Electronic Supplementary Information

Free-standing, Hierarchically Porous Carbon Nanotube Film as Binder-free Electrode for high-energy Li-O_2 batteries

Shaohong Liu, Zhiyu Wang, Chang Yu, Zongbin Zhao, Xiaoming Fan, Zheng Ling and Jieshan Qiu

*Carbon Research Laboratory, Liaoning Key Lab for Energy Materials and Chemical Engineering, State Key Lab of Fine Chemicals, Dalian University of Technology, Dalian 116024, P. R. China. E-mail: jqiu@dlut.edu.cn

b Physical Chemistry, Technical University of Dresden, Bergstraße 66b, 01062 Dresden, Germany. E-mail: wangzy1980@gmail.com

Experimental Details

Preparation of the suspension of functionalized CNTs: Pristine CNTs were refluxed in the solution of concentrated H_2SO_4/HNO_3/H_2O (3:1:1 in volume) at 100 °C for 4 h, followed by washing to neutrality with deionized (DI) water. The obtained functionalized CNTs were dispersed into DI water under ultrasonic for 1 h. After centrifuging at 9,000 rpm for 15 min, the supernatant containing well dispersed CNTs was harvested and its concentration is tuned to 0.5 mg mL\(^{-1}\) for later use.

Preparation of the hierarchically porous CNT film: Surface charged PS colloidal particles were prepared by emulsion polymerization.\(^{[43]}\) In a typical run, 9 mg of surface-charged PS particles was dispersed in 40 mL of CNT suspension made above under ultrasonic for 10 min. Afterwards, the mixed suspension was vacuum filtered onto a 0.22 micron cellulose ester filter paper to make CNT/PS composite films. These films were peeled off from the filter paper and were annealed in N_2 flow at 500 °C for 2 h with a ramp rate of 2 °C min\(^{-1}\). After complete removal of the PS particles, FHP-CNT films were obtained and were directly used as the air electrode in Li-O_2 batteries. For comparison, CNT films without large tunnels were also prepared by the same procedure except the introduction of the PS colloids.

Materials characterization: The morphology of the films were characterized with field-emission scanning electron microscopy (FESEM, FEI Nova Nano SEM 450 at 3 kV). Powder X-ray diffraction (XRD) patterns were recorded on a D/Max-III type X-ray spectrometer with Cu Kα radiation (\(\lambda = 1.5406\) Å). Before test, the discharged electrodes were sealed inside the glovebox to avoid exposure to air. N_2 adsorption/desorption isotherm of the samples were measured by Micrometrics ASAP 2020 Surface Area and Porosity Analyzer at 77 K.
**Electrochemical Measurements:** The electrochemical measurements were conducted using meshed CR2032 coin cells (Shenzhen Kejingstar, China) with pure Li foil as the counter electrode. The air electrodes were fabricated by punching FHP-CNT films into discs with a diameter of ca. 1.0 cm and mass loading of ca. 0.8 g cm\(^{-2}\), which are directly used as the air electrodes without using any auxiliary binders. The cells were assembled in an argon-filled glove box with 1 M LiPF\(_6\) in tetraethylene glycol dimethyl ether (TEGDME) as the electrolyte. All tests were performed on a Land CT2001A battery tester at different current densities within a cut-off voltage window of 2.2–4.4 V in 1 atm dry O\(_2\) at room temperature.

![Figure S1](image1.png)

**Figure S1** N\(_2\) adsorption-desorption isotherm of (a) FHP-CNT film and (b) CNT film.

![Figure S2](image2.png)

**Figure S2** SEM images of densely packed CNT films, which were synthesize by vacuum filtration of CNT suspension without using PS template.
Figure S3 XRD profiles of FHP-CNT electrode before and after discharge, showing the formation of Li$_2$O$_2$.

Figure S4 Discharge-charge profiles of FHP-CNT electrode with a capacity of 500 mA h g$^{-1}$. 
Figure S5 Nyquist plots of FHP-CNT and CNT electrodes.