Supplementary Information

Electrospun nanofibers with a core-shell structure of silicon nanoparticles and carbon nanotubes in carbon for use in lithium-ion battery anodes

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1. Experimental details

Preparation of electrospun SiNP-CNT-core carbon-shell nanofibers

SCNFs were prepared by coaxial electrospinning, as illustrated in **Figure S1**. In this, the multi-walled CNTs (20-nm diameter, 10-μm length, ACN Co., Korea) were modified before use by employing a wet chemical oxidative process to ensure a good dispersion in the polymer solution. SiNPs (0.684 g, <100 nm particle size, Sigma Aldrich Chemical, USA) and activated

CNTs with concentrations of 0.5, 1, 2, 5, or 10 wt% (mass ratio of CNTs:SiNPs) were then dispersed in a co-solvent of acetone and *N,N*-dimethylformamide (DMF) (8.8 g, w:w = 1:1, Sigma Aldrich Chemical, USA) by ultrasonifying for 1 h. Next, polyvinylpyrrolidone (PVP) (1.2 g, M_w: 1,300,000; Acros Organics, USA) was completely dissolved in the SiNPs-CNTs solution to a PVP concentration of 12 wt%. This mixture was then stirred for 24 h at 50 °C to obtain a polymer solution that was used to form the core. The solution to be used for the shell was prepared by dissolving polyacrylonitrile (PAN, 1 g, Sigma Aldrich Chemical, USA) in DMF (9 g) to obtain a polymer concentration of 10 wt%. Both of these solutions were then loaded into 5-mL plastic syringes equipped with a coaxial stainless-steel needle. Coaxial electrospinning was carried out using an aluminum foil collector and an electrospinning system (ESR200R2, NanoNC, Ltd., Korea) with a voltage of 12 kV and a distance of 15 cm between the stainless-steel needle and collector. The syringe flow rate was maintained at 1 $mL \cdot h^{-1}$ for both the core and shell solutions.

Carbonization of the PAN shell

After electrospinning, the SCNFs were thermally treated to stabilize and carbonize the PAN shell. The initial stabilization of the PAN shell was carried out at 200–300 °C for 1 h under the air atmosphere, creating a dense ladder-polymer structure through oxidation that prevents it melting during subsequent carbonization. This carbonization was carried out at 1000 °C for 1 h under a nitrogen atmosphere, the temperature being increased gradually at a rate of 3 $°C \cdot min^{-1}$. Through carbonization, non-carbon elements are removed from the stabilized PAN fibers as different gases within a temperature range of 300 to 1000 °C. Beyond 800 °C, de-nitrogenation also takes place, resulting in the formation of carbon network structure in the core. This

carbonization process is mainly concentrated on converting the raw PAN in the shell into carbon, whereas the sacrificial PVP core is simply burnt out to leave a SiNPs-CNTs composite.

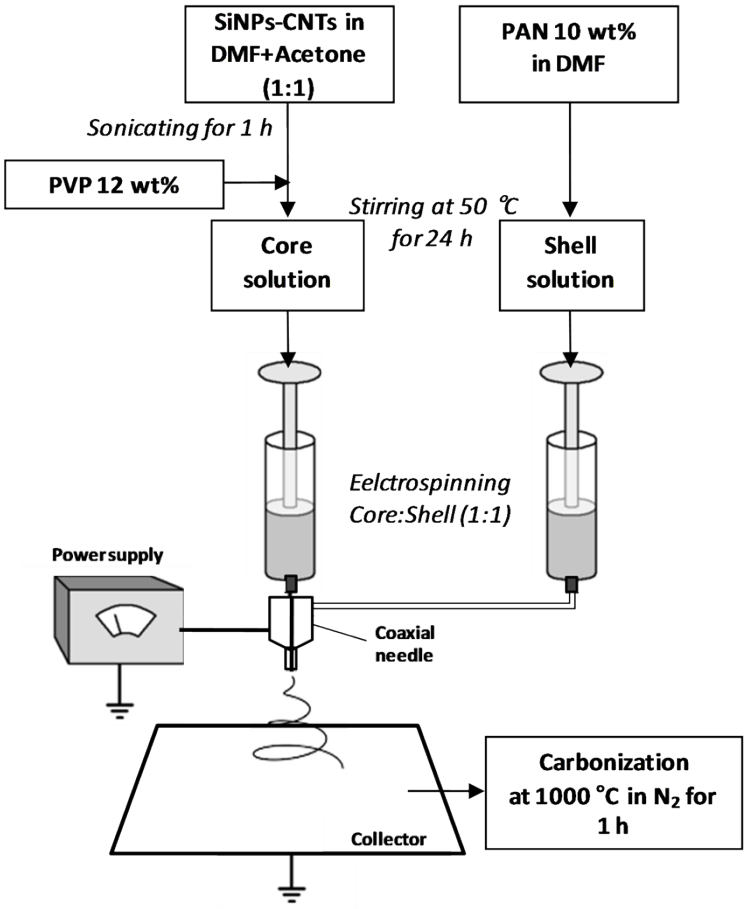

Figure S1: Schematic for the preparation of SCNFs.

