Electronic Supplementary Material (ESI) for RSC Advances

Supporting information for

Porous TiO_2 nanoribbons and TiO_2 nanoribbons/carbon dots composites for an enhanced Li-ion storage

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Material and Characterization

Preparation of porous TiO_2 nanoribbons (P-TNRs) and TiO_2 nanoribbons/carbon dots composites (TNRs/C): All the chemicals were used as received without further purification. In a typical synthesis, 4 g Glucose and 1 g TiO_2 was dissolved into the 10 M NaOH solution sufficiently, and then the solution was sealed in the Teflon-lined stainless steel autoclave and heated at 190 ^{o}C for 48 h. Finally, the as-prepared yellow-white powders was treated by HCl (pH = 1) and then was calcined at 500 ^{o}C for 4 h under the nitrogen atmosphere, giviung rise to black TNRs/C. Alternatively, the product of P-TNRs was obtained after the calciantion of intermediates in air atmosphere.

Electrode fabrication

The electrochemical rate-capability and cycling performance of samples were carried out with coin-shaped cells using a metallic lithium film as both the counter and reference electrodes. The anode was prepared by a coating method; the 80% (weight percent) active material (the powder was ground and sieved before used), 10% conducting carbon black (Super P), and 10% polyvinyli-dene fluoride (PVDF) binder homogeneously added into N-methyl pyrrolidinone (NMP). And then the slurries were stirring by a magnetic stirring apparatus until that the powder mixed uniformly. The slurries were coated on the copper foil with an automatic film applicator, dried in a vacuum oven at 120 ^{o}C for 12 h, and cut into circular sheets (Ø is 14 mm). Then these sheets were dried in a vacuum oven at 120 ^{o}C for 12 h again. The mass of Li metal was about 15 mg, and the mass of electrode was 2.45 mg, in which the active material was about 1.96 mg. The electrode thickness was about 15 μm. The cells were assembled into CR2016 coin cells in a glove box filled with pure argon, in which the moisture and oxygen were strictly controlled to less than 0.1 ppm. Microporous polypropylene film (Celgard2400) was used as the separator. The electrolyte was 1.0 mol L^{-1} $LiPF_6$ in a mixture of diethyl carbonate (DEC) and ethylene carbonate (EC) in the ratio of 1 : 1 (w : w). The cells had a configuration of Li metal (−) | electrolyte | Sample (+) filled with a liquid electrolyte.

Characterization

The obtained products were characterized by X-ray powder diffraction (XRD) using a X ‘Pert-ProMPD (Holand) D/max-γA X-ray diffractometer with Cu Kα radiation (λ = 0.154178 nm). The XRD measurement conditions: the scanning current is 40 mA, the scanning voltage was 40 kV and the scanning step was 0.026 ^{o}. Scanning electron microscopy (SEM) images and EDX were taken on a FEI-quanta 200F scanning electron microscope with acceleration voltage of 30 kV. Transmission electron micrographs (TEMs) were taken on a FEI-Tecnai F20 (200 kV) transmission electron microscope (FEI). X-ray Photoelectron Spectroscopy (XPS) was obtained by using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatised Mg Kα X-ray (hν = 1283.3 eV). The XPS samples were prepared by drying a dispersion of powders on a piece of silicon wafer. Nitrogen adsorption-desorption isotherms were obtained using a ASAP2050 (Micromeritics Industrument Corp.) surface area & porosity Analyzer at 77 K. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Thermogravimetric analysis (TGA) was carried out under a flow of air with a temperature ramp of 5 ^{o}C min^{-1}. The electrochemical properties of products were tested in CR2016 coin cells. All the measurements were controlled and recorded automatically by the LAND CT2001C charge-discharge detector (China, Wu han). Cyclic voltammetry (CV) tests were performed over the potential range of 0.01 - 3.00 V using a CHI660B electrochemical workstation. And electrochemical impedance spectroscopy (EIS) was measured on CHI660D (Chenhua, Shanghai) with the frequency range from 100 kHz and 10 mHz. Fourier transform infrared (FTIR) was recorded on a Ventrix (Brukle) spectrophotometer in the wavelength range of 400-4000 nm. The electronic conductivities were collected by the 4-probe DC method (Advanced Instrument Technology, CMT-SR1000N),

