Silicon Nanoparticles-Graphene Paper Composites for Li Ion Battery Anodes

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Supporting Information

Experimental

1. **Preparation of Graphite oxide**:

Graphite oxide (GO) was synthesized from flake graphite (Asbury Carbons, 230U Grade, High Carbon Natural Graphite 99+) by a modified Hummers method originally reported by Kovtyukhova et al.[1], in which pre-oxidation of graphite is followed by oxidation with Hummers' method. In the pre-oxidation, the graphite power (2.0 g) was added with stirring into the concentrated H_2SO_4 (20 mL) solution in which $K_2S_2O_8$ (1.0 g) and P_2O_5 (1.0 g) were completely dissolved at 80°C. The mixture, in a beaker, was kept at 80°C for 4.5 h using an oil bath after which the mixture was cooled down and was diluted with 1 L of distilled deionized (DDI) water. The pretreated product was filtered with a Nylon Membrane filter (0.2 μm, Milipore) and washed on the filter until the pH of filtrate water became neutral. The shiny, dark-gray, pre-oxidized graphite was dried in air overnight. Then, it was dispersed by stirring into chilled H_2SO_4 (75 mL) in an Erlenmeyer flask in an ice bath. $KMnO_4$ (10g) was added slowly with stirring to keep the temperature of reaction mixture below 20°C. The resulting thick, dark green paste was allowed to react at 35°C for 2 h followed by addition of DDI water (160 mL) to give a dark brown solution. To avoid over-flow of mixture due to rapid temperature rise with foaming by water addition, the flask was chilled in an ice bath and water was added in ~5 mL aliquots with close monitoring of temperature (kept below 50°C). After additional stirring for 2 h, the dark brownish solution was further diluted with distilled water (500 mL) after which H_2O_2 (30%, 8.3 mL) was added slowly and the color of the mixture turned into brilliant yellow. The mixture was allowed to settle overnight and the supernatant was decanted. The remaining product was washed with 10% HCl solution (800 mL) with stirring and the brownish solution was allowed to settle overnight. The supernatant was decanted and the remaining product was centrifuged and washed with DDI water. The washing process was repeated until the pH of the solution became neutral (at this stage, the Mn concentration in the supernatant was below 0.1 ppm by AAS). Thus obtained product was diluted to make a ~0.7 % w/w aqueous dispersion for storage.

2. Preparation of Si-Graphene Paper Composites:

In a typical preparation, Si nanoparticles (H-terminated, <30 nm, Meliorum Nanotechnology, stored in Ar) were removed from an Argon glovebox and exposed to air overnight to ensure that a hydrophilic oxide layer was formed on the surface of the nanoparticles. Then the Si nanoparticles were weighed and dispersed in ~1 ml DDI water by sonication for 15 minutes. A desired amount of the graphite oxide dispersion was then added to the suspension of Si nanoparticles. In some preparations, the pH was adjusted to ~10 with NH_4OH (29% in H_2O, Fischer Scientific), whereas in some others, no pH adjustment was made. No clear trend on the effect of pH adjustment could be identified. The composite mixture was then sonicated for 60 minutes and vacuum-filtered (47 mm, 0.22 μm pore nylon filters, Whatman) until the surface of the composite appeared dry. After filtering, the composite paper was removed from the nylon filter carefully with forceps and allowed to air-dry for approximately 24 hours. Once dried, a razor blade was used to cut the composite paper into smaller ribbons to allow them to fit into a quartz tube for thermal reduction. Samples for electrodes were cut from these ribbons either before or after thermal reduction, although the fragility of the reduced samples made it more difficult to cut out electrodes. Composite papers were reduced with a 10% H_2 in Argon flow (~100 ml/min total rate) at 700°C for 1 hour. Afterwards, the samples were ready for testing.

3. Sample characterization: X-ray diffraction (Rigaku X-ray diffractometer miniflex) measurements were carried out with Cu K_α radiation using an operating voltage of 40 kV, a step size of 0.01°, and a step time of 1 s^2. High-resolution transmission electron microscopy (HRTEM) was performed on a Hitachi HF-2000 operated at 200 kV with a energy dispersive spectroscopy (EDS) detector. Samples dispersed in ethanol were applied onto the 400 mesh Cu grid with lacey carbon film and dried in air before TEM imaging. For thermogravimetric analysis (TGA) (Mettler Toledo, TGA/SDTA851^e) in air, the samples were heated to 100°C and held at 100°C for 10 min to remove any volatiles and water adsorbed on the samples. Then, the temperature was ramped to 800°C at the rate of 10°C/min in flowing air. The weight loss, after correcting for oxidation of Si, was used to calculate the carbon content. Separate TGA with bare silicon nanoparticle was run at the same conditions to obtain data to correct the weight gain of Si-graphene paper composites due to oxidation of silicon particles in air. For atomic force microscopy (AFM) images of graphene oxide sheets, a droplet of the dilute, aqueous dispersion was dried onto a freshly cleaved mica surface at room temperature with N_2 purge. A normal tapping mode silicon cantilever (125 kHz, 16 N/m, SI-DF20, Seiko Nano Instruments Inc.) was used for AFM imaging. An AFM instrument (Nanoscope IV, Digital Instrument, Santa Barbara, USA) was used for surface imaging. The dispersion and size distribution of graphene oxide sheets dispersed in water (0.25mg/mL) were measured with dynamic light scattering (DLS) at 25^{o}C. Scanning Electron Microscopy (SEM) images were taken with a Hitachi S-3400N-II microscope operated at 5 kV accelerating voltage in the secondary electron (SE) mode. Sheet resistance and conductivity measurements were made with a four-point probe technique with an electrode separation of 1 mm using a Keithley 2400 sourcemeter.

4. Electrochemical experiments: The electrochemical response of the samples was tested using two-electrode Swagelok-type cells, with a Li metal reference electrode that was separate from a Li metal counter electrode. For the Si-graphene composite paper samples, the sample was weighed ten consecutive times on an analytical balance (Mettler Toledo AX205) to enhance accuracy. These samples were typically ~2 mg/cm^2 and 5