2. Water contact angle measurements

Measurement of the water contact angle (WCA) of the as-electrospun SNF and SCNF membranes returned a large WCA (99°) for the PAN fiber membrane, and a narrow WCA (20°) for the PVP fiber membrane, as shown in **Figure S2(a)** and **(b)**. The results shown in **Figure S2(c)** and **(d)** indicate WCAs of 87° for SNF and 89° for SCNF membranes, respectively. The fact that these values of SNFs and SCNFs are closed to the WCA of PAN indicates that SiNP-

CNT/PVP composite in the core is wrapped by a PAN shell, this demonstrating a core-shell structure in coaxially electrospun fibers.

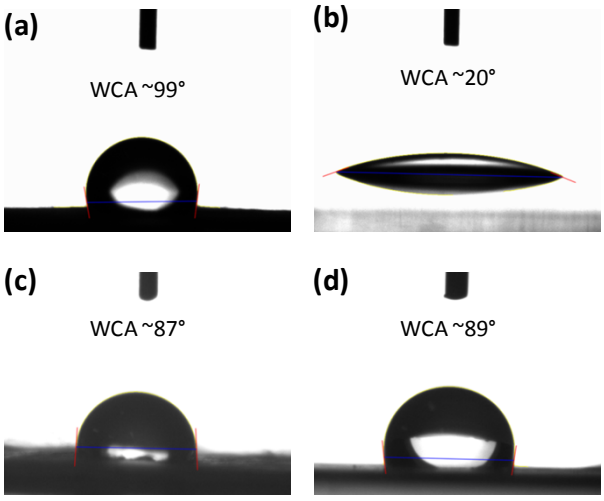

Figure S2: Photographs showing the water contact angle of as-electrospun (a) PAN fiber membrane; (b) PVP fiber membrane; (c) SiNP-core carbon-shell fiber (SNF) membrane; and (d) SiNP-CNT-core carbon-shell fiber with 1 wt% of CNTs (SCNF) membrane.

3. TGA data

The decomposition of PVP and carbonization of PAN in the carbonization process are demonstrated within a temperature range of 25–600 °C under nitrogen by the TG thermograms shown in **Figure S3**. The TG curve (a) of PVP shows a sharp decline at 450 °C, indicating a notable weight loss due to the thermal decomposition of PVP. The TG thermogram (b) of PAN, on the other hand, reveals its dehydrogenation over a temperature range 300–500 °C. The remaining weight of PAN is around 60 %, which is retained during de-nitrogenation in the carbonization process over a temperature range 500–1000 °C. The contributing mass component of SiNPs in the carbonized SCNFs is determined from the TG thermograms over a temperature range of 25–700 °C in air, as shown in **Figure S3(c)**. This curve remains unchanged between

25–450 °C, but shows a decrease and therefore weight loss over the range of 450–600 °C that is attributed to the oxidation of carbon in the SCNFs. The 50 wt% of remaining solid is found to be mainly SiNPs, from which a mass ratio of SiNPs:C = 1:1 was used as the basis for the analysis of electrochemical performance.

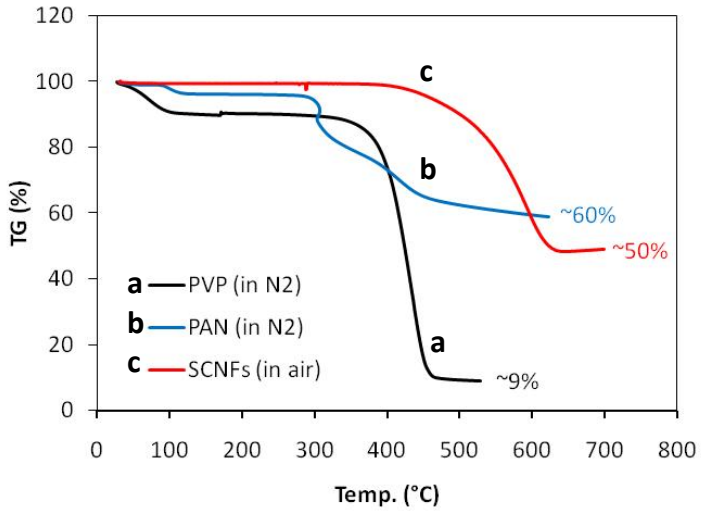

Figure S3: TG thermograms of (a) polyvinylpyrrolidone (PVP) in nitrogen, (b) polyacrylonitrile (PAN) in nitrogen, and (c) carbonized SiNPs-CNTs/carbon core/shell nanofibers with 1 wt% of CNTs (SCNFs) in air.

