ELECTRONIC SUPPLEMENTARY INFORMATION

Topographically triplex-roughened Ti_3O_5/TiP_2O_7@MPCNFs hierarchical nanocomposite delivering synergistic lithium storage

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Experimental

Preparation: Polyacrylonitrile (PAN) fibril (5 g, 100, 000 g mol^{-1}, UK Courtaulds Co.) was dissolved into N, N-dimethyl formamide (DMF, 50 ml) under ultrasonic stirring. A mixed solution containing tetrabutyl titanate ($Ti(OC_4H_9)_4$, 6ml) and acetic anhydride (HAc, 4 ml) was slowly dripped into the PAN/DMF solution at ambient temperature under ultrasonic stirring until to obtain a homogeneous solution. The mixture was electrospun at an electrostatic potential of 12 kV with a feed rate of 0.4 ml h^{-1}. As-spun nanofibers were collected on a 20 cm-distant aluminium roller at a rotating linear speed of 15 m s^{-1}. The spun nanofibers were stabilized at 250 °C for 2 h in air, and subsequently immersed into 20 vol. % phosphoric acid (H_3PO_4) aqueous solution at ambient temperature for 6 h. The impregnated nanofibers were calcined in a tube furnace at 1000 °C for 2 h with a heating rate of 3 °C min^{-1} in highly pure N_2. The as-obtained Ti_3O_5/TiP_2O_7@MPCNFs web was repeatedly washed with distilled water and then dried to remove surficial impurities. For comparison, PAN nanofibers were electrospun, stabilized and carbonized under the same conditions to prepare CNFs without H_3PO_4 pre-impregnation and MPCNFs with H_3PO_4 activation, respectively.

Structural characterization: The morphologies and structures of samples were observed using a field emission scanning electron microscope (FESEM, Hitachi S-4700) with an energy dispersive X-ray (EDX) spectrometer and a transmission electron microscope (TEM, Hitachi H-800) with a select-area electron diffractometer (SAED). According to Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH), Horvath-Kawazoe (HK) and Kelvin equations, specific surface areas, pore size distributions, micropore volumes and mesopore volumes were calculated, respectively, 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. Thermogravimetric analysis was performed on a TG analyzer (Q500, TA) from 100 to 700 °C at a heating rate of 10 °C/min in air. Contact angles of water on the samples under ambient conditions were recorded by a contact angle goniometer (OCA 20, Dataphysics). All the contact angles were averaged over at least five measurements of water droplets at different positions on the samples. Every water droplet of about 4 μl was placed on the sample surface and the initial contact angle was recorded immediately after 30 s evaporation. Contact angle hysteresis was calculated from the subtraction between initial contact angle and instantaneous contact angle after 25 min evaporation. Crystal-phase structural variations were identified by X-ray diffraction (XRD, Rigaku D/max 2500 VB2+/PC, Cu Kα, λ = 0.154056 nm) and Raman spectroscopy (Renishaw inVia, λ = 532 nm).

Electrochemical characterization: The electrical conductivities of samples were measured by conventional four-point probe technique. Electrochemical measurements were carried out using a standard three-electrode CR 2025 coin cell system. The as-obtained web (~2 mg) sandwiched in two nickel meshes (diameter of 1.5 cm) was punched at 20 MPa and directly used as working electrode without any binder or conductor. The electrode was dried in vacuum at 120 °C for 24 h and then assembled with lithium foil as reference and counter electrode and PP/PE/PP trilayer membrane (Celgard 2300) as separator in an argon-filled glove box (VAC Omni-Lab, moisture content < 0.5 ppm, oxygen content < 0.1 ppm). The electrolyte was 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume). Cyclic voltammetry (CV) measurements were performed at a scan rate of 0.1 mV s^{-1} from 0.001 to 3.000 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) from 0.001 to 3.000 V at a current density of 50 mA g^{-1} for 100 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.

Table S1 Surface structural parameters, physical behaviors and electrochemical features of (i) CNFs, (ii) MPCNFs and (iii) Ti_3O_5/TiP_2O_7@MPCNFs.

