

Supplementary date

Multimodal Porous CNT@TiO₂ Nanocables with Superior Performance in Lithium-ion Batteries

Huijuan Zhou^a, Lang Liu^{*a}, Xingchao Wang^a, Fuxin Liang^b, Shujuan Bao^a, Dongmei Lv^b,
Yakun Tang^a, Dianzeng Jia^{*a}

^a *Key Laboratory of Material and Technology for Clean Energy, Ministry of Education;
Institute of Applied Chemistry, Xinjiang University. Urumqi 830046, Xinjiang, China.*

E-mail: liulang@xju.edu.cn; jdz@xju.edu.cn

^b *State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese
Academy of Sciences, Beijing 100190, China.*

Experimental

Materials Synthesis:

Sulfonated polydivinylbenzene nanotubes (SPNTs): The pristine crosslinked bamboo-like polydivinylbenzene nanotubes (PNTs) with a mean exterior diameter of 100-150 nm were prepared by the cationic polymerization [*Chem. Commun.*, 2011, **47**, 4727]. 0.2 g of vacuum dried PNTs were immersed in 30 mL of concentrated sulfuric acid and stirred at 50 °C for 12 h. The mixture was diluted by a large amount of deionized water, and the sample was collected by suction filtration and washed with water and ethanol.

SPNT@titania-gel nanocables: 0.1 g of SPNTs were dispersed in 10 ml of ethanol under sonication for 90 min. The suspension was placed in 0 °C ice bath under high speed magnetic stirring for 20 min. 1.33 g of tetrabutyl titanate (TBT) was rapidly added to the mixture and stirred for 2 h to allow a saturated adsorption of TBT on the surface of SPNTs. Afterwards, 1 ml of water was introduced into the system and kept stirring at 0 °C for 2 h. The precipitates were separated by centrifugation (4000 rpm) and the product was dried at ambient temperature and subsequently stored in a vacuum oven at 50 °C overnight. SPNT@titania-gel nanocables T1, T2, T3, T4, T5, T6 were prepared by a various mass of TBT for 0.2, 0.5, 0.8, 1.33, 2.0 and 4.0 g.

CNT@TiO₂ nanocables and TiO₂ nanotubes: The black CNT@TiO₂ nanocables and the white TiO₂ nanotubes were obtained by calcinating SPNT@titania-gel nanocables (T4) at 700 °C for 2 h in N₂ atmosphere and in air environment (heating rate: 5 °C min⁻¹), respectively.

Bamboo-like carbon nanotubes (CNTs): SPNTs were carbonized in N₂ for 2 h at 500 °C, 700 °C, 900 °C and 1100 °C, respectively.

Materials characterization:

Morphology, microstructure and composition of the samples were investigated by FESEM (Hitachi S-4800), TEM (Hitachi H-600) and HRTEM (JEM 2100). XRD measurements were carried out with a Bruker D8 using filtered Cu Ka radiation. TGA were carried out with a Netzsch STA 449C. FT-IR spectra were recorded on a BRUKER VERTEX70 spectrometer. Nitrogen adsorption/desorption isotherms were obtained using an ASAP 2020 Xtended Pressure Sorption Analyzer at 77 K. The specific surface area was

calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated by the Density Functional Theory (DFT) method.

Electrochemical characterization:

The electrodes were fabricated by a conventional coating method. A slurry consisting of the as-synthesized active material (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) in N-methyl-2-pyrrolidone (NMP) was uniformly spread onto a Cu foil. The electrodes were dried at 110 °C for 12 h in a vacuum oven before transferring into an Argon-filled glovebox. Coin cells were fabricated using lithium metal as the counter electrode, Celgard 2,300 membrane as the separator and LiPF₆ (1 M) in ethylene carbonate/dimethyl carbonate/(EC/DMC, 1:1 vol%) as the electrolyte. The cyclic voltammograms (CVs) were collected on an electrochemical workstation (CHI660B, Chenhua, China) and the galvanostatic charge/discharge of the cells were tested with a battery test instrument (CT2001A, Land, China).

