

## Electronic Supplementary Material

# Ultrathin nanobelts-assembled Chinese knot-like 3D TiO<sub>2</sub> for fast and stable lithium storage

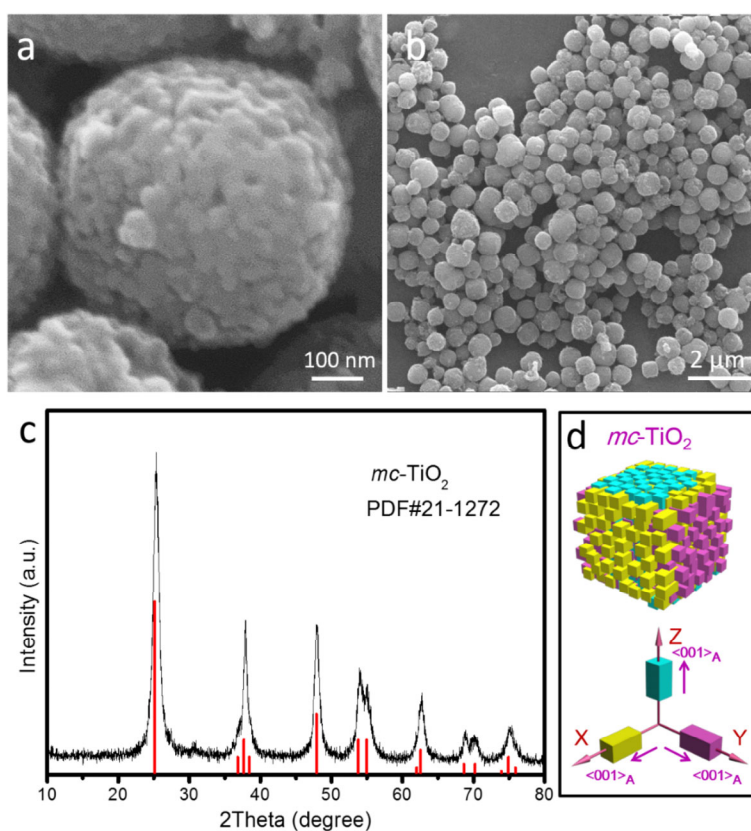
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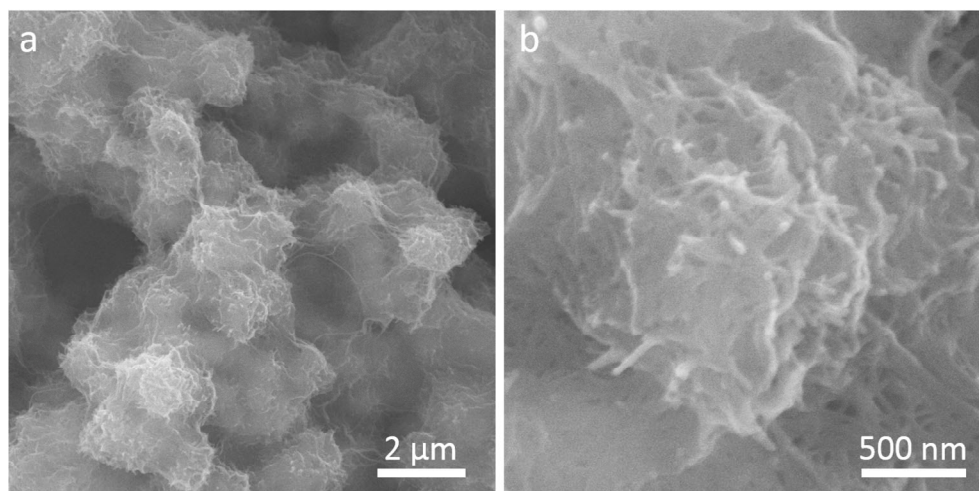
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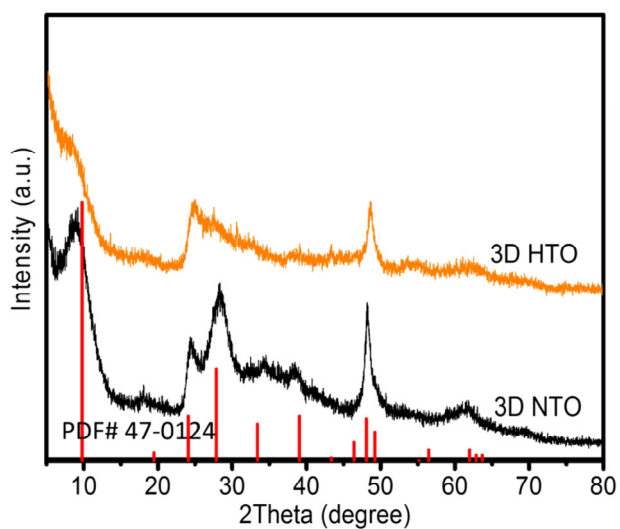


