

Supporting Information

Embedding Silicon Nanoparticles in Graphene Based 3D Framework by Cross-Linking Reaction for High Performance Lithium Ion Batteries

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1 Experimental Section

Materials synthesis

First, Si nanoparticles were prepared through a typical magnesiothermic reduction of commercial silica aerogels, which is feasible to scale up. Magnesium (Mg) and silica aerogels with a molar ration of 2 to 1 were mixed uniformly and heated to 650 °C for 10 h. The product was collected and washed with diluted hydrochloric acid, distilled water, and absolute ethanol for several times. The residual silicon oxides were removed by soaking the product in ethanol-based hydrofluoric acid. Then, 100 mg of Si nanoparticles was dispersed into GO suspension, synthesized by modified Hummer's method. After ultrasonic dispersion for 30 minutes, PAM solution (2wt.%) was added drop by drop in above suspension to start the cross-linking reaction with magnetic stirring, until the floccule appeared and the solution became clear and transparent. Finally, the product was collected and treated by annealing at 650 °C in

Ar atmosphere for 2 h, leading to thermal reduction of GO as reduced graphene oxides (RGO).

Characterization

The structure and morphology of the samples in this work were characterized by X-Ray diffraction (Philips X'Pert Super diffractometer with Cu K α radiation ($\lambda=1.54178\text{\AA}$)), Raman spectrometer (Lab-RAM HR UV/VIS/NIR), scanning electron microscopy (SEM) (JSM-6700F), transmission electron microscopy (TEM) (JEOL-2010).

Electrochemical measurements

Charge/discharge tests were carried out using coin-type cells (CR 2016). Lithium foil was acted as counter and reference electrode. A solution of 1 mol/L LiPF₆ dissolved in ethylene carbonate/dimethyl carbonate (EC/DEC) (1:1 volume ratio) was used as the electrolyte. To prepare the working electrode, a mixed slurry of active material, super P carbon black, and carboxymethylcellulose sodium (CMC-Na) at a weight ratio of 70:25:5 was coated on Cu foil (99.9%). After dried at 100 °C for 10 h in a vacuum oven, the active material density of each electrode was determined to be around 1.0~1.5 mg cm⁻². The cells were assembled in an argon-filled glove box (Mikrouna, Super 1220/750/900, China). Galvanostatic charge/discharge measurements were performed on a LAND-CT2001A instruments in the voltage range of 0.005–1.5 V (vs Li/Li⁺). Electrochemical impedance spectroscopy (EIS) was also measured with an electrochemical workstation (CHI660D) by applying an alternating current (AC) voltage of 5 mV in the frequency range from 100 kHz to 0.1

Hz. Unless otherwise noted, charge/discharge rate and specific capacity were calculated based on the total mass of active materials.