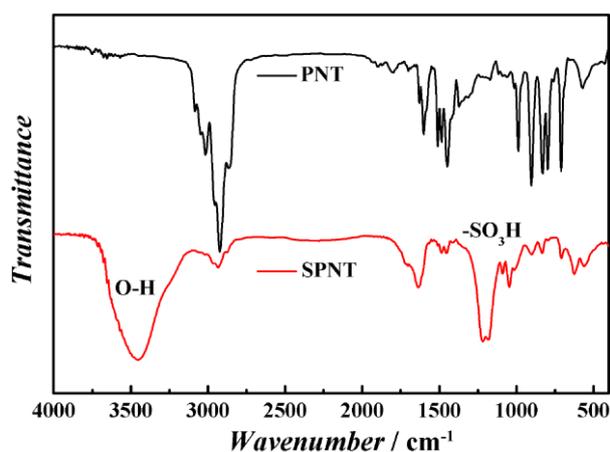


Fig. S1 FT-IR spectra of PNT (a) and SPNT (b).

In Fig. S1, some new peaks at 1199 and 1046 cm⁻¹ appear in IR spectrum of the SPNT, which are attributed to the stretching vibration of sulfonic acid groups. The result indicates that PNT has been successfully sulfonated, and sulfonic acid groups (SO₃H) are introduced on the surface of polymer nanotubes.

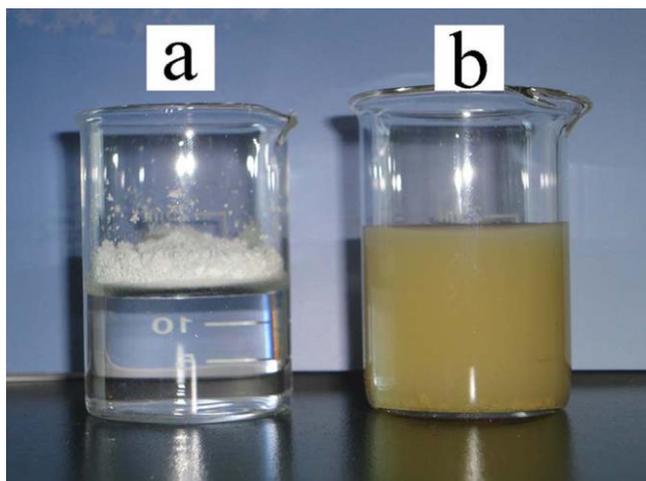


Fig. S2 Pictures for PNT (a) and SPNT (b) dispersed in water.

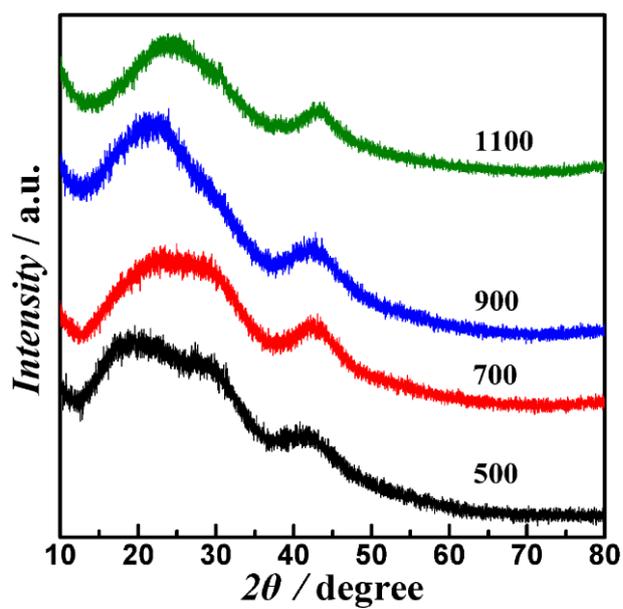


Fig. S3 XRD patterns of CNT by the calcination of SPNT at different temperatures.