**Figure S1** High (a) and low (b) magnification SEM images of the *mc*-TiO<sub>2</sub> microcages, and the corresponding XRD patterns (c). (d) A structure model of *mc*-TiO<sub>2</sub> (up) and the illustration of the perpendicular relationship between the corresponding building blocks (down).

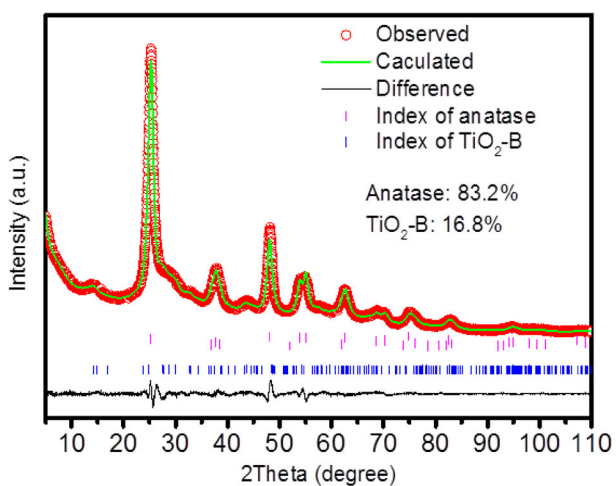
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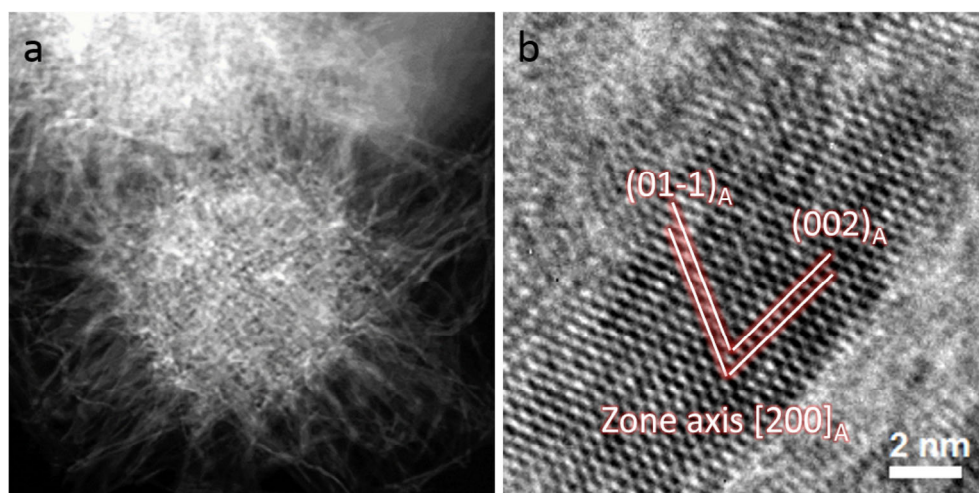
**Figure S2** SEM images of 3D NTO.