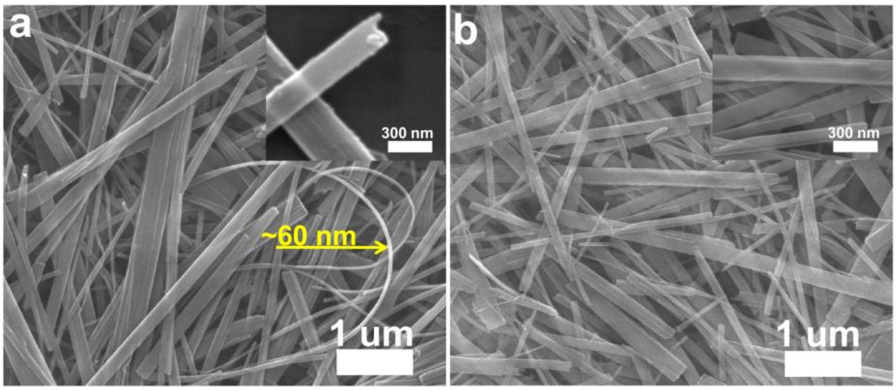

Fig. S1 SEM images of (a) TNRs/C and (b) P-TNRs.

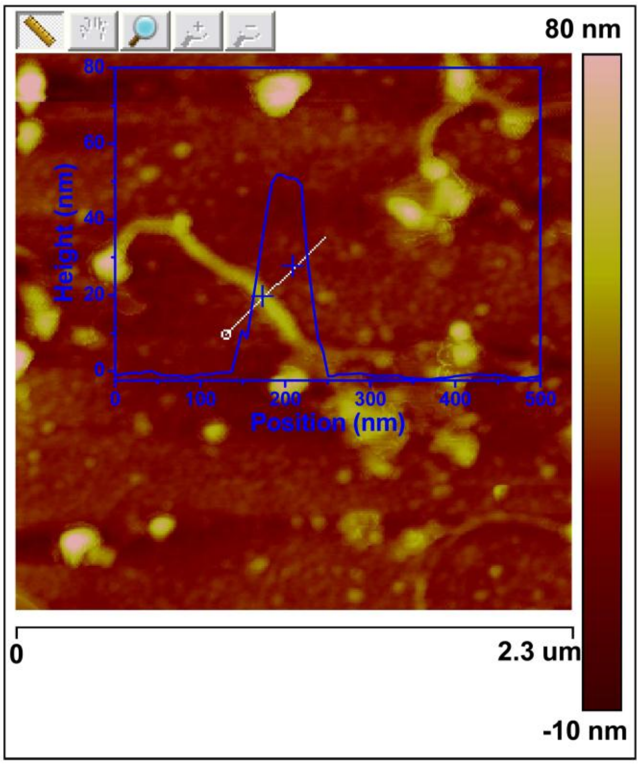

Fig. S2 AFM image of TNRs/C and insert image is the relationship between the height and position of the selected area.

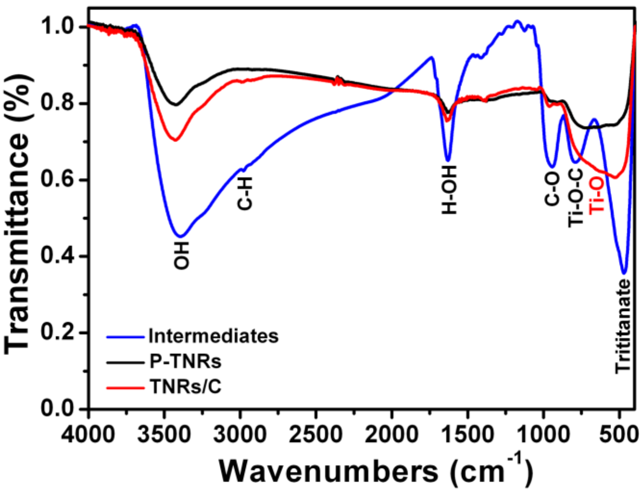

Fig. S3 FTIR spectra of intermediates (blue), TNRs/C (red), and P-TNRs (black).