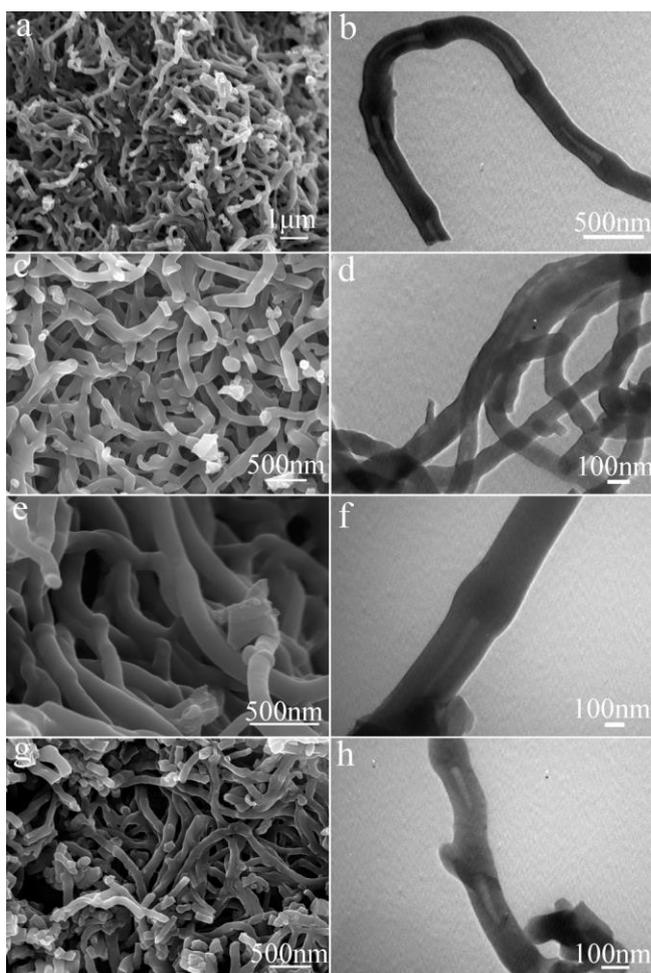


Fig. S4 SEM and TEM images of CNTs obtained at 500 °C (a, b), 700 °C (c, d), 900 °C (e, f) and 1100 °C (g, h), respectively.

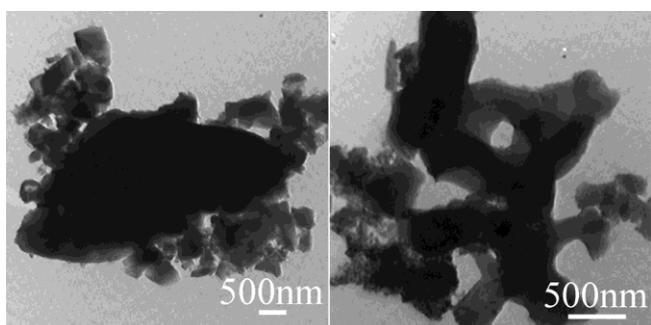


Fig. S5 TEM images of products by carbonizing PNT at 700 °C in N₂ atmosphere.

Table S1. Synthesis parameters for the SPNT@titania-gel nanocables

Sample number	SPNT [g]	Ethanol [mL]	TBT [g]	H ₂ O [mL]	Titania-gel thickness [nm]
T1	0.1	10	0.2	1	\
T2	0.1	10	0.5	1	~15nm
T3	0.1	10	0.8	1	~47nm
T4	0.1	10	1.33	1	~120nm
T5	0.1	10	2.0	1	~132nm
T6	0.1	10	4.0	1	Fleck-like structure