2 Fabrication of Si/GO/PAM composite through cross-linking reaction

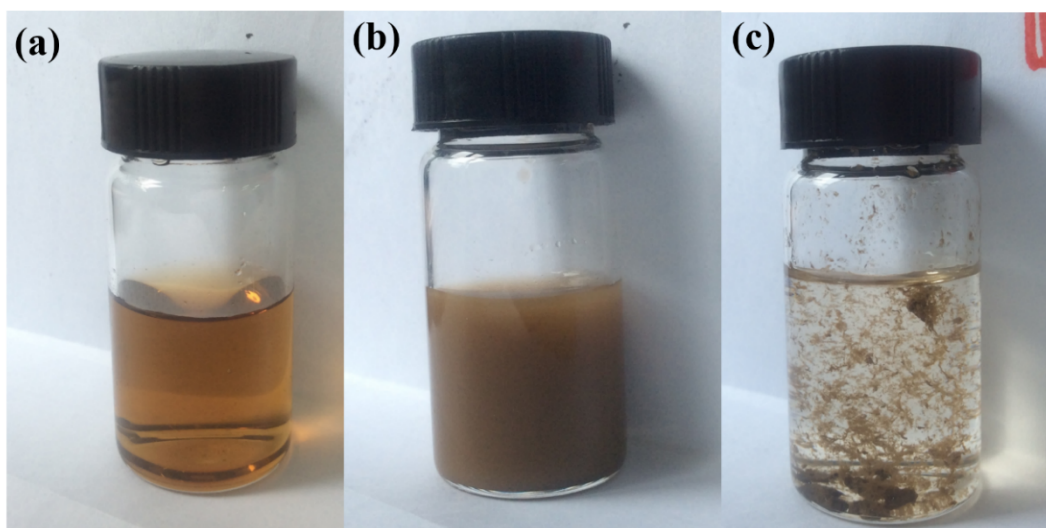


Figure S1. Digital photos of (a) GO suspension, (b) mixed suspension Si and GO, and (c) Si/GO/PAM floccule obtained by dropping PAM solution into suspension (b).

GO powder was made according to a slightly modified Hummer's method. [1]

3 Fourier transformed infrared spectroscopy was measured by Hyperion 3000.

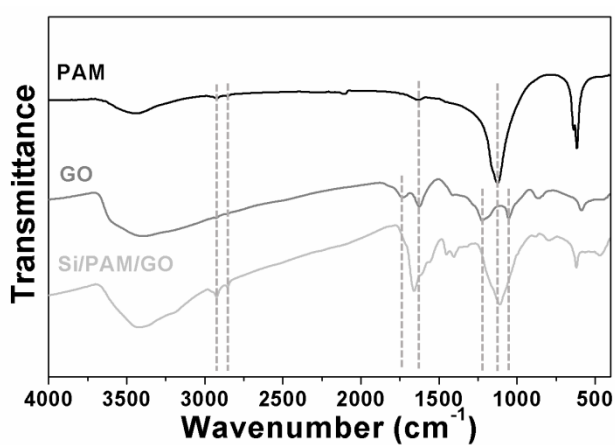


Figure S2. FTIR spectra of PAM, GO, and Si/PAM/GO composite.

Figure. S2 exhibits the FTIR spectra of PAM, GO, and Si/PAM/GO composite. For PAM, the peaks at 1648 cm^{-1} and 1141 cm^{-1} are assigned to the characteristic bands of the C=O stretching and $-\text{NH}_2$ rocking vibration of amide groups, respectively. [2-3] The characteristic peaks in the spectrum of GO at 1055 cm^{-1} , 1236 cm^{-1} , 1626 cm^{-1} , and 1730 cm^{-1} are ascribed to C–O–C stretching vibrations, C–OH stretching vibration, aromatic C=C stretching vibration, and C=O stretching vibration for carbonyl, respectively. [4-6] Therefore, we can infer that GO is rich of oxygen-containing functional groups which would be responsible for the formation of hydrogen bond. After cross-linking, these characteristic peaks of both GO and PAM all appears in the FTIR spectrum of Si/PAM/GO composite except that some weak peaks are covered by the adjacent strong peaks. Notably, the characteristic peak of C=O displays a obvious shift from 1648 cm^{-1} to a higher wavenumber at 1660 cm^{-1} , which is attributed to the presence of the hydrogen bonding between the N–H bond of PAM and O–H bond of GO nanosheets. [7]

4 Thermal gravimetric analysis (TGA) measurement was carried out on TGA Q5000 V3.15 Build 263 from room temperature to $650\text{ }^{\circ}\text{C}$ in air, with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

