

Supporting Information:

Freestanding Carbon-Coated CNT/Sn(O₂) Coaxial Sponges with Enhanced Lithium-Ion Storage Capability

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Experimental Details

Carbon coated CNT/Sn(O₂) sponge preparation. Carbon nanotube sponges were synthesized by chemical vapor deposition using 1,2-dicyclobenzene as the carbon source and ferrocene as the catalyst.¹ After growth, the CNT sponge is peeled off the glass substrate and cut into 5 × 5 × 1 mm pieces. In order to increase the hydrophlicity of CNT surface, the CNT sponge pieces were solvothermally treated by concentrated HNO₃ (63%) in an autoclave at 110 °C for 5 h. Afterwards, the pieces were thoroughly washed with ultrapure water and absolute alcohol. CNT supported SnO₂ nanoparticles (CNT/SnO₂) sponge were prepared by a hydrolyzation process of tin salts in a ethylene glycol (EG)-water system. In a typical experiment, as-prepared CNT sponge pieces (100 mg) was first suspended in 200 mL aqueous solution of EG (10 mL water) that was hosted

in a round-bottom flask. Then 3.0 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (dissolved in 100 mL EG) was added to the above CNT containing solution. After a slow magnetic stirring for 20 min, 0.72 g NaOH was added to facilitate the hydrolyzation process of tin salts. Then, the solution was heated to 120°C under atmospheric pressure and refluxed for 72 h with constant but slow stirring to guarantee uniform coating of tin oxide throughout the CNT sponge. After washing and desiccation, the grey black pieces, CNT supported SnO_2 nanoparticles (CNT/ SnO_2) sponge, was obtained. The weight of a certain amount of sponge pieces were measured before and after the SnO_2 deposition to quantify the mass loading of SnO_2 which is typically around 1.0 mg on each piece ($\sim 0.25 \text{ cm}^2$, $\sim 1.0 \text{ mm}$ thick). That is to say, the areal mass loading of SnO_2 was approximately 4.0 mg cm^{-2} .

For carbon coating, the CNT/ SnO_2 sponge pieces was immersed in 40 mL of 0.1-0.3 M aqueous glucose solution for different thickness of carbon coating. The resulting suspension was transferred to a 50 mL teflon autoclave, which was then heated in an electric oven at 180°C for 10 h. The dark gray product was collected by centrifugation, washed with deionized water, and then dried in a vacuum oven at 110°C . The glucose-coated CNT/ SnO_2 was then annealed at 450°C for 2 h in argon atmosphere, forming carbon coated CNT/ SnO_2 (CNT/ SnO_2 @C). For synthesizing CNT/Sn@C, the carbon coated CNT/ SnO_2 was further heated at 550°C under a gas mixture of H_2 and Ar (volume ratio: 1: 9) with a flow rate of 200 sccm for 1 h. Finally the system was cooled down to room temperature under Ar atmosphere.

Characterization: X-ray diffraction (XRD) with Cu $\text{K}\alpha$ radiation (Rigaku D/max-2500B2+/PCX system) was used to determine the phase composition and crystallinity. The composition and microstructure of the samples were further investigated by FE-SEM (Hitachi S4800), FE-TEM (FEI *Tecnai G2 20 ST*), and TGA (Perkin Elmer, Diamond TG) measurements. After battery

testing samples were washed in acetonitrile to remove the electrolyte before being introduced to the SEM or TEM.

Electrochemical Measurements. Electrochemical cycling tests were performed in the half cell configuration in standard coin (2032 size), which were assembled in an argon environment glove box with an oxygen concentration of less than 0.1 ppm. Coin cells were made using freestanding sponge pieces as the working electrode, Celgard 3501 as the separator, and lithium foil as the counter and reference electrode. The electrolyte was 1M LiPF₆ with 1:1 ethylene carbonate: diethylene carbonate (EC: DEC). The cycle life of the cells was tested at the rate of 100 mA g⁻¹ and different rates in the range from 50 mA g⁻¹ to 1600 mA g⁻¹ within a fixed voltage window of 3.0 V-5 mV.

