Supporting Information

Surface graphited carbon scaffold enables simple and scalable fabrication of 3D composite lithium metal anode

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Experiments

Synthesis method: A total of 0.5 g polyacrylonitrile (PAN) (Mw=150000, Sinopharm Chemical Reagent Co., Ltd) and 0.04 g FS-51 (surfactant) were added into 10 ml dimethylformamide (DMF) (analytically pure, Sinopharm Chemical Reagent Co., Ltd). The as-prepared solution was stirred at 70 ^{o}C for 12 h. The electrospinning process was conducted with the following parameters: 20-cm nozzle-to-collector distance, 15-kV voltage, 1-mL/h pump rate, 10-cm × 10-cm graphite paper collector size and 12-h electrospinning time. The as-prepared fiber film was stabilized in air at 300 ^{o}C for 2 h in a box furnace (MTI). The oxidized fiber was carbonized at 650 ^{o}C under argon atmosphere for 2 h with a heating rate of 10 ^{o}C min^{-1} in a tube furnace (Zhonghuan Experiment Electric Furnace) to obtain LT-CNFs. The LT-CNFs were then heated at 800 ^{o}C under argon atmosphere for 2h with a heating rate of 5 min^{-1} in a tube furnace. Finally, the 800 °C carbonized nanofibers were further carbonized under argon atmosphere at relatively high temperatures of 1000 ^{o}C and 1200 ^{o}C for 2h with a heating rate of 5 min^{-1} in a tube furnace to obtain HT-CNFs. To fabricate the 3D composite Li, 3 mg of Li was put on the piece of HT-CNFs (1 cm^{-2}), and heated together with the HT-CNFs at the temperature of 250 ℃.

Electrochemical measurements: 2032-type coin cells (MTI) were constructed in an Ar-filled glove box (Etelux, Lab2000). The carbonate-based electrolyte is composed of hexafluorophosphate ($LiPF_6$, 1M) as Li salt, ethylene carbonate and diethyl carbonate (volume ratio 1:1) as co-solvent. A 25 μm-thick microporous polypropylene membrane (Celgard) was used as the separator. For the galvanostatic cycling test, Li foils (1 cm^{-2}, 200 μm thick, 99.9%, Alfa Aesar) were used as the control electrodes. For the symmetrical cell test, the cells were assembled with two identical electrodes (1 cm^2). To prepare $LiCoO_2$ electrodes, the $LiCoO_2$ powders (MTI) were mixed with polyvinylidene fluoride (MTI) and carbon black (TIMCAL) at a ratio of 8:1:1 with N-Methyl-2-pyrrolidone as the solvent. For the full cell test, the as-prepared $LiCoO_2$ electrode (the areal density is 5 mg cm^{-2}) was used as the cathode and a Li foil (1 cm^{-2}, 50 μm thick, 99.9% for cycling test, 1 cm^{-2}, 200 μm thick, 99.9% for rate test) was used as the control anode, the 3D composite Li as the modified anode. To standardize

the measurement, a fixed amount (40 µl) of electrolyte was used in each coin cell. All electrochemical tests were conducted using the Land 8-channel battery tester. EIS measurements were obtained over the frequency range of 100 kHz to 10 mHz with an amplitude of 5 mV using an electrochemical analyzer (CHI800D, Shanghai Huachen Instruments).

Characterizations: The microstructure of all the samples was investigated by scanning electron microscopy with a MERLIN Compact Zeiss scanning electron microscope. The XRD patterns of the as-fabrication materials were evaluated using a D/max-2500 diffractometer (Rigaku, Japan) equipped with a CuK_{α} radiation source. TEM observations were conducted on JEOL-ARM-200F TEM operated at 200 kV. Raman patterns were observed by a spectrograph (Princeton sp-2500).