Samples	Specific surface area [m^2 g^{-1}]	Total pore volume [cm^3 g^{-1}]	Micro-pore volume [cm^3 g^{-1}]	Meso-pore volume [cm^3 g^{-1}]	Micro-pore width [nm]	Meso-pore width [nm]	Contact angle [°]	Contact angle hysteresis [°]	Electrical conductivity [S cm^{-1}]	Charge transfer resistance [Ω]	Warburg diffusion impedance [Ω]
i	320	0.45	0.24	0.22	0.39	7.8	110.7	26.2	1.954	212	203
ii	1350	0.84	0.61	0.26	0.95	9.1	127.5	13.7	1.028	174	120
iii	780	0.56	0.38	0.20	0.87	8.3	153.1	5.8	0.573	255	176

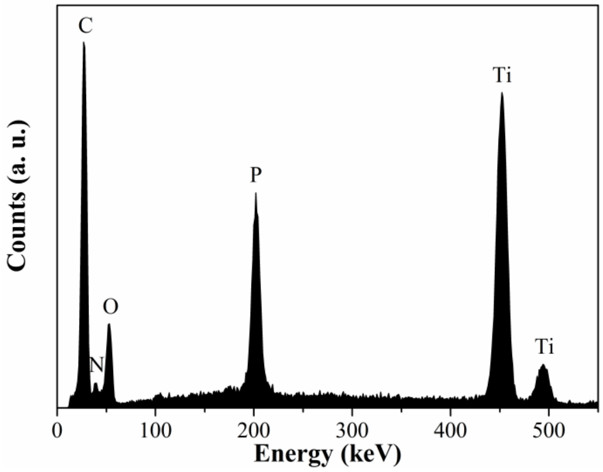

Fig. S1 EDX spectrum of Ti_3O_5/TiP_2O_7@MPCNFs.

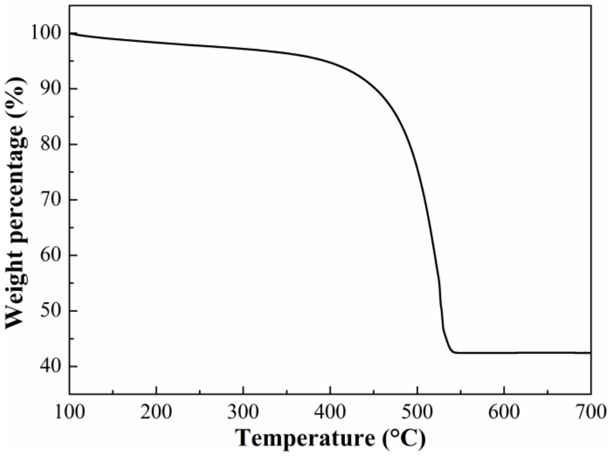

Fig. S2 TGA curve of Ti_3O_5/TiP_2O_7@MPCNFs at a heating rate of 10 °C/min in air.

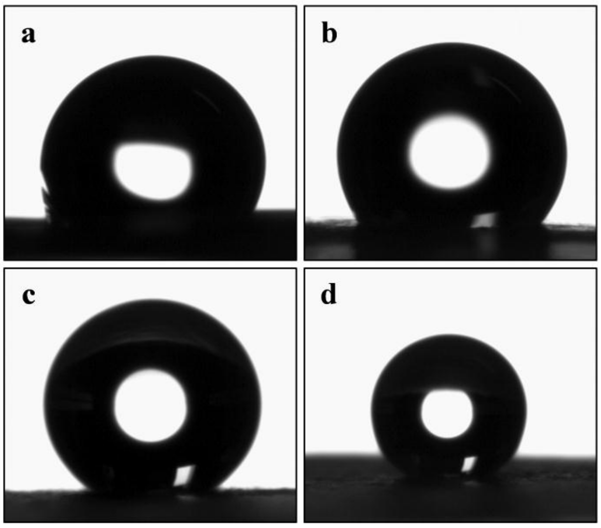

Fig. S3 Photographs of water droplets on the surfaces of (a) CNFs, (b) MPCNFs and (c) Ti_3O_5/TiP_2O_7@MPCNFs after 30 s evaporation at ambient temperature. (d) Photograph of the same water droplet shown in (c) after 25 min evaporation at ambient temperature.