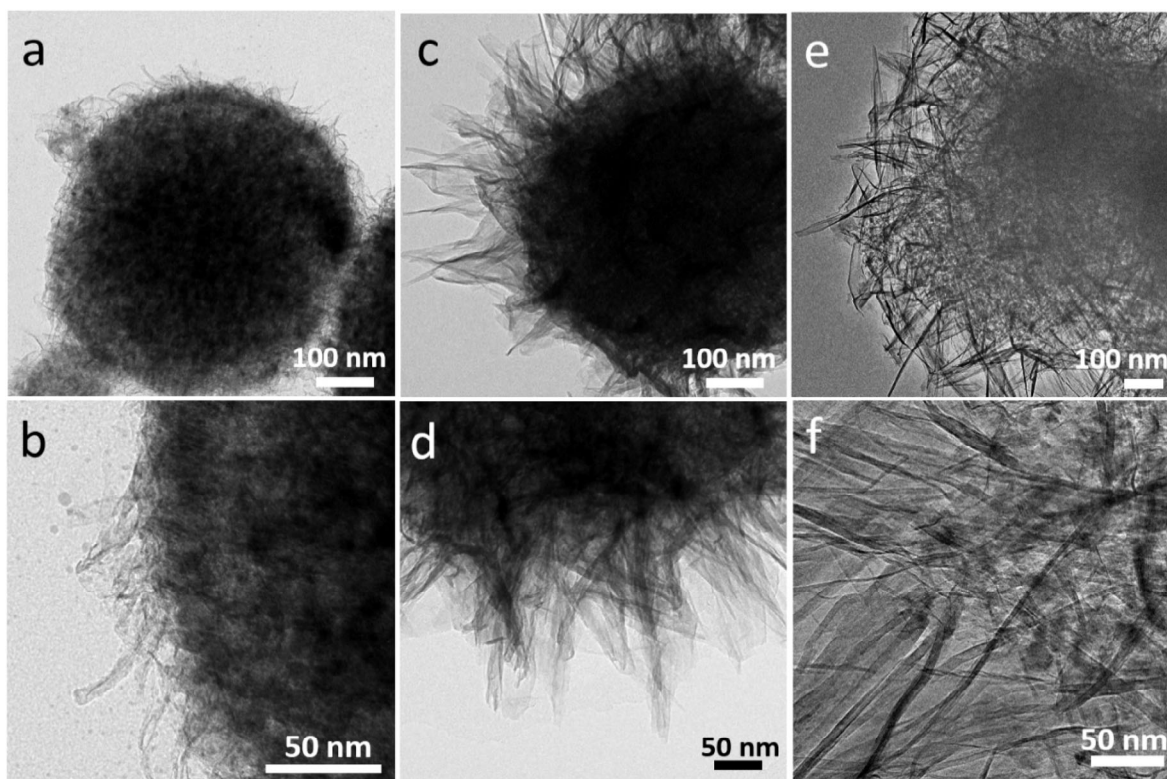
**Figure S3** XRD patterns of 3D NTO and 3D HTO. The red lines are the standard diffractions of  $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$  (PDF#47-0124,  $a = 0.3784$  nm,  $b = 1.803$  nm and  $c = 0.2998$  nm).



**Figure S4** Rietveld refinement analysis of XRD pattern of 3D  $\text{TiO}_2$ . Anatase: PDF#21-1272,  $\text{TiO}_2$ -B: PDF#35-0088.

