

Electronic Supporting Information

A nanofibrous polypyrrole/silicon composite derived from cellulose substance as anode material for lithium-ion batteries

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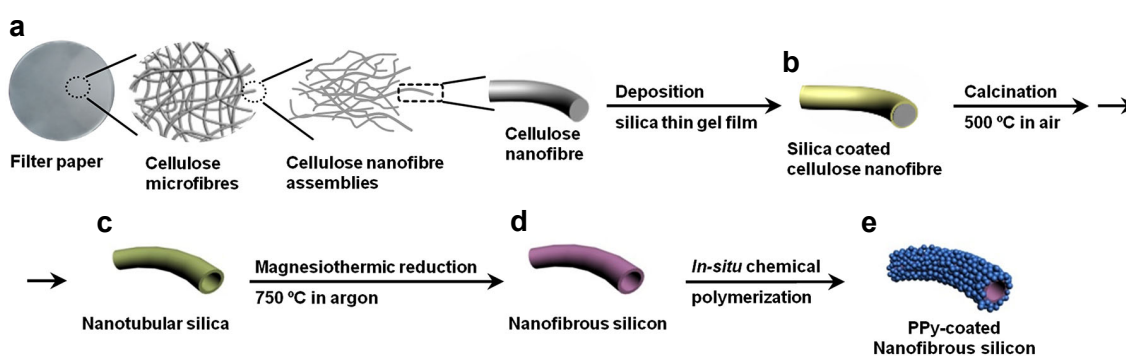
Material fabrication: The synthetic process of the nanofibrous polypyrrole/silicon composite derived from the cellulose substance (commercial laboratory quantitative ashless filter paper) is schematically illustrated in Scheme S1. All the chemicals used were guaranteed reagents and were used without further purification. The water used in all relevant experiments was purified by using a Milli-Q Advantage A10 system (Millipore, Bedford, MA, USA) with resistivity higher than 18.2 MΩ cm. The filter paper used was washed with ethanol and dried prior to use. Thin silica gel films were deposited by a sol-gel process to coat the surfaces of the cellulose fibres of the filter paper giving the silica/cellulose composite (Scheme S1b) which was done as follows. Tetraethoxysilane (TEOS, 98%, J&K Chemical Ltd.) was dissolved in ethanol with a concentration of 50 mM and stirred for 30 min; and into which, a mixture solution of water, ethanol and 1 M HCl (38:11:2, v/v/v) was droplet added, followed with continuous stirring for 10 min to give the precursor solution. Pieces of filter paper were immersed into the precursor solution for 45 min, then washed several times with ethanol and dried under 60 °C for 24 h, resulting in the as-deposited silica/cellulose composite; which was thereafter calcined at 600 °C (heating rate 2 °C min⁻¹) for 6 h in air to remove the cellulose component, giving nanotubular structured silica as replica of the initial cellulose substance (Scheme S1c). The nanotubular silica was reduced by a magnesiothermic reduction process employing a home-made stainless steel autoclave, where a mixture of magnesium powder (99%, Aldrich) and the nanotubular silica obtained (1:1, w/w) was heated at 750 °C (heating rate 3 °C min⁻¹) for 3 h under argon atmosphere. The product mixture was washed with 1 M HCl to remove the excessive magnesium and the magnesia produced, resulting in nanofibrous silicon derived from the initial cellulose fibres (Scheme S1d). An *in-situ* polymerization process was adopted to deposit polypyrrole (PPy) coatings on the silicon nanofibres. The resultant nanofibrous silicon (4.0 mg) was dispersed in isopropanol (10.0 mL) with ultrasonic treatment for 5 min, then 10.0 μL of pyrrole (98%, Sinopharm Chemical Reagent Co. Ltd.) was added into the suspension under stirring; thereafter, an isopropanol solution of copper(II) chloride dihydrate (99.9%, Aldrich) with a concentration of 10 mg mL⁻¹

was added dropwisely with the final molar ratio of CuCl_2 and pyrrole was 3:1. The resultant suspension was stirred for 24 h at room temperature, and the black powder produced was collected by centrifugation, which was thoroughly washed with water for six times and dried at 60 °C for 24 h to give the nanofibrous PPy/silicon composite (Scheme S1e). The content of PPy in the resultant composite was 66.2% by weight as determined by thermogravimetric analysis (TGA); and to adjust the content of PPy in the PPy/silicon composite, another sample with 50.1 wt.% of PPy was also fabricated by the same experimental procedure except 6.0 μL of pyrrole was used. Moreover, as a comparison material for the electrochemical study, pure PPy powder was synthesized by the *in-situ* chemical polymerization process.

