Electronic Supplementary Information for

Three-Dimensional porous silicon-MWNT heterostructure with superior lithium storge performance†

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Experimental details

Preparation of the pSi-MWNT composite:

Preparation of mesoporous silica (KIT-6):

4.0 g Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Sigma-Aldrich) was dissolved in 30 g distilled water and 120 g HCl (2M) under vigorous stirring. After complete dissolution, 4.0g 1-butanol (BuOH, Sinopharm Chemical Reagent Co. Ltd., 99%) and 8.4 g tetraethoxysilane (TEOS, Sinopharm Chemical Reagent Co. Ltd, 99%) were added to the homogeneous clear solution. The solution was stirred at 35 °C for 24 h, then hydrothermally heated at 100℃ for 24 h using a stainless-steel autoclave with a Teflon inlet. The resulting silica (KIT-6) was isolated by centrifugation and calcined at 550 °C for 2 h for template removal.

Preparation of 3D porous silicon (pSi):

0.3 g KIT-6 Silica and 0.3 g magnesium powder (Sinopharm Chemical Reagent Co. Ltd, 100~200 mesh) were put in a corundum boat and heated at 700 °C for 7h under Ar (95 vol. %)/H_2 (5 vol. %) mixed gas flow with a heating speed of 2 °C min^{-1}. The resulting powder was immersed in 2 M HCl solution and kept under stirring for 12 h. After etching, the obtained 3D porous silicon (pSi) was washed with distilled water and isolated by centrifuge at a speed of 4000 rpm for 4 times, followed by vacuum drying at 80 °C for 12 h.

Preparation of 3D porous silicon-MWNT composite (pSi-MWNT):

The pSi particles were dispersed in the iron(III) nitrate solution (5 wt. % iron metal amount) in water-ethanol mixed solvents and dried in a vacuum oven at 100°C for an hour. For chemical vapour deposition (CVD), the iron modified pSi was put into the quartz tube furnace and first flushed with argon gas (200 ml/min) for 30 min to flush away any oxygen in the reactor. Then the temperature of the furnace was increased up to 550°C under a mixed gas flow of argon (200 ml/min) and hydrogen (20 ml/min) and held for 30 min for the reduction of iron(III) to iron nanoparticles by hydrogen gas. Then the temperature was increased to 750°C, whereupon acetylene (C_2H_2) was introduced for 20 min for MWNT growth, under $H_2/C_2H_2/Ar$ (5/30/200 ml/min) mix-gas flow. For carbon coating, the furnace temperature was further increased to 900°C for 30 min under C_2H_2/Ar (40/200 ml/min) mix-gas. After carbon deposition, the furnace was turned off and cooled down to room temperature under the argon atmosphere (200 ml/min flow).

For comparison, the porous silicon/MWNT mixture (pSi/MWNT) was prepared by ball milling (300 r/min for 4 h) with ethanol as dispersing agent, followed by carbon coating via CVD at 900°C using acetylene as the carbon source. The amounts of MWNT and coated carbon of the pSi/MWNT mixture were controlled to be the same as those of the pSi-MWNT composite.

Structural and morphological characterization:

X-Ray diffraction (XRD) measurements were carried out using a Rigaku D/MAX-2200/PC X-ray diffractometer at 40 kV and 30 mA, with a Cu Kα radiation source. Raman spectra were taken by a BRUKER optic SENTERRA (R-200L) Raman spectrometer using a laser of a wavelength of 633 nm at room temperature. The specific surface area and pore size distribution were determined from the results of nitrogen adsorption/desorption measurements using an ASAP 2020 Accelerated Surface Area and Porosimetry (Micromeritics Inc., USA).

Thermogravimetric analysis (TGA) was performed using a STA 449F3 analyzer (NETZSCH Co., Germany) to evaluate the MWNT and carbon coating amounts of the composite after CVD process. We prepared the sample without carbon coating after MWNT deposition under the same CVD conditions for exact measurement of the MWNT content. The carbon coating amount was determined by the difference between the MWNT content and total carbon amount.

