Electronic Supplementary Information

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

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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 (λ = 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.

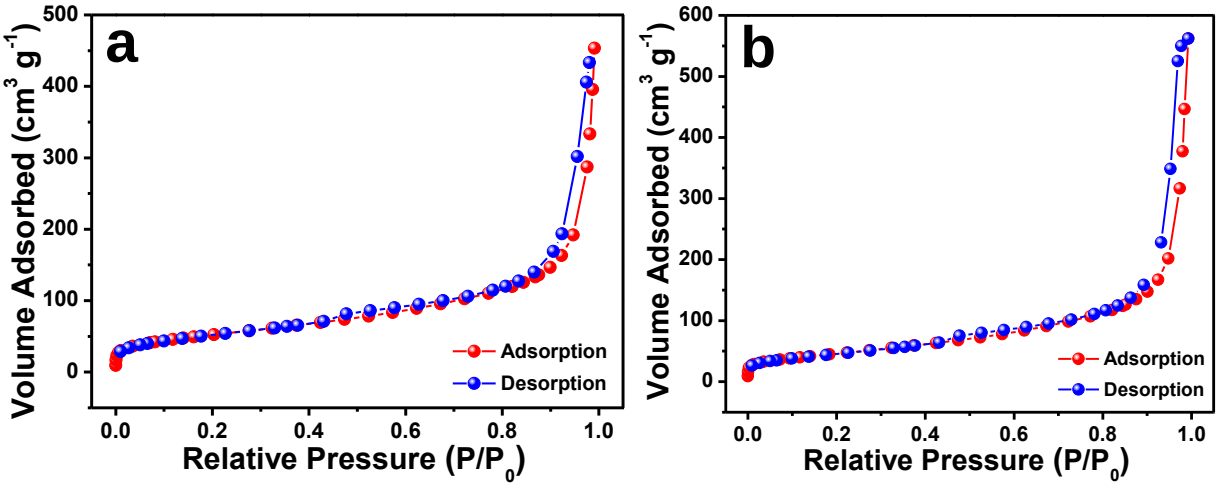

Figure S1 N_2 adsorption-desorption isotherm of (a) FHP-CNT film and (b) CNT film.

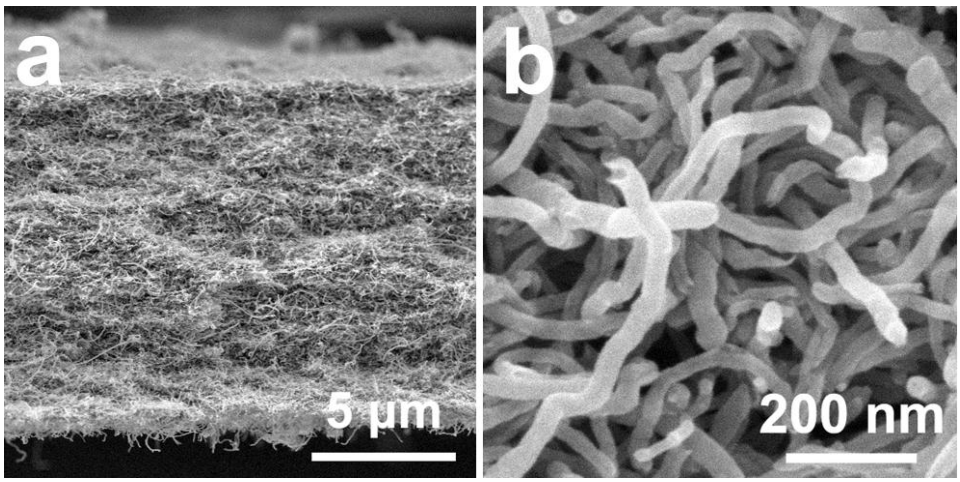

Figure S2 SEM images of densely packed CNT films, which were synthesize by vacuum filtration of CNT suspension without using PS template.

