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Supporting Information

Carbon-coated TiO_2 (B) nanosheets composite for lithium ion batteries

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Synthesis of C-coated TiO_2 (B) nanosheets composite: Typically, 1.0 mL of $TiCl_3$ dissolved in HCl aqueous solution was added into 30 mL of the mixture of ethylene glycol (5 mL) and *N*-methyl-pyrrolidone (25 mL), which was then transferred into a 100-mL Teflon-lined autoclave. We should point out that air must be avoided during the process to prevent the oxidation of Ti^{3+} to Ti^{4+}. Otherwise, TiO_2 will not be obtained due to the difficulty of the hydrolysis of Ti^{4+} in acidic medium at temperatures $T \leq 150$ °C. Subsequently, the system was subjected to thermal treatment at 150 °C for 14 h. The precipitate was isolated by ultracentrifugation and washed with deionized water and ethanol three times, and then dried at 75 °C overnight. Upon annealing of the sample at 300 °C under vacuum or in air, C-coated TiO_2 (B) nanosheets composites were obtained. Besides ethylene glycol, we found that C-coated TiO_2 (B) could also be produced in the presence of other alcohols such as 1,2-propylene glycol and glycerol.

Characterization: X-ray powder diffraction (XRD) was performed with a D/MAX−RC diffractometer operated at 30 kV and 100 mA with Cu Kα radiation. XPS measurements were carried out in an ultra-high vacuum (UHV) setup equipped with a monochromatic Al Kα X-ray source (hv = 1486.6 eV), operated at 14.5 kV and 35 mA. The base pressure in the measurement chamber was maintained at about 2×10^{-9} mbar. The resolution spectra were carried out in the fixed transmission mode with pass energy of 200 eV, resulting in an overall energy resolution of 0.25 eV. A flood gun was applied to compensate the charging effects. The binding energy scales were re-calibrated based on the Ti^{4+} $2p_{5/2}$ peak at ~458.8 eV. Scanning electron microscopy (SEM) was carried out using a field emission microscope (FEI Quanta 600 FEG) operated at 20 kV and equipped with an energy-dispersive X-ray spectrometer (EDX). Transmission electron microscopy (TEM) and high-resolution TEM images were recorded with a transmission electron microscope (Cs-corrected Titan) operated at 300 kV. TEM specimens were prepared by pipetting a few millilitres of the sample dispersion in ethanol onto holey copper grids.

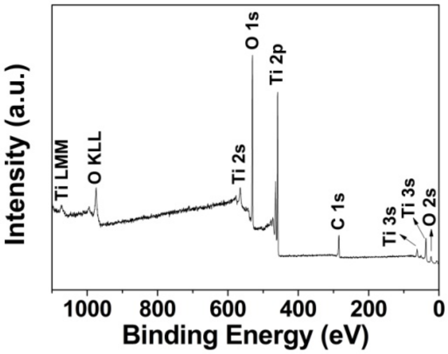

Fig. S1 The wide-survey XPS spectrum of the annealed TiO_2 (B) (300 °C in vacuum for 6 h plus 1 h in air).

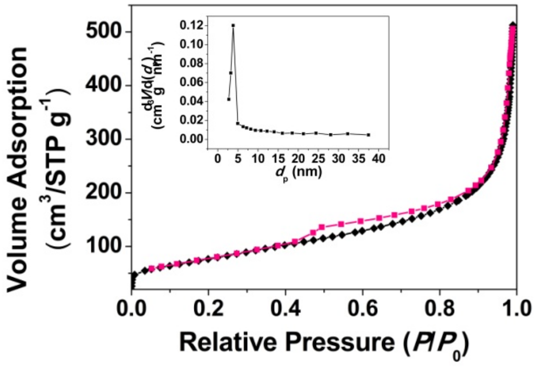

Fig. S2 Nitrogen adsorption-desorption isotherm of the annealed TiO_2 (B) (300 °C in vacuum for 6 h plus 1 h in air). Inset: the plot the pore size distribution. The results for pristine TiO_2 (B) and those other annealed samples are very similar to this kind and thus were not shown here.

