

B₄C nanowires and carbon nanotubes composite as a novel bifunctional electrocatalyst for high energy lithium oxygen batteries

Wen-Bin Luo, Shu-Lei Chou*, Jia-Zhao Wang, Hua-Kun Liu

Experimental Section

Method: Firstly, 25 mg Ni(NO₃)₂ · 6H₂O and 10 mg amorphous boron nanopowder were dissolved into 20 ml ethanol to form a Ni–B emulsion under 2 h ultrasonication. Then, 60 mg CNTs was mixed into the above solution. After stirring for 2 h, the solution was dried at 70 °C under stirring and finally dried at 105 °C for 3 h. The BC composite was synthesized in a tube furnace (diameter: 55 mm, length: 1200 mm) by heating at 1200 °C for 6 h with 50 ml min⁻¹ continuous flow of nitrogen.

Characterization: The phase purity and the structure were analyzed by X-ray powder diffraction (GBC MMA) on an instrument equipped with Cu K α radiation that was operated over a 2 θ range of 10 – 70° in a continuous scan mode with a scan rate of 2° min⁻¹. The morphology of the samples was examined using field emission scanning electron microscopy (FE-SEM; JEOL JSM-7500). Transmission electron microscopy (TEM) investigations were performed using a 200 kV JEOL 2011 instrument. Atomic resolution analytical microscope (ARM) investigations were performed using a 200 kV JEOL 2011 instrument. Raman spectroscopy was performed using a Raman spectrometer (Jobin Yvon HR800) employing a 10 mW neon laser at 632.8 nm.

Electrochemical measurements: Electrochemical experiments were performed using CR2032 type coin cells with holes in the cathode shell. For preparing working electrodes, a mixture of the as-synthesized hybrid materials and poly(tetrafluoroethylene) (PTFE) at a weight ratio of

90:10, using Nafion (5wt.%) as the solvent, was pasted on the round carbon paper. Typical loadings of cathode powder for a cathode area of 1.1 cm² were $\sim 1.5 - 2.0$ mg cm⁻². The electrolyte consisted of a solution of LiCF₃SO₃ in tetraethylene glycol dimethyl ether (TEGDME) (molar ratio = 1:4). Pure lithium foil was used as the counter electrode. The cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany). Galvanostatic deep, full charge-discharge curves were collected at various current densities from 0.2 to 0.5 mA cm⁻² between 4.4 and 2.5 V vs. Li⁺/Li, and discharge-charge cycling was tested with 1000, 2000 and 3000 mAh g⁻¹ cut-off discharge capacity, followed by charging to 4.5 V vs. Li⁺/Li. All tests were carried out on LAND CT 2001A multi-channel battery testers at room temperature in oxygen atmosphere (High purity oxygen, 99.95%) using our specially designed facility. Measurements were repeated at least three times to ensure reliability.

The aqueous electrochemical tests involving the rotating disk electrode (RDE) were carried out using computer-controlled potentiostats (Princeton 2273 and 616 Princeton Applied Research) with a typical three-electrode cell. Platinum foil was used as the counter-electrode and an Ag/AgCl (saturated KCl filled) electrode as the reference electrode. The working electrodes were prepared by applying the respective catalyst inks onto pre-polished glassy carbon (GC) disk electrodes. Briefly, 5 mg of sample and 100 μ L 5wt.% Nafion solution were dispersed in 1 mL water/isopropanol (3/1; v/v) solution and ultrasonicated for 30 min to form the uniform catalyst ink (~ 5 mg mL⁻¹). A total of 4.5 μ L well-dispersed catalyst ink was applied onto a pre-polished glassy carbon (GC) disk electrode (5 mm in diameter). The electrodes thus prepared were dried at room temperature overnight prior to the electrochemical tests. The detailed kinetic analysis was conducted according to Koutecky-Levich plots:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}} \quad (1)$$

where j_k is the kinetic current and B is Levich slope, which is given by:

