

Supplemental Information

Amorphous Si/SiO_x/SiO₂ Nanocomposites via Facile and Scalable Synthesis as Anode Materials for Li-ion Batteries with Long Cycling Life

Fang Dai, Ran Yi, Mikhail Gordin, Shuru Chen, and Donghai Wang*

Preparation of Si/SiO_x/SiO₂ nanocomposite: all procedures except for the washing process were carried out in a glovebox filled with Ar. Sodium potassium alloy (NaK) was prepared by mixing 0.7 g (0.03 mol) of sodium (Aldrich, 99.9 %) and 2.7 g (0.07 mol) of potassium (Aldrich, 98 %). The as-prepared NaK alloy was added to 120 mL of toluene solution of anhydrous SiCl₄ (1.8 mL, 0.0157 mol, Aldrich). This mixed solution was heated under reflux for 4 h, by the end of which time black particles formed. After cooling the solution down to room temperature, 20 mL of diethyl ether solution of hydrogen chloride (Aldrich) was added slowly while the mixture was under magnetic stirring. The stirring was then stopped and 40 mL of de-gassed DI water was added slowly while bubbling in N₂. After addition of water, the reaction mixture was placed in a sonic bath for around five minutes. (Warning: A lot of heat was generated during the addition of the H₂O and may result in explosion if the addition of H₂O is too fast.) The products were then collected by filtration, washed several times with DI water, and annealed at 500°C for 2 h under Ar atmosphere.

Characterizations: The composite anode material was characterized by scanning transmission electron microscopy with an EDX accessory (STEM-EDX, Hitachi, HD-2700), transmission electron microscopy (TEM, JEOL, EM-2010F), and X-ray photoelectron spectroscopy (XPS, Kratos Analytical Axis Ultra). The X-ray powder diffraction spectrum (XRD) was obtained using a Rigaku Miniflex II spectrometer. FT-IR spectroscopy was performed as diffuse reflectance measurements with powder samples using a Bruker IFS 66/S FT-IR spectrometer and Spectra-Tech Collector II DRIFTS accessory. Thermogravimetric analysis (TGA) was performed on TA Instruments SDT 2960.

Electrochemical Measurements: CR2016-type coin cells consisting of the Si/SiO_x/SiO₂-based electrode and lithium foil anode separated by a Celgard 2400 membrane were used for battery tests. The electrode contained 70 wt% active material, 20 wt% Super P and 10 wt% sodium carboxymethyl cellulose. The electrolyte was 1 M LiPF₆ dissolved in a mixed solvent of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) (2:1:2, v/v/v) with 10 wt% fluoroethylene

carbonate (FEC) as additive. The density of the electrode is 0.68 g/cm^3 and the loading of the active material is 1.02 mg/cm^2 . The cells were assembled in an argon-filled glove box (MBraun GmbH, Germany). The charge-discharge experiments were performed on a BT2000 battery testing system (Arbin Instruments, USA) in the potential range of 0.02-1.5 V using galvanostatic charging and discharging method with different current rates. Lithium foil acted as both the reference and counter electrode. Electrochemical tests were performed at room temperature.

Structure modification

The particle size of the composite can be adjusted by using different calcinations temperature. When the as-prepared material was calcinated at 700°C , the average particle size of the material increased to around 100 nm without the composition changing. The XRD pattern showed similar broad peaks as those of the sample calcinated at 500°C (Figure S5). Although the initial cycle coulombic efficiency increased, the long cycling stability of the 700°C -calcined composite was worse than that of the 500°C -calcined composite (Figure S6). The ratio of Si and silicon oxides can be also controlled by disproportionation of the SiO_x .¹ When calcinated to 900°C , the SiO_x inside the composite disproportionated to form crystalline Si and amorphous SiO_2 . (Figure S5) The electrochemical performance of the 900°C -calcined composite was tested and shown in Figure S6. The composite also showed an increased 1st cycle coulombic efficiency and a good long cycling stability. However, the stable capacity of the composite was not as high as the 500°C -calcined composite (Figure S6).

