Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2019

Dendrite-Free Deposition on Lithium Anode Toward Long-Life and High-Stable Li//Graphite Dual-Ion Battery

Xiao-Tong Xi,[a] Xi Feng,[a] Xue-Jiao Nie,[a] Bao-Hua Hou,[a] Wen-Hao Li,[b] Xu Yang,[a] Ai-Bo Yang,[a] Wen-Dong Sun,[a] Xing-Long Wu*[abc]

[a] *National & Local United Engineering Laboratory for Power Batteries, and Faculty of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China. E-mail: xinglong@nenu.edu.cn*
[b] *Key Laboratory for UV Light-Emitting Materials and Technology of Ministry of Education, Northeast Normal University, Changchun, Jilin 130024, P. R. China*
[c] *Institute of Advanced Electrochemical Energy, Xi'an University of Technology, Xi'an 710048, P. R. China*

1. Experimental Details:

The preparation of CNFs-Li: 1 g zinc oxide solid and 20 ml methanol were added to 50 ml circular bottom bottle, then 20 ml methanol solution containing 1.0 g 2-methylimidazole was added to the above solution under strong mechanical stirring. After stirring at room temperature for 72 h, 0.5 g 2-methylimidazole was added and stirred for 48 h. The obtained white product was centrifuged at 9000 rpm for 5 min and washed with ethanol for five times. Thus, ZIF-8 was obtained by drying with infrared lamp for 12 h. Then 0.6 g ZIF-8 particles were added to 8 ml dimethylformamide (DMF) and dispersed under ultrasonic wave for 30 h. Then 20 ml DMF solution of 11% PAN was added to the above solution and stirred for 18 h at room temperature. The evenly dispersed solution was added to the syringe with 20 ml, needle volume of 0.9 mm. The electrospinning device is then installed with the 10-15 cm distance between the needle and aluminum foil and the voltage setting is 10.5 kV. The resultant ZIF-8/PAN composite fibers were stabilization in a tubular furnace under air at 270 ^{o}C for 2 h with a heating rate of 1 ^{o}C min^{-1}. Further, the carbonization process was

measured in Ar atmosphere with a heating rate of 5 ^{o}C min^{-1}, the heating time is kept at an hour when the temperature is up to 500 ^{o}C. Then raising the temperature to 700 ^{o}C with identical heating rate, the heating time was hold for 2 h, finally natural cooling. The resultant fabric pellicles were named as CNFs. These obtained products of CNFs were soaked in 11% HCl aqueous solution for 24 h to remove resultant zinc metal and other basic impurities. These products were washed with distilled water and drying in a vacuum oven at 100 ^{o}C for 12 h.

Electrochemical Measurements: Electrochemical tests were analyzed in the CR2032 coin-type cells. The graphite electrode was prepared by mixing Natural graphite powder, acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 80:10:10. N-methyl-2-pyrrolidone (NMP) was added to the as-obtained mixture and grounded to form a uniform slurry. The slurry was cast uniformed onto aluminum foil and then dried at 100^{o}C under vacuum for 12 h. The mass loading of the graphite positive electrode was about 1 mg cm^{-2}. The carbonate ester-based electrolyte of 4 mol L^{-1} $LiPF_6$ dissolved in ethyl methyl carbonate (EMC) by purchasing from Shanghai Xiaoyuan. Glass fiber from Whatman was used as separator and lithium foils obtained from DodoChem were used as counter electrode. The specifications of Li foils are cylindrical shape with 15.6 mm in diameter and 0.45 mm in thickness. Therefore, the total amount of Li metal for each cell is about 45.9 mg. According to the charge curve at the 5th cycle in Fig. 3a in main text, the mass of Li metal utilized in a cycle is about 0.027 mg. The CNFs-Li electrode was prepared by directly pressing the CNFs film on the Li surface at a pressure of 1~2 MPa. And then, the metallic Li with CNFs modified assembled into Li//G DIB with 4 mol L^{-1} $LiPF_6$/EMC as the electrolyte. The bare Li anode was also matched with the graphite cathode in a coin cell to form Li//G DIB with 4 mol L^{-1} $LiPF_6$/EMC electrolyte for comparison. In the procedures of cell fabrication, 150 µL of electrolyte was used in each cell. The preparation of electrolyte and fabrication of batteries were conducted in an Ar-filled glove box followed by an overnight aging before test. The electrochemical properties of symmetric Li cells with different CNFs-Li and bare Li electrode were measured on the Arbin Instrument. Galvanostatic discharge/charge tests were carried out on the LAND-CT2001A battery test system in a voltage range of 3-5 V at various current densities. Electrochemical impedance spectroscopy (EIS) was performed with an amplitude voltage of 5 mV in the frequency range from 0.1 MHz to 100 MHz by using VersaSTAT 3 workstation.

