Supplementary Information for

A simple integrated design and manufacturing by electrospinning for stabilized lithium battery tin-based anodes

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Experimental Part

Materials synthesis

Experimentally, all chemicals were of analytical grade and used as received. The samples in this work were all prepared by an electrospinning method based on the previous studies.[1-3] Typically, 2.5 g of polyacrylonitrile (PAN, M_w about 150 000) was dissolved in 25 ml of N, N-dimethylformamide (DMF), and then 1.70 g of $SnCl_2 \cdot 2H_2O$ and 0.80g $Cu(NO_3)_2 \cdot 3H_2O$ were added to form a mixed solution. After vigorous stirring for 40 h at 60 °C, a sticky sol was obtained. For comparison, 25 ml of DMF solution containing 2.5 g PAN was also prepared without adding metal salts. A high voltage power supply was used to provide a 15 kV high voltage for the as-prepared electrospinning solutions. The feed speed rate and needle-to-collector distance were set up at 0.6 ml h^{-1} and 15 cm, respectively. The PAN nanofibers were collected on a self-manufactured collector, and then dried for 24 h in vacuum at 80 °C. The dried nanofibers were further stabilized in air at 260 °C for 3 h with a heating rate of 2 °C min^{-1}. Finally, the stabilized nanofibers were annealed in a Ar flow at 830

°C for 1 h with a heating rate of 2 °C min^{-1} for forming N-doping carbon nanofibers (N-CNFs). N-CNFs loaded with $SnCu/SnO_x$ material was also prepared by the same process. Finally, the annealed products were abtained as self-standing paper. The self-standing N-CNF paper was cut into disks (φ = 1.25 cm, *wt* = 1.7 ~ 2.1 mg), which were directly used as electrodes. These self-standing N-CNF paper electrodes were denoted as N-CNF-PE.

Materials Characterization

The structures and morphology of these samples were characterized by X-ray diffraction (XRD, RIGAKU SCXmini), X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB MK II), Raman Spectra (Renishaw, excited at 514.5 nm), scanning electron microscope (SEM, JSM-6700F) transmission electron microscope (TEM, Tecnai G2 F20), CHNOS Elemental Analyzer (Vario MICRO) and inductively coupled plasma atomic emission spectrometer (ICP-AES, Ultima2).

Electrochemical measurements

The electrochemical behaviors were measured via CR2025 coin-type cells assembled in a dry argon-filled glove box. The cell consisted of N-CNF-PE and lithium sheet cathode which were separated by a Celgard 2300 membrane and electrolyte of 1 M $LiPF_6$ in EC:EMC:DMC (1:1:1 in volume). The cells were cycled by LAND2001A at room temperature. Cyclic voltammetry (CV) tests were preformed on a CHI660D Electrochemical Workstation with scan rates of 0.1 and 0.5 m Vs^{-1}.