$$B = 0.2nF(D_{O_2})^{2/3} \nu^{-1/6} C_{O_2} \quad (2)$$

Here, n is the number of electrons transferred in the reduction of one O_2 molecule, F is the Faraday constant ($F = 96485 \text{ C/mol}$), D_{O_2} is the diffusion coefficient of O_2 ($D_{O_2} = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinematics viscosity for KOH ($\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$), and C_{O_2} is the concentration of O_2 in the solution ($C_{O_2} = 1.2 \times 10^{-6} \text{ mol cm}^{-3}$). The constant 0.2 is adopted when the rotation speed is expressed in rpm. According to Equations (1) and (2), the number of electrons transferred (n) can be obtained from the slope of Koutecky-Levich plot of j^{-1} vs. $\omega^{-1/2}$. The non-aqueous cyclic voltammograms (CV) tests were carried out using computer-controlled potentiostats (Princeton 2273 and 636 Princeton Applied Research) in a three-electrode system. $LiCF_3SO_3$ in TEGDME (molar ratio = 1:4) was used as electrolyte, the details can be found in our previous work. [1]

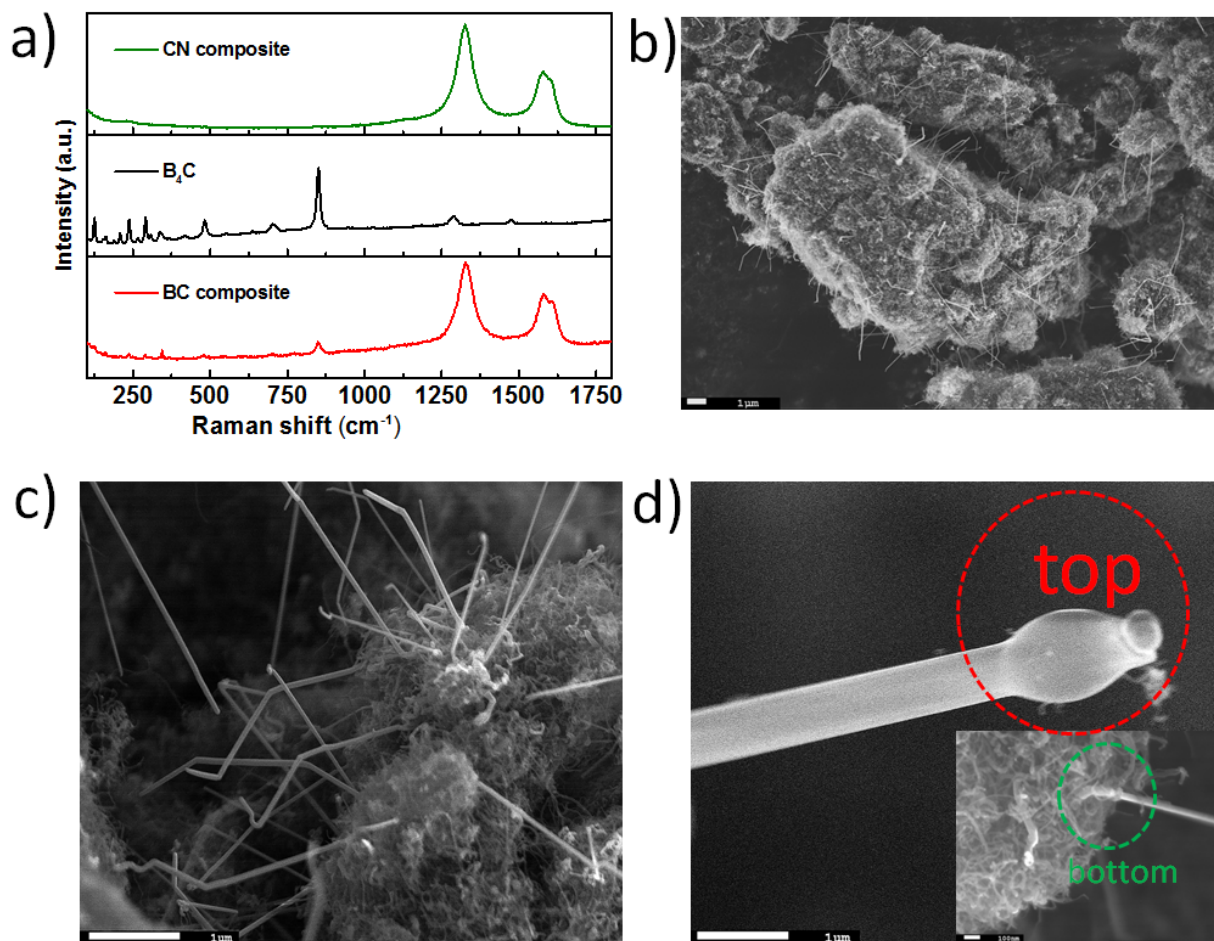


Figure S1. (a) Raman spectra of the pure B_4C , CN, and BC composite; (b, c, d) FESEM images of the BC composite;

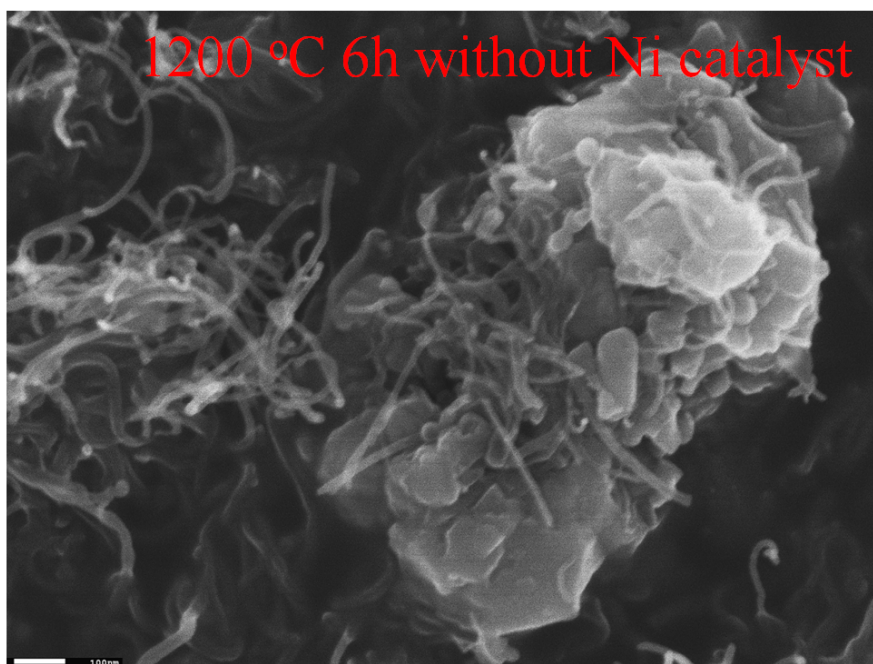


Figure S2. FESEM image of the reference composite grown without using Ni catalyst.