The morphologies and microstructures of the samples were investigated using a FEI Nova SEM 230 ultra-high resolution FESEM and a JEM-2100F TEM (JEOL Ltd., Japan). For SEM observation, the cycled electrode (in fully de-lithiated state) was taken out of the cell in an argon-filled glove box and washed with dimethyl carbonate (DMC) to remove the residual lithium salt. The electrode was first immerged in water and then in toluene for days to remove the binder. Then the electrode material was centrifuged several times for complete purification.

Electrochemical characterization:

Electrode preparation:

The working electrodes were composed of active material, Super P conductive carbon black (40 nm, Timical) and styrene butadiene rubber/sodium carboxymethyl cellulose (SBR/SCMC, 1:1 by weight) as binder at a weight ratio of 60:20:20. After casting the mixture onto a copper foil and drying, the electrodes were cut to Φ12 mm disks, pressed at 3 MPa and finally dried at 60 °C in vacuum for 8 h.

Cells assemble:

Coin-type CR 2016 cells were assembled in an Argon filled glove box (MBraun, Unilab, Germany) using ENTEK ET20-26 membrane as separator and lithium-foil as counter electrode. The oxygen and water contents in the glove box were less than 10 ppm. The electrolyte was 1M $LiPF_6$ electrolyte in a mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 by volume) containing 2 wt% vinylene carbonate (VC). The testing cells were charged/discharged at room temperature between 0.01 V and 1.2 V versus Li/Li^+ using a commercially available battery test system (LAND CT2001A model, Wuhan Jinnuo Electronics Co., Ltd.). The specific capacity was calculated according to the total composite weight.

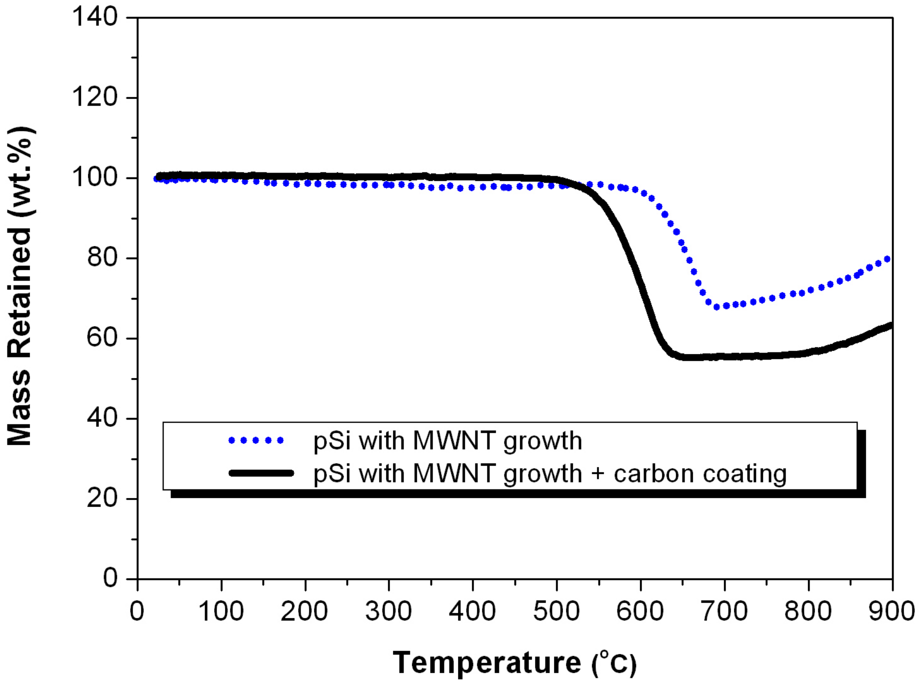

Fig. S1 Thermogravimetry analysis (TGA) results of the porous silicon (pSi) composite with MWNT growth and carbon coating. The weight increase after 750°C is due to the oxidation of silicon in air above 750°C.