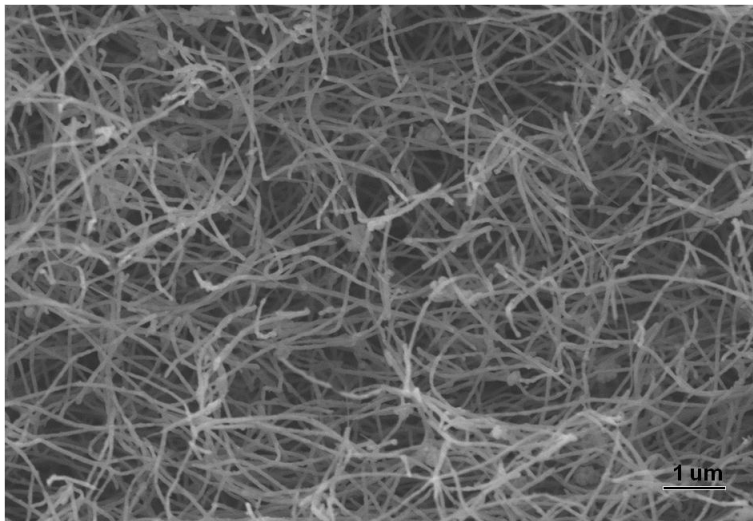


Figure S1. Low-magnification SEM image of a piece of CNT/SnO₂@C coaxial sponge after incision. The CNT surface coating is uniform throughout the entire structure due to the porous nature of the sponge.

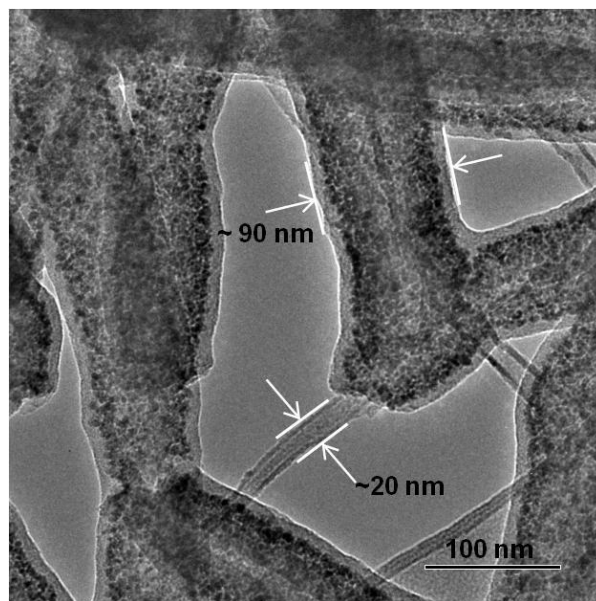


Figure S2. TEM image of CNT/SnO₂@C-2 sponge, showing the average diameter of the hybrid coaxial structure increased from ~20 nm to ~90 nm after the hydrolysis and hydrothermal processes.

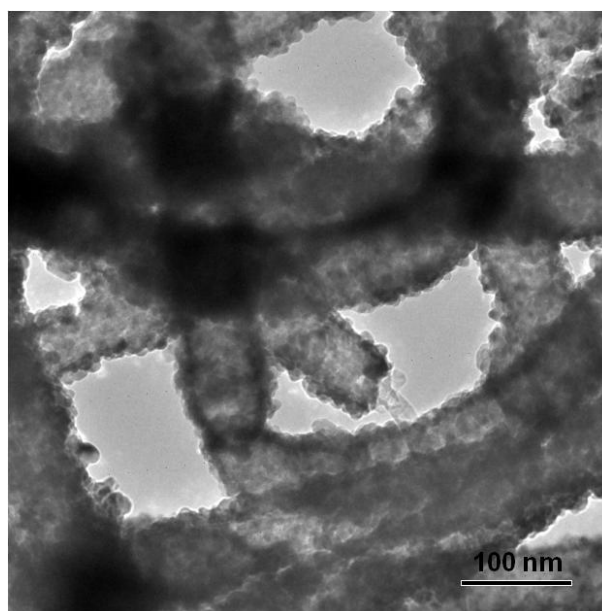


Figure S3. TEM image of CNT/SnO₂ sponge without carbon coating after thermal annealing.