The FTIR spectra of intermediates, TNRs/C, and P-TNRs show a strong and broad O-H stretching mode at 3400 cm^{-1} and an H-O-H bending mode at 1630 cm^{-1}[1], demonstrating a lot of hydroxyl groups (-OH) existed in the intermediates and also one part of -OH presented on the surface of the TNRs/C and P-TNRs. The IR modes of TNRs/C and P-TNRs in the 450-1000 cm^{-1} range can be attributed to Ti-O-Ti bending vibrations.[2] While a strong C-O stretching mode at 947 cm^{-1} in the IR spectrum showed the presence of carbonaceous materials and residual carbohydrate in the intermediates.[3,4] The Ti-O-C vibration at 626 cm^{-1} and a rather sharp absorption band at 470 cm^{-1} also indicates the formation of trititanate structure.[5]

References

[1] M. Ray, S. Chatterjee, T. Das, S. Bhattacharyya, P. Ayyub and S. Mazumdar, *Nanotechnology*, 2011, **22**, 415705.

[2] Y. Suzuki, S. Pavasupree and S. Yoshikawa, *J. Mater. Res.*, 2005, **20**, 1063.

[3] B. J. Jiang, C. G. Tian, W. Zhou, J. Q. Wang, Y. Xie, Q. J. Pan, Z. Y. Ren, Y. Z. Dong, D. Fu, J. L. Han and H. G. Fu, *Chem. Eur. J.*, 2011, **17**, 8379.

[4] J. Ming, R. X. Liu, G. F. Liang, H. Y. Cheng, Y. C. Yu and F. Y. Zhao, *J. Mater. Chem.*, 2011, **21**, 10929.

[5] G. W. Peng, S. K. Chen and H. S. Liu, *Appl. Spectrosc.*, 1995, **49**, 1646.