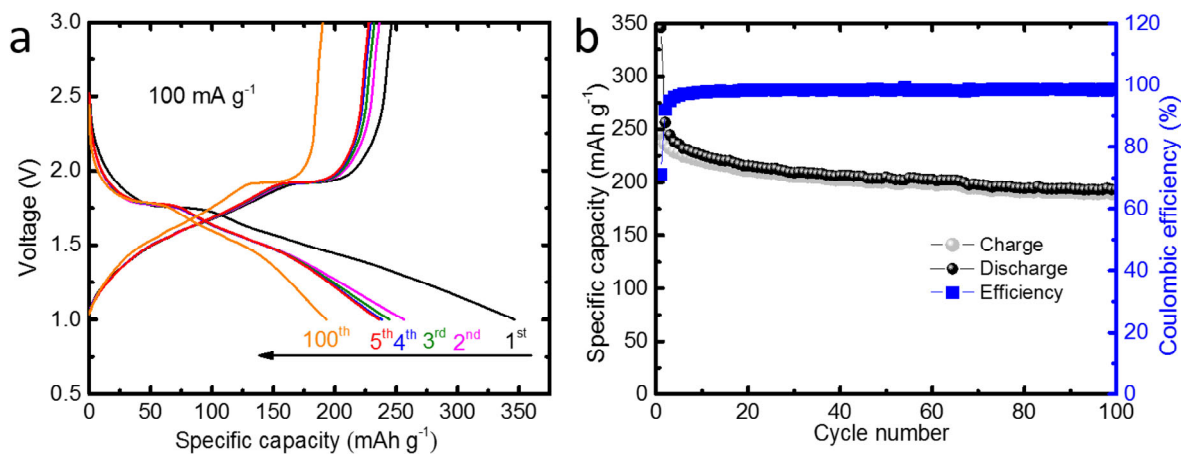


**Figure S5** (a) STEM and (b) HRTEM images of 3D TiO<sub>2</sub>.

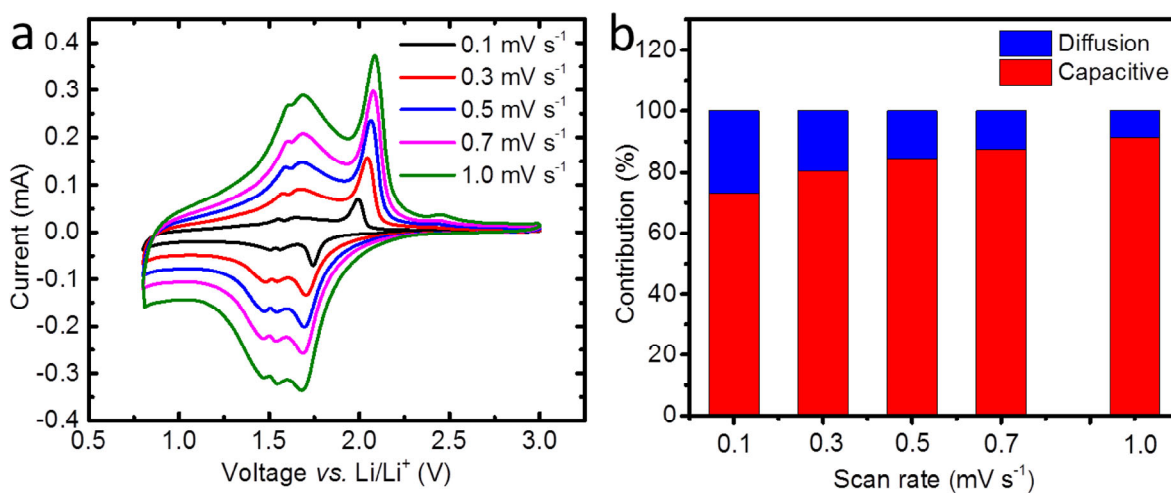


**Figure S6** TEM images of *mc*-TiO<sub>2</sub> treated in 10M NaOH for 1 h (a, b), 2 h (c, d), and 4 h (e, f).

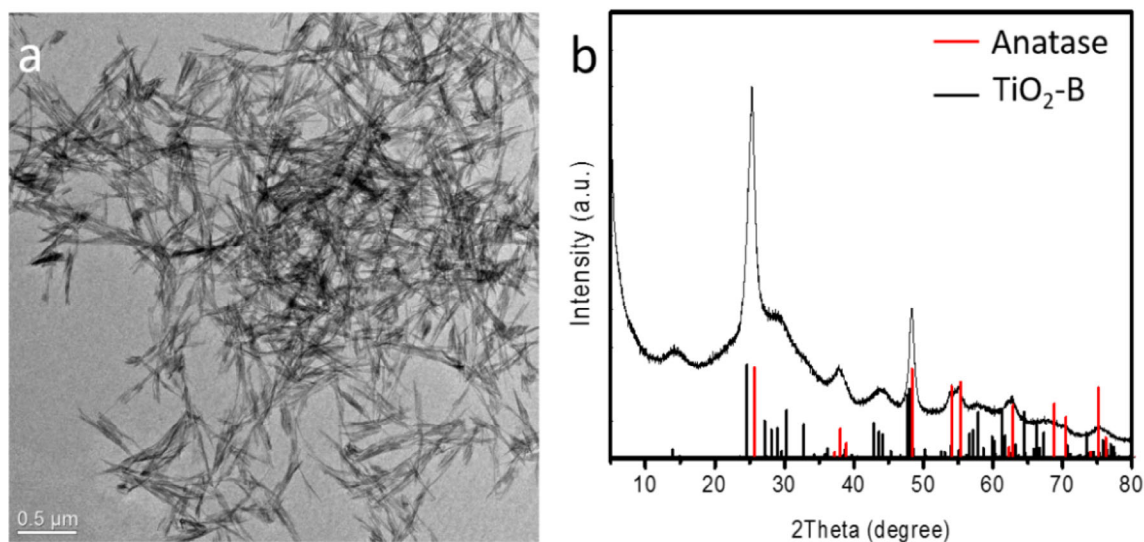
When treated with 10 M NaOH for 1 h, some tiny nanosheets were observed at the surface of the microcages (Fig. S6a and S6b). The nanosheets all tilt to the same direction forming a similar angle with the surface of the microcage, confirming that anatase nanoparticles oriented in the same direction will be delaminated in the same direction. These small nanosheets grew to be larger and longer after 2 h reaction (Fig. S6c and S6d). But the interior of the microcage remained non-delaminated. When the reaction time extended to 4 h, 3D nanoarchitecture constructed by perpendicularly oriented ultrathin nanobelts was clearly observed with few anatase nanoparticles inside (Fig. S6e and S6f).