Characterizations: For the field-emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM) measurements, the specimens were made by sonicating a small amount of the related sample in 1.0 mL ethanol for tens of seconds to obtain a suspension, which was thereafter dropped onto silicon wafer or carbon-coated copper grid followed by drying in air prior to the measurements. FE-SEM measurements were performed on a Hitachi SU-70 field emission scanning microscope working at an accelerating voltage of 25.0 kV with EDAX HORIBA X-Max80006 equipment, and the specimens were sputtered with platinum to increase conductivity. TEM observations were acquired on a Hitachi HT-7700 electron microscope operating at an accelerating voltage of 100 kV. Powder X-ray diffraction (XRD) measurements were performed on a Philips X'Pert PRO diffractometer with a $\text{Cu}_{K\alpha 1}$ ($\lambda = 0.15405$ nm) radiation source in the range of 10° – 80° . Raman spectra were recorded using a Jobin Yvon LabRam HR UV Raman spectrometer operating at an excitation wavelength of 514 nm. X-ray photoelectron spectra (XPS) were measured using a VG Escalab Mark 2 spectrophotometer equipped with an $\text{Mg}_{K\alpha}$ X-ray source at an energy of 1253.6 eV. High-resolution XPS scans in the silicon, carbon and nitrogen regions were operated at 0.2 eV increments with a sweep time of 1000 ms eV^{-1} and 30 energy sweeps for each region. All of the binding energies were referenced to the C 1s peak at 285.0 eV. The thermogravimetric analyses (TGA) were performed using a Netzsch STA 409 PC/PG thermal analyzer and carried out in air at a heating rate of 10 °C min^{-1} in the temperature range of 25–800 °C.

Electrochemical measurements: The synthesized nanofibrous PPy/silicon composites with varied contents of PPy, the nanofibrous silicon matter and the PPy powders were employed as anode materials for lithium-ion batteries, and the corresponding electrochemical performances were evaluated. The specific material was mixed with acetylene carbon black and poly(vinylidene fluoride) (PVDF) with a weight ratio of 75:10:15 and was stirred to form a homogeneous slurry using 1-methyl-2-pyrrolidone (NMP) as solvent; the slurry was spread onto nickel foam and dried at 80 °C for 12 h in a vacuum oven and then pressed at a pressure

of 10 atm to obtain the anode electrode. Standard CR2025 type coin cells were assembled in an argon-filled glovebox with oxygen and water contents less than 0.1 ppm using the anodes fabricated, Celgard 2300 film and metallic lithium foil were used as the separator and counter electrode, respectively; and 1.0 M lithium hexafluorophosphate (LiPF_6) dissolved in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) was used as the electrolyte. The cyclic voltammetry (CV) tests were carried out on a CHI760D electrochemical workstation (CH instruments, Inc., China) over a voltage range from 0.01 V to 1.50 V with a scan rate of 0.1 mV s^{-1} . The half cells were charged and discharged galvanostatically on a Neware Battery Testing System (Neware Technology Co., Ltd., Shenzhen, China) at a current density of 300 mA g^{-1} or at different current densities of 300, 600, 1500 and 3000 mA g^{-1} in the voltage window of 0.01–1.50 V vs. Li/Li^+ at $25 \text{ }^\circ\text{C}$. The specific capacities of the anodes made by the nanofibrous PPy/silicon composites were calculated based on the mass of silicon contained.



Scheme S1 Schematic illustration of the preparation process of the nanofibrous PPy/Si composite derived from the natural cellulose substance (ordinary laboratory quantitative cellulose filter paper). (a) The hierarchical structures of the filter paper. (b) Ultrathin silica gel layers are deposited to coat the cellulose nanofibres by a sol–gel process. (c) Calcination of the as-prepared silica/cellulose composite in air yields nanotubular silica as replica of the initial cellulose nanofibres. (d) The nanotubular silica is applied with magnesiothermic reduction to give nanofibrous silicon. (e) *In-situ* deposition of PPy layer on the silicon nanowires to give the nanofibrous PPy/Si composite.