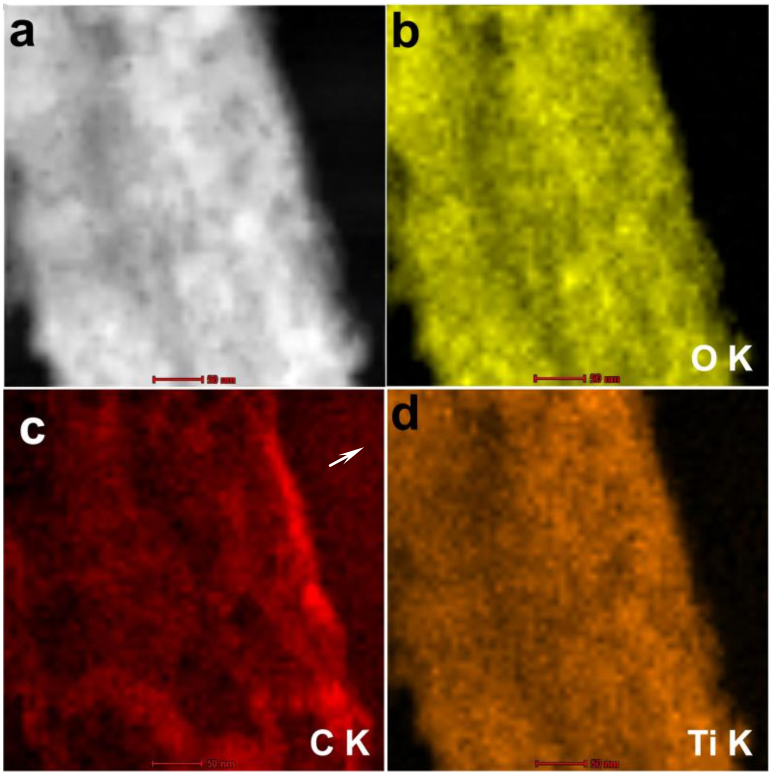

Fig. S4 (a) HAADF-STEM image of TNRs; EDS mapping images of (b) O element, (c) C element and (d) Ti element from TNRs/C. Note that the light signals of the C element in the blank area (Fig. 3c, right, arrow-labeled) were resulted from the carbon supporter over the copper grids which used for the TEM test, but the obvious boundaries of TNRs/C and deeper color well demonstrated the existence of carbon in the structure of TNRs/C.

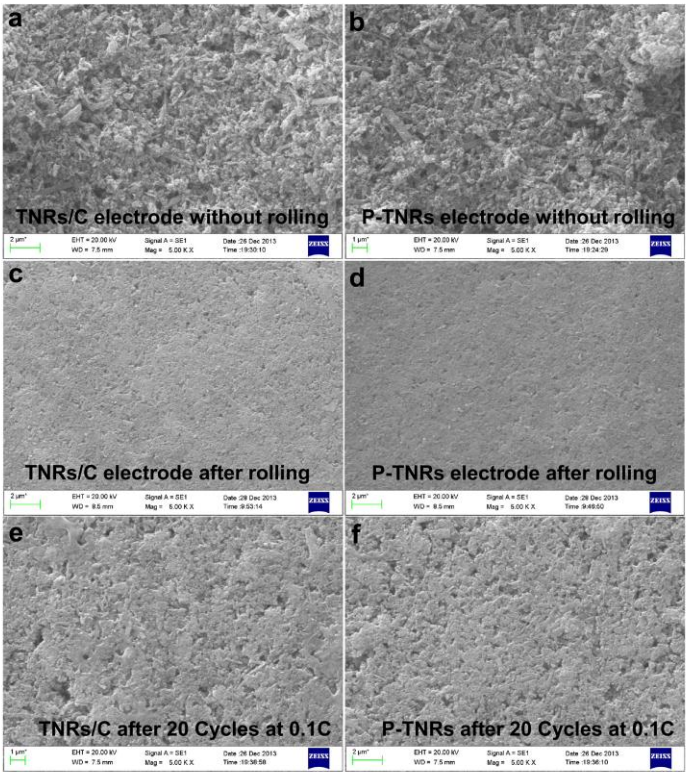

Fig. S5 SEM images of (a) TNRs/C and (b) P-TNRs electrodes without rolling process; (c) TNRs/C and (d) P-TNRs electrodes after rolling process; (c) TNRs/C and (d) P-TNRs electrodes after 20 cycles at the rate of 0.1 C.

Table S1 Comparative performance of P-TNRs, TNRs/C and other TiO_2-based materials in previous literatures

Kind of Sample	Cell Type	Electrolyte	Active materials:Carbon: Binder	Capacity at 1 C (mAh g^{-1})	Capacity at 10 C (mAh g^{-1})
P-TNRs	2016	DEC:EC	8:1:1	138	45
TNRs/Ce	2016	DEC:EC	8:1:1	225	73
Mesoporous TiO_2 [1]	--	EC:DMC	8.5:1:0.5	150 (1.2 C)	--
TiO_2@carbon nanofiber[2]	--	EC:DMC	7:1.5:1.5	179 (~1C)	100 (~10 C)
TiO_2 nanofiber [2]	--	EC:DMC	7:1.5:1.5	135 (~1C)	42 (~10 C)
Graphene/TiO_2[3]	--	DMC :EC	--	160	140
Porous TiO_2[4]	--	DMC: EC	8:1:1	140	65
TiO_2 hollow peanuts[5]	2032	EC/DMC/EMC	8:1:1	156(~0.2 C)	--
hollow TiO_2[6]	2025	EC:DMC	8:1:1	150 (~1 C)	130 (~10 C)
TiO_2 hollow nanofibers[7]	2016	EC:DEC	8:1:1	85	15
N-doped TiO_2 hollow nanofibers[7]	2016	EC:DEC	8:1:1	125	30
TiO_2 nanocrystals/RGO sheets[8]	--	EC/DMC/EMC	8.5:1:0.5	175(0.59 C)	135(11.8 C)

The blank column without label means no note in the literatures. Note that all the listed data were just a simple compare and not strictly because different battery system, electrolyte and mass of electrode were used in different literatures.

