

# Supplementary Information for

## Ultrasmall titanium oxide/titanium oxynitride composite nanoparticles embedded carbon nanofiber mats as high-capacity and free-standing electrodes for lithium sulfur batteries

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### Experimental procedure

**Materials** The titanium (IV) propoxide ( $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , 98%), polyvinylpyrrolidone (PVP,  $M_w = 1,300,000$ ), polyacrylonitrile (PAN,  $M_w = 150,000$ ), and *N,N*-dimethyl formamide (DMF, anhydrous, 99.8%) were purchased from Sigma-Aldrich. Acetic acid ( $\text{CH}_3\text{COOH}$ , glacial, 99.7%) was purchased from Samchun Chemical. We used all materials without further purification.

**Lithium polysulfide ( $\text{Li}_2\text{S}_6$ ) solution preparation:** The  $\text{Li}_2\text{S}_6$  solution was prepared through a chemical reaction between sulfur (S) and lithium sulfide ( $\text{Li}_2\text{S}$ ) by dissolving a desired amount of stoichiometric S and  $\text{Li}_2\text{S}$  in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) solution (1:1 in volume) with the addition of 1 M of lithium nitrate ( $\text{LiNO}_3$ ). To yield the fully dissolved  $\text{Li}_2\text{S}_6$  solution, the mixture was stirred at 300 rpm and heated at 80 °C overnight. The final solution had a red-brown color and contained 3-M sulfur.

**$\text{TiO}_2/\text{TiO}_x\text{N}_y$ -carbon nanofiber current collector preparation:** 0.75 g of PAN, 0.75 g of PVP, 0.9 g of titanium propoxide, and 0.6 g of acetic acid were dissolved in 15 ml of DMF by heating at 80 °C and stirring at 500 rpm. The prepared solution was electrospun using a conventional

electrospinning setup with the following parameters: an applied voltage of 15 kV, solution flow rate of 1.3 ml h<sup>-1</sup>, and distance between the nozzle-tip to the collector of 15 cm. The prepared electrospun membranes were left overnight in air and then transferred into a box furnace, heated up to 280 °C at a heating rate of 5 °C min<sup>-1</sup> and held for 4 h to stabilize the PAN nanofibers. After the stabilization process, the membranes were formed into free-standing films. The obtained free-standing films were punched into disks with diameter of 1.8 cm. The free-standing stabilized PAN nanofiber films were further carbonized under an argon atmosphere at 1000 °C for 2 h at a heating rate of 5 °C min<sup>-1</sup> to synthesize TiO<sub>2</sub>/TiO<sub>x</sub>N<sub>y</sub>-carbon nanofiber films. For comparison, bare-carbon nanofibers were synthesized without adding titanium precursor, titanium propoxide, and acetic acid, at same electrospinning and heating conditions.

