

ELECTRONIC SUPPLEMENTARY INFORMATION

Hierarchical flower-like TiO₂/MPCNFs as a free-standing anode with superior cycling reversibility and rate capability

Donghua Teng, Yunhua Yu and Xiaoping Yang*

State Key Laboratory of Organic-Inorganic Composites, Beijing University of

Chemical Technology, Beijing, China.

* Corresponding author, E-mail: yangxp@mail.buct.edu.cn.

Experimental

Preparation: Tetrabutyl titanate/polyacrylonitrile ($\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{PAN}$) nanofibers were electrospun and stabilized at 250 °C for 2 h in air following our previous work.¹ Subsequently, the stabilized webs (each size of $\sim 5 \times 5$ cm and total weight of ~ 500 mg) were immersed into urea-containing (0.5 g) ethylene glycol aqueous solution (EG/ H_2O , 100 ml, 3:7 by volume), which was loaded in a 150 ml Teflon-lined stainless steel autoclave and kept at 180 °C for 4 h. After cooling down to ambient temperature, the impregnated webs were repetitively washed with ethanol and finally calcined at 600 °C for 2 h under 3 °C min^{-1} in highly pure N_2 . For comparison, nanoparticulate (EG solvothermal treatment) and micro-particulate (H_2O solvothermal treatment) $\text{TiO}_2/\text{MPCNFs}$ were also prepared under similar conditions.

Structural characterization: Microstructures of samples were observed using a field emission scanning electron microscope (FESEM, Hitachi S-4700) with an energy dispersive X-ray (EDX) spectrometer, a transmission electron microscope (TEM, Hitachi H-800) and a high-resolution transmission electron microscope (HRTEM, JEM-3010) with a select-area electron diffractometer (SAED). Thermogravimetric analyses (TGA) were performed on a TG analyzer (Q500, TA) from 100 to 750 °C at a heating rate of 10 °C/min in air. According to Brunauer-Emmett-Teller (BET) equation, specific surface areas were calculated from adsorption/desorption isotherms for N_2 using an automatic gas adsorption analyzer (Micromeritics ASAP 2010) at -196 °C. Prior to the measurements, all samples were

degassed and dehydrated at 200 °C for 24 h. Crystal phases were identified by X-ray diffraction (XRD, Rigaku D/max 2500 VB2+/PC, Cu K α , λ = 0.154 nm).

Electrochemical characterization: Electrochemical measurements were carried out using standard three-electrode CR 2025 coin cells, which were identically assembled following our previous work.¹ Cyclic voltammetry (CV) measurements were performed at a scan rate of 0.2 mV s⁻¹ or at different scan rates of 0.2-1.0 mV s⁻¹ in the voltage windows of 1-3 or 0.001-3 V using an electrochemical workstation (Metrohm Autolab PGSTAT 302N). Electrochemical impedance spectroscopic (EIS) analyses were carried out on the same electrochemical workstation by applying a potentiostatic signal amplitude of 10 mV over 200 kHz to 0.1 Hz. The cells were discharged and charged on a cell testing instrument (LAND CT2001A) in the voltage windows of 1-3 or 0.001-3 V at a current density of 50 mA g⁻¹ for 200 cycles or at different current densities of 50, 100, 200, 500, 1000, 2000 and again 50 mA g⁻¹ for every sequential 20 cycles, respectively.

References

1 D. H. Teng, Y. H. Yu, P. W. Li, X. Bai and X. P. Yang, *RSC Adv.*, 2013, **3**, 14237.

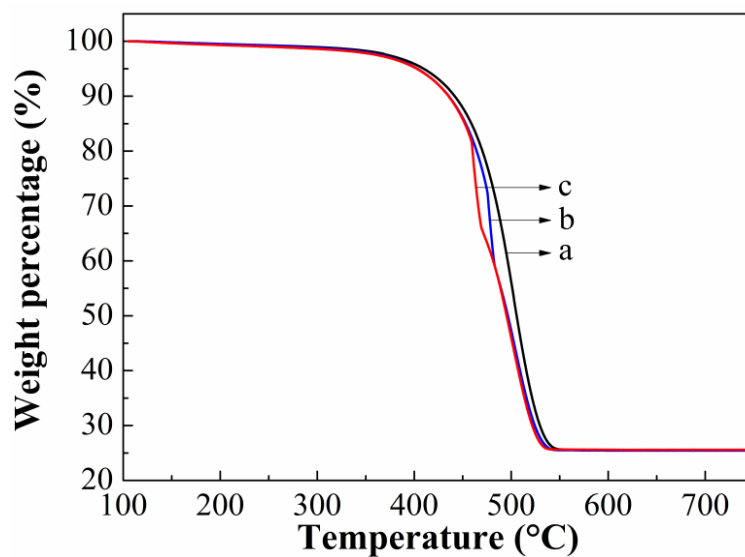


Fig. S1 TGA curves of (a) nano-particulate, (b) micro-particulate and (c) flower-like $\text{TiO}_2/\text{MPCNFs}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in air.