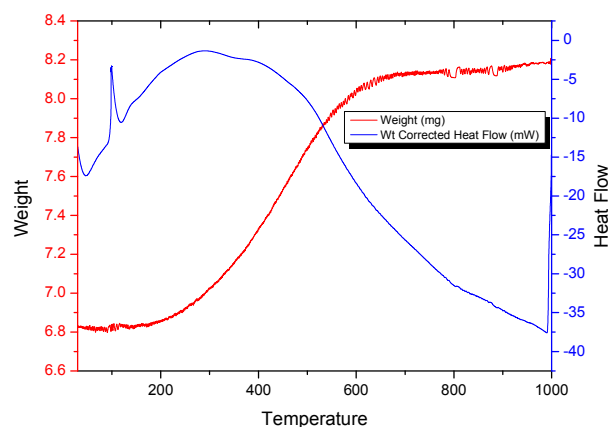


Figure S1. Thermogravimetric analysis (TGA) of the Si/SiO_x/SiO₂ nanocomposite.

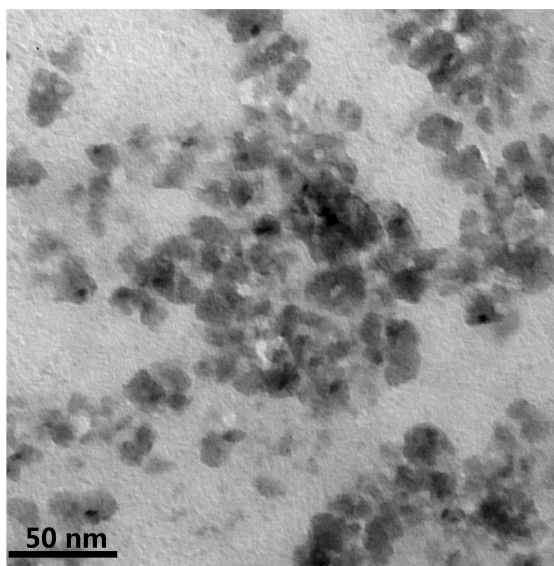


Figure S2. Low-magnification TEM image of the Si/SiO_x/SiO₂ nanocomposite.

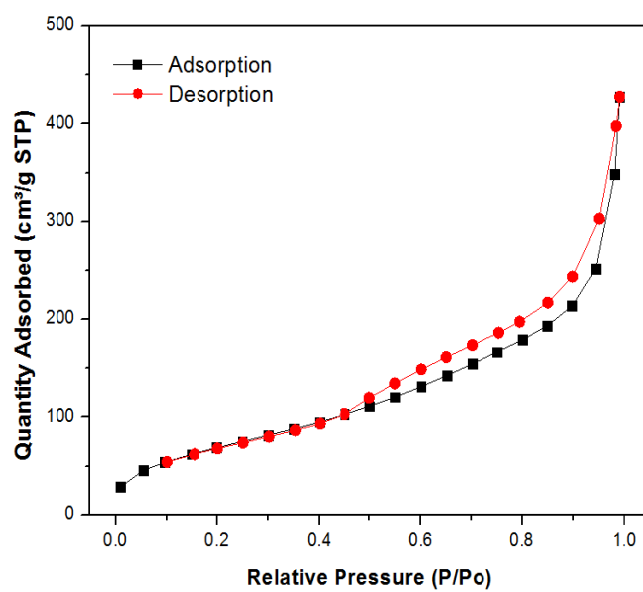


Figure S3. BET isothermal profile of the Si/SiO_x/SiO₂ nanocomposite.