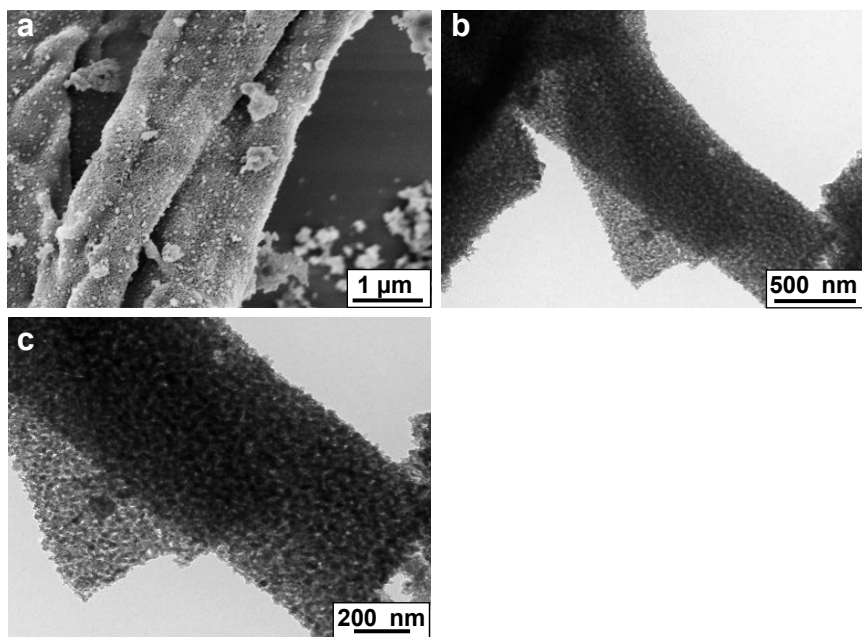


Fig. S1 (a) FE-SEM and (b, c) TEM images of the nanofibrous silicon matter derived from natural cellulose substance.

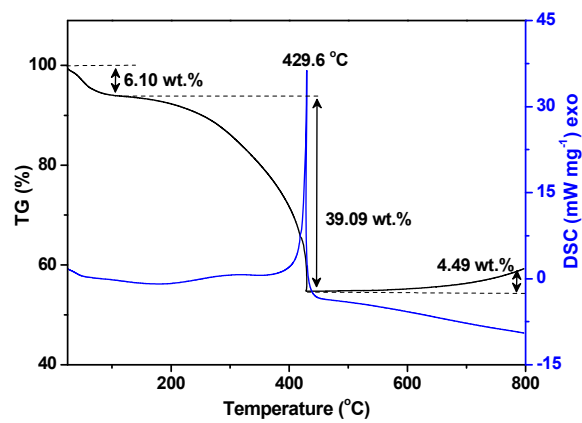


Fig. S2 TG and DSC curves for the nanofibrous PPy/Si composite calcined in air.

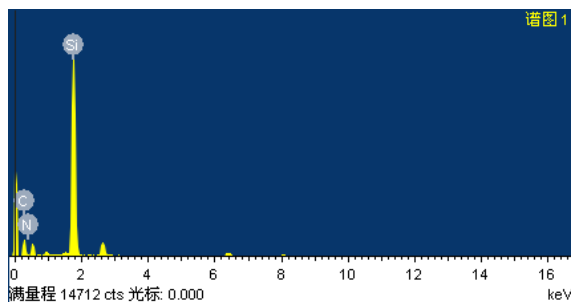


Fig. S3 Energy dispersive X-ray (EDX) analysis of the nanofibrous PPy/Si composite.

