Supporting Information

A molten salt strategy for deriving porous Si@C nano-composite from Si-rich biomass for high-performance Li-ion batteries

Ning Lin, Tianjun Xu, Ying Han, Kangze Shen, Yongchun Zhu, and Yitai Qian*

Experimental section

Materials synthesis: Typically, dried natural bamboo leaves were ball-milled into fine powder, which was immersed into 2.0 M HCl solution for 2 h. After dried at 60 ^{o}C, the precursors were loaded in a covered alundum crucible and calcinated at 400 ^{o}C for 100 min under air atmosphere. Next, a mixture of 1.0 g of the obtained SiO_2/C intermediate, 0.6 g metallic Mg powder and excess $AlCl_3$ was sealed in a stainless steel autoclave (20 ml), and heated at 200 ^{o}C for 6 h. The ramping speed for the heating process was kept at 5 ^{o}C min^{-1}. The obtained sample was soaked in 1 M HCl solution for 2 h, then washed with ethanol and water for several times. The obtained sample was then immersed in diluted ethanol-based hydrofluoric acid (HF) solution for 10 min to remove the residual silicon oxides. After washing, the sample is vacuum-dried at 50 ^{o}C.

Characterization: The structure and morphology of the product were characterized by X-ray diffractometer (Philips X' Pert Super diffract meter with Cu Kα radiation (λ=1.54178 Å)), Raman spectrometer (Lab-RAM HR UV/VIS/NIR), FTIR instrument

(FTIR, Hyperion 3000), scanning electron microscopy (SEM, JEOL-JSM-6700F), and transmission electron microscopy (TEM, Hitachi H7650 and HRTEM, JEOL 2010). Thermal gravimetric analysis (TGA) measurement was carried out on TGA Q5000 V3.15 Build 263 from room temperature to 800 °C in air.

Electrochemical Measurement: The electrochemical properties of the prepared Si@C sample were evaluated through coin-type cells (2016 R-type) which were assembled under an argon-filled glove box (H_2O, O_2 < 1 ppm). Metallic Li sheet was used as counter and reference electrode. 1 M $LiPF_6$ in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC; 1:1 by volume) was served as the electrolyte (Zhuhai Smooth way Electronic Materials Co., Ltd (china)). For preparing working electrode, the slurry mixed with as-prepared active Si@C material, carbon black (super P) and sodium alginate (SA) binder in a weight ratio of 8:1:1 in water solvent was pasted onto a Cu foil, and then dried in a vacuum oven at 80 ^oC for 10 h. The active material density of each electrode was determined to be about 1.0 mg cm^{-2}. Galvanostatic measurements were conducted using a LAND-CT2001A instrument at room temperature with a fixed voltage range of 0.01-1.5 V (*vs.* Li/Li^+). Cyclic voltammetry (CV) was performed on electrochemistry workstation (CHI660D), with a scanning rate of 0.1 mV s^{-1} at room temperature.

For assembling the full cells, the commercial available $LiCoO_2$ is employed as cathode. The $LiCoO_2$ cathode electrode was prepared by mixing the commercial $LiCoO_2$ material, carbon black, and poly(vinyl difluoride) (PVDF) binder in a weight ratio of 8:1:1. N-Methyl-2-pyrrolidone (NMP) was used as the solvent to form slurry.

The resulting slurry was coated onto the Al foil and dried at 120 °C for 12h for further use. A pre-lithiation treatment of Si@C anodes was performed in half-cells which is discharged at cut-off voltage of 0.1 V vs. Li/Li^+ at 0.3 A g^{-1}. For Si@C /$LiCoO_2$ full cell assembly, the anode capacity is limited and the excess capacity of cathode is controlled at about 10%. The reversible capacity and energy density of the full cells were calculated based on the weight of Si@C. Galvanostatic measurements of the full cells were conducted using a LAND-CT2001A instrument at room temperature with a voltage range of 2.5-4.2 V.

(1)

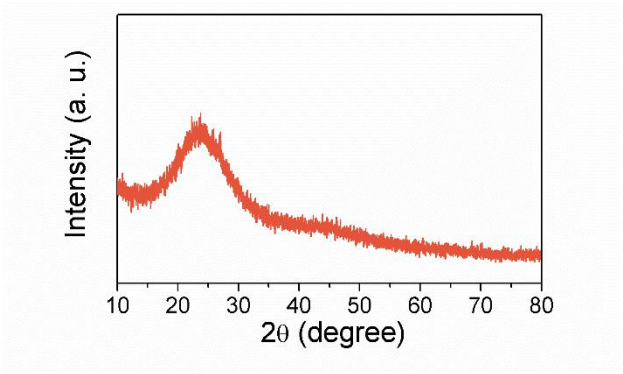

Figure S1. The XRD pattern of the baked bamboo leaves.