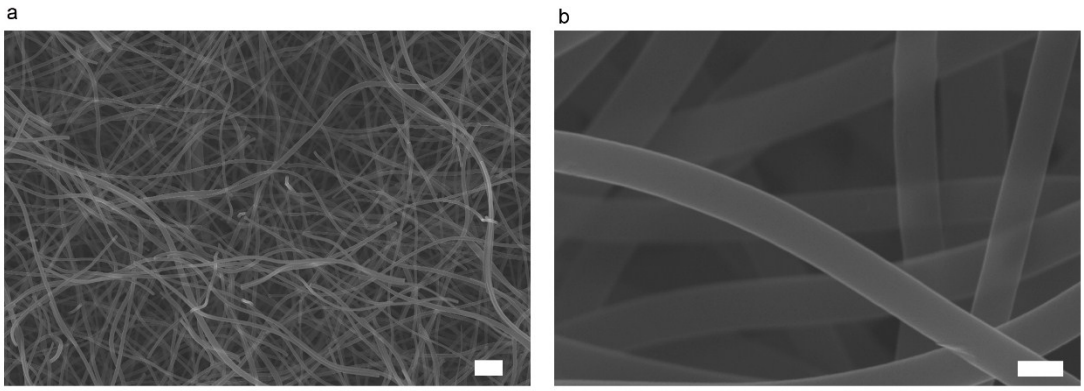

Fig. S1 SEM images of the LT-CNFs. (a) Low magnification. (b) high magnification. Scale bar, 2 µm (a), 200 nm (b).

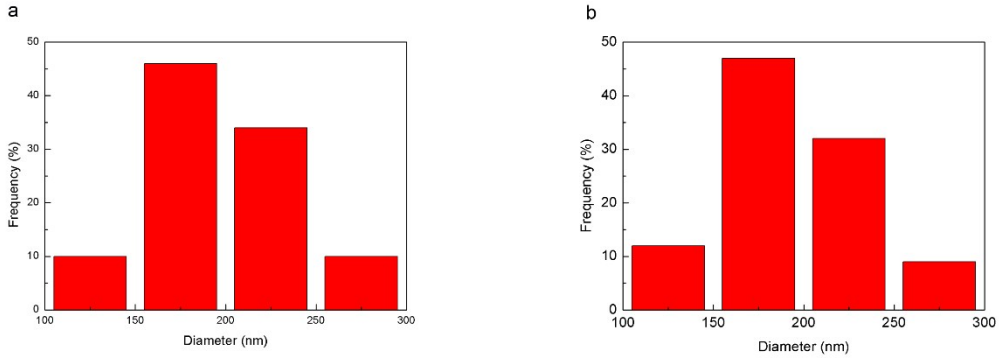

Fig. S2 Statistics of the carbon nanofiber diameter distribution. (a) Diameter distribution of the LT-CNFs. (b) Diameter distribution of the HT-CNFs.