2. Calculation of Apparent Diffusion Coefficient by EIS Method

The EIS Nyquist plots of both Li//G DIBs before cycling are shown in Fig. S6 in supporting materials. According to the fitting inclined lines in low frequency region, apparent diffusion coefficient (*D*) can be evaluated by the following eq 1:

$$D = (R^2T^2)/(2A^2n^4F^4C^2\sigma^2) \quad (1)$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the electrode (here, 1.13 cm^2), n is the number of electrons per reaction species, F is Faraday constant, C is the concentration of ion in the electrode, and σ is Warburg factor obtained by linear fitting of the inclined lines at low frequency as the eq 2:

$$Z_{re} \propto \sigma\omega^{-1/2} \quad (2)$$

The slopes of the straight line fitted and corresponding apparent diffusion coefficient of both Li//G DIBs are exhibited in Table S1, respectively.

Table S1. Apparent diffusion coefficient calculated from the EIS for CNFs-Li and bare Li electrode.

	CNFs-Li	**Bare Li**
slope	6.0228	33.3947
D（×10^{-11} cm^2/s）	4.27	0.12

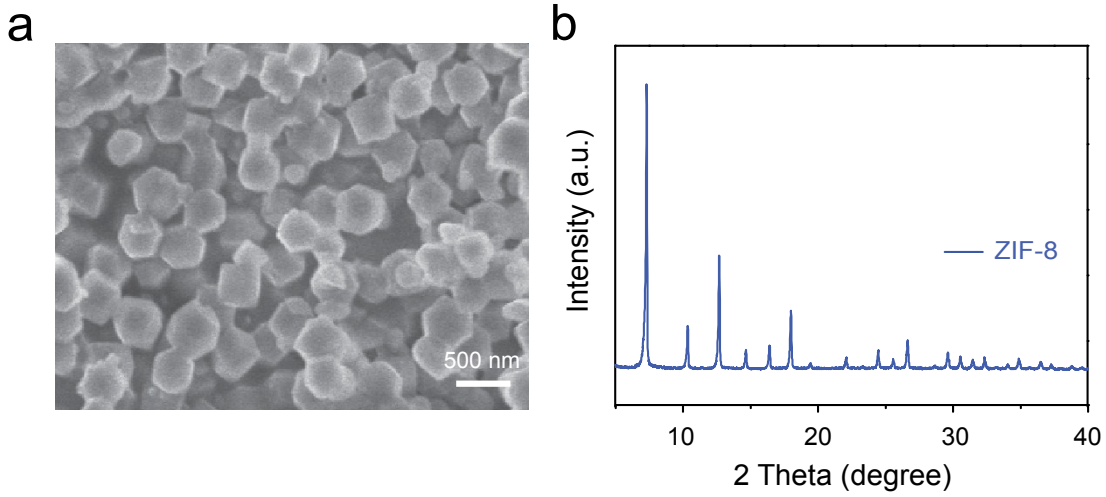

Fig. S1 SEM image (a) and XRD pattern (b) of the ZIF-8 nanoparticles.