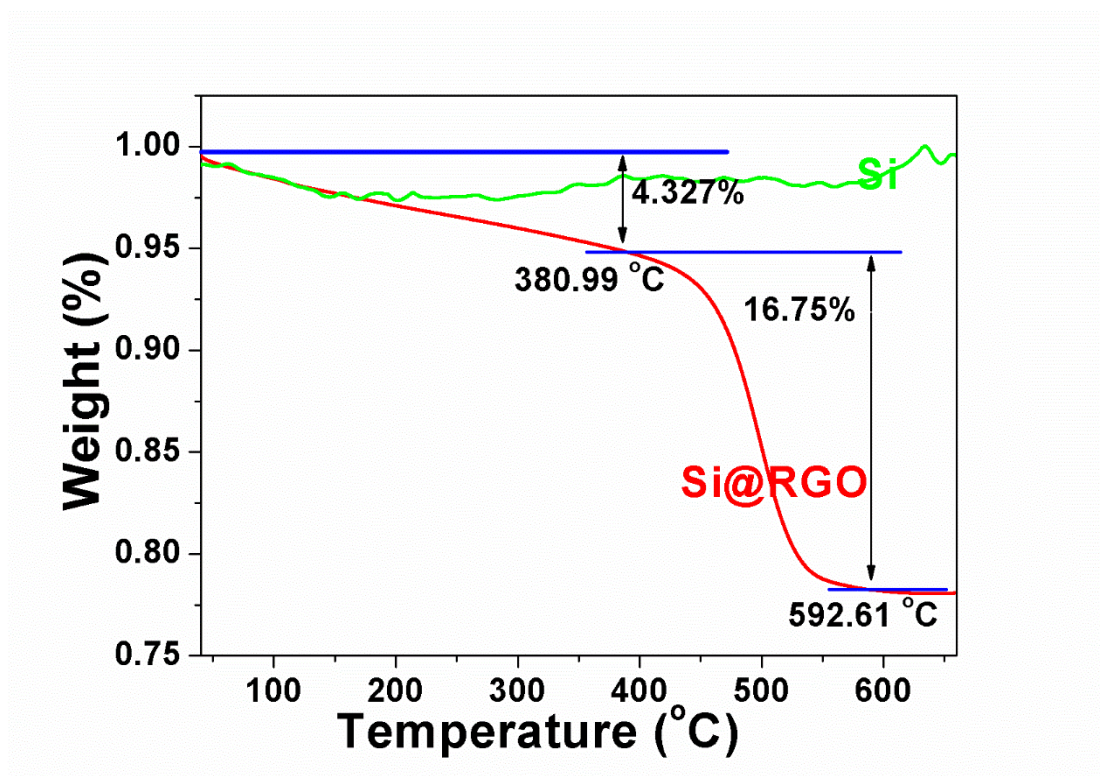


Figure S3. TGA curves of Si @RGO composites and bare Si nanoparticles.

5 TEM and corresponding elemental mapping measurement of Si@RGO composite.

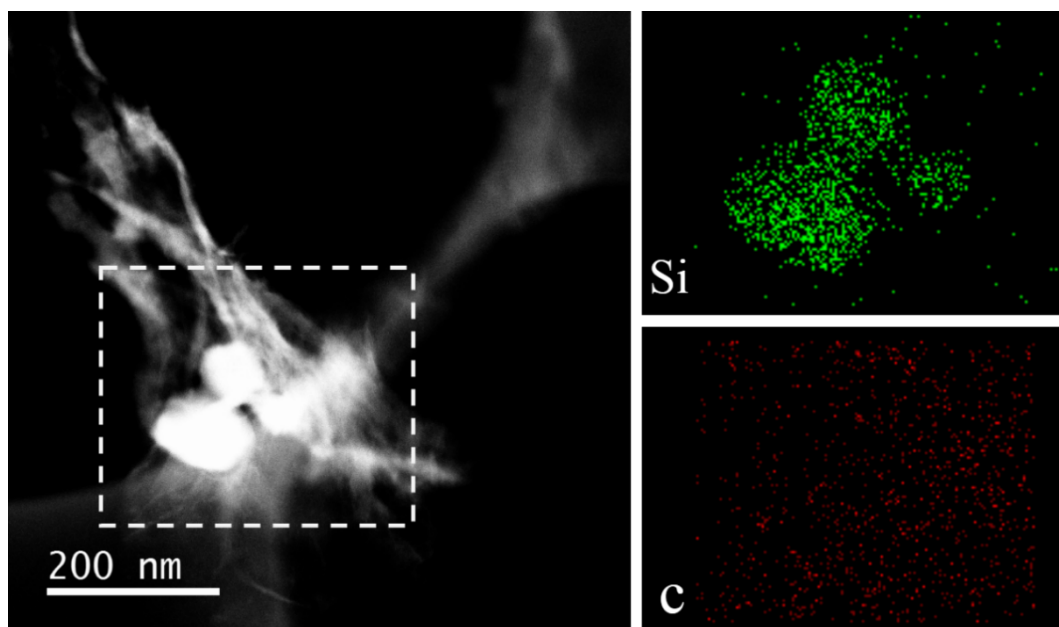


Figure S4. TEM image of Si@RGO composite and corresponding mapping pictures of Si and C elements.