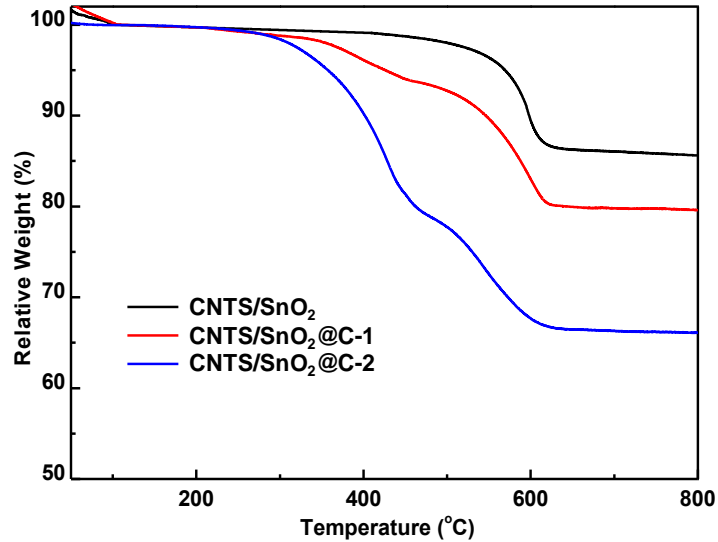


Figure S4. Thermal gravimetric analysis (TGA) of the as-prepared CNT based sponges. The SnO₂ contents of CNT/SnO₂, CNT/SnO₂@C-1, and CNT/SnO₂@C-2 estimated from the thermal analysis are ca. 85.7, 81.0, and 72.8 wt%, respectively. The analysis was taken in air with a heating rate of 10°C min⁻¹.

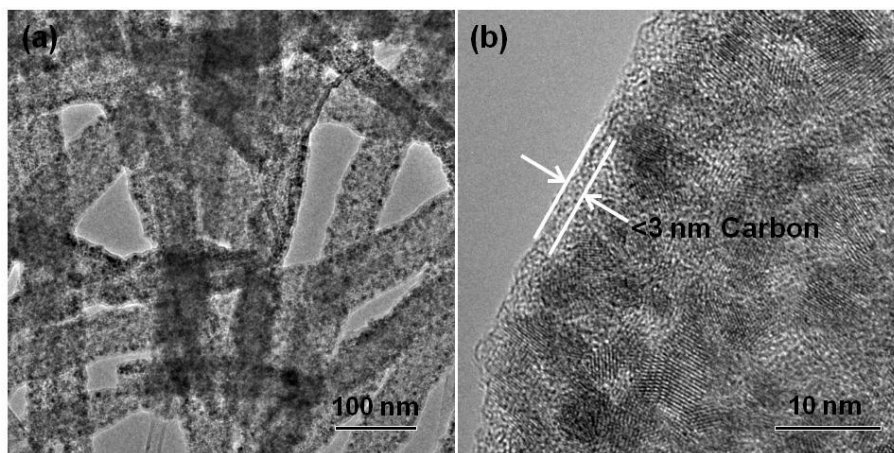


Figure S5. TEM images of CNT/SnO₂@C-1 sponge with carbon coating thickness as thin as less than 3 nm.