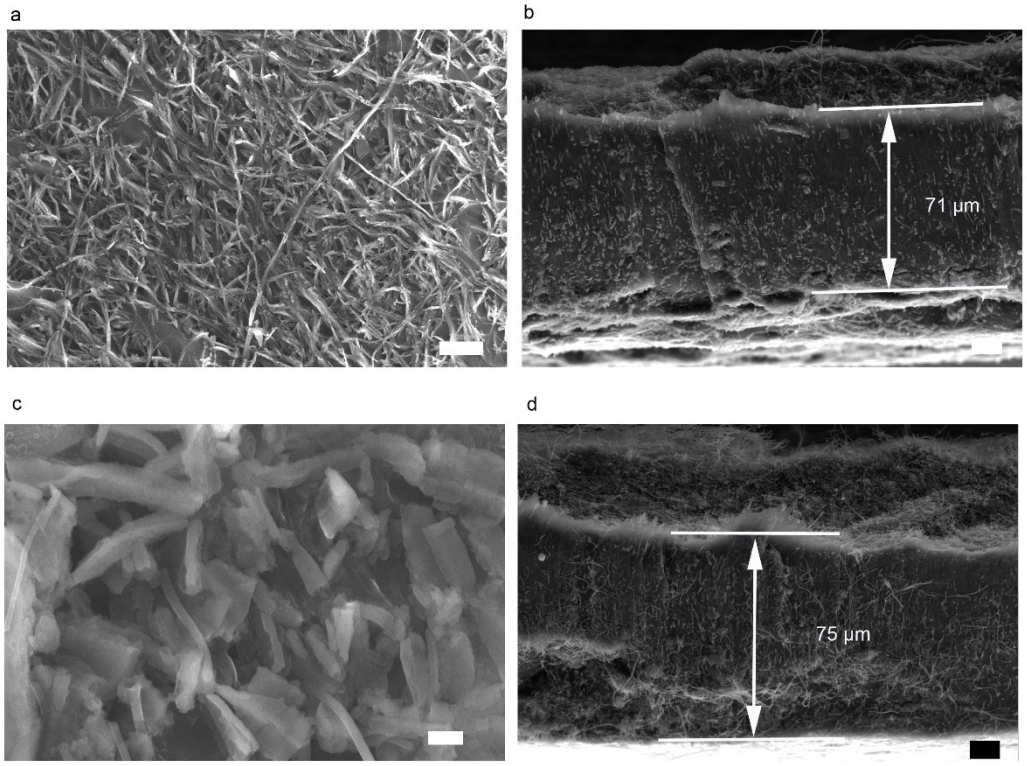

Fig. S3 Top-view SEM image (a), cross section SEM images (b,c) of the 3D composite Li before cycling and cross section SEM image of the 3D composite Li after 100 cycles at a current density of 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2} (d). Scale bar, 10 μm (a,b,d) and 1 μm (c).

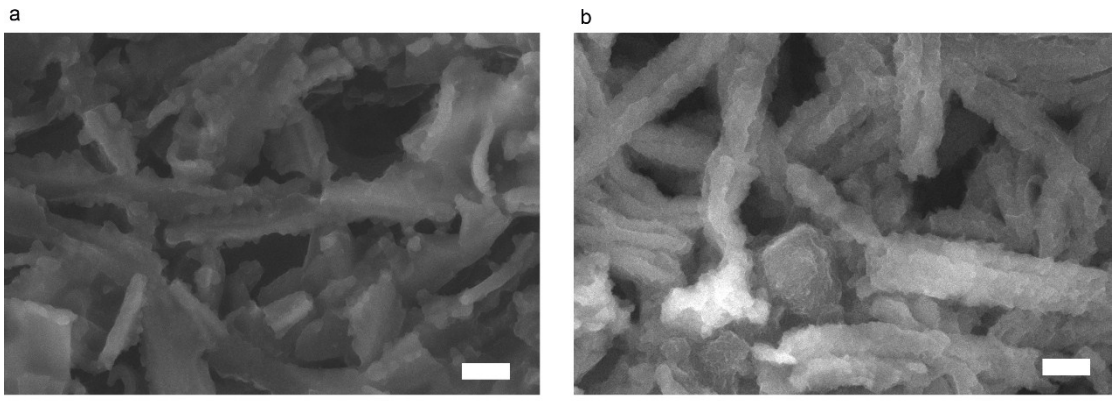

Fig. S4 Top-view SEM images of the internal structure of the 3D composite Li before cycling (a) and after 100 cycles at a current density of 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2} (b). Scale bar, 1 μm (a,b).

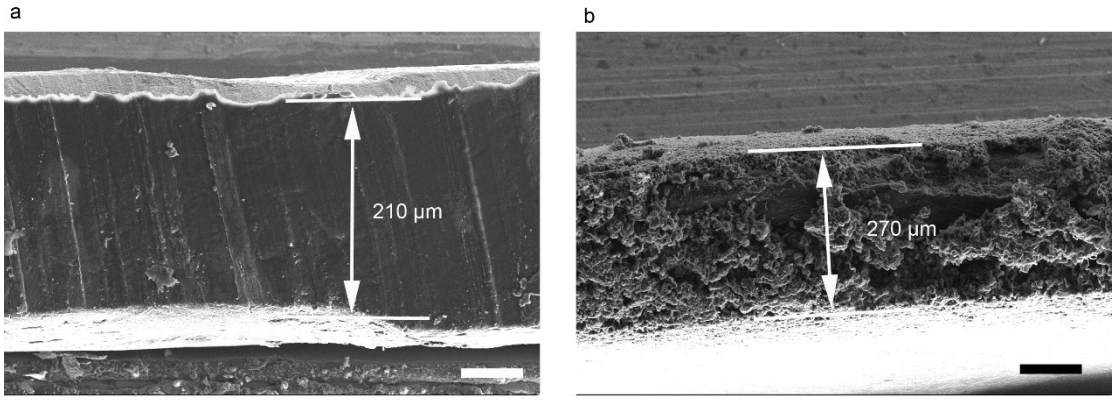

Fig. S5 Cross section SEM images of the bare Li before cycling (a) and after 100 cycles at a current density of 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2} (b). Scale bar, 60 µm (a) and 100 µm (b).