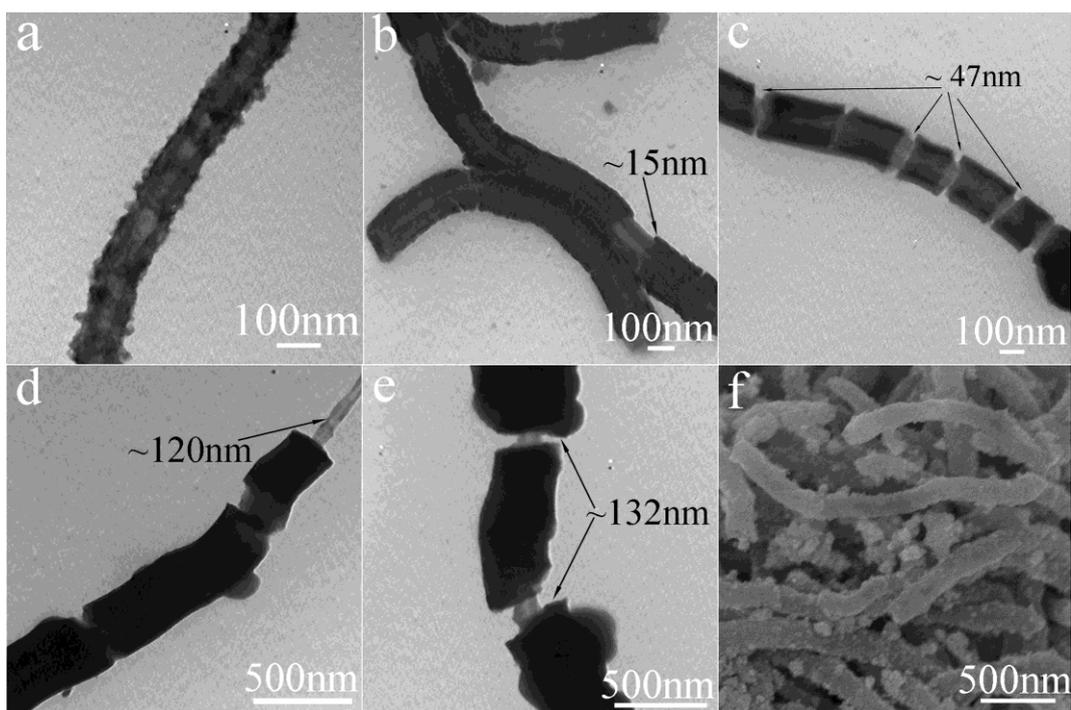


Fig. S6 TEM and SEM images of SPNT@titania-gel nanocables prepared at varied feeding amount of TBT: a) T1, b) T2, c) T3, d) T4, e) T5, f) T6.

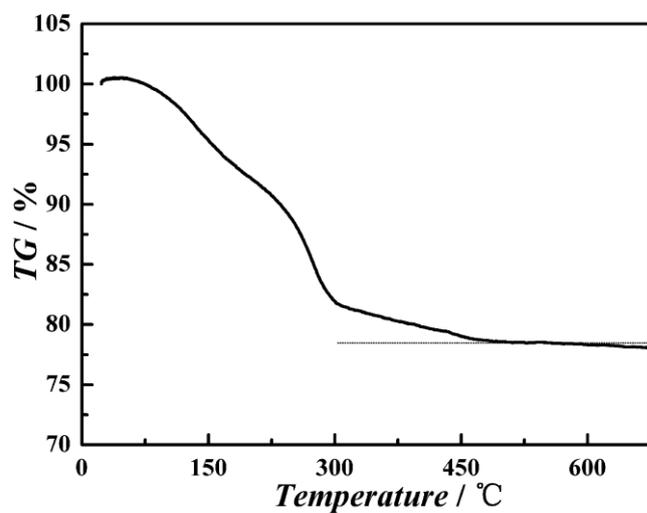


Fig. S7 TGA curve of the SPNT@titania-gel nanocables (T4) in N₂ atmosphere.

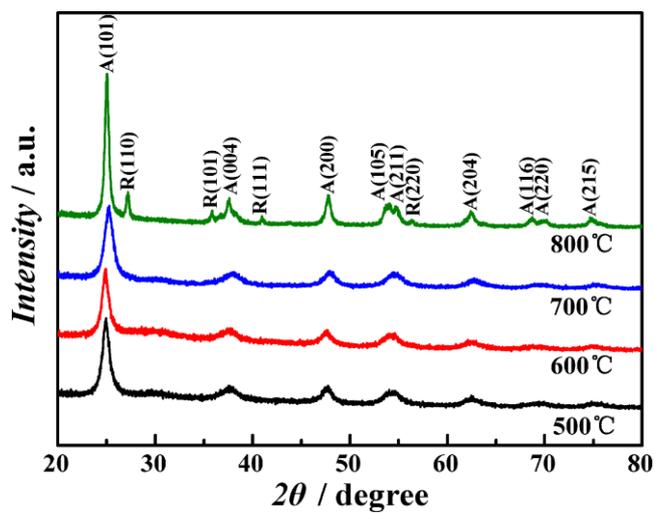


Fig. S8 XRD patterns of CNT@TiO₂ composite nanocables obtained by calcinating T4 at different temperatures in N₂ atmosphere.