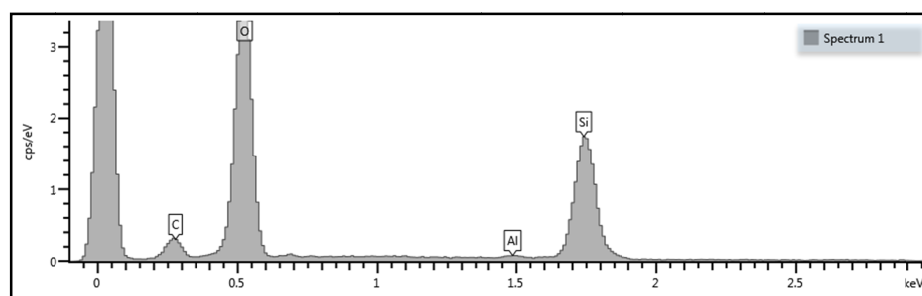


Figure S4. EDS spectrum of the Si/SiO_x/SiO₂ nanocomposite.

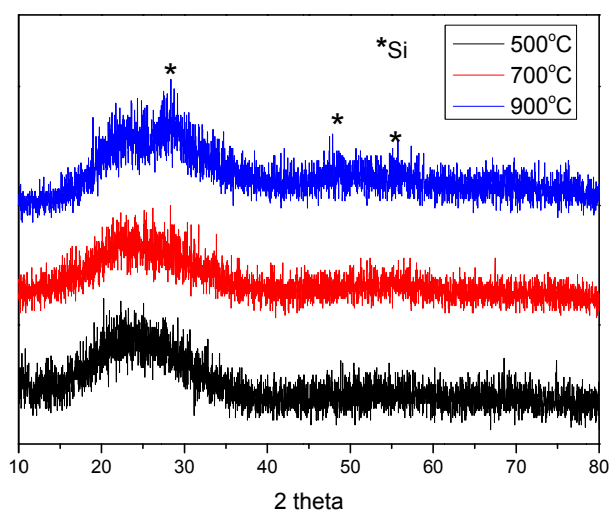


Figure S5. XRD spectra of the composites with different calcinations temperature

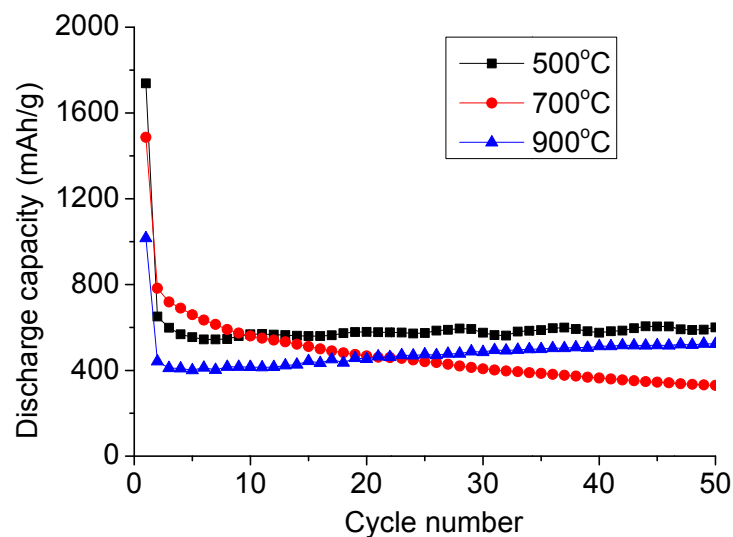


Figure S6. Discharge capacity of the composites with different calcinations temperature (0.02-1.50V at 0.4A/g current density)

Reference

1. a) C. M. Hessel, D. Reid, M. G. Panthani, M. R. Rasch, B. W. Goodfellow, J. Wei, H. Fujii, V. Akhavan and B. A. Korgel, *Chem. Mater.*, 2011, **24**, 393-401;
b) J.-I. Lee, N.-S. Choi and S. Park, *Energy Environ. Sci.*, 2012, **5**, 7878.
2. C. M. Park, W. Choi, Y. Hwa, J. H. Kim, G. Jeong and H. J. Sohn, *J. Mater. Chem.*, 2010, **20**, 4854-4860.