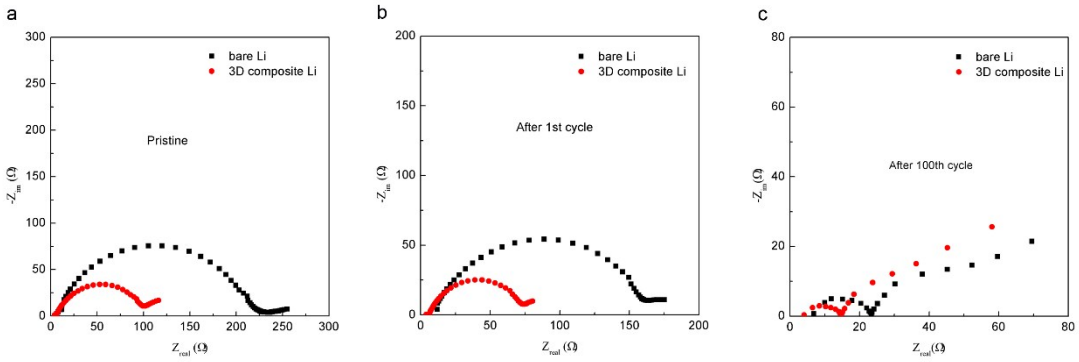

Fig. S6 (a) Electrochemical impedance spectroscopy of the 3D composite electrode and the bare Li electrode before cycling. (b) Electrochemical impedance spectroscopy of the 3D composite electrode and the bare Li electrode after the 1st cycle at the current density of 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2}. (c) Electrochemical impedance spectroscopy of the 3D composite electrode and the bare Li electrode after the 100th cycle at the current density of 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2}.

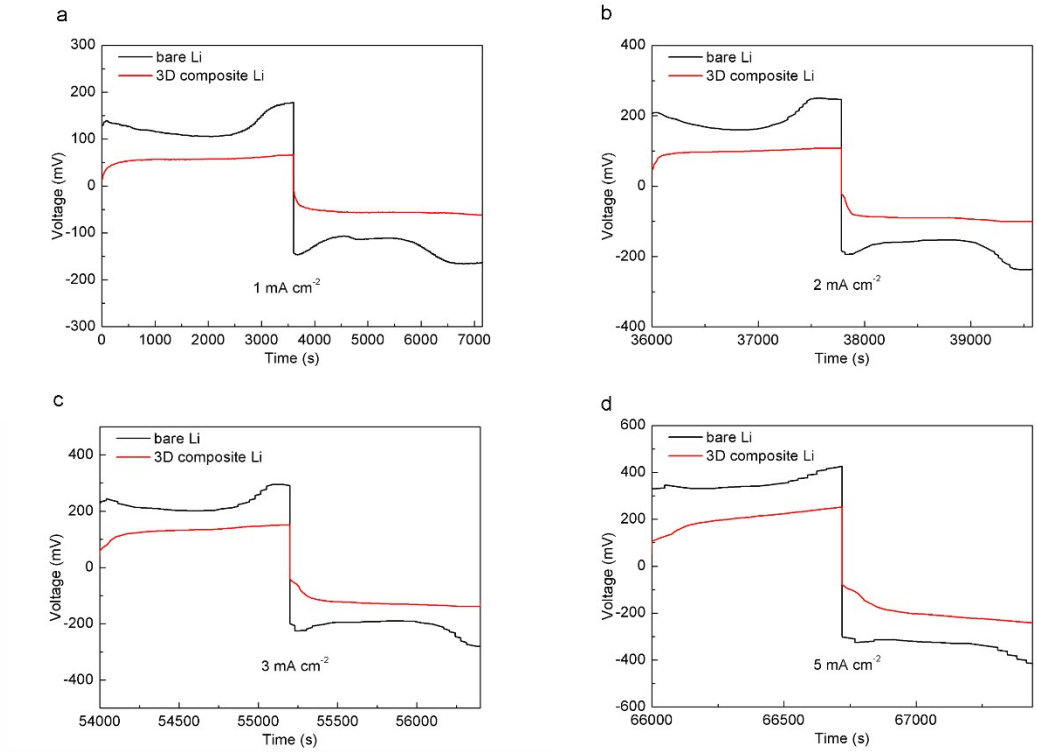

Fig. S7 The detailed voltage profiles of the 1st cycle for the 3D composite Li electrode and bare Li electrode at 1 mA cm^{-2} (a), 2 mA cm^{-2} (b), 3 mA cm^{-2} (c) and 5 mA cm^{-2} (d) in Fig. 3e.