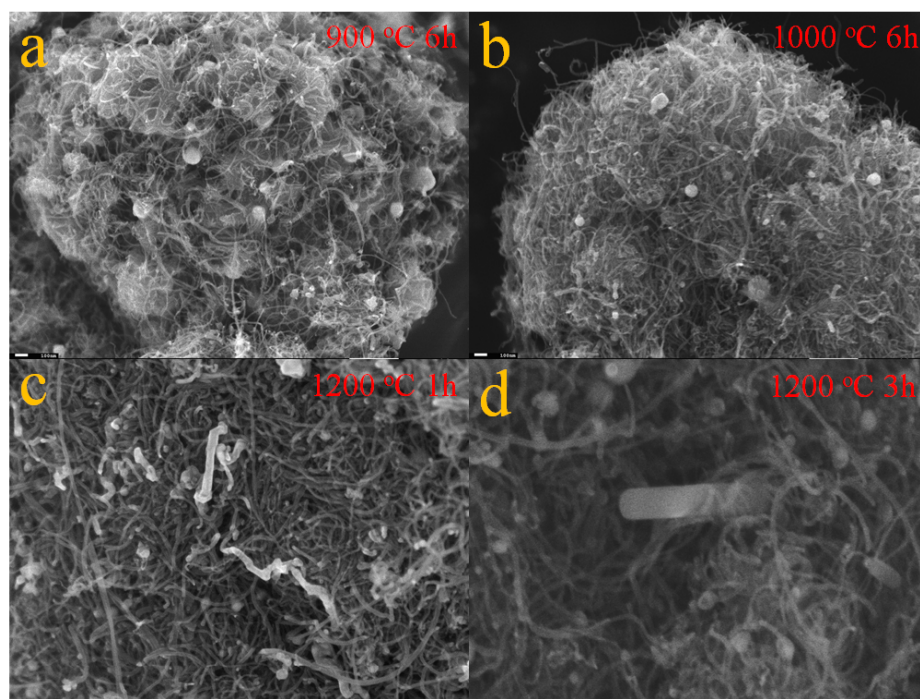


Figure S3. FESEM images of the composite with different annealing temperatures and times

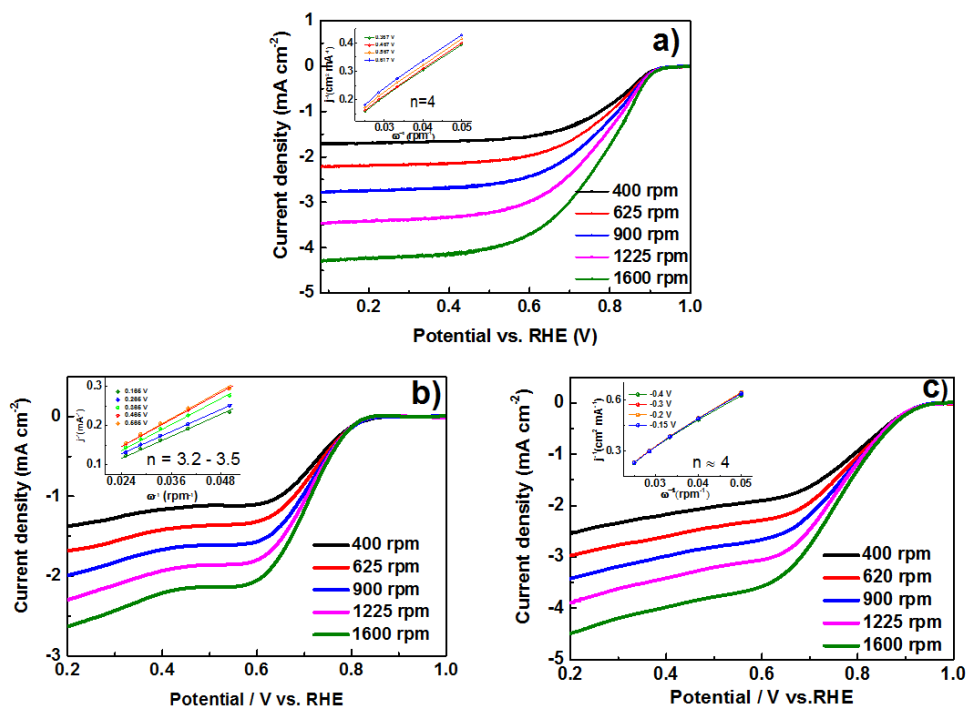


Figure S4. RDE curves of commercial Pt/C (20 wt% Pt on Vulcan XC-72)(a), CN composite (b), BC composite in O₂-saturated 0.1 M KOH solution with various rotation speeds with a sweep rate of 10 mV s⁻¹; K–L plots (J^{-1} versus $\omega^{-1/2}$) at different potentials are shown in the insets.

