Supporting Information for

Highly stable and flexible Li-ion battery anodes based on TiO_2 coated 3D carbon nanostructures

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Experiments Section

Materials Synthesis: Growth of carbon nanowire arrays on the microfibers of carbon cloth (CC, CeTech Co., Ltd.) was carried out via the thermal chemical vapor deposition (TCVD) method. Typically, 1 nm thick Fe film deposited on CC by electron beam evaporator was used as the catalyst, acetylene (C_2H_2) with a flowing rate of 100 sccm was used as the carbon source, and a mixture of Ar (400 sccm) and H_2 (50 sccm) was used as the carrying gas. The growth temperature and time were 800 °C and 20 mins, respectively.

Prior to atomic layer deposition (ALD) TiO_2, the fabricated carbon nanowire arrays on CC were treated with oxygen plasma. The reactive ion etching (RIE) was performed on a March PX-250 plasma etching system with 10 sccm oxygen gas flow. The chamber pressure, RF power and exposure time were 70 mTorr, 100 W and 10 min, respectively. ALD coating of TiO_2 was carried out in the

Beneq system (TFS 200) at 120 °C using $TiCl_4$ and water as the titanium and oxygen source, respectively. During the deposition, the reaction chamber was maintained at 1.0 mbar with a steady N_2 steam (200 sccm). Each ALD cycle consisted of a 300 ms precursor pulse and 2 s purging time with N_2. 500 cycles were applied to obtain TiO_2 thin film in this work. The mass loading of the TiO_2 coating was determined by weighing before and after ALD deposition using a microbalance (Mettler, XP26) with an accuracy of 0.002 mg. The mass loading density of the carbon naonowire arrays and TiO_2 was calculated to be ~1.0 and 4.0 mg/cm^2, respectively. Besides, 830 ALD cycles were employed to obtained ~60 nm TiO_2, corresponding to a higher mass loading density of 7.0 mg/cm^2.

Structural Characterization: The morphology of the prepared samples was investigated using field-emission scanning electron microscopy (SEM, LEO 1550 Gemini) with accelerating voltage of 5.00 kV and transmission electron microscopy (TEM, JEOL 2010F) with accelerating voltage of 200 kV.

Electrochemical Characterization: Electrochemical measurements were carried out using CR-2032 type coin cell with Li foil serving as both reference and counter electrode. CC with C@TiO_2 core-shell nanocable arrays (NCAs) was used directly as the binder-free working electrode. The cells were assembled in a high purity Ar filled glove box (H_2O < 0.5 ppm, O_2 < 0.5 ppm, Innovative Technology). The electrolyte was made from 1 M lithium hexafluorophosphate ($LiPF_6$) dissolved in ethylene carbonate and dimethyl carbonate (EC/DMC, 1:1 by volume) containing 5.0 vol% fluoroethylene carbonate (FEC, Aldrich). Similarly, the whole battery was assembled by using the CC with C@TiO_2 core-shell NCAs as the anode and an Al foil with commercial $LiMn_2O_4$ as the cathode. The whole flexible battery was sealed by polyethylene tapes (3M) in glove box. The galvanostatic discharge-charge measurements were carried out using a multichannel battery tester (Neware, BTS-610). The discharge of the first cycle was performed from the open circuit potential to 1 V, and all the

following tests were carried out within a voltage window of 1-3 V.

Supplementary Figure

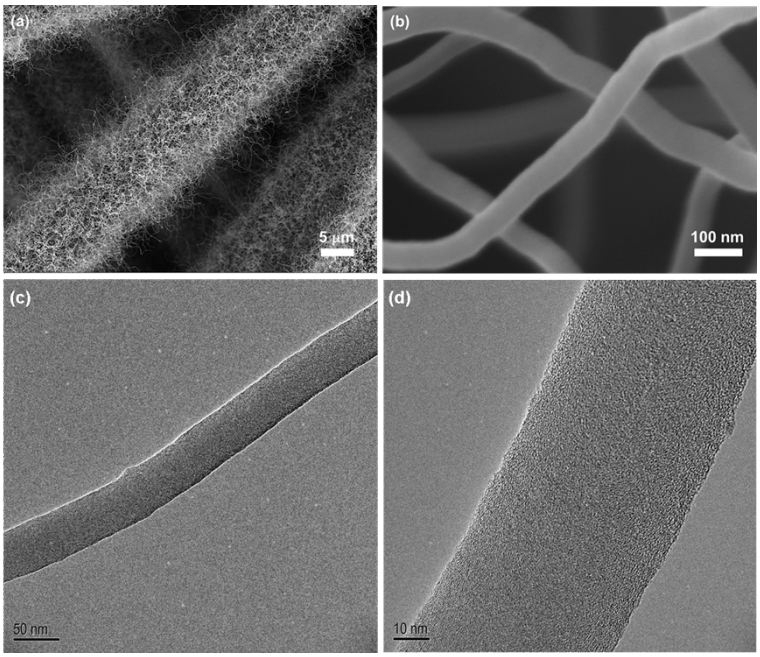

Fig. S1 Morphology characterization of the hierarchical 3D carbon nanowire arrays (CNWAs) on carbon cloth. (a) Low and (b) high magnification SEM images of the hierarchical 3D 3D CNWAs. (c) TEM and (d) HRTEM images of a carbon nanowire.