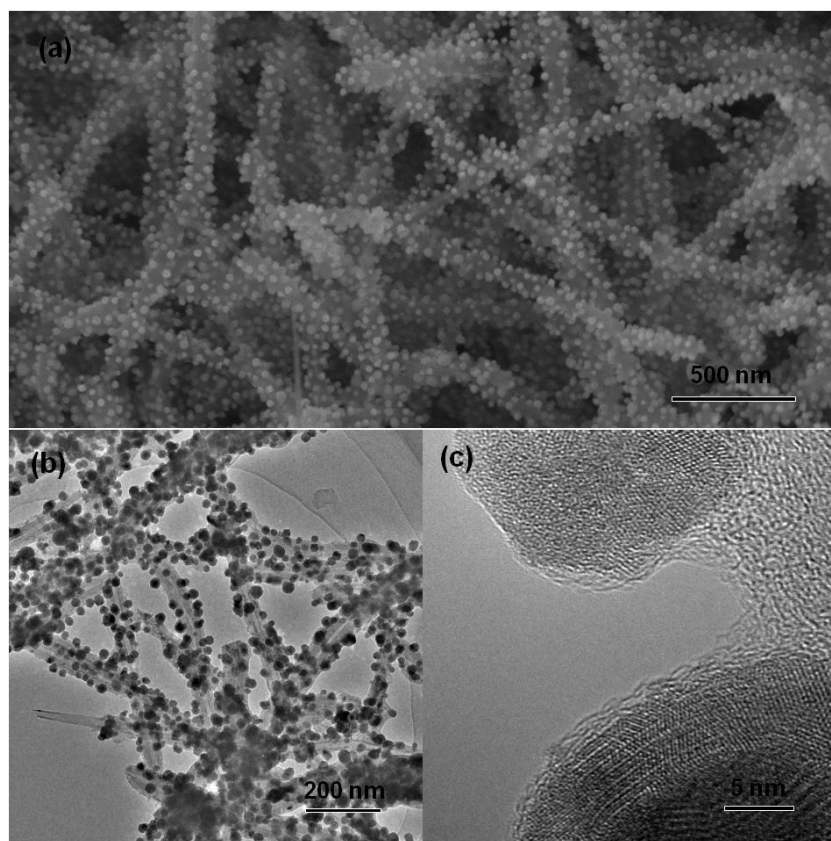


Figure S6. a) SEM and b, c) TEM images of CNT/Sn@C-1 sponge, showing tin nanoparticles with an average diameter larger than 30 nm are affixed on CNTs with or partly with very thin carbon coating layer on the particle surface.