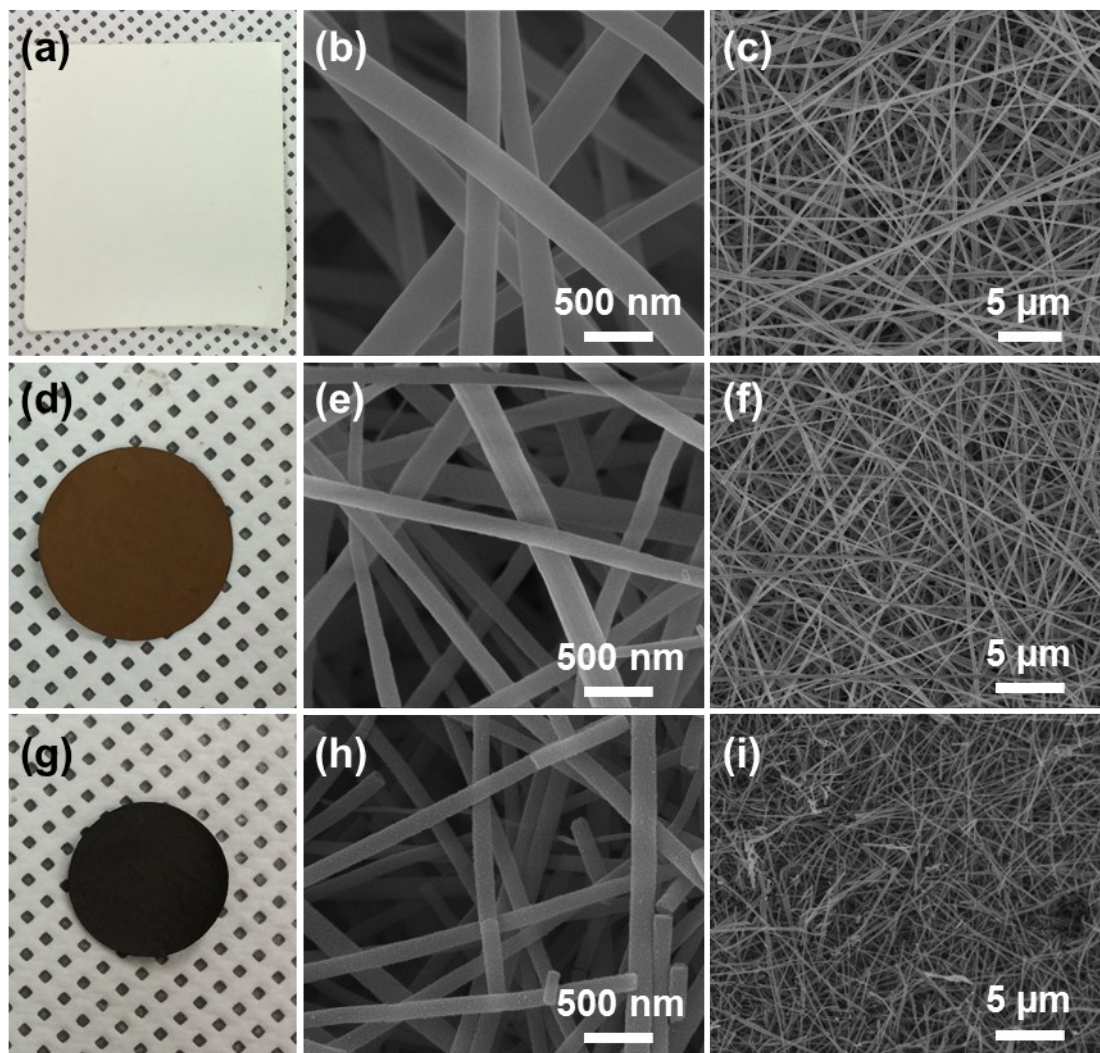
**Characterization:** The morphology of the fibers was observed with field-emission scanning electron microscope (Field Emission SEM, Nova 230, FEI) and transmission electron microscope (TEM, tecnai F30 S-Twin, 300 kV, FEI). The thickness of the synthesized mat was measured using a micrometer (MDC-25PJ, Mitutoyo). To investigate the nature of backbone CNFs, Raman spectroscopy and four-probe measurement were carried out. The crystalline phase of the nanoparticles attached on carbon nanofiber was confirmed by X-ray diffraction pattern (XRD, RIGAKU, D/MAX-2500). The elemental analysis of the TiO<sub>2</sub>/TiO<sub>x</sub>N<sub>y</sub>-CNF was conducted by energy-dispersive X-ray spectroscopy (EDS) equipped in SEM and TEM devices and element analyzer (FLASH 2000 series for carbon and nitrogen and FlashEA 1112 for oxygen). XPS data were collected to confirm the composition of nanoparticles by a K-alpha. The absorption capacities of TiO<sub>2</sub>/TiO<sub>x</sub>N<sub>y</sub>-CNF and CNF mats were measured via UV-vis spectroscopy (Agilent 8453).

**Electrochemical Characterization:** To evaluate the electrochemical performance of the cell with TiO<sub>2</sub>/TiO<sub>x</sub>N<sub>y</sub>-CNF current collector, 2032-type coin cells were assembled in an argon-filled glove box using lithium metals as the counter/reference electrode. The separator used is Celgard 2325 with the thickness of 25 μm. Synthesized free-standing electrospun nanofiber mats were directly used as current collector and fabricated Li<sub>2</sub>S<sub>6</sub> solution was used as the active material. For a sulfur mass

loading of 2 mg, 20  $\mu\text{l}$  of  $\text{Li}_2\text{S}_6$  solution was added into a cell. The electrolyte was prepared as 1 M lithium bis(-trifluoromethanesulphonyl)imide (LiTFSI) in DOL/DME mixed solution (1:1 in volume) containing 1 M  $\text{LiNO}_3$  as additive. 20  $\mu\text{l}$  of electrolyte was added in one cell. The cells were galvanostatically charged and discharged between 1.7 and 2.6 V vs.  $\text{Li/Li}^+$  at various current densities with a battery testing system (WBCS3000, WonATech). The electrochemical impedance spectroscopy (ZIVE SP1, WonATech) of the cells were measured in a frequency ranging from 1 MHz to 10 mHz with AC voltage amplitude of 5 mV.