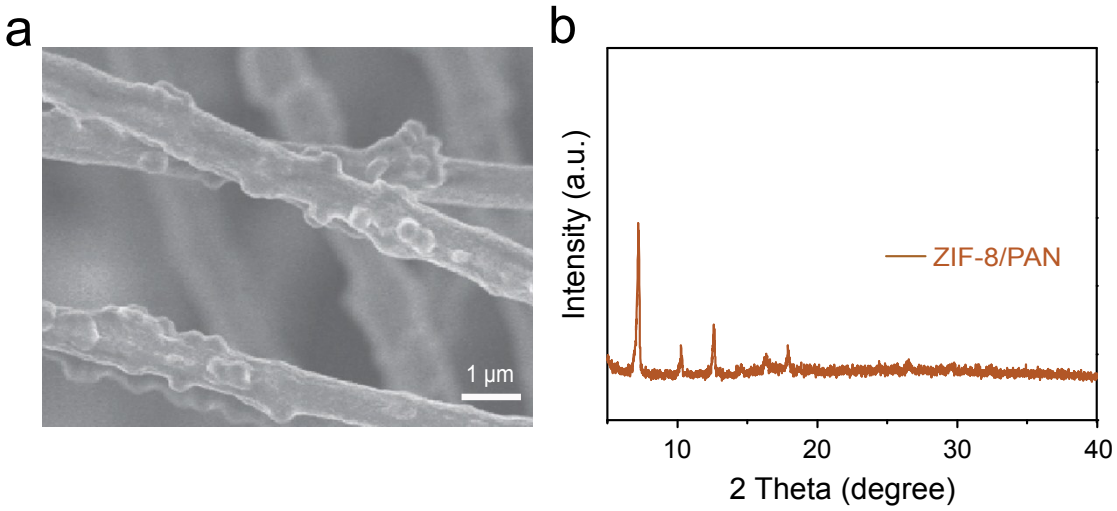

Fig. S2 SEM image (a) and XRD image (b) of the ZIF-8/PAN nanofibers.

As shown in Fig. S2, all the peak intensities of the ZIF-8/PAN nanofibers are much weaker than those of ZIF-8 nanoparticles, which is due to the PAN fibers encased part of the ZIF-8 particles,

thus weakening the peak intensities.

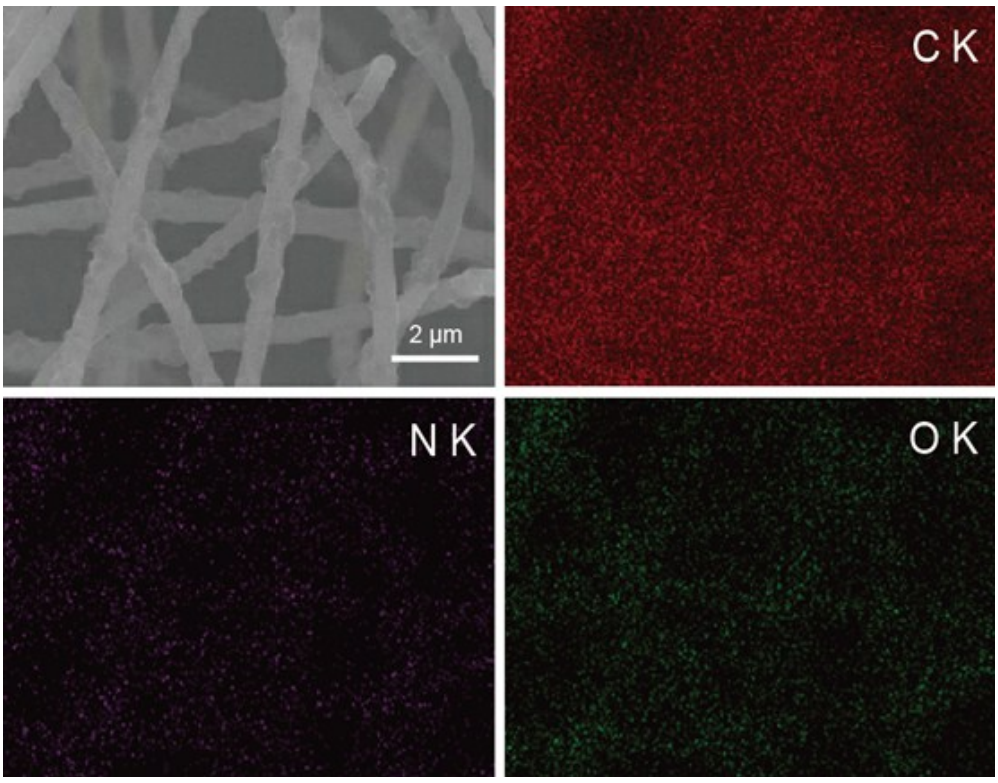

Fig. S3 SEM image of CNFs film and the corresponding elemental mappings for C, N and O, respectively.

Fig. S3 exhibits the surface of CNFs film with a great deal of relatively uniform nanofibers and the corresponding elemental mappings (C, N, and O), in which the elements are well-distributed homogeneously. This indicates that the CNFs film is doped with a small amount of nitrogen atoms.