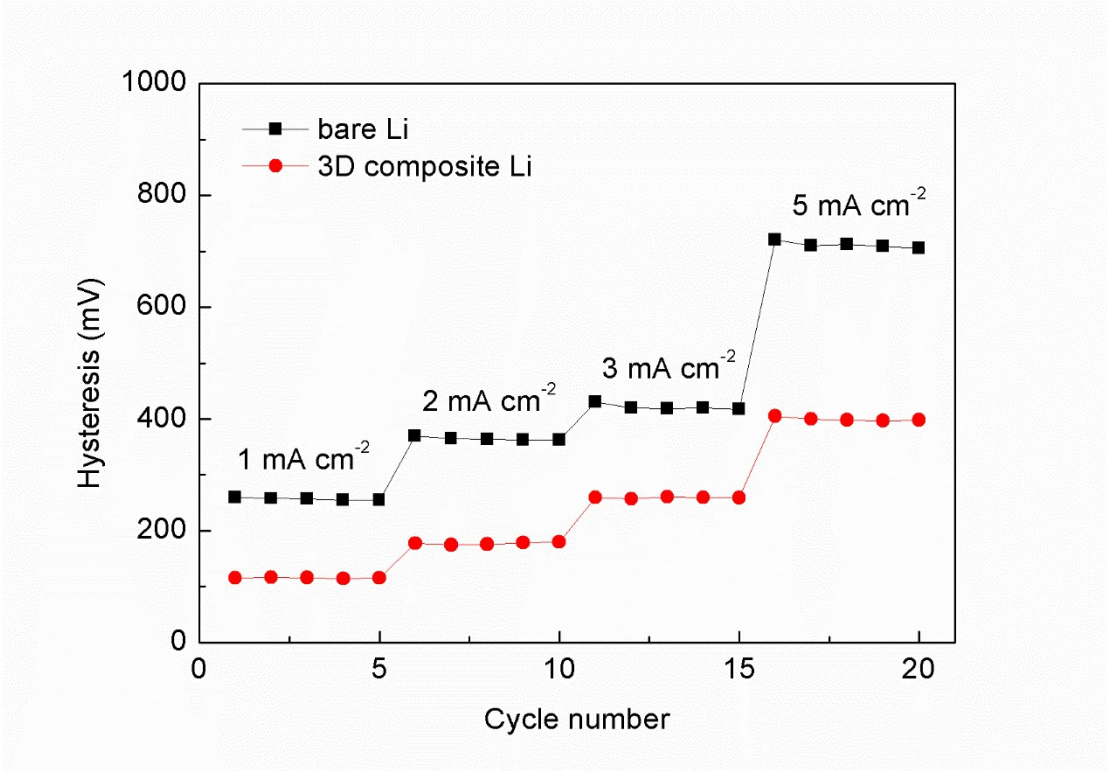

Fig. S8 Voltage hysteresis of the 3D composite Li electrode and the bare Li electrode under various current density.