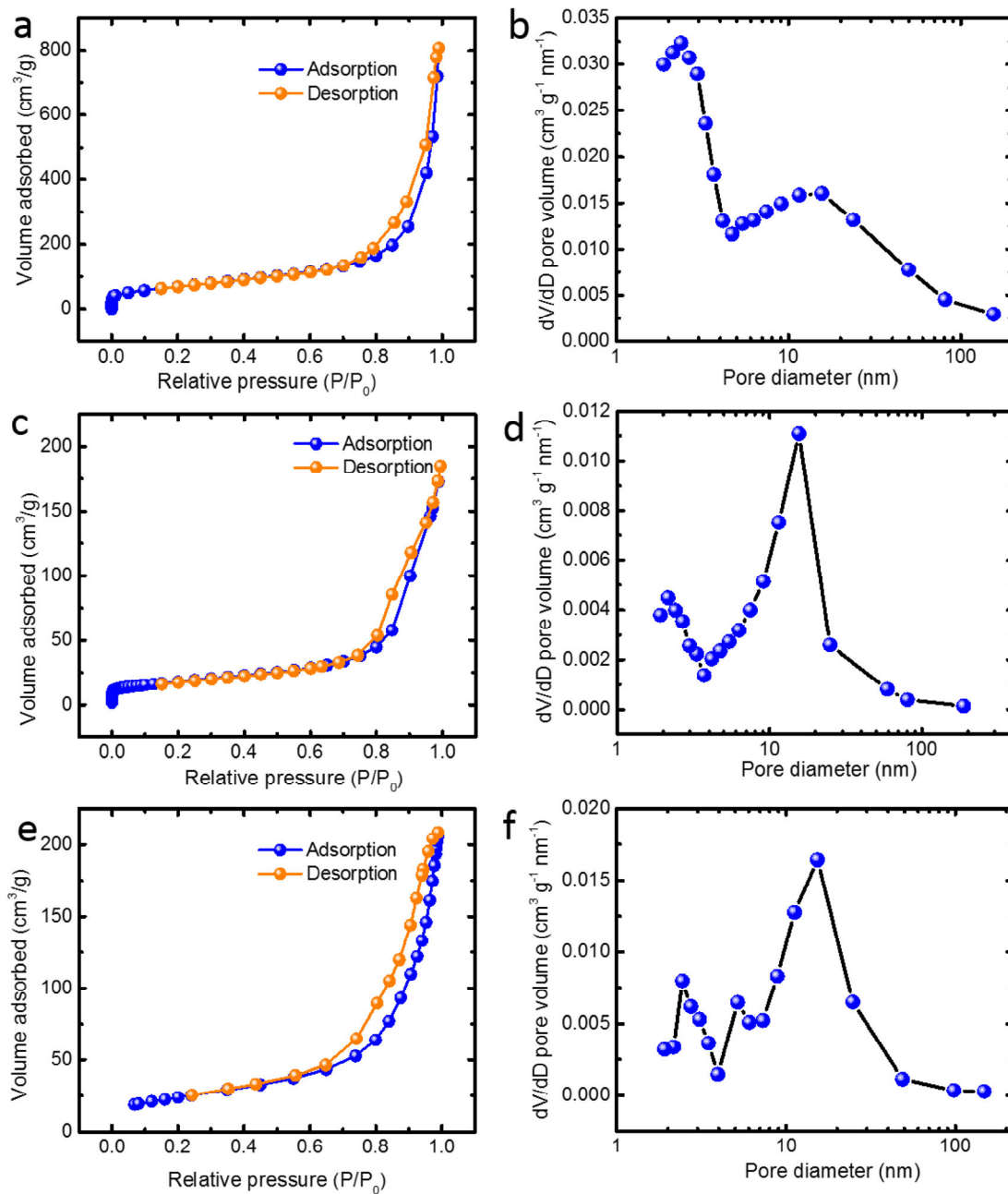
**Figure S7** (a) The galvanostatic discharge-recharge curves of 3D TiO<sub>2</sub> at the current densities of 100 mA g<sup>-1</sup> (0.5 C). (b) Cycling capacity of 3D TiO<sub>2</sub> at 100 mA g<sup>-1</sup> (0.5 C) for 100 cycles.



**Figure S8** (a) CV curves of 3D TiO<sub>2</sub> at the scan rates from 0.1 to 1 mV s<sup>-1</sup>. (b) Normalized contribution ratio of capacitive effect (red) and diffusion-controlled reactions (blue) at the corresponding scan rates in (a).



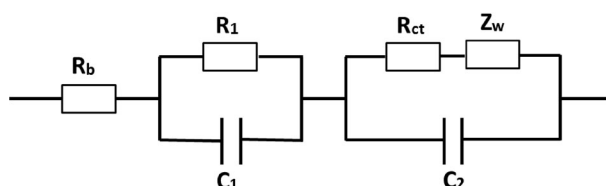
**Figure S9** TEM image (a) and XRD patterns (b) of dispersive TiO<sub>2</sub> nanobelts.



**Figure S10** Nitrogen adsorption and desorption isotherms and the pore size distributions of dispersive nanobelts (a, b), AB550 (c, d) and *mc*-TiO<sub>2</sub>-400 (e, f).

**Table S1** Porous structure parameters of 3D TiO<sub>2</sub>, dispersive nanobelts, AB550, and *mc*-TiO<sub>2</sub>-400.