6 The cyclic voltammetry (CV) measurements were carried out at room temperature at scanning rates of $0.5 \text{ mV}\cdot\text{s}^{-1}$ between 0.005 and 1.5 V (vs Li/Li⁺) on an electrochemical workstation (CHI660E).

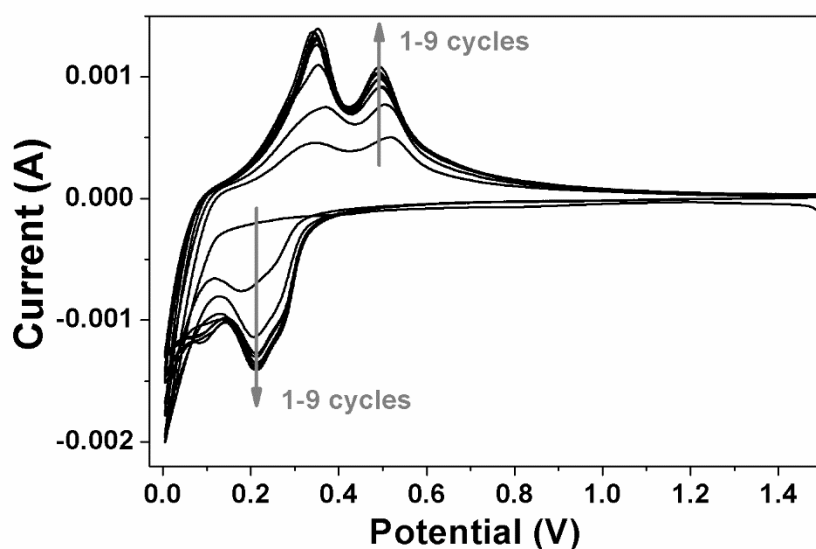


Figure S5. CV curves of Si@RGO electrode.

7 As a contrast, the Si and graphene composite with a weight ratio of 8/2 is prepared by simple filtration of the mixed suspension, followed by heating treatment at 650 °C under Ar atmosphere for 2 h. And the cycling behavior is measured by galvanostatic discharge/charge tests. The obtained Si/graphene composite delivers a reversible capacity of 349 mAh g^{-1} at 1.2 A g^{-1} over 50 cycles, which is better than bare Si electrode.

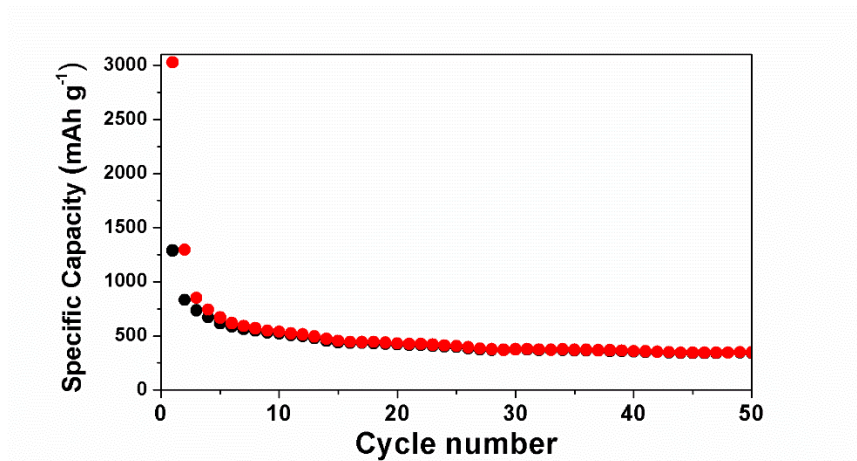


Figure S6. Cycling performance of the Si/graphene prepared by simple filtration at a current density of 1.2 A g⁻¹.

References

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