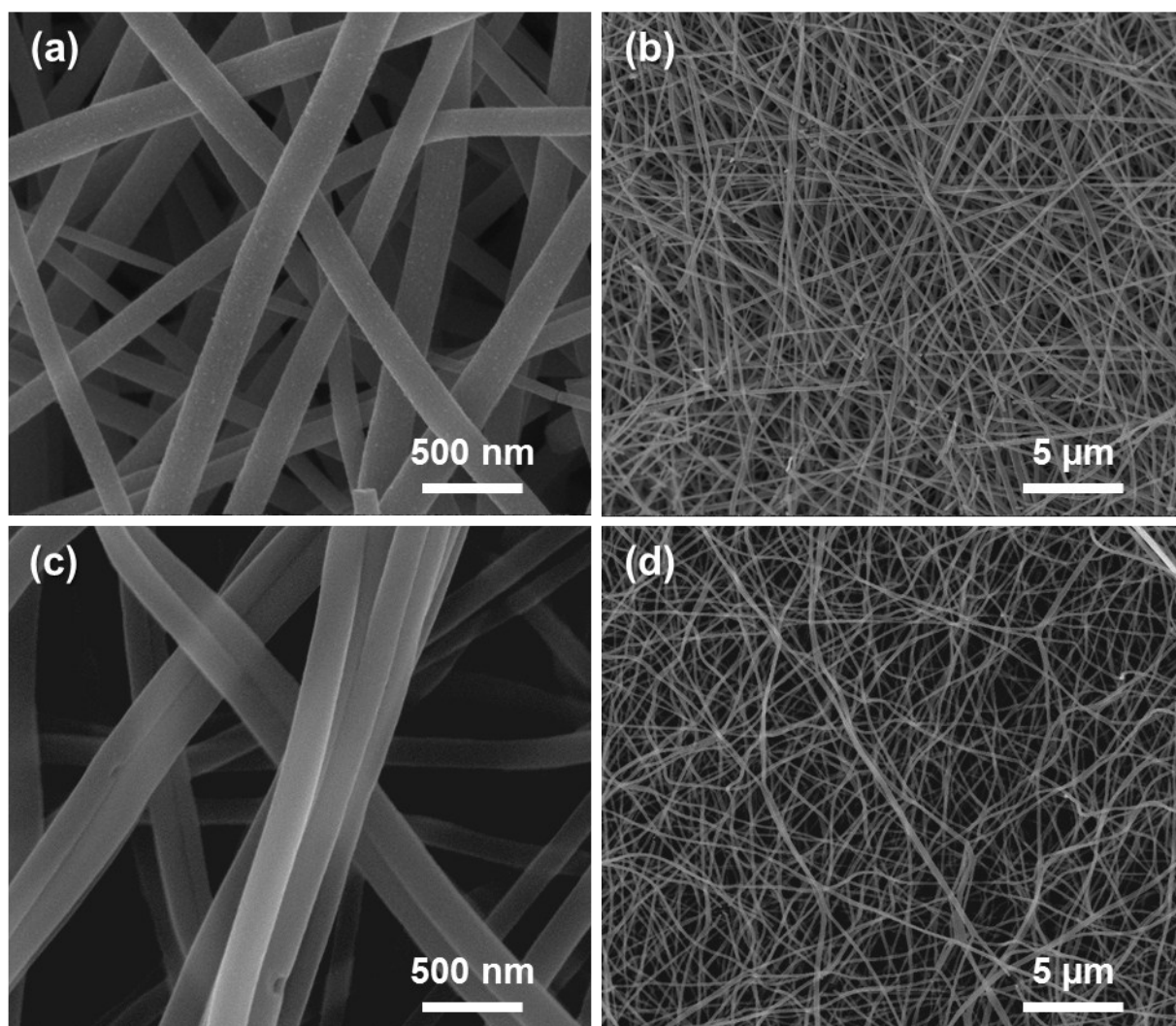
***Absorption experiment of polysulfides:*** For preparing 1 mM  $\text{Li}_2\text{S}_6$  solution, equivalent amount of lithium and sulfur powders were dissolved in tetrahydrofuran (THF) and stirred for 24 h. As-synthesized  $\text{TiO}_2/\text{TiO}_x\text{N}_y$ -CNF and CNF mats with the same weight of 15 mg were separately soaked in the 1 mM  $\text{Li}_2\text{S}_6$  solution for 24 h. After taking out the  $\text{TiO}_2/\text{TiO}_x\text{N}_y$ -CNF and CNF mats, each solution was centrifuged with 13,000 rpm for 3 h and then, the supernatant was finally obtained for UV-visible absorption analysis. All procedures were conducted in an Ar-filled glovebox.