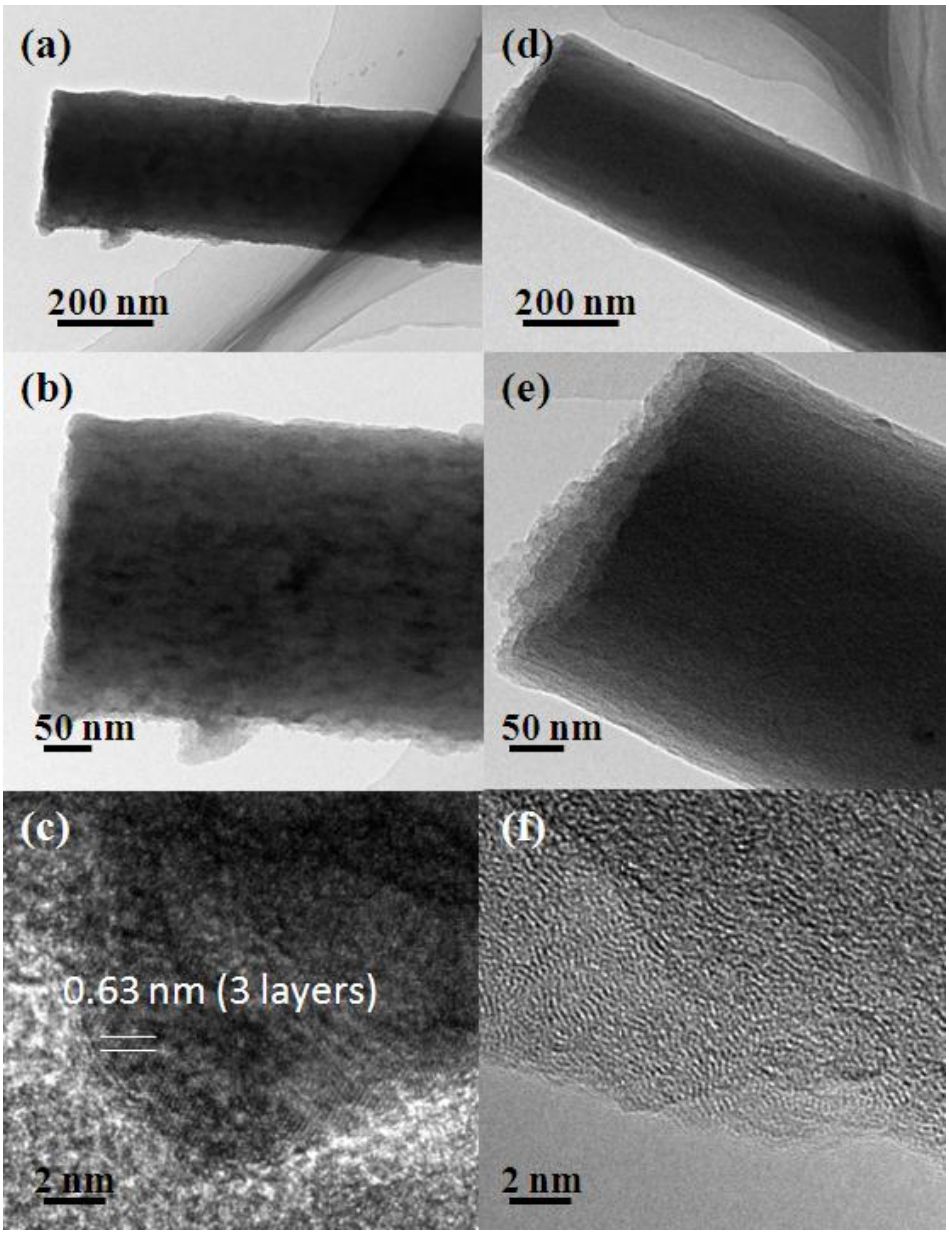

Fig. S1 TEM and high-resolution TEM images of (a)-(c)SnCu/SnOx N-CNFs and (d)-(f) pure N-CNFs.

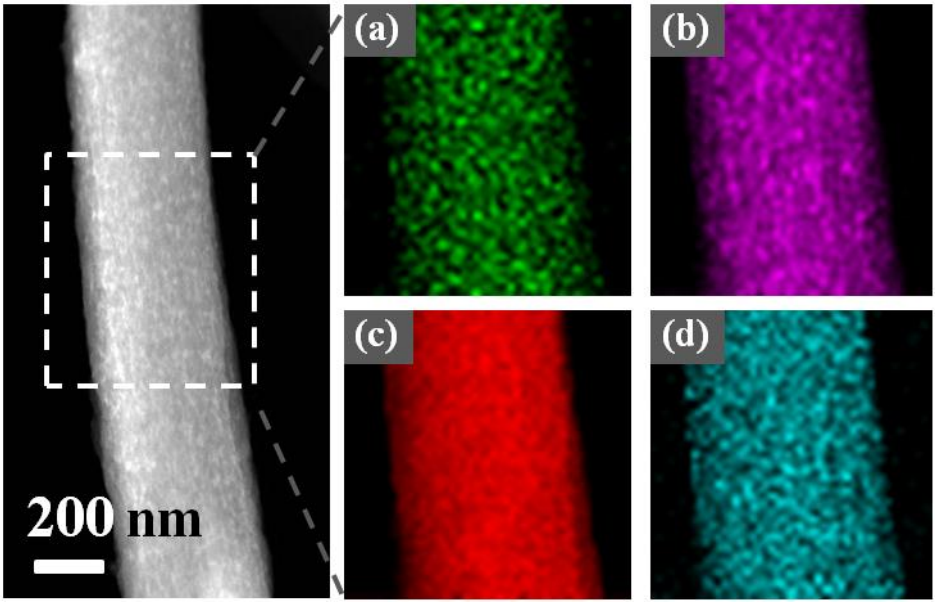

Fig. S2. STEM image and (a)O, (b) Sn, (c) C, and (d) Cu element mapping images of as-obtained