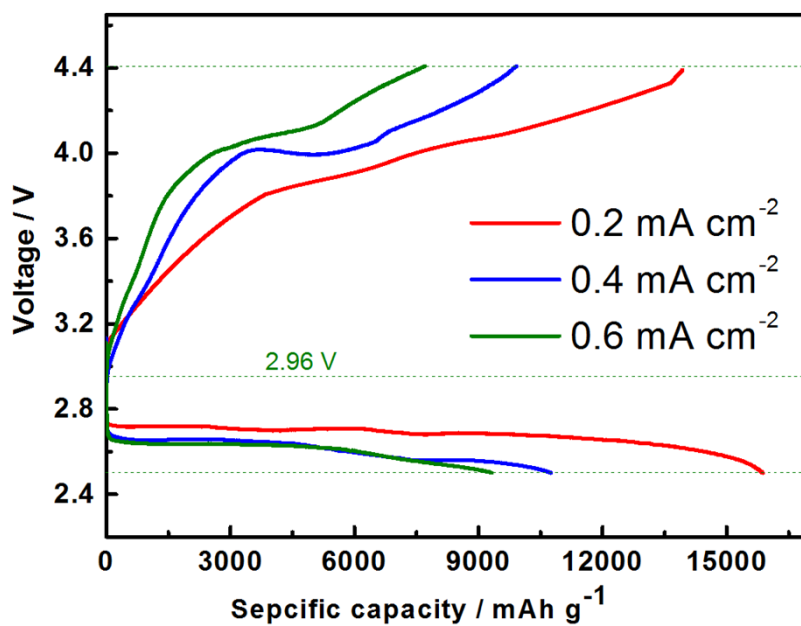
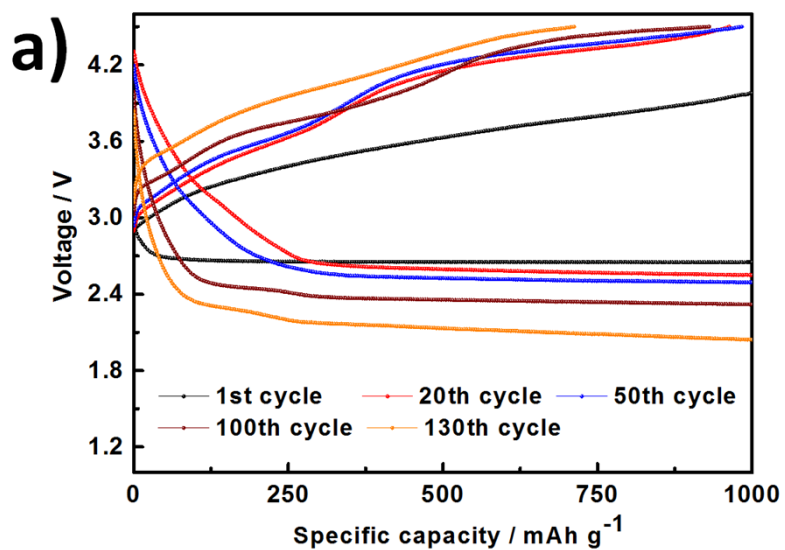