[Figure S1]



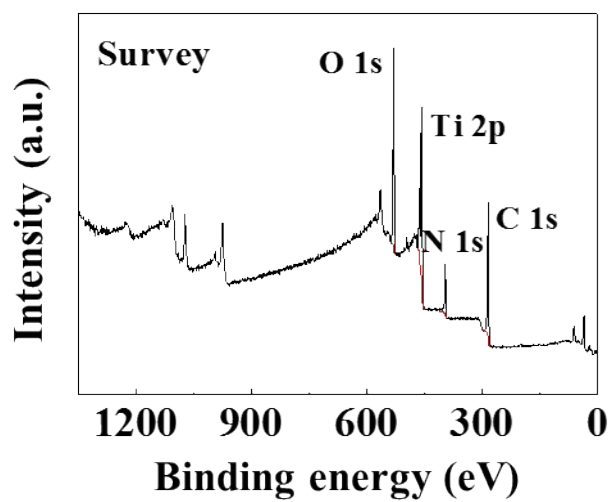
**Figure S1.** Photograph and SEM images of (a-c) as-spun, (d-f) stabilized, (g-i) carbonized  $\text{TiO}_2/\text{TiO}_x\text{N}_y$ -CNF mats.

[Figure S2]



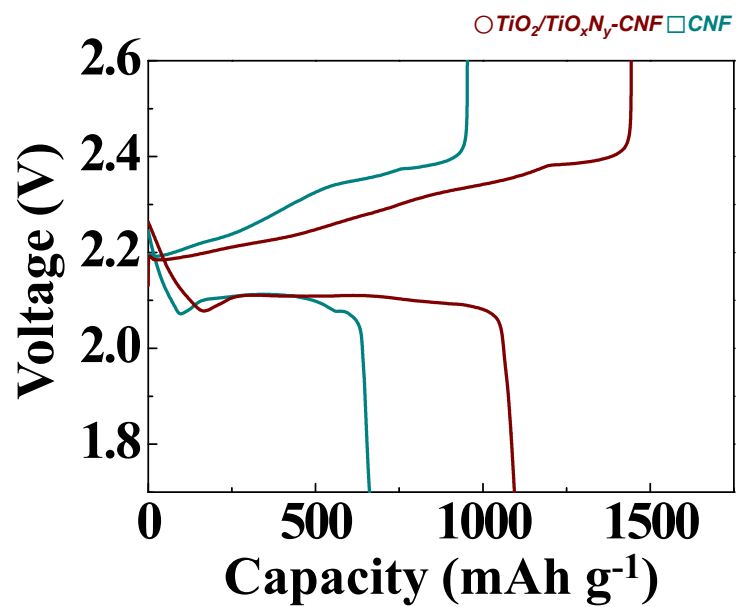
**Figure S2.** High magnification and low magnification SEM images of (a, b)  $\text{TiO}_2/\text{TiO}_x\text{N}_y$ -CNF and (c, d) CNF mats.