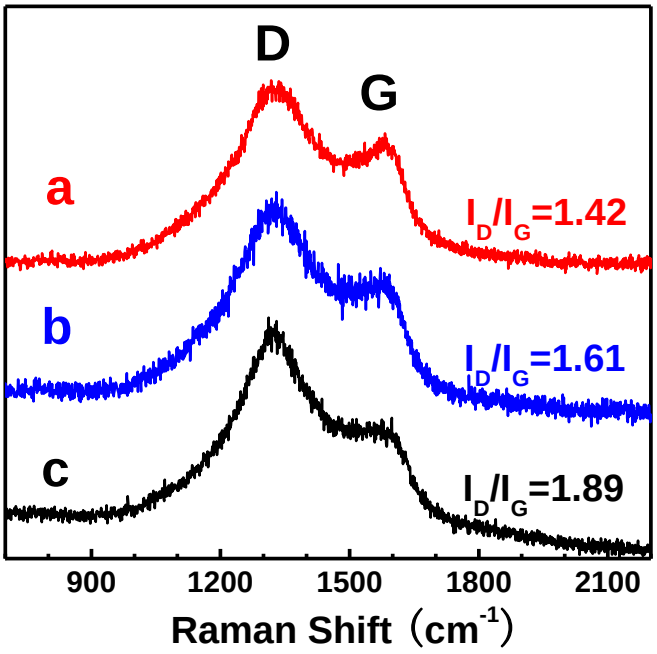

Fig. S3. Raman spectra of the (a) without N-doping CNFs derived from PVA(polyvinyl alcohol), (b) pure N-CNFs and (c) SnCu/SnOx N-CNFs with the excitation wavelength of 514.5 nm.

In addition, Raman Spectra is also considered to be a useful technique to detect the N doping in carbon materials. As shown in the **Fig. S3**, Raman results (Renishaw, excited at 514.5 nm) for all samples exhibit the well-known D and G peaks respectively associated with the disordered and graphitized structures, showing the characteristics of microcrystalline graphitic materials. The increasing ratio of the integral intensities I_D/I_G indicates that the defectiveness of the graphite-like layers grows with increasing of N concentration in the materials. The $SnCu/SnO_x$ N-CNF sample with the highest N concentration 3.2 wt.% was the most defective. The similar results have also been observed in the previous report.[4] Herein, a part of carbon content in the $SnCu/SnO_x$ N-CNFs has been consumed in the redox reaction, leading to a higher N concentration compared to that of 2.4 wt. % in pure N-CNFs.

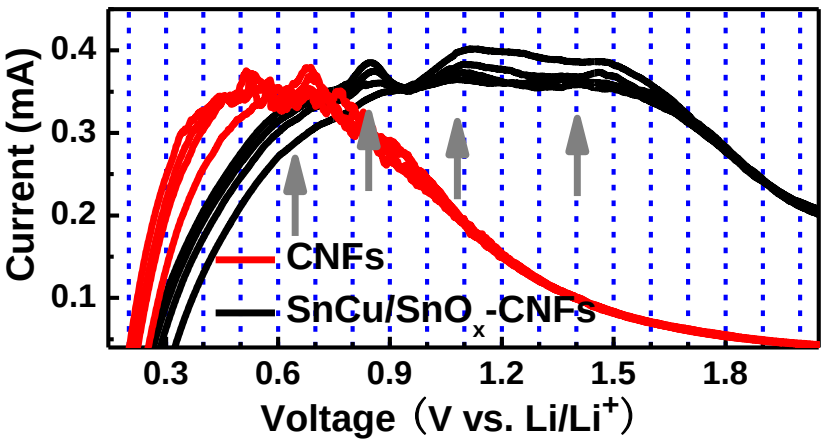

Fig. S4. The magnified cyclic voltammetry curves at 0.5 mV/s for N-CNF-PE $SnCu/SnO_x$ N-CNF-PE.

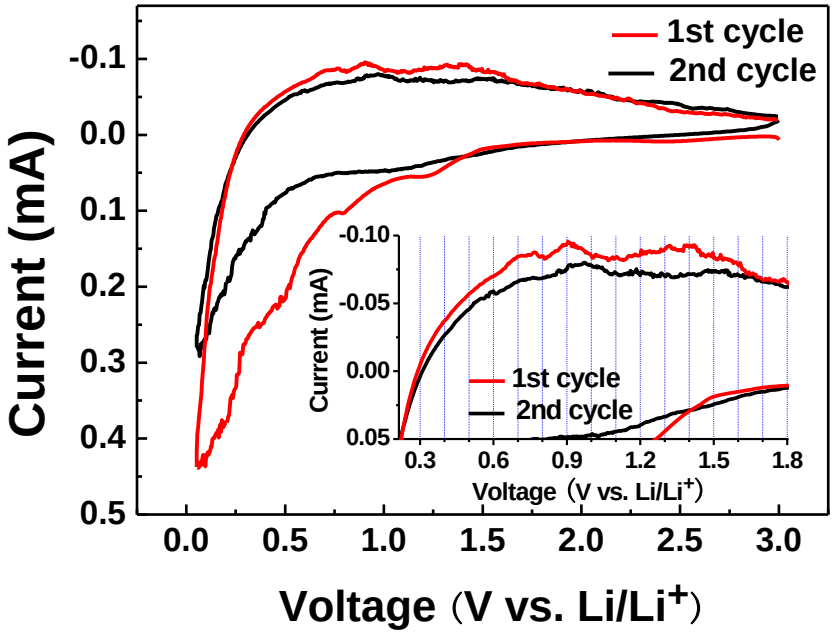

Fig. S5. The cyclic voltammetry curves of SnCu/SnOx N-CNFs at 0.1 mV/s. The inset is the corresponding magnified cyclic voltammetry curve.

