Supporting Information

In-situ carbonized cellulose-based hybrid film as flexible paper-anode for lithium-ion batteries

Shaomei Cao[†], *Xin Feng*[*,†], *Yuanyuan Song*[‖], *Hongjiang Liu*[‡], *Miao Miao*[†], *Jianhui Fang*[‡], *Liyi Shi*[†]

[†] Research Center of Nano Science and Technology, Shanghai University, Shanghai 200444, P. R. China

[‡] Department of Chemistry, College of Science, Shanghai University, Shanghai 200444, P. R. China

[‖] School of Materials Sciences and Engineering, Shanghai University, Shanghai 200444, P. R. China.

*Corresponding Author:

*E-mail: fengxin@shu.edu.cn (X. Feng).

Experimental section

Materials

$Li_4Ti_5O_{12}$ (LTO) powders with particle size of 100-200 nm were synthesized in laboratory according to our previous literature[S1]. Cellulose nanofiber (CNF) with fiber diameter of 20-30 nm and aspect ratios of 20-200 was extracted from dealginate kelp residues by according to our reported procedures[S2-S4]. Carbon nanotubes (CNTs) aqueous dispersion (solid content: 4 wt%) with diameter of 30-50 nm and length of 5-12 μm was provided by Shenzhen Susn Sinotech New Materials Co., Ltd (China). Sodium dodecyl benzene sulfonate (SDBS) and glycerol were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Lithium hexafluorophosphate ($LiPF_6$), ethylene carbonate (EC) and diethyl carbonate (DEC) electrolyte were purchased from Zhangjiagang Guotai Huarong New Chemical Material Co., Ltd.

Fast fabrication of LTO/CNF/CNT hybrid film

Free-standing LTO/CNF/CNT hybrid network film was prepared by pressure-controlled aqueous extrusion papermaking process as described in our previous work[S5]. Firstly, a conductive slurry containing 10 mL CNF suspension (0.1% w/w), 20 mL CNT aqueous (0.1% w/w, SDBS as stabilizer), 70 mL LTO dispersions (0.1% w/w) and 1.0 g glycerol (used to improve the film forming ability) was prepared by sonication in 10 ℃ water bath for about 30 min. Secondly, the conductive slurry was poured into a pressured extruder and filtrated through a PC membrane (nuclepore track-etch membrane, pore size 200 nm, Whatman, U.K) under a controlled pressure of 1.0 MPa, and the process took about 30 min to obtain the filter cake. Then, the filter cake with the PC membrane was subsequently sandwiched between two glass sheets and dried at 95 °C under vacuum for 15 min. Finally, the free-standing hybrid film was easily separated from the PC membrane.

In situ carbonization of LTO/ CNF/CNT hybrid film

The LTO/CNF/CNT hybrid film was carbonized at 400 °C with a slow heating rate of 5 °C·min^{-1} for 2 h in a tube furnace (FRH-100/520/1250, Linn High Therm, Germany) under high purity argon flow. After cooling to ambient temperature, the flexible free-standing LTO/C-CNF/CNT hybrid film with high conductivity was ultimately obtained. The LTO/C-CNF/CNT hybrid film for LIBs anode was marked as LCC-A. The comparative anode

fabricated using the same method without carbonization process was marked as LCC-U.

Characterization

The surface and cross section topography of the paper-anode before/after cycling were imaged using a field emission scanning electron microscope (FESEM) (JSM-6700F, JEOL, Japan). The morphology of LTO/CNF/CNT in aqueous suspension was observed using a transmission electron microscope (TEM) (JEM-2010F, JEOL, Japan). X-ray diffraction (XRD) patterns (D/max 2550, Rigaku, Japan) were taken to detect the different components in the hybrid film. Raman spectra were recorded with amicro Raman spectroscope (INVIA, Renishaw, England) using 633 nm laser as the excitation source to verify the structure characteristics of carbon nanomaterials Thermogravi metric analysis (TGA) was carried out on a combined thermal analyzer (STA 409 PC, Netzsch, Germany) with a heating rate of 10 °C·min^{-1} in different (nitrogen/oxygen) atmosphere. Nitrogen adsorption-desorption isotherms were measured at 77 K (NOVA2000, Quantachrome, America) and the samples were degassed in a vacuum at 200 °C for 2 h before measurement. Electron conductivity was measured by the standard four probe technique (RTS-8, China) and the measurements were averaged on 3 replicates.

Electrochemical Measurement

The electrochemical performance of the LCC-A and LCC-U flexible electrode was investigated in the coin half-cells. The obtained hybrid films were cut into disks with diameter of 15 mm, and then dried at 80 °C in vacuum overnight. CR2016 coin-type half-cells were assembled in an argon-filled glove box (O_2 and H_2O content＜0.5 ppm) using Li-foil as counter electrode as well as reference electrode, Celgard 2400 as separator, and 1 M $LiPF_6$ in a 1:1 (v:v) mixture of EC and DEC as the electrolyte. Galvanostatic discharge/charge tests were carried out on Land CT2001A auto cycler in a voltage window of 1.0~2.5 V (vs. Li/Li$^+$) at room temperature (25 °C). Cycle voltammograms (CV) were recorded from 0.8 V to 2.5 V at a scanning rate of 0.2~5.0 mV·s^{-1} using a CHI660D Electrochemical Workstation, and the electrochemical impedance spectrums (EIS) were measured by CHI660D Impedance Analyzer in the frequency range from 10 mHz to 100 kHz with a potential perturbation at 5 mV. All the LIBs measurements mentioned above are based on the mass of $Li_4Ti_5O_{12}$ in the electrode.