Electrode preparation. TiO_2 (B) was mixed with C65 carbon black (Timcal, Bodio, Switzerland) and PVdF binder (Solef S5130, Solvay) in NMP at a weight ratio of 70:20:10 (TiO2:C65:PVdF). The mixture was cast onto copper foil using Doctor-Blade technique. The solvent was evaporated at room temperature and then dried at 110°C under vacuum overnight. The electrode loading was *ca.* 1 mg cm^{-2} and the geometric electrode area was 1.13 cm^{-2}.

Cell assembly and electrochemical characterization. Three-electrode Swagelok cell was assembled in Ar-filled glovebox (O2 < 2 ppm and H2O < 1 ppm). Pure lithium metal was used as counter and reference electrodes. Whatman GF/D glass fibre filters served as separators. LP40 electrolyte (150 µL of 1 M LiPF6 in ethylene carbonate/diethyl carbonate) was purchased from Merck (Darmstadt, Germany) and was used as-received. Electrochemical measurements were performed with a Bio-Logic VMP-3 (Bio Logic SAS, Claix, France) at charge rate of 0.5 C, 1 C, 3 C, 10 C and 30C, being 1 C equivalent to 336 mA g^{-1} . Potential window was 1.0 - 3.0 V.

Fig. S3 shows the retention of the initial reversible capacity (oxidation) for several samples upon cycling. In terms of retention, TiO_2_6hVac_1hAir delivered again the best results, followed by TiO_2_1hVac, TiO_2_1hAir, TiO_2_1hVac and TiO_2_2hAir.

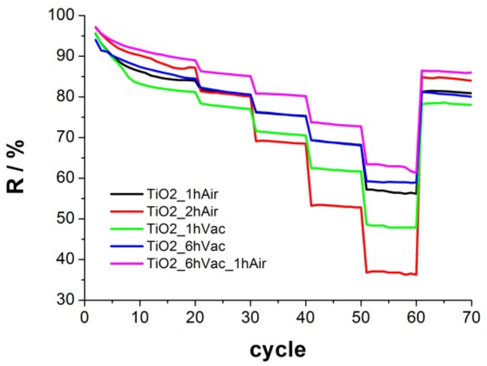

Fig. S3 Retention of initial reversible capacity for TiO_2_1hAir, TiO_2_2hAir, TiO_2_1hVac, TiO_2_6hVac and TiO_2_6hVac_1hAir upon cycling at 0.5, 1, 3, 10 and 30 C.

The efficiencies of the samples, that is, the ratio between the charge inserted in and extracted from TiO_2 (B) is plotted in Fig. S4. In this case, TiO_2_2hAir shows the best values followed closely by TiO_2_6hVac and TiO_2_6hVac_1hAir. The worst efficiencies were obtained for TiO_2_1hVac followed by TiO_2_1hAir. In general, short annealing procedures resulted in low efficiency.

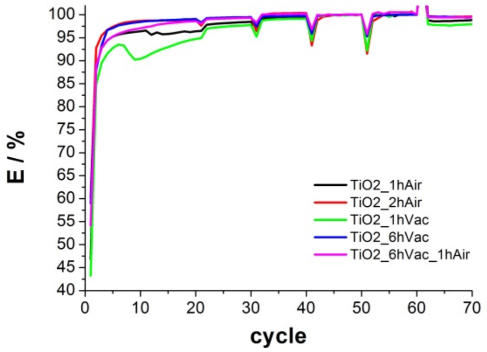

Fig. S4 Efficiency of TiO_2_1hAir, TiO_2_2hAir, TiO_2_1hVac, TiO_2_6hVac and TiO_2_6hVac_1hAir upon cycling at 0.5, 1, 3, 10 and 30 C.