Samples	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore size (nm)
3D TiO <sub>2</sub>	302	1.23	11
Dispersive nanobelts	247	1.25	2.5 and 14
AB550	62.3	0.29	15
<i>mc</i> -TiO <sub>2</sub> -400	79.1	0.42	2.5 and 15



**Figure S11** A proposed equivalent circuit for the data in Fig. 3d.

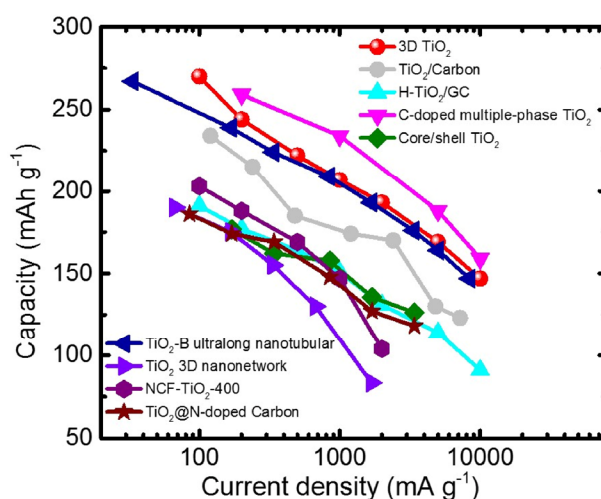
**Table S2** Fitted Impedance Parameters of the Equivalent Circuit in Fig. S10.

Sample	$R_b/\text{Ohm}$	$R_1/\text{Ohm}$	$R_{ct}/\text{Ohm}$	$Z_w/\text{Ohm}$
3D TiO <sub>2</sub>	1.74	12.2	61.8	120
Dispersive TiO <sub>2</sub>	2.05	16.7	114	258
AB550	1.60	17.5	102	157
<i>mc</i> -TiO <sub>2</sub> -400	2.07	29.9	132	304

The lithium-ion diffusion coefficients of the four samples are estimated using the inclined lines in the Warburg region and based on the following equation (Eq. s1):

$$D_{Li} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (\text{S1})$$

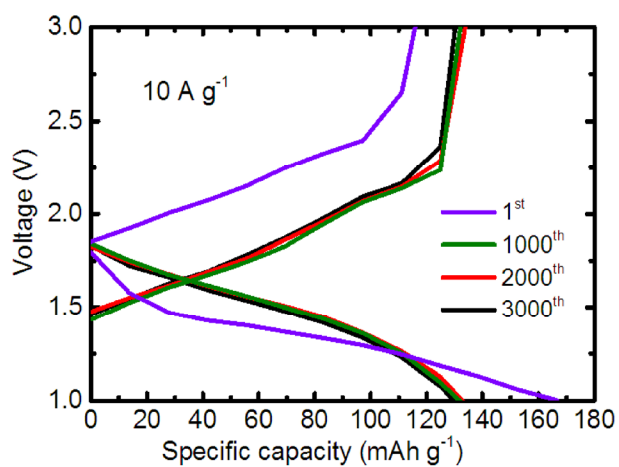
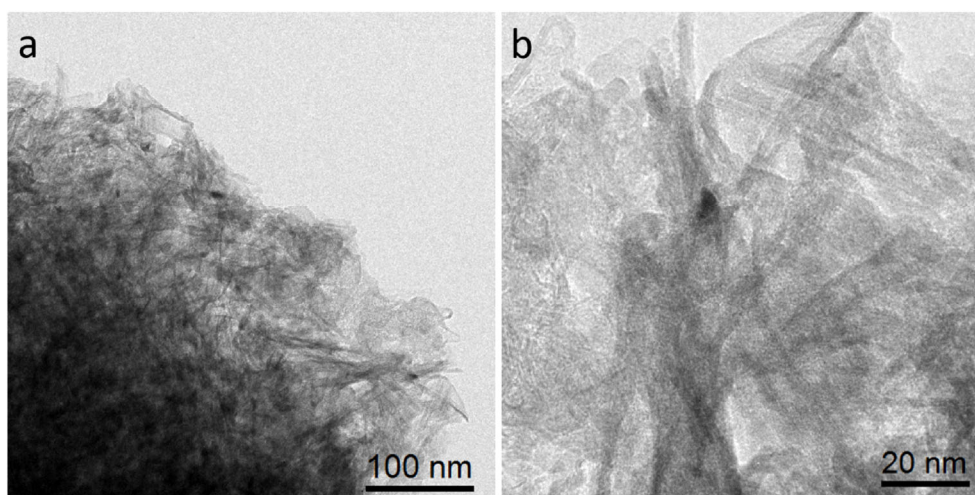
where  $R$  is the gas constant ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature ( $T = 298 \text{ K}$ ),  $A$  is the surface area of the cathode ( $A = 1.13 \text{ cm}^2$ ),  $n$  is the number of electrons per molecule during reaction ( $n = 1$ ),  $F$  is the Faraday constant ( $F = 96485 \text{ C/mol}$ ),  $C$  is the concentration of lithium ions ( $C = 7.69 \times 10^{-3} \text{ mol cm}^{-3}$ ), and  $\sigma$  is the Warburg factor which can be determined by linearly fitting the  $Z'$  vs. the square root of frequency  $\omega^{-1/2}$ . The lithium ion diffusion coefficients in the 3D TiO<sub>2</sub>, dispersive nanobelts, AB550 and *mc*-TiO<sub>2</sub>-400 were calculated to be  $8.37 \times 10^{-15}$ ,  $3.29 \times 10^{-15}$ ,  $5.44 \times 10^{-14}$ ,  $6.91 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ . These results conflict with the lithium storage performances presented in Figure 3c, therefore, the superior lithium storage performance of 3D TiO<sub>2</sub> can be attributed to the high surface area and in favored pseudocapacitance at high current rates.



