

Electronic Supplementary Information (ESI)

Fabrication of TiO₂@carbon core-shell nanosheets for advanced lithium-ion batteries with excellent cyclability

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Material preparation

Synthesis of titanate nanosheets

Lepidocrocite-type cesium titanate (Cs_{0.7}Ti_{1.825}O₄) and its protonated derivative were prepared by the high temperature solid state reaction followed by exchange of interlayer cesium ions with protons via 1.0 M HCl treatment).^{1, 2} The titanate nanosheets were prepared by exfoliation of the protonated titanate with tetrabutyl ammonium hydroxide (TBAOH).^{1, 2}

Synthesis of TiO₂@carbon

The TiO₂@carbon (TC) nanosheets were synthesized by the following procedure. Firstly, the exfoliated titanate nanosheets (40 mL, 5 g L⁻¹) sol was added dropwise into CTAB solution (330 mL, 6 g L⁻¹) under vigorous agitation to obtain a white mixed sol. Then, P123 solution (20 mL, 100 g L⁻¹) was added into the mixed sol under stirring for 2 h. To the above mixed solution, NaCl solution (80 mL, 50 g L⁻¹) was added slowly into the homogeneous mixture under vigorous stirring. The obtained homogeneous mixture was freeze-dried and then calcined at 873 K in N₂ atmosphere for 4 h. NaCl was removed through washing by the mixed solvent of water and ethanol. The final black product was dried in a vacuum oven at 80 °C overnight. As a comparison, pure TiO₂ was prepared from exfoliated titanate nanosheets by the similar method but without addition of CTAB and P123.

Material Characterization

X-ray diffraction (XRD) analysis was performed on a Philips X'Pro X-ray diffractometer with Cu K_α irradiation. The X-ray source was operated at 40 kV and 40 mA. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements were conducted with JEM-1011S and JEM-2010 electron microscopes, using an accelerating voltage of 80 kV and 200 kV, respectively. Scanning electron microscopy (SEM) measurements were conducted with a Hitachi S4800 instrument. Nitrogen sorption/desorption isotherms are collected at 77K using

Micromeritics ASAP2020 equipment. Raman spectra were recorded in a Bruker Multi RAM FT-Raman spectrometer. (Laser source: 532 nm light). X-ray photoelectron spectra (XPS) were recorded on a Thermo Fisher by using Al K α radiation (15 kV, 150W). A 30 s argon ion etching, which was operated with an accelerating voltage of 4 kV, was used to remove the surface species and examine the compositions in the bulk. All binding energies (BEs) were referenced to the C1s peak at 284.6 eV.

Electrochemical measurement

Electrochemical experiments were carried out using CR2032 type coin cells with lithium metal as both the counter and reference electrodes at room temperature. The working electrodes, which were fabricated by a conventional coating method, were composed of a mixture of the as-synthesized active material (60 wt %), super-P (conducting additive, 20 wt %), and polyvinylidene fluoride (binder, 20 wt %). N-Methyl-2-pyrrolidone (NMP) was used as the solvent to make slurry, which was uniformly spread onto a copper foil current collector. The electrodes were dried at 353 K for four hours in an oven and then pressed and dried at 393 K overnight under vacuum. The mass loading of the active materials is about 0.5 mg cm⁻² and the thickness of the electrodes is 0.15 mm. Cell assembly was carried out in an argon-filled glove box in which both oxygen and moisture levels were kept less than 1 ppm. 200 μ L electrolyte of 1.0 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC)–DMC–ethyl methyl carbonate (EMC) (1: 1: 1 in weight) was used as an electrolyte solution. A Celgard 2325 film was used as the separator. Cyclic voltammetry (CV) was performed at room temperature on an electrochemical station (CHI660D). CV tests were carried out over the potential range from 3.0 to 0.01 V (vs. Li⁺/Li) at a scanning rate of 0.2 mV s⁻¹. Galvanostatic discharge–charge experiments were tested at various current densities in a voltage range of 0.01 to 3.0 V (vs. Li⁺/Li) using a battery test system (LAND CT2001A model, Wuhan Jinnuo Electronics Co. Ltd.).