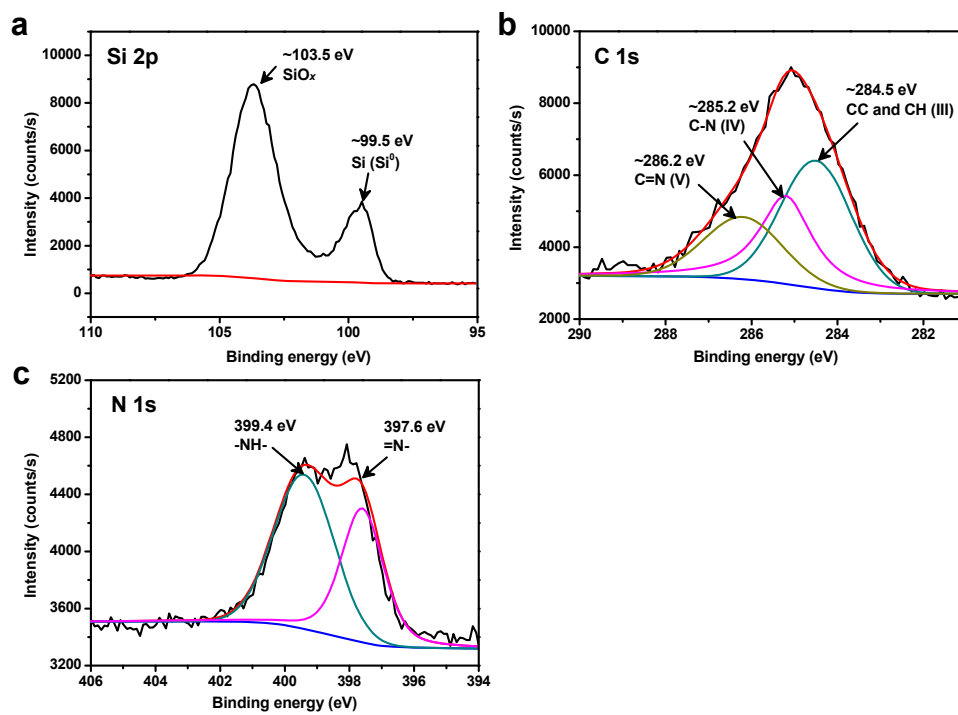


Fig. S4 High-resolution X-ray photoelectron spectra (XPS) of (a) Si 2p, (b) C 1s and (c) N 1s regions of the nanofibrous PPy/Si composite.

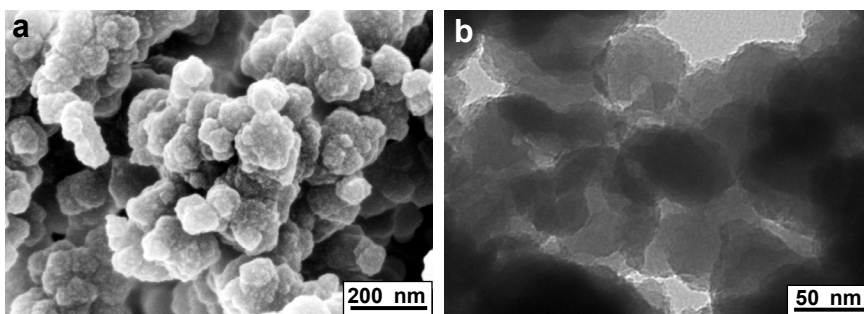


Fig. S5 a) FE-SEM and b) TEM micrographs of the PPy powder synthesized by *in-situ* chemical polymerization.

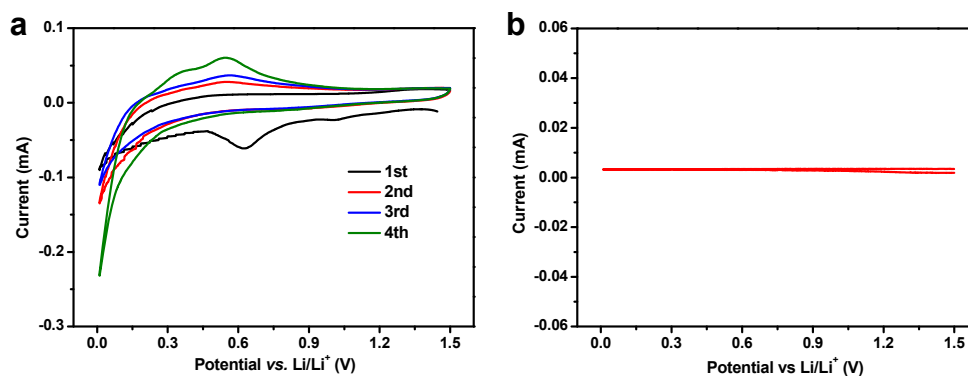


Fig. S6 Cyclic voltammetry curves of a) the nanofibrous silicon matter, and b) the PPy powder electrodes at a scan rate of 0.1 mV s^{-1} over the potential window of 0.01–1.50 V vs. Li/Li^+ .

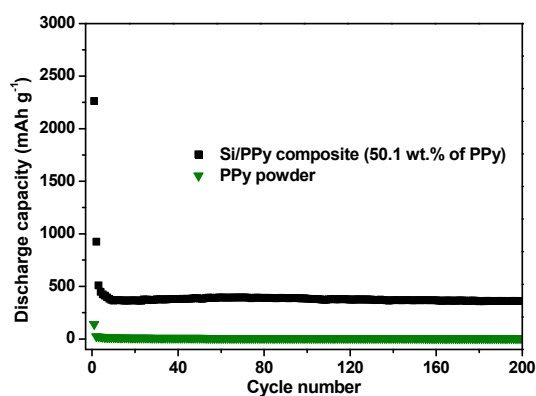


Fig. S7 The discharge cycling performance of the PPy/Si composite (50.1 wt.% of PPy and 49.9 wt.% of silicon) and the PPy powder at a current density of 300 mA g^{-1} .