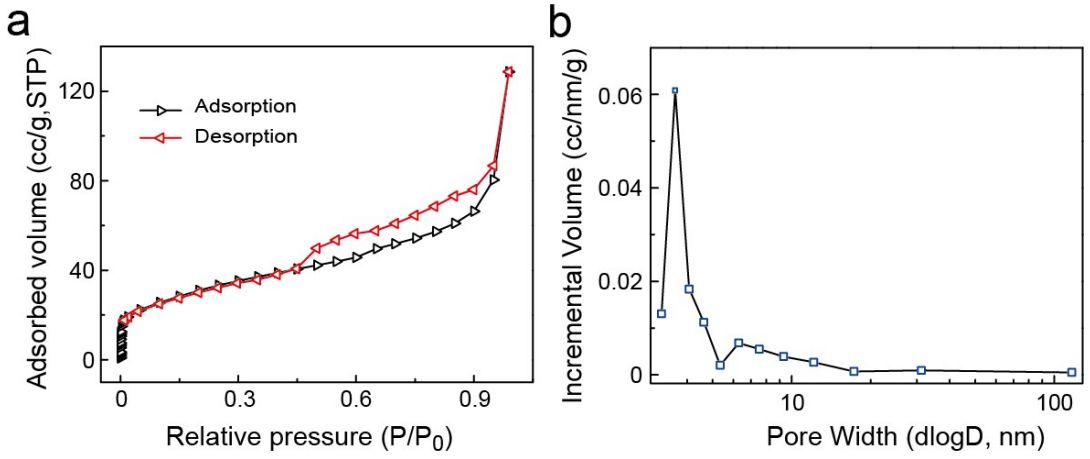

Fig. S4 (a) Nitrogen adsorption-desorption isotherms of the CNFs film and (b) the corresponding profile

of pore-size distribution.

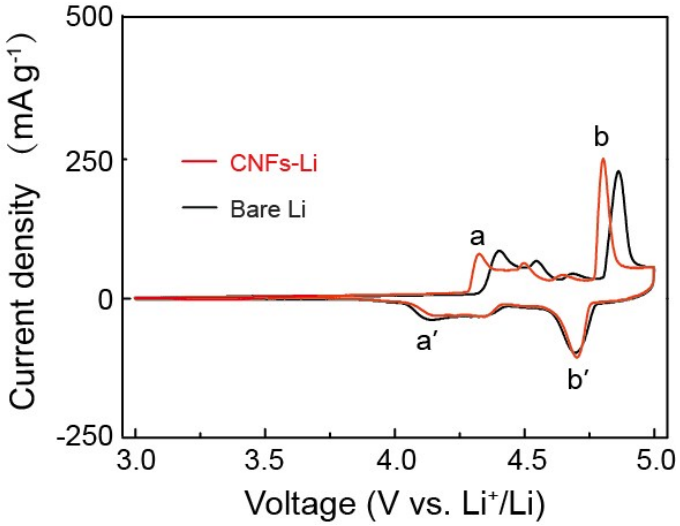

Fig. S5 The CV curves of CNFs-Li and bare Li in Li//G DIBs at a scan rate of 0.1 mV s^{-1}. The voltage range is 3-5 V vs. Li^+/Li.

As can be seen from Fig. S5, the CNFs-Li anode exhibits smaller voltage polarization than the bare Li in the Li//G DIBs.

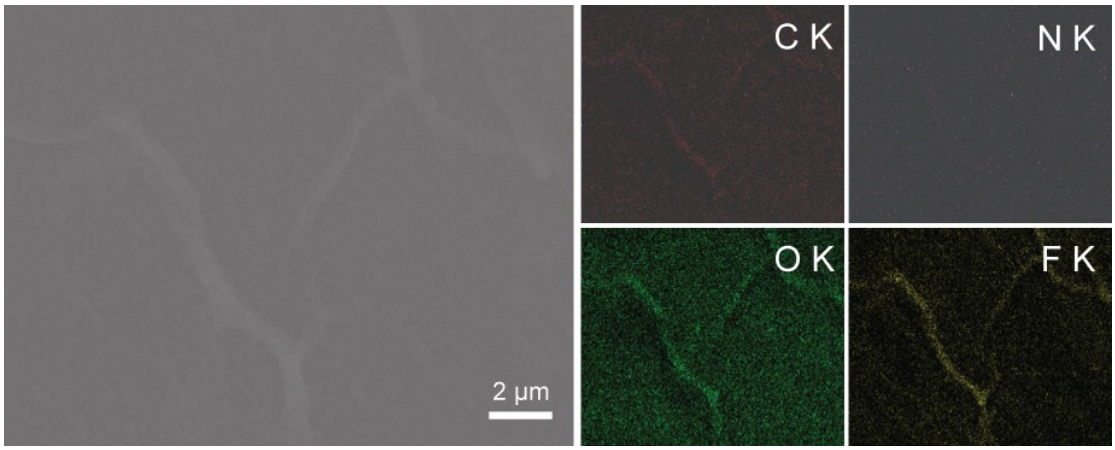

Fig. S6 SEM image of bare Li surface for Li//G DIB over 200 cycles at 0.2 A g^{-1} and the corresponding elemental mappings for C, N, O and F, respectively.