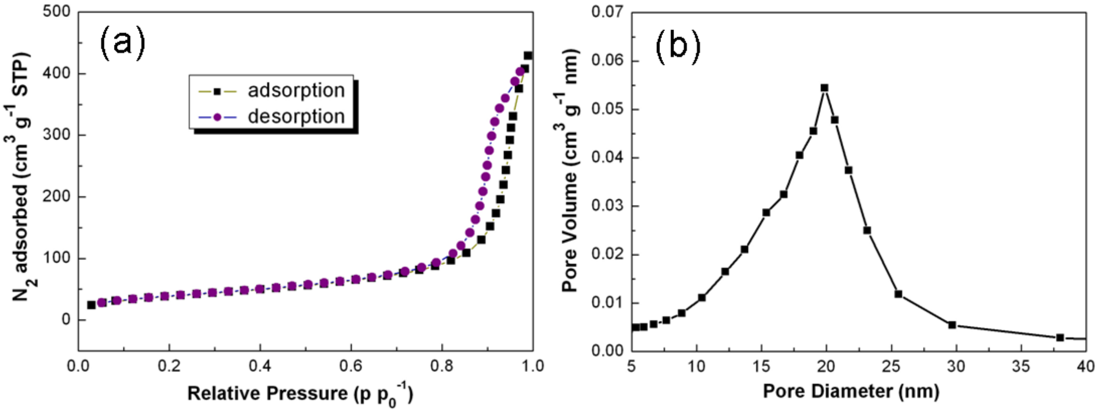

Fig. S2 (a) Nitrogen adsorption-desorption isotherm linear plot and (b) Barrett-Joyner-Halenda (BJH) pore size distribution of the pSi.

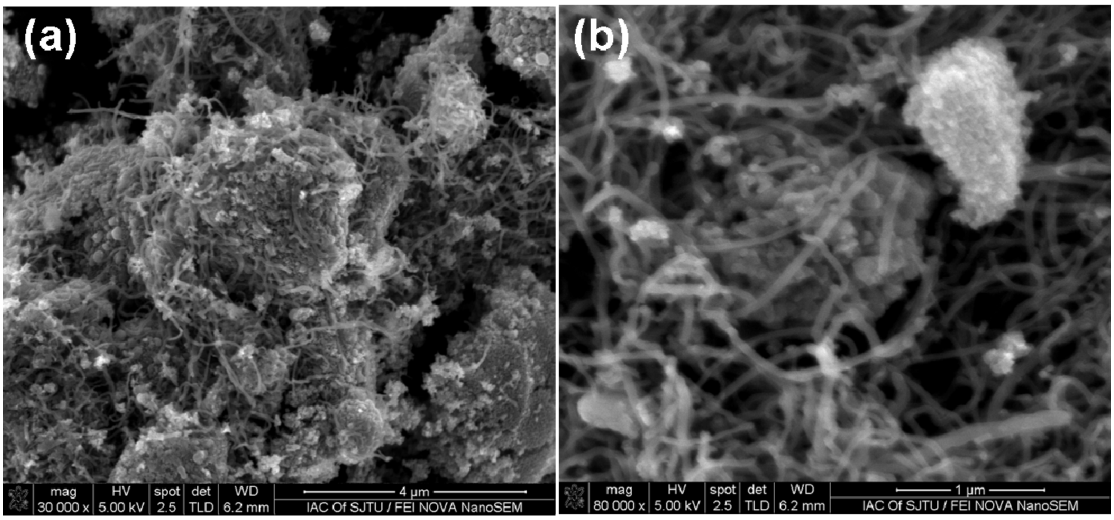

Fig. S3 (a, b) SEM micrographs of the pSi/MWNT mixture.