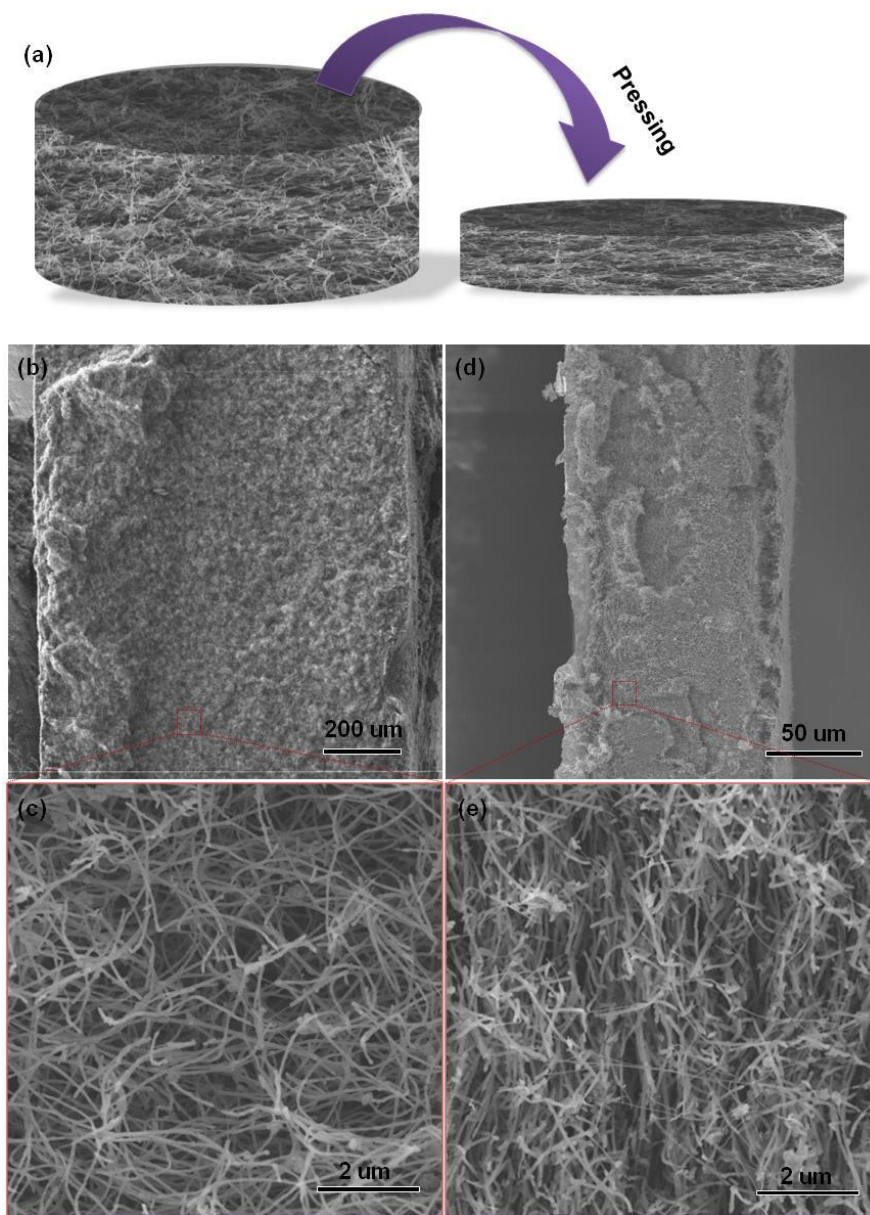


Figure S7. a) The hybrid sponge can be pressed and used as the free standing electrode. The thickness of the sponge is b, c) ~ 1 mm before and d, e) ~ 110 μm after compression.