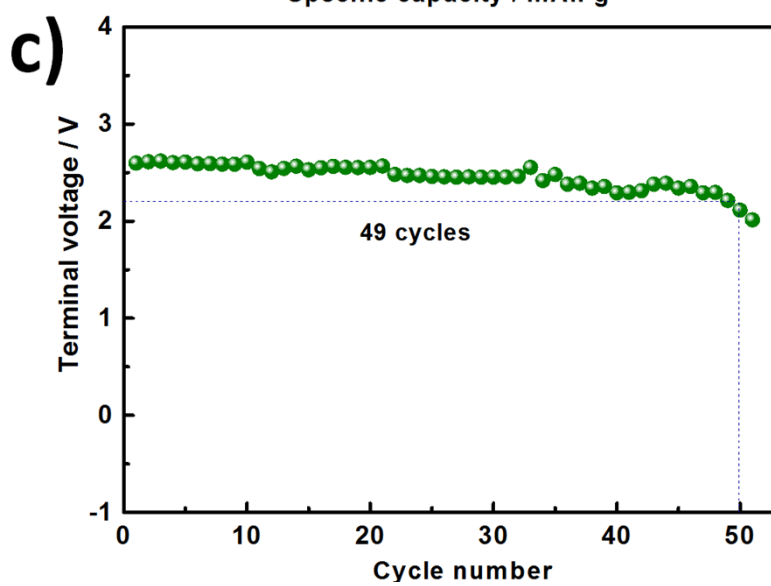
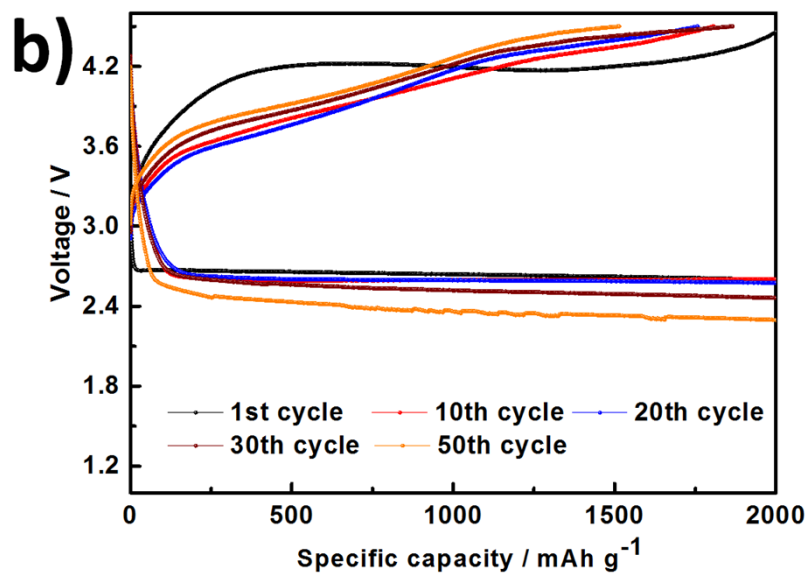