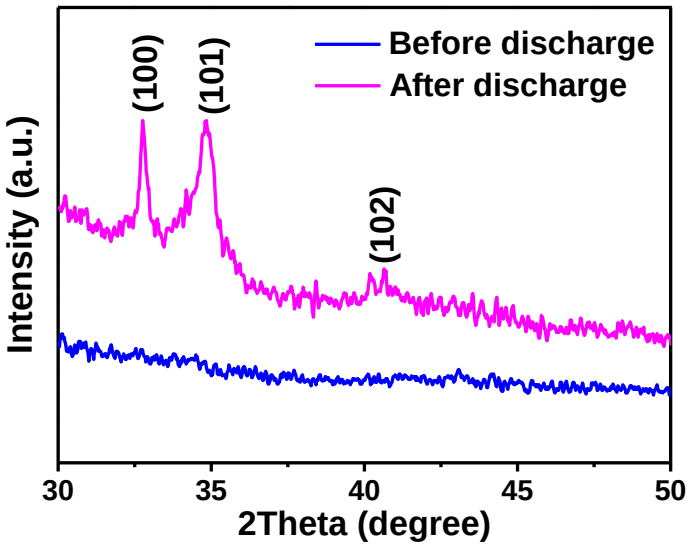

Figure S3 XRD profiles of FHP-CNT electrode before and after dishcharge, showing the formation of Li_2O_2.

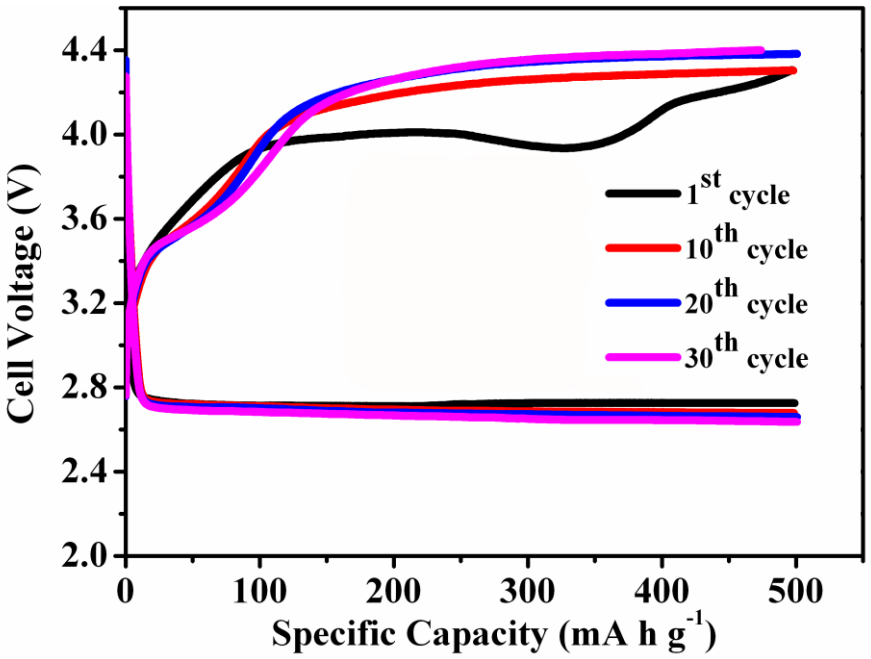

Figure S4 Discharge-charge profiles of FHP-CNT electrode with a capacity of 500 mA h g^{-1}.

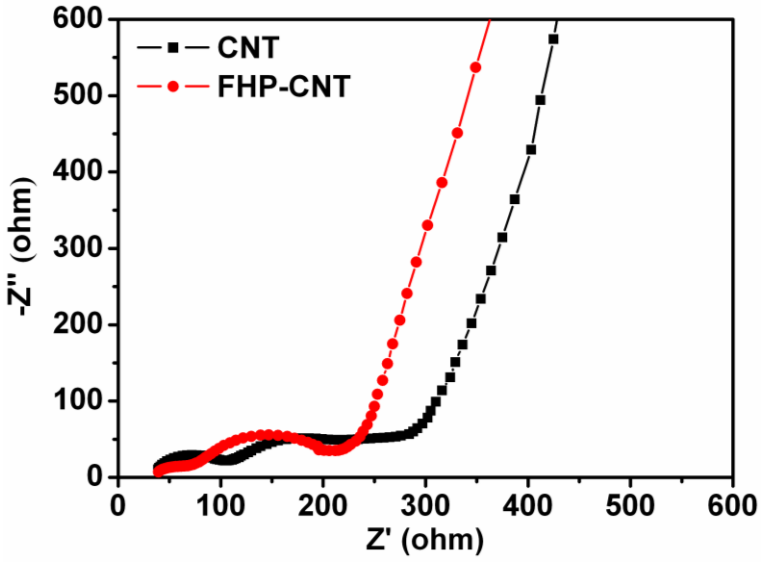

Figure S5 Nyquist plots of FHP-CNT and CNT electrodes.