(2)

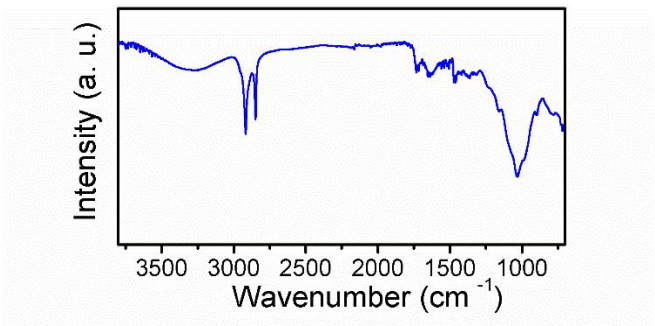

Figure S2. The FT-IR plots of the dried bamboo leaves.

(3)

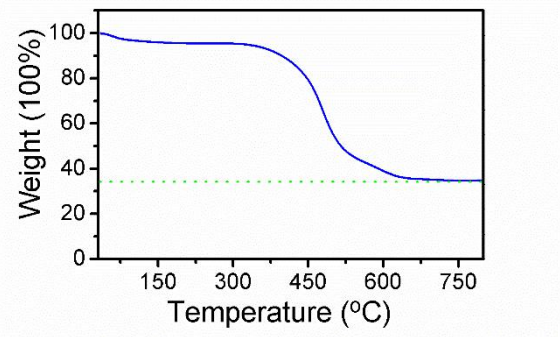

Figure S3. Thermal gravimetric analysis (TGA) plot of the Si@C composite from room temperature to 800 °C in air.

(4)

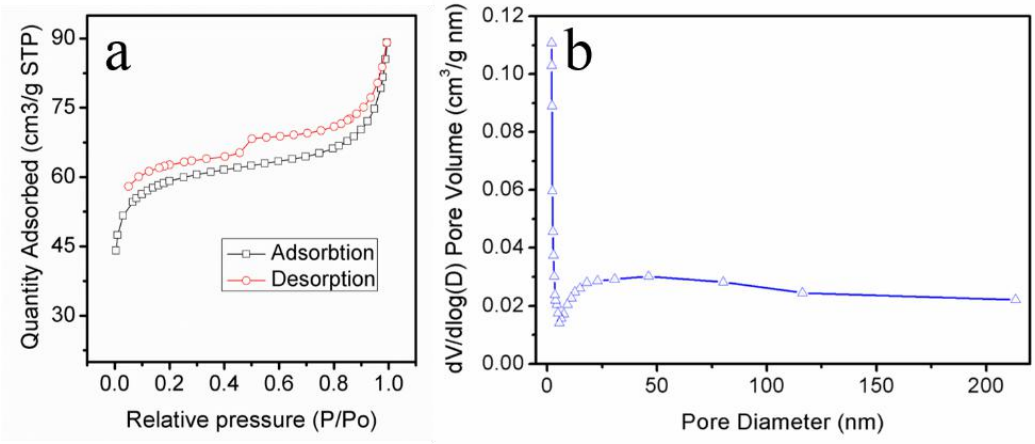

Figure S4. The BET Isotherm Linear Plot, and (b) the BJH pore distribution of the Si@C composite.

The Figure S5 exhibits the discharge/charge voltage curves of the Si@C electrode. In the first cycle, the discharge potential plateau is below 0.2 V which is mainly resulted from the Li-alloying reaction with Si. In the subsequent cycle, the discharge plateau shift to higher potential, because Si nanoparticles in the composite changed from crystallized to amorphous structure during the lithiation/delithiation process. On the other hand, the charge voltage plateaus are located at around 0.4 V that is corresponding to the de-alloying reaction of LixSi. This section has been provided in the revised supporting information, please check, thank you.

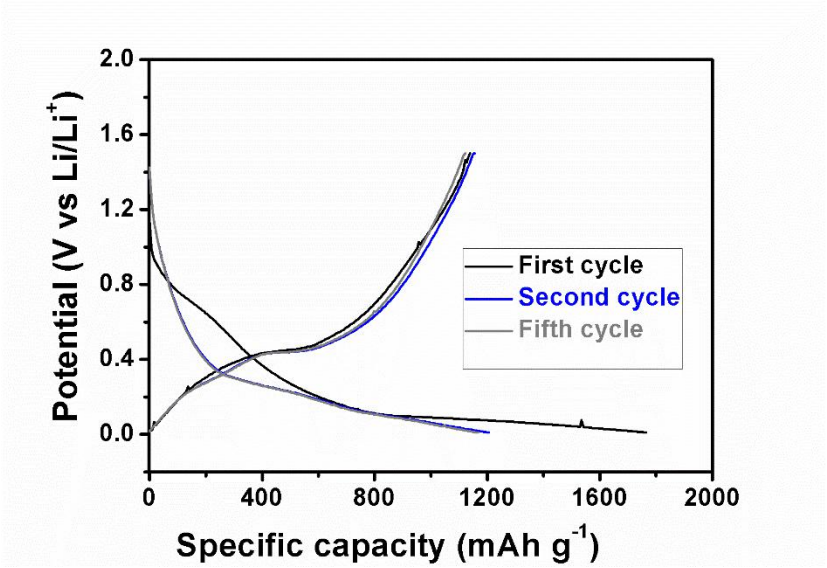

Figure S5. Charge/discharge voltage curves of Si@C composite.