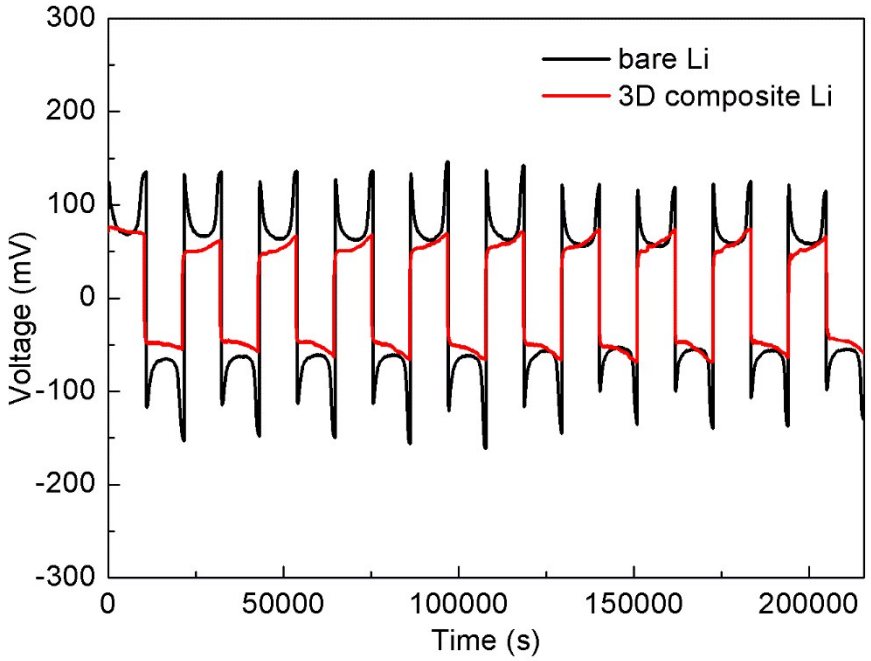

Fig. S9 Galvanostatic cycling of a symmetric 3D composite Li electrode and bare Li for 10 cycles at the current density of 1 mA cm^{-2} with a capacity of 3 mAh cm^{-2}.

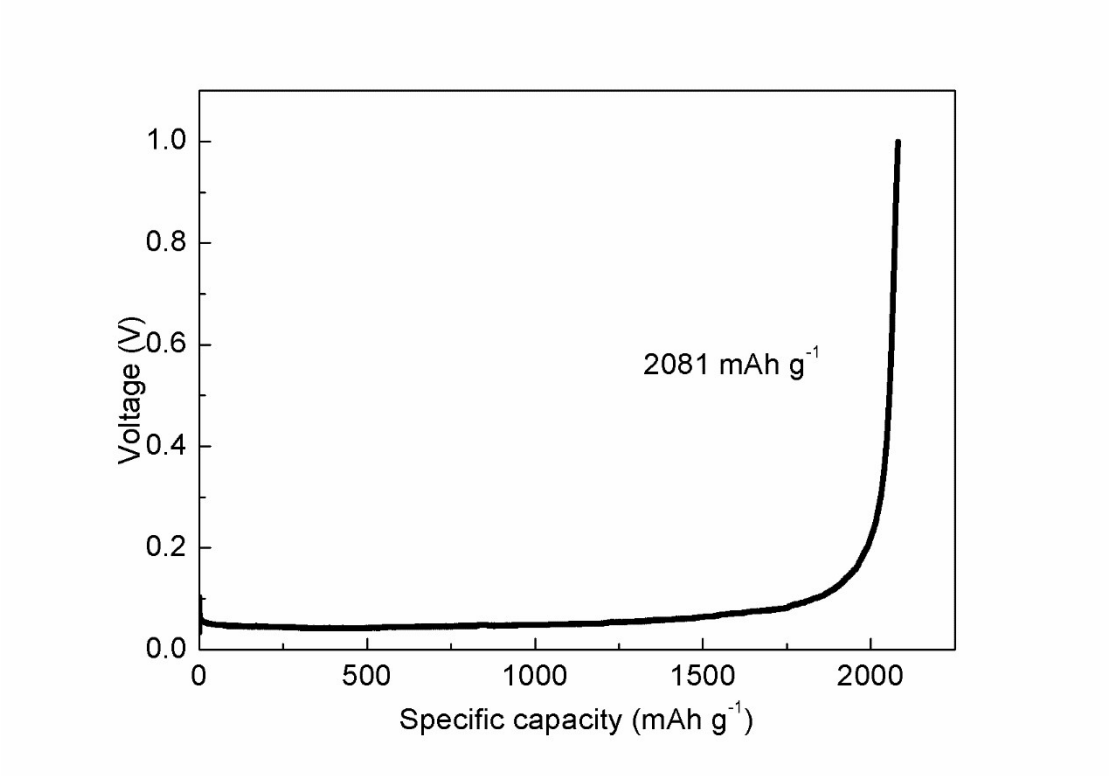

Fig. S10 Electrochemical stripping curve for the 3D composite Li electrode at the current density of 1 mA cm^{-2}. The cutoff voltage is set at 1 V.

Table S1. Weight of the HT-CNF film and the 3D composite Li

Materials	Average weight (mg)
HT-CNF film	1.9
3D composite Li	4.9

Video S1. Observation of Li melt infusion into the HT-CNFs film.