exhibited the similar peak shape, which can be divided into three peaks associated to in situ produced carbon from PVP and hydrocarbon contamination (284.6 eV), C-O type carbon (285.7 eV) and small amounts of COO type carbon (288.9 eV) (Fig. S5c&e). The slightly increased amount of C-O and COO carbon types in the 3D-TiO_2/C sample suggested that the carbon surface was functionalized due to the concentrated alkali environment during the hydrothermal treatment. This process may allow the carbon surface to be more easily connected with the TiO_2 nanotubes so that the nanotubes will not be dispersed in the solution.
Fig. S6. FE-SEM images of the hydrothermally treated ST-TiO2/C with 10 M NaOH solution at 150 °C for different time: (a, b, c) 1 h, (d, e, f) 3 h, (g, h, i) 10 h, (j, k, l) 17 h and (m, n, o) 24 h; (a, b, d, e, g, h, j, k, m, n) surface of the corresponding film; (c, f, i, l, o) cross-section of the corresponding film; the white round marks in (c, f, i, l, o) indicate the cross-section of the carbon nanofiber sites.
Fig. S7. High-resolution FE-SEM images of the hydrothermally treated ST-TiO$_2$/C with 10 M NaOH solution at 150 °C for 1 h.
Fig. S8. Differential capacity plot of the 3D-TiO$_2$/C electrode at the first cycle. The lithium storage in TiO$_2$(B) and anatase was determined through PsVoigt1 functions.
**Fig. S9.** Comparison of the capacities at different current densities for the 3D-TiO$_2$ electrode with other hydrothermally synthesized TiO$_2$-based electrodes that were reported previously. The capacities were calculated on the basis of the total weight of the electrode materials (active materials+conductive carbon+binder). Here, the capacities of the 3D-TiO$_2$ electrode were calculated on the basis of the total weight of the TiO$_2$/C composite films, which were used without the application of any additional conductive agent or binder. The listed ratio (e.g., 75:18:7) is the mass ratio of the active materials:conductive carbon:binder.
Fig. S10. (a, b) TEM images of the 3D-TiO$_2$/C electrode after cycling 2160 times at 30 °C; (c) XRD pattern of the 3D-TiO$_2$/C electrode after cycling 1941 times at 30 °C; (d) differential capacity plot of the 3D-TiO$_2$/C electrode at the 500th cycle in Fig. 12a.

As shown in Fig. S8 a-c, the 3D-TiO$_2$/C electrode exhibited excellent structure and morphology durability (The peaks in Fig. S8c of the Ag phase were due to the modified rough surface layer on the current collector [38]). Fig. S8d shows that the redox peaks could be sustained even after 500 cycles, which also indicates the excellent structure durability.
**Table S1.** Textural properties of ST-TiO$_2$/C and 3D-TiO$_2$/C.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
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<tbody>
<tr>
<td>ST-TiO$_2$/C</td>
<td>267.1</td>
<td>0.270</td>
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<tr>
<td>3D-TiO$_2$/C</td>
<td>502.9</td>
<td>2.062</td>
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