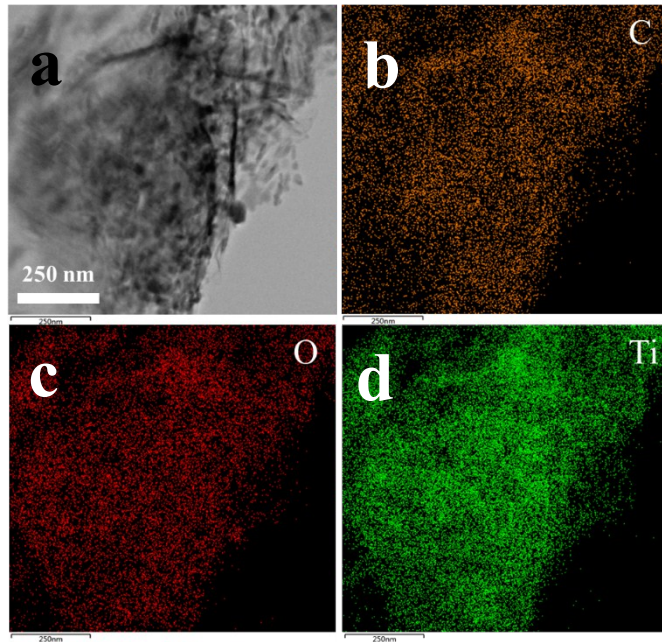


Fig. S1 STEM and corresponding element mapping of TiO₂@C nanosheets.

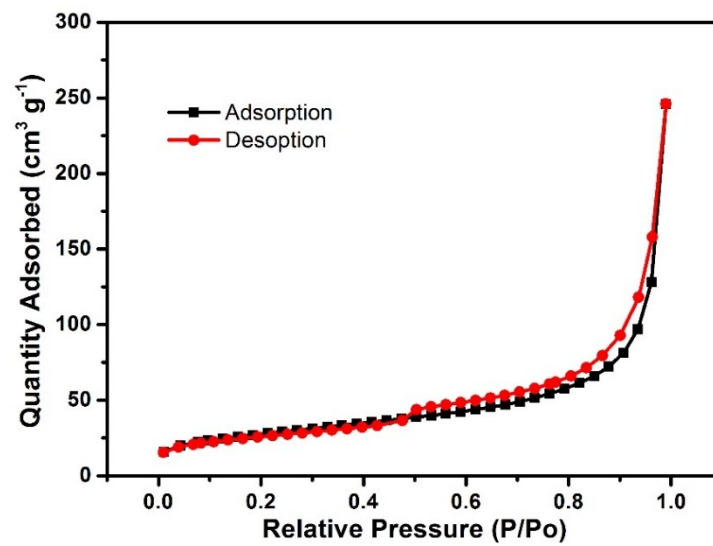


Fig. S2 Nitrogen adsorption-desorption isotherms of TiO₂@C nanosheets.

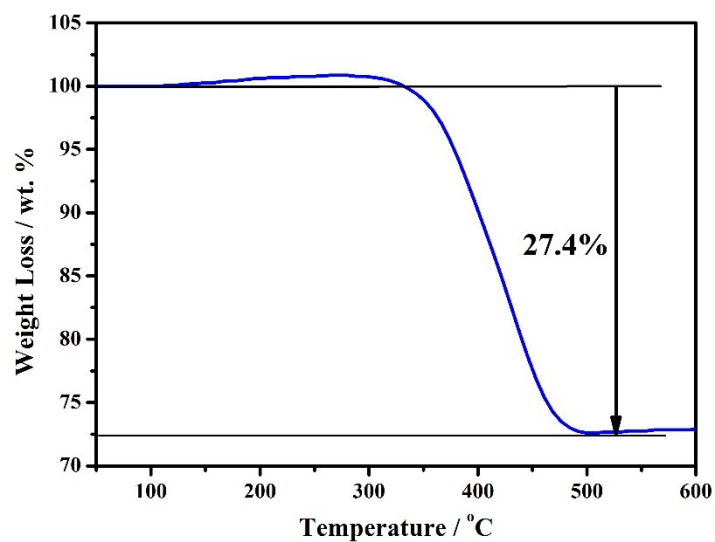


Fig. S3 TGA curve of TiO₂@C nanosheets measured under air atmosphere.