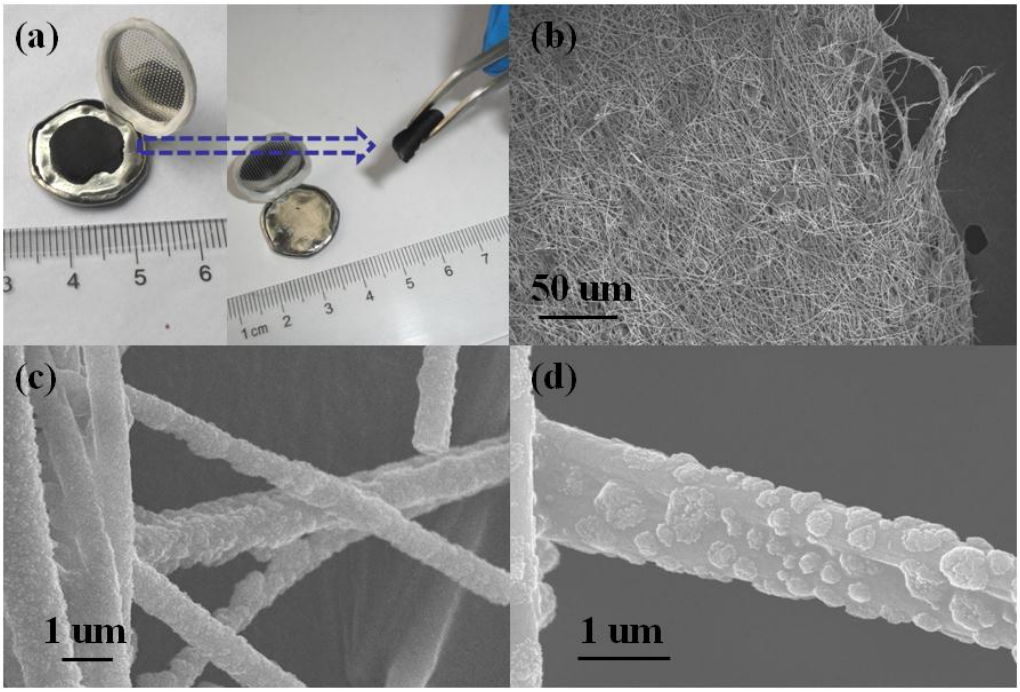

Fig. S6. (a), Digital camera images of SnCu/SnO_x N-CNF-PE after cell test; (b),(c) and (d),The corresponding SEM images of the SnCu/SnO_x N-CNFs.

The detailed calculation:

The XPS, Elemental Analyzer and ICP have been used to exactly detect the ratio of Sn, Cu, N, O and C in SnCu/SnO_x N-CNFs. The contents of Sn, Cu, N, O and C in the SnCu/SnO_x N-CNFs are 35 wt.%, 10.3 wt.%, 3.2 wt.%, 1.5 wt.% and 50 wt.%, respectively. Herein, we assume that most of O element in SnCu/SnO_x N-CNFs is from SnO_2. Accordingly, the Sn and SnO_2 in the SnCu/SnO_x N-CNFs are about 29.5 wt.% and 7 wt.%. Thus, the capacities of both Sn and SnO_2 are ~343 mA/g [i.e., C - ($C_{N\text{-}CNFs}$ * 50 wt.%) = 470 - (255 * 0.50) = 343]. When the specific theoretical capacities of Sn and SnO_2 (994 and 782 mAh g^{-1}) were all utilized reversibly, the contribution of Sn and SnO_2 to the SnCu/SnO_x N-CNFs are about 347 mA/g [i.e., (994 * 29.5 wt.%) + (782 * 7 wt.%) = 347]. Thus, we can know that the capacity of 343 mA/g is close to 347 mA/g, indicating ~100 % of the theoretical capacities of Sn and SnO_2.

Thus, the reversible capacity of SnCu/SnO_x embedding in N-CNHs can almost achieve its theoretical capacity under low current densities in this current study. It is concluded that the electrochemical performance of SnCu/SnO_x N-CNFs can be strongly improved by using this simple integrated design and manufacturing.

Refs:

[1] Jang B. O., *et al.*,***J. Alloys Compounds***, **2013**, 574, 325.

[2] Bonino C. A. *et al.*, ***ACS Appl. Mater. Interface.,*** **2011**, 3, 2534.

[3] Jung H. R. *et al.*, ***J. Electrochem. Soc.***, **2011**,158 (6), A644.

[4] Ismagilov Z. R. *et al.* ***Carbon*****, 2009**, 47,1922.