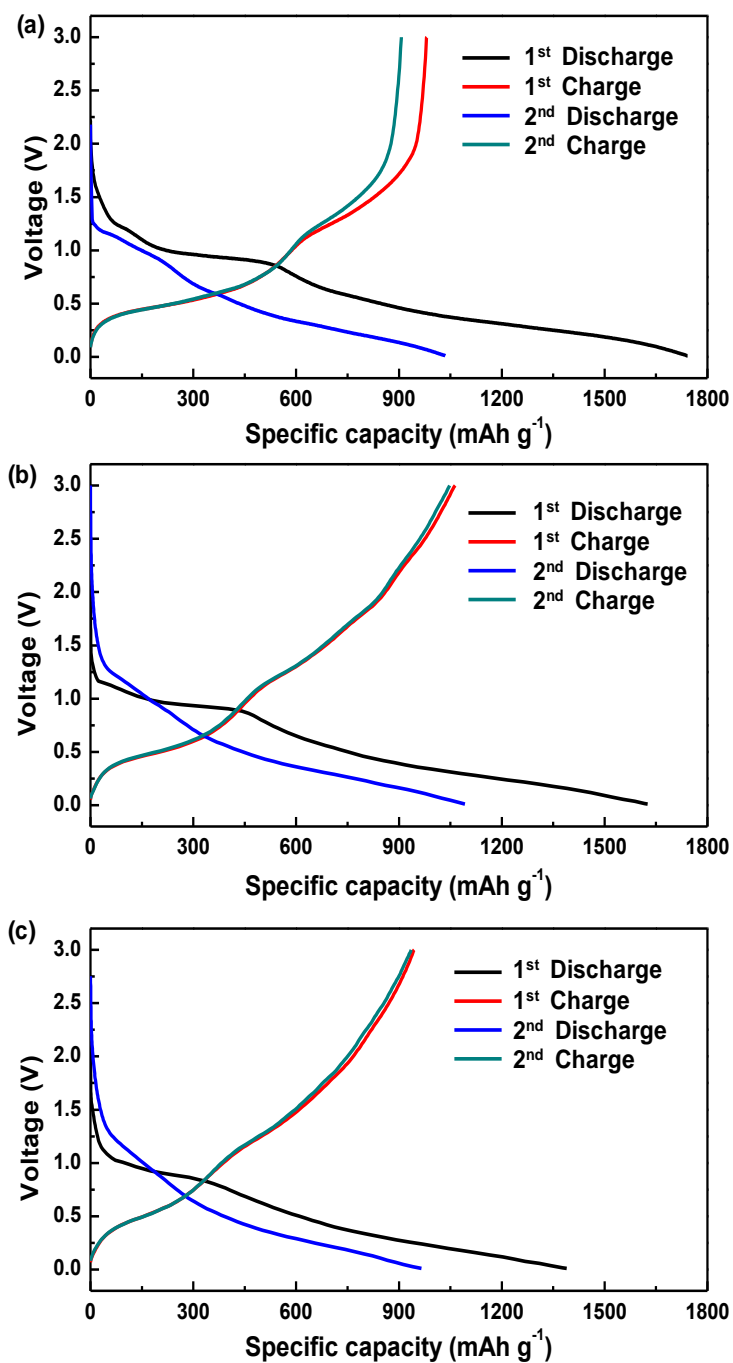


Figure S8. Charge/discharge voltage profiles of the first two cycles of a) CNT/SnO₂, b) CNT/SnO₂@C-1, and c) CNT/SnO₂@C-2, respectively.

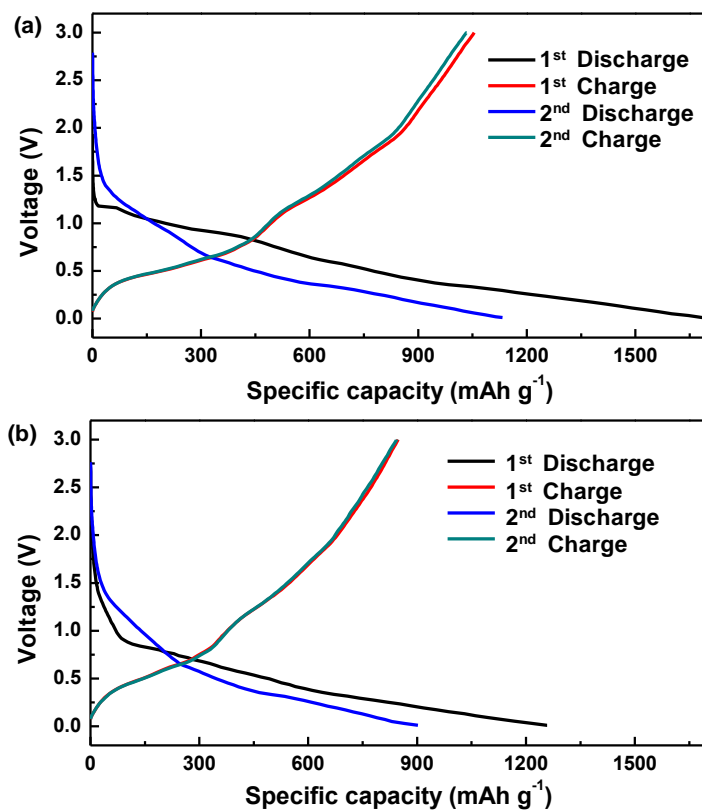


Figure S9. Charge/discharge voltage profiles of the first two cycles of a) CNT/Sn@C-1 and b) CNT/Sn@C-2, respectively.