Figure S5. Discharge/charge curves of BC composite at different current densities.





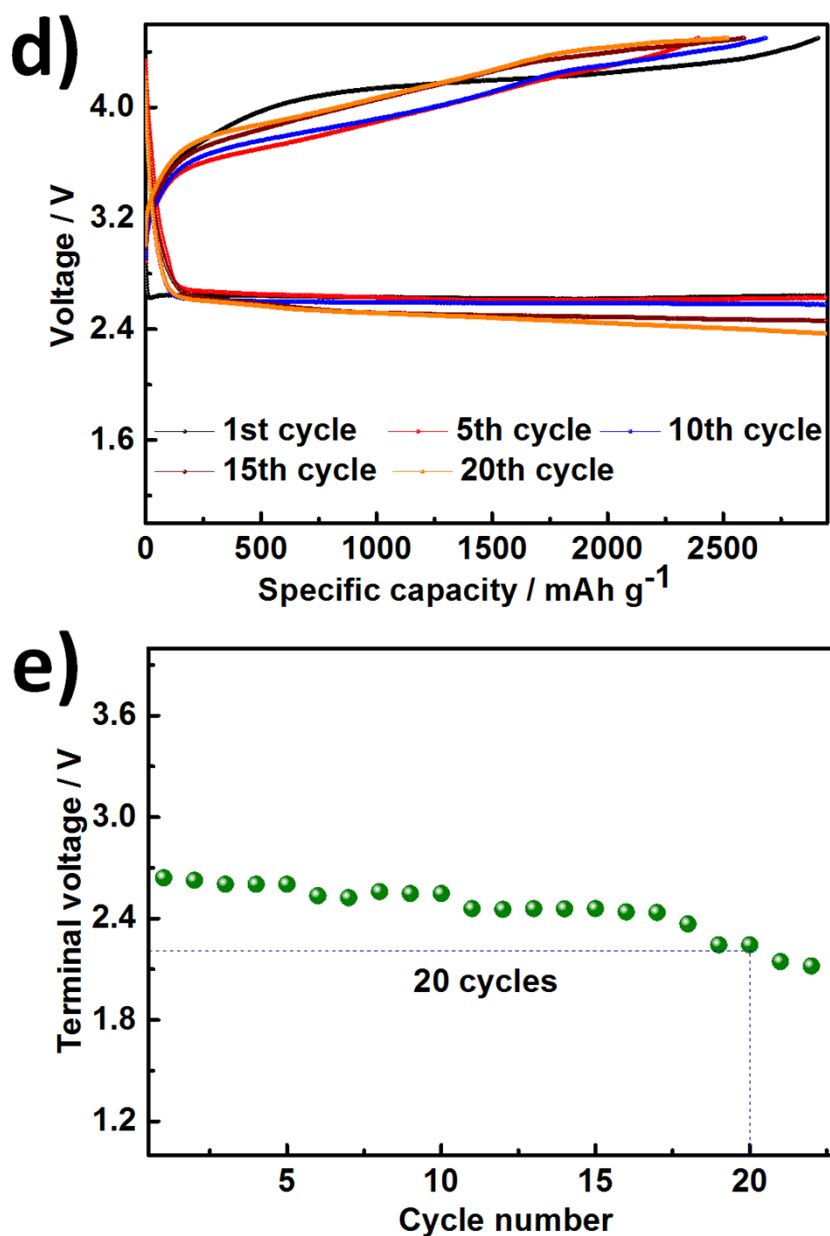


Figure S6. (a) Discharge/charge curves for selected cycles of the BC composite at 0.4 mA cm^{-2} with a fixed capacity of 1000 mAh g^{-1} ; (b) Discharge/charge curves for selected cycles of the BC composite, and (c) the cycling performance at 0.4 mA cm^{-2} with a fixed capacity of 2000 mAh g^{-1} ; (d) Discharge/charge curves of the BC composite, and (e) the cycling performance at 0.4 mA cm^{-2} with a fixed capacity of 3000 mAh g^{-1} .

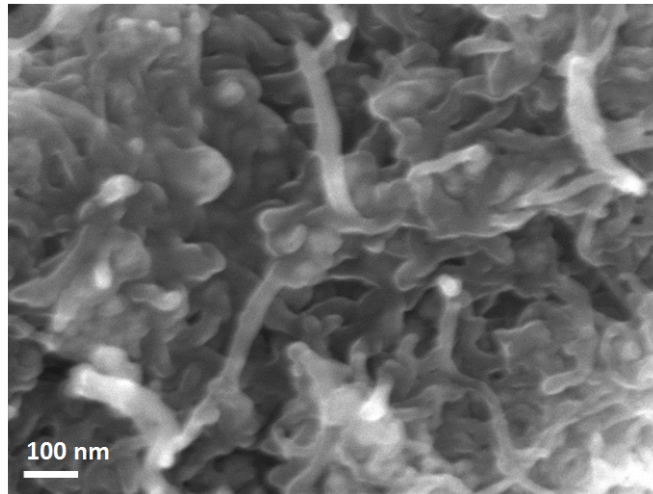


Figure S7. FESEM images of the CN composite after 1st full discharge.

[1] W.B. Luo, S.L. Chou, J.Z. Wang, Y.C. Zhai, H.K. Liu, *Small* 2015,**10**,1002.