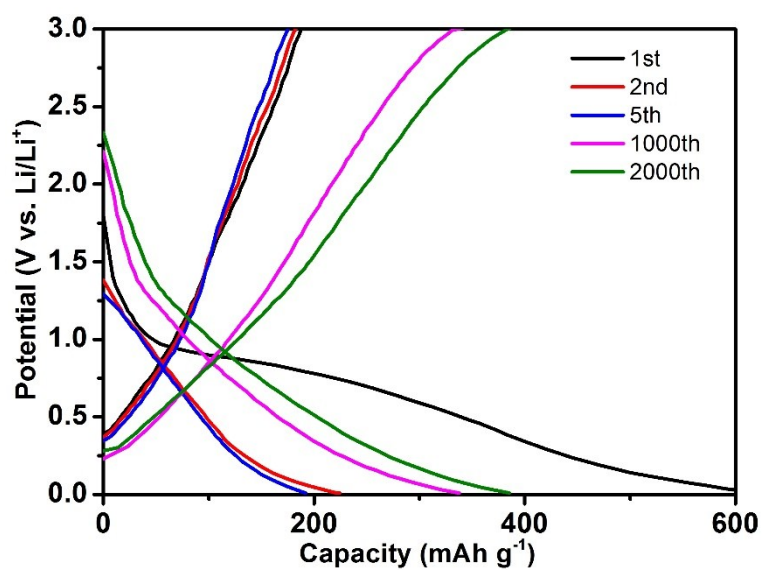


Fig. S4 Discharge curves for different cycles at 4.6 A g⁻¹.

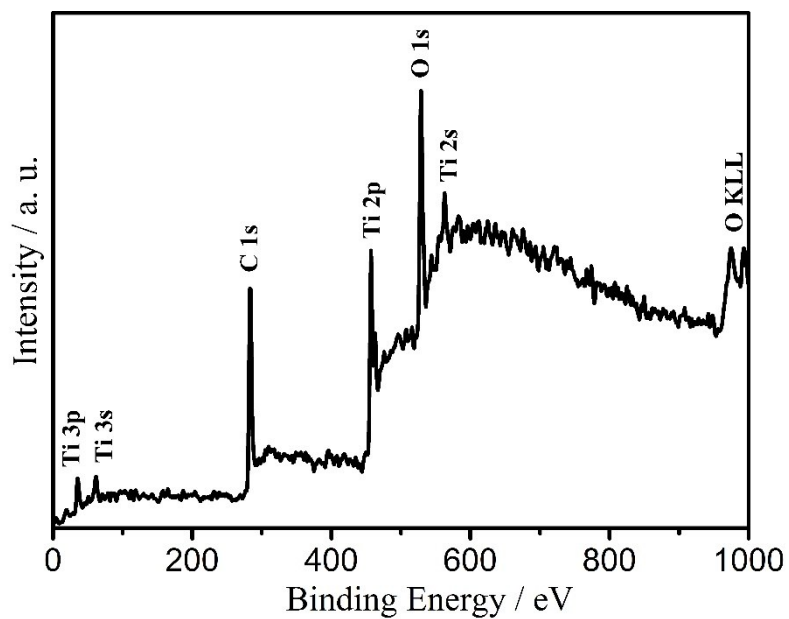


Fig. S5 X-ray photoelectron spectrum (XPS) of TiO_2 @C nanosheets.