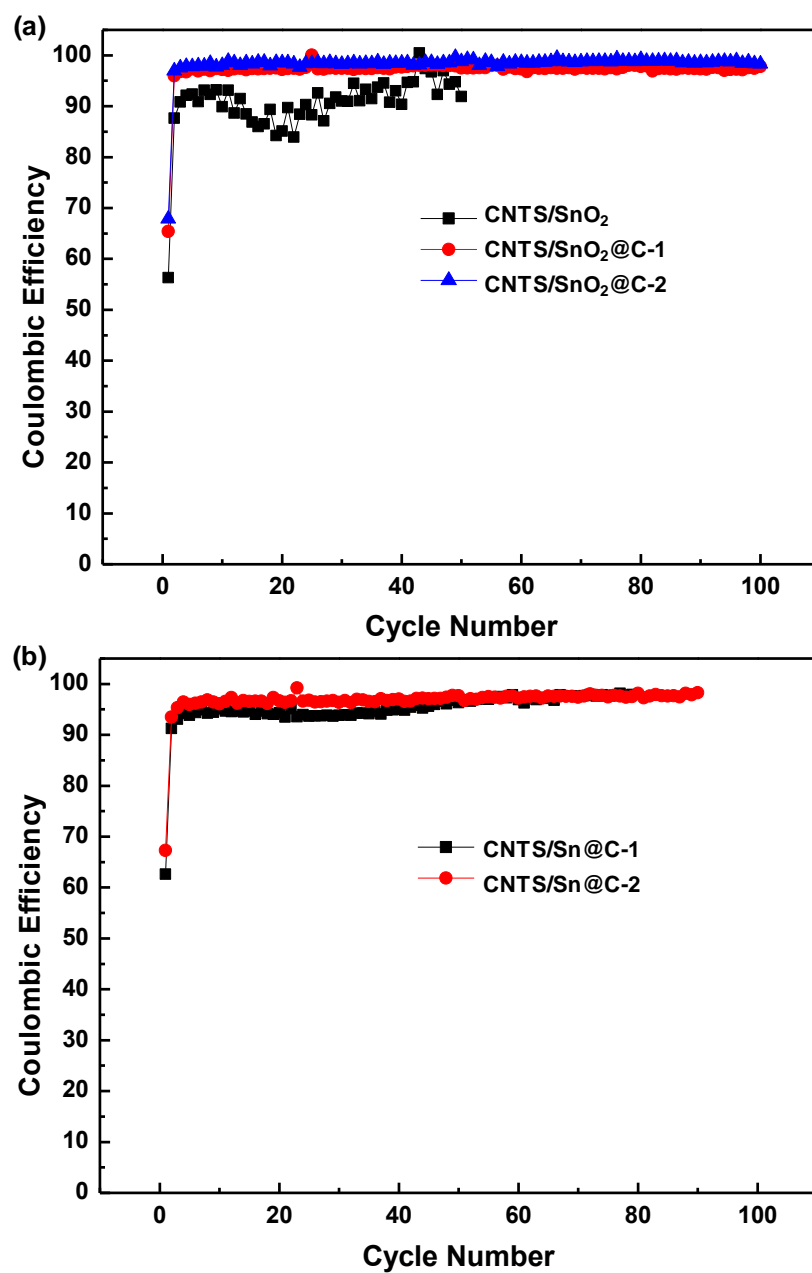


Figure S10. Coulombic Efficiency of a) CNT/SnO₂@C and b) CNT/Sn@C composite electrodes.

Reference

1. Gui, X. C.; Wei, J. Q.; Wang, K. L.; Cao, A. Y.; Zhu, H. W.; Jia, Y.; Shu, Q. K.; Wu, D. H., Carbon Nanotube Sponges. *Advanced Materials* **2010**, *22* (5), 617-621.