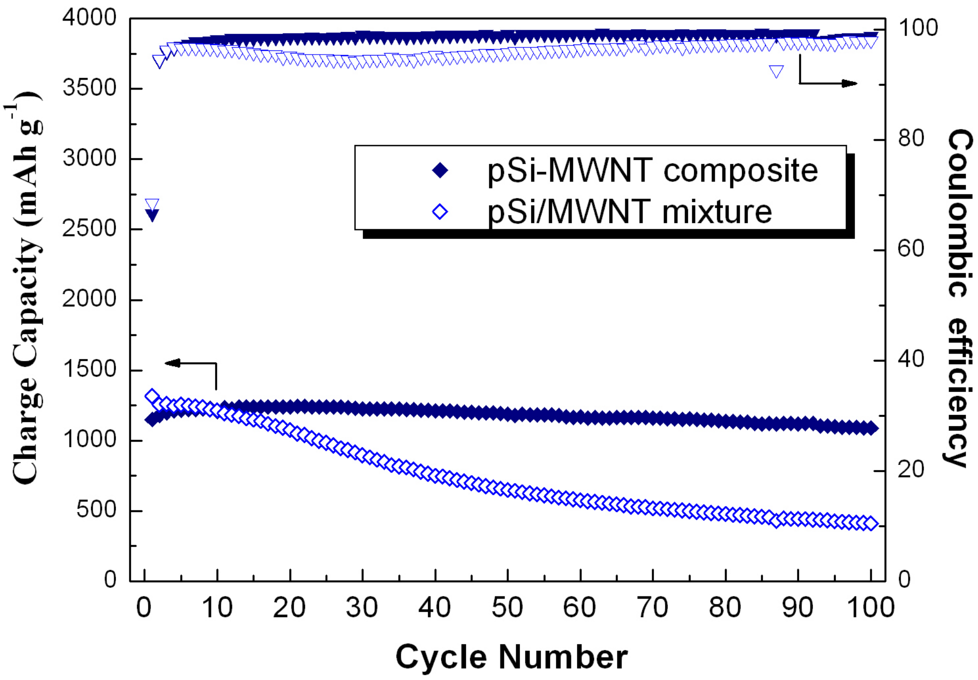

Fig. S4 Reversible capacities of the pSi-MWNT composite and the pSi/MWNT mixture at a current density of 300 mA g^{-1} for 100 cycles (solid symbols: pSi-MWNT composite; open symbols: pSi/MWNT mixture).

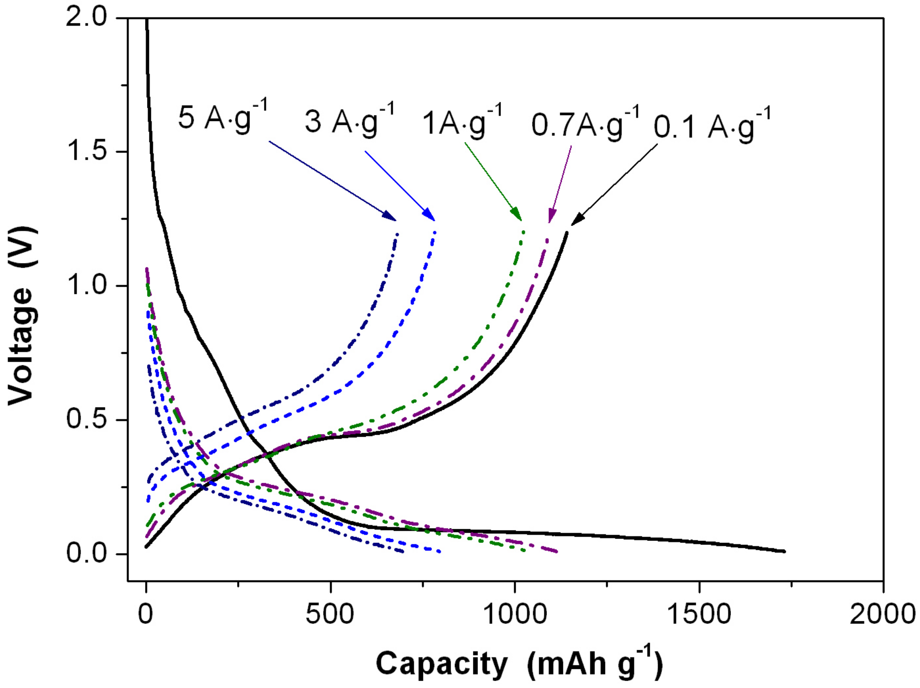

Fig. S5 Charge–discharge profiles of the pSi-MWNT composite at different current densities from 0.1 to 5 A g^{-1}.