4. EDS data

The energy dispersive X-ray spectroscopy (EDS) of SCNFs in the Figure S4 displays that the core-shell nanofibers mainly consist of C and Si. The quantitative weight ratio of Si and C in SCNFs is found to be 1:1.7, which is smaller than the weight ratio Si:C (1:1) in TGA thermogram . It implies that a portion of Si enveloped by carbon shell. The observed Si is outer surface of SCNFs because of the grind for the EDS analysis.

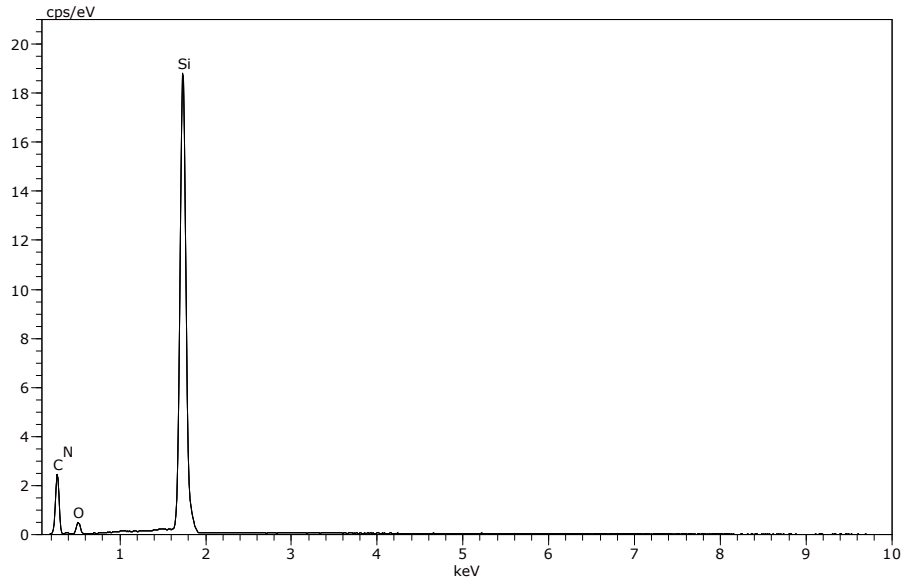

Figure S4: EDS profile of carbonized SiNPs-CNTs/carbon nanofibers (SCNFs) with 1 wt% of CNTs.

5. TEM images of SCNF with over 1 wt% of CNT

Figure S5 shows TEM images of SCNFs containing 2, 5, and 10 wt% of CNTs in the core before and after carbonization. These also show clusters of SiNPs on the fiber surface, the density of these clusters increasing with the amount of CNTs in the core.

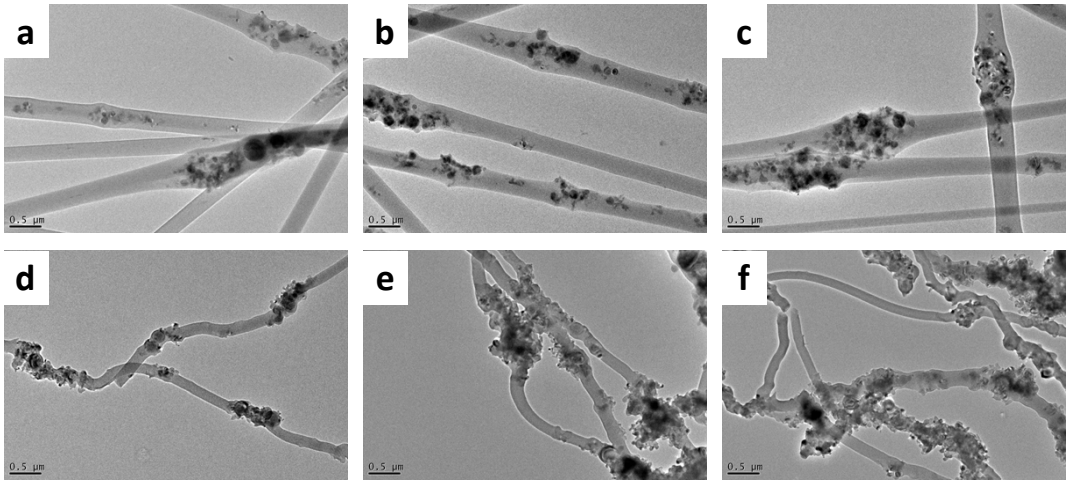

Figure S5: TEM images of SCNF (a,b,c) before and (d,e,f) after carbonization at 1000 °C in nitrogen for 1 h with CNT:SiNP ratios of (a,d) 2, (b,e) 5, (c,f) 10 wt%.