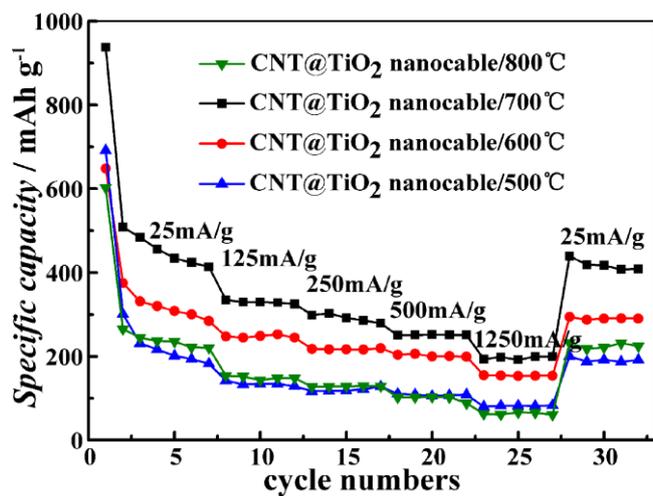


Fig S9 Rate capability of the CNT@TiO₂ nanocables obtained at different temperatures in the voltage range of 0.01-3.0 V.

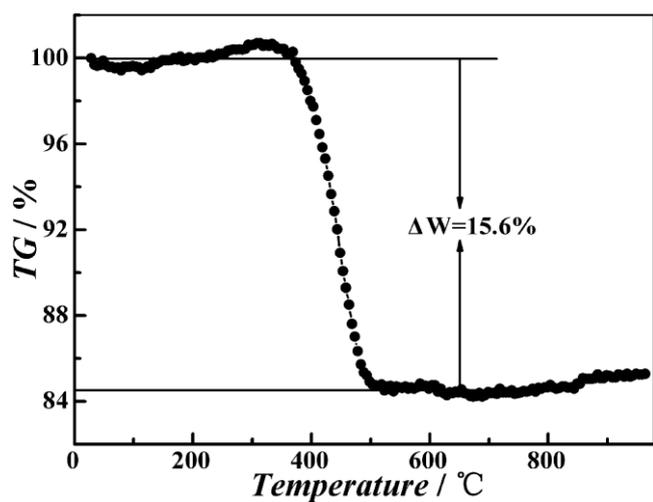


Fig. S10 TGA curve of the CNT@TiO₂ nanocables obtained at 700 °C in air atmosphere to completely remove CNT.

From the TGA curve, the composite CNT@TiO₂ nanocables contain approximately 84.4% titania and 15.6% carbon.

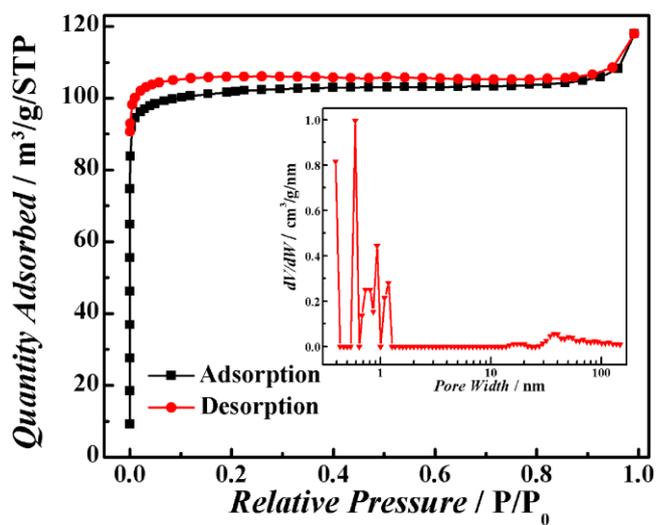


Fig. S11 The N₂ adsorption/desorption isotherms and pore size distribution of the pure carbon nanotubes.

The N₂ adsorption/desorption isotherms show strong adsorption at $p/p^0 = 0-0.1$ and $0.9-1.0$, indicating that the sample contains micropores and macropores. The BET surface area is $410 \text{ m}^2 \text{ g}^{-1}$ and the pore size distribution contains micropores (0.4-1.2 nm) and macropores (30-60 nm).