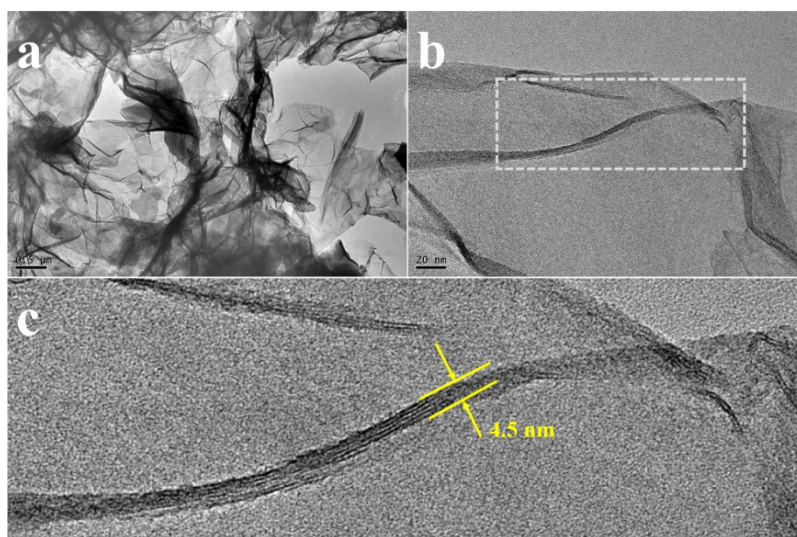


Fig. S6 TEM images of pure TiO_2 nanosheets without coating carbon.

Table S1 Comparison of the LIBs performances of the TiO₂@C in our work and the recent TiO₂-based nanostructures from literatures.

	Electrode	Voltage window(V)	Current density (mA g ⁻¹)	Cycle number	Capacity (mAh g ⁻¹)	Refs.
	TiO ₂ @C nsnosheets	0.01-3	230 4600	300 2000	549 385	This work
1	TiO ₂ QDs in C	0.01-3	1000 2000	300 2000	333 189	3
2	TiO ₂ -C nanofibers	0-3	100 5000	250 1600	680 260	4
3	Hybrid of TiO ₂ nanobelts and graphene	0-3	150 3000	100 -	430 210	5
4	TiO ₂ @TiN/Carbon cloth	0.01-3	3350 335	650 300	240 260	6
5	TiO ₂ nanorods/RGO	0.01-3	670 6700	300 -	200 140	7
6	TiO ₂ @porous C/RGO	0.01-3	800	500	159	8
7	TiO ₂ NPs/Graphene	0.01-3	1000 3000	-	230 150	9
8	TiO ₂ -NSs@CNT	0.01-3	840	120	221	10
9	TiO ₂ /Nanoporous graphene	0.01-3	305	100	290	11
10	TiO ₂ @C	0.01-3	335	100	162	12

References

- 1 T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada and H. Nakazawa, *J. Am. Chem. Soc.*, 1996, **118**, 8329-8335.
- 2 T. Sasaki and M. Watanabe, *J. Am. Chem. Soc.*, 1998, **120**, 4682-4689.
- 3 Y. Tang, L. Liu, X. Wang, D. Jia, W. Xia, Z. Zhao and J. Qiu, *J. Power Sources*, 2016, **319**, 227-234.
- 4 X. Li, Y. Chen, L. Zhou, Y.-W. Mai and H. Huang, *J. Mater. Chem. A*, 2014, **2**, 3875.
- 5 H. Huang, J. Fang, Y. Xia, X. Tao, Y. Gan, J. Du, W. Zhu and W. Zhang, *J. Mater. Chem. A*, 2013, **1**, 2495.
- 6 M.-S. Balogun, C. Li, Y. Zeng, M. Yu, Q. Wu, M. Wu, X. Lu and Y. Tong, *J. Power Sources*, 2014, **272**, 946-953.
- 7 M. Zhen, S. Guo, G. Gao, Z. Zhou and L. Liu, *Chem Commun (Camb)*, 2015, **51**, 507-510.
- 8 S. Jiang, R. Wang, M. Pang, H. Wang, S. Zeng, X. Yue, L. Ni, Y. Yu, J. Dai, S. Qiu, et al., *Electrochim. Acta*, 2015, **182**, 406-415.
- 9 D. Cai, P. Lian, X. Zhu, S. Liang, W. Yang and H. Wang, *Electrochim. Acta*, 2012, **74**, 65-72.
- 10 S. Ding, J. S. Chen and X. W. Lou, *Adv. Funct. Mater.*, 2011, **21**, 4120-4125.
- 11 C. Chen, X. Hu, Y. Jiang, Z. Yang, P. Hu and Y. Huang, *Chemistry*, 2014, **20**, 1383-1388.
- 12 J. Y. Liao, D. Higgins, G. Lui, V. Chabot, X. Xiao and Z. Chen, *Nano Lett*, 2013, **13**, 5467-5473.