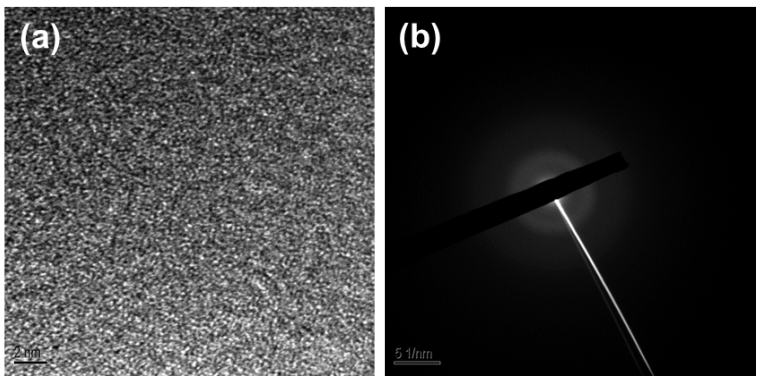

Fig. S2 (a) The HRTEM image and (b) selected-area electron diffraction (SAED) pattern of the TiO_2 layer.

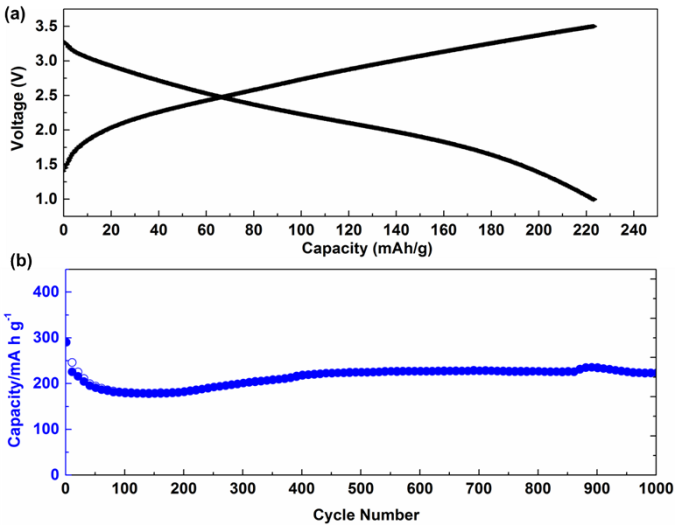

Fig. S3 (a) The typical voltage profile and (b) capacity retention of C@TiO_2/$LiMn_2O_4$ whole battery at a current density of 5 C in the voltage range of 1-3.5 V.

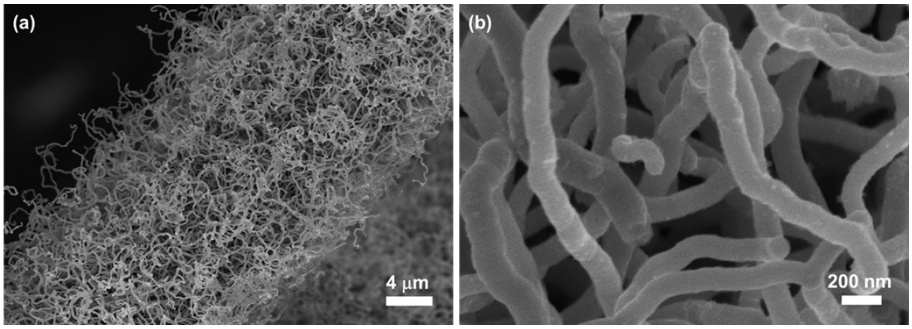

Fig. S4 (a) Low and (b) high magnification SEM images of the the hierarchical 3D C@TiO_2 core-shell NCAs after 2000 cycles at a high rate of 5 C.

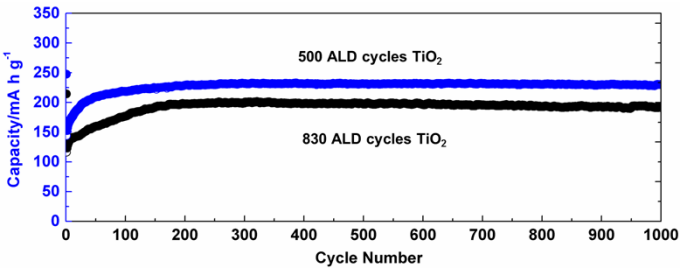

Fig. S5 Capacity retention of the C@TiO_2 core-shell NCAs electrodes with 500 and 830 ALD cycles at a current rate of 1 C.