References

1. J. Wang, Y. K. Zhou, Y. Y. Hu, R. O'Hayre and Z. P. Shao, *J. Phys. Chem. C*, 2011, **115**, 2529-2536.
2. Z. X. Yang, G. D. Du, Q. Meng, Z. P. Guo, X. B. Yu, Z. X. Chen, T. L. Guo and R. Zeng, *J. Mater. Chem.*, 2012, **22**, 5848-5854.
3. Y. H. Ding, P. Zhang, H. M. Ren, Q. Zhuo, Z. M. Yang, Y. Jiang, *Mater. Res. Bullet.*, 2011, **46**, 2403-2407.
4. H. E. Wang, H. Cheng, C. P. Liu, X. Chen, Q. L. Jiang, Z. G. Lu, Y. Y. Li, C. Y. Chung, W. J. Zhang, J. A. Zapien, L. Martinu and I. Bello, *J. Power Sources*, 2011, **196**, 6394-6399.
5. Y. Wang, X. W. Su and S. Lu, *J. Mater. Chem.*, 2012, **22**, 1969-1976.
6. J. Ming, Y. Q. Wu, S. Nagarajan, D. J. Lee, Y. K. Sun and F. Y. Zhao, *J. Mater. Chem.*, 2012, **22**, 22135-22141.
7. H. Han, T. Song, J. Y. Bae, L. F. Nazar, H. Kim and U. Paik, *Energy Environ. Sci.*, 2011, **4**, 4532-4536.
8. W. Li, F. Wang, S. S. Feng, J. X. Wang, Z. K. Sun, B. Li, Y. H. Li, J. P. Yang, A. A. Elzatahry,Y. Y. Xia and D. Y. Zhao, *J. Am. Chem. Soc.*, 2014, DOI: 10.1021/ja4100723

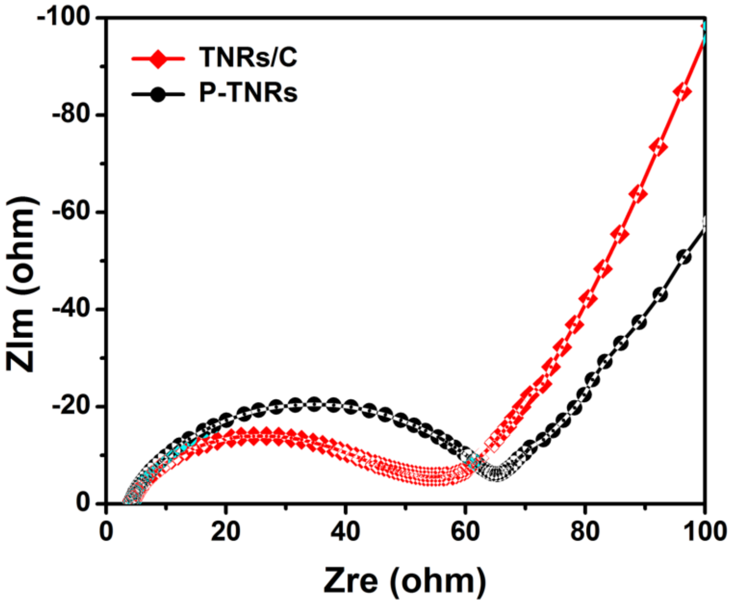

Fig. S6 Nyquist plots of TNRs/C and P-TNRs electrodes.