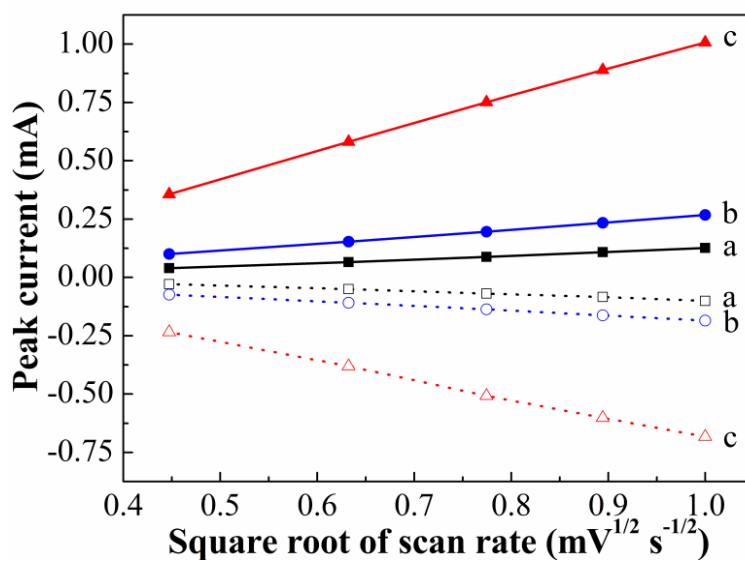


Fig. S2 Plots of peak current vs. square root of scan rate of (a) nano-particulate, (b) micro-particulate and (c) flower-like $\text{TiO}_2/\text{MPCNFs}$.

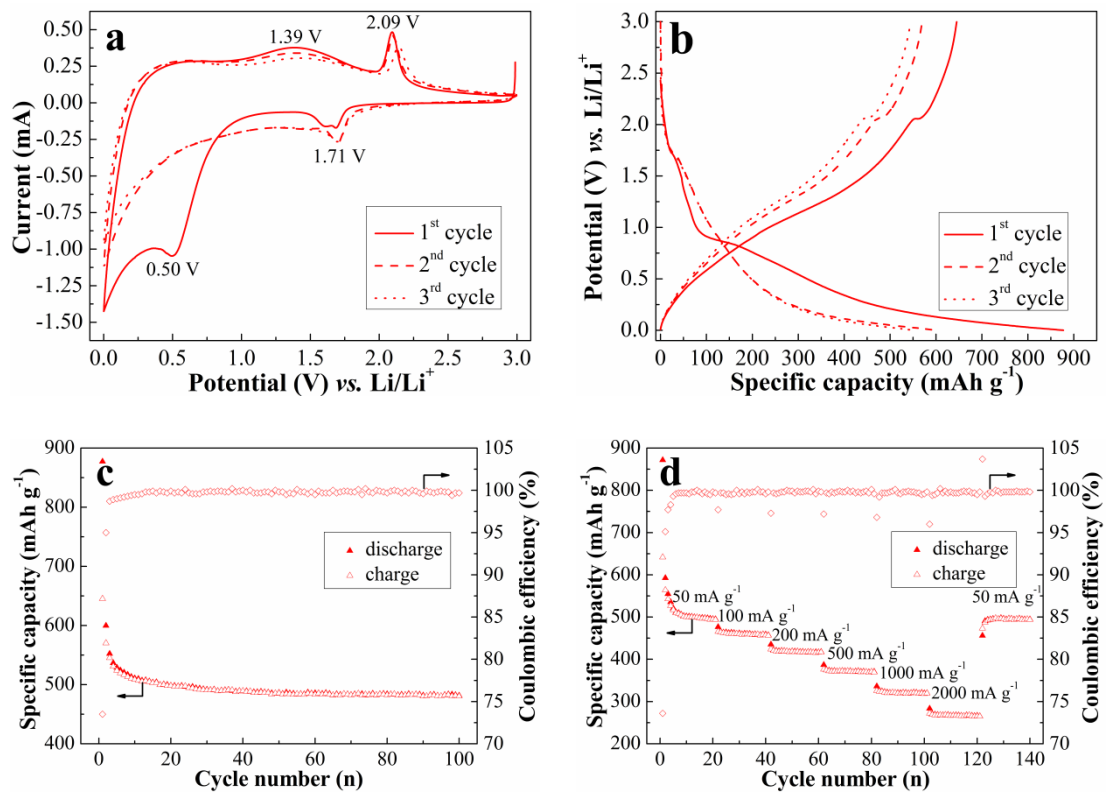


Fig. S3 (a) CV curves for the initial three cycles of flower-like $\text{TiO}_2/\text{MPCNFs}$ at a scan rate of 0.2 mV s^{-1} from 0.001 to 3 V. (b) Discharge/charge curves for the initial three cycles of flower-like $\text{TiO}_2/\text{MPCNFs}$ anode at 50 mA g^{-1} from 0.001 to 3 V. (c) Cycling performance at 50 mA g^{-1} and (d) rate capability of flower-like $\text{TiO}_2/\text{MPCNFs}$ from 0.001 to 3 V.