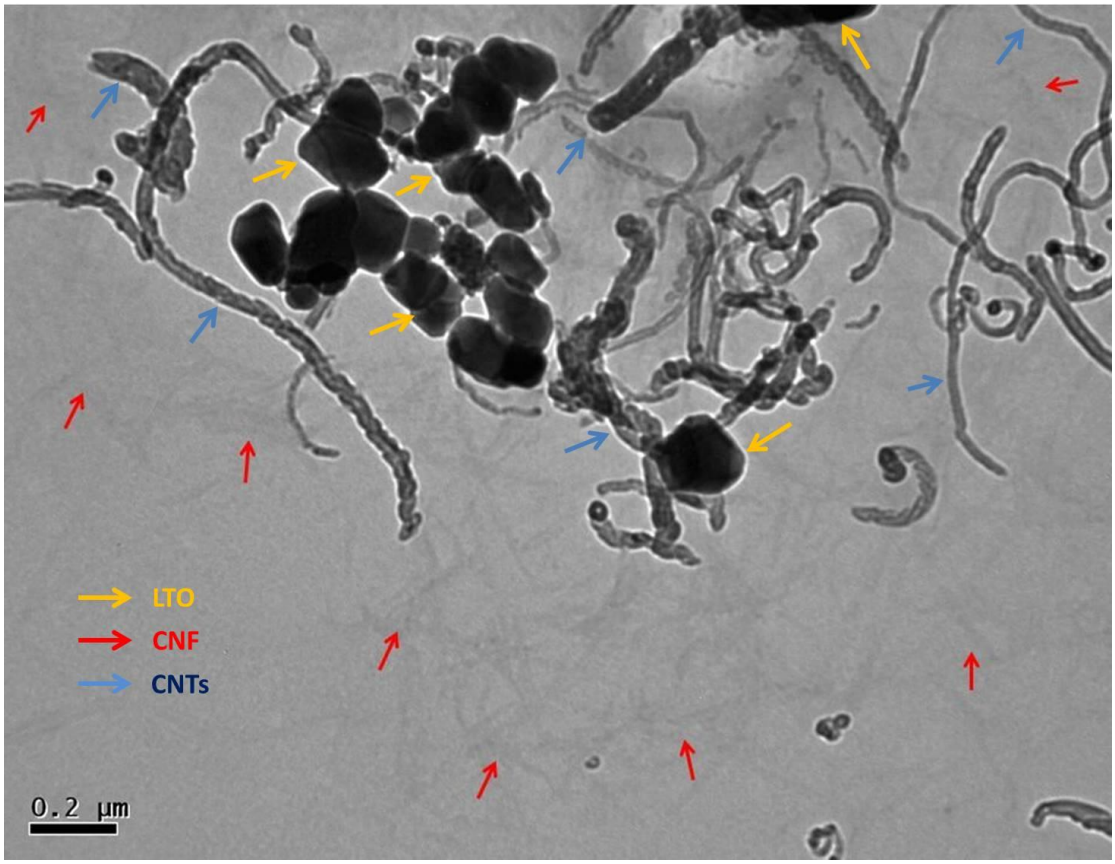

Fig. S1 TEM image of LTO/CNF/CNT

S1. Cheng, C.; Liu, H.; Xue, X.; Cao, H.; Shi, L. Highly Dispersed Copper Nanoparticle Modified Nano $Li_4Ti_5O_{12}$ with High Rate Performance for Lithium Ion Battery. *Electrochim. Acta* **2014**, *120*, 226-230.

S2. Miao, M.; Zhao, J. P.; Feng, X.; Cao, Y.; Cao, S. M.; Zhao, Y. F.; Ge, X. Q.; Sun, L. N.; Shi, L. Y.; Fang, J. H. Fast Fabrication of Transparent and Multi-Luminescent TEMPO-Oxidized Nanofibrillated Cellulose Nanopaper Functionalized with Lanthanide Complexes. *J. Mater. Chem. C* **2015**, *3*, 2511–2517.

S3. Feng, X.; Meng, X. H.; Zhao, J. P.; Miao, M.; Shi, L. Y.; Zhang, S. P.; Fang, J. H. Extraction and Preparation of Cellulose Nanocrystals from Dealginate Kelp Residue: Structures and Morphological Characterization. *Cellulose* **2015**, *22*, 1763-1772.

S4. Cao, Y.; Jiang, Y. Q.; Song, Y. Y.; Cao, S. M.; Miao, M.; Feng, X.; Fang, J. H.; Shi, L. Y. Combined Bleaching and Hydrolysis for Isolation of Cellulose Nanofibrils from Waste Sackcloth. *Carbohydr. Polym.* **2015**, *131*, 152-158.

S5. Cao, S. M.; Feng, X.; Song, Y. Y.; Xue, X.; Liu, H. J.; Miao, M.; Fang, J. H.; Shi, L. Y. Integrated Fast Assembly of Free-Standing Lithium Titanate/Carbon Nanotube/Cellulose Nanofiber Hybrid Network Film as Flexible Paper-Electrode for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2015**, *7*, 10695-10701.