After 200 cycles, there exists lithium dendrites (about 10 μm in length and 1 μm in diameter) on the bare Li surface, as well as the elements C, N, O and F did not distribute evenly in the corresponding elemental mappings. As shown in Fig. S6, the largely increased F content reveals

that the continuous decomposition of electrolyte during the charge/discharge processes.

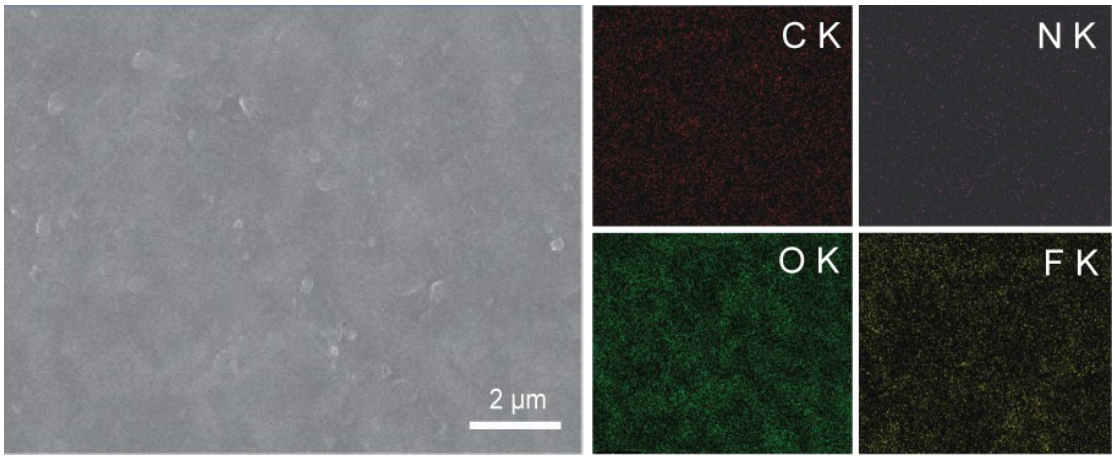

Fig. S7 SEM image of CNFs-Li surface for Li//G DIB after 200 cycles at 0.2 A g^{-1} and the corresponding elemental mappings for C, N, O and F, respectively.

After 200 cycles, the surface of the protected Li anode is still neat and smooth, as well as the elements (C, N, O and F) uniformly distribute in the corresponding elemental mappings. Compared with the bare Li surface, the content of F decreases largely, which shows that the decomposition of electrolyte is alleviated greatly.

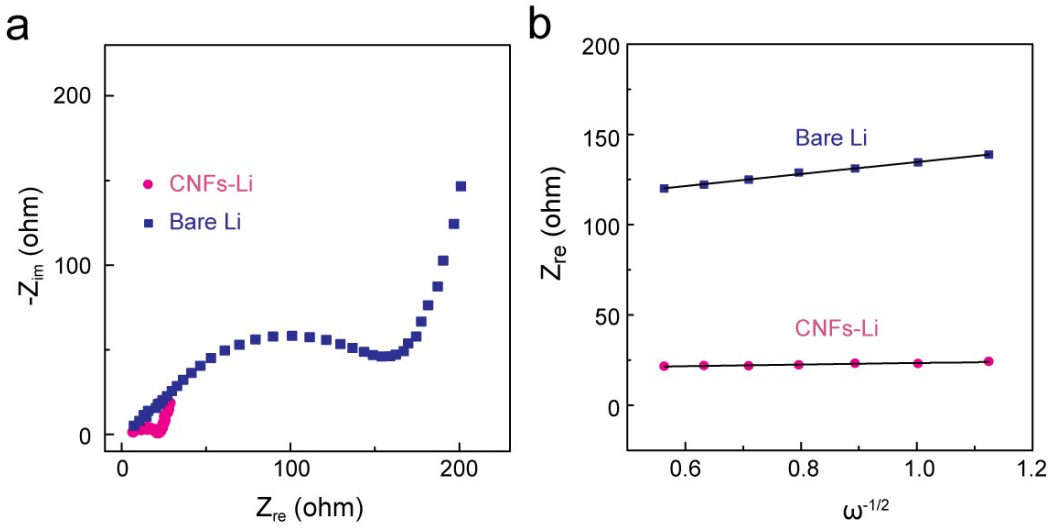

Fig. S8 (a) The Nyquist plots of impedance spectra of CNFs-Li and bare Li electrode before cycling. (b) The linear fitting between Z_{re} and reciprocal square root of frequency ($\omega^{-1/2}$) in the low-frequency region

for CNFs-Li and bare Li electrode, respectively.