**[Figure S3]**



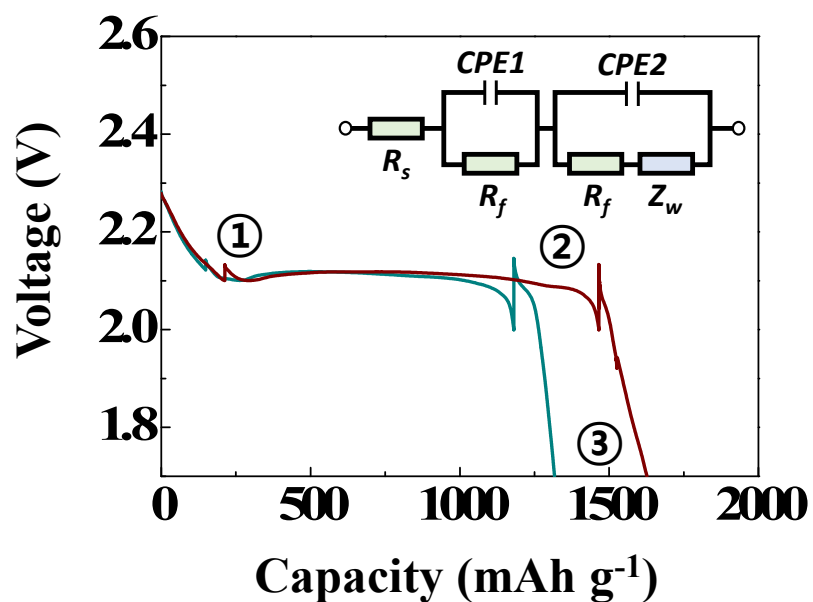
**Figure S3.** XPS survey spectra of the  $\text{TiO}_2/\text{TiO}_x\text{N}_y\text{-CNF}$  mats.

[Figure S4]



**Figure S4.** Galvanostatic discharge/charge profiles of the cells using  $\text{TiO}_2/\text{TiO}_x\text{N}_y\text{-CNF}$  and  $\text{CNF}$  current collectors.

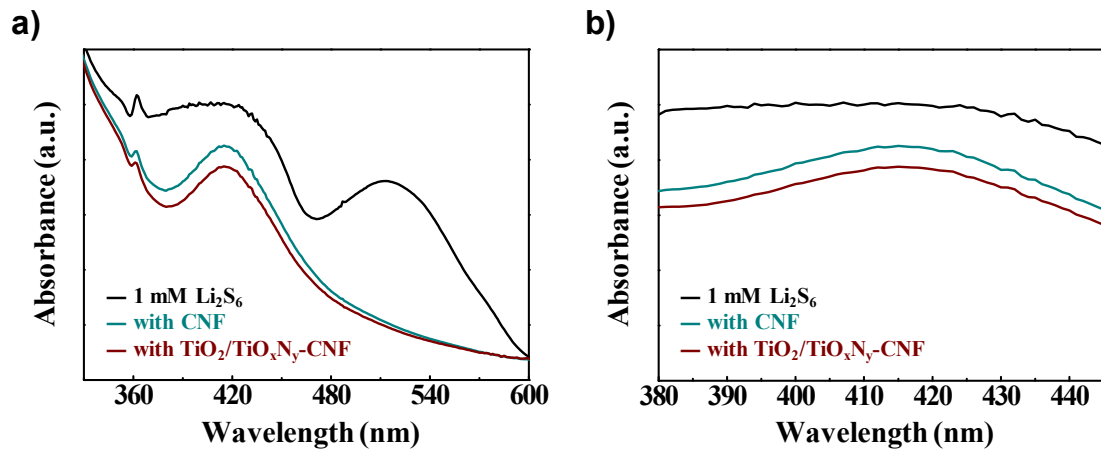
[Figure S5]



**Figure S5.** The 1<sup>st</sup> discharge curve of the cells using TiO<sub>2</sub>/TiO<sub>x</sub>N<sub>y</sub>-CNF and CNF current collectors corresponding to impedance spectra. (Inset: proposed equivalent circuit for of the cells using TiO<sub>2</sub>/TiO<sub>x</sub>N<sub>y</sub>-CNF and CNF current collectors)



[Figure S6]



**Figure S6.** a) UV/Vis absorption spectra of lithium polysulfide ( $\text{Li}_2\text{S}_6$ ) solution before and after the addition of CNF and  $\text{TiO}_2/\text{TiO}_x\text{N}_y\text{-CNF}$  mats. b) magnified UV/Vis absorption spectra near 415 nm.