**Figure S12** Rate performance comparison of the as-prepared 3D TiO<sub>2</sub> and other recently reported TiO<sub>2</sub> nanostructures. 3D TiO<sub>2</sub> (this work, 70:20:10), TiO<sub>2</sub>/Carbon (80:15:5) [1], H-TiO<sub>2</sub>/GC (90:0:10) [2], C-doped multiple-phase TiO<sub>2</sub> (80:15:5) [3], core/shell TiO<sub>2</sub> (70:20:10) [4], TiO<sub>2</sub>-B ultralong nanotubular (100:0:0) [5], 3D TiO<sub>2</sub> nanonetwork (66:26:8) [6], NCF-TiO<sub>2</sub>-400 (100:0:0) [7] and TiO<sub>2</sub>@N-doped Carbon (50:30:20) [8].

**Table S3** Cycling stability comparison of 3D TiO<sub>2</sub> and other reported TiO<sub>2</sub> nanostructures.

Sample	Current density (mA g <sup>-1</sup> )	Initial/Final capacity (mAh g <sup>-1</sup> )	Cycle number	Capacity retention	Capacity fading of each cycle (mAh g <sup>-1</sup> )
3D TiO <sub>2</sub> (this work)	10000	167/130	3000	77.8%	0.0123
TiO <sub>2</sub> /Carbon [1]	1200	174/154	300	88.5%	0.0667
H-TiO <sub>2</sub> /GC [2]	1000	150/137	1000	91.3%	0.012
C-doped multiple-phase TiO <sub>2</sub> [3]	2000	220/204	280	92.7%	0.571
Core/shell TiO <sub>2</sub> [4]	170	385/151	100	39.2%	2.34
TiO <sub>2</sub> -B ultralong nanotubular [5]	8400	175/114	10000	65.1%	0.0061
3D TiO <sub>2</sub> nanonetwork [6]	335	154/128	200	83.1%	0.13
NCF-TiO <sub>2</sub> -400 [7]	1000	149/223	100	66.8%	0.74
TiO <sub>2</sub> @N-doped Carbon [8]	1700	130/117	2000	90%	0.0065

**Figure S13** The galvanostatic discharge-recharge curves of 3D TiO<sub>2</sub> at the current density of 10 A g<sup>-1</sup> (50 C).**Figure S14** TEM images of 3D TiO<sub>2</sub> after 1000 cycles at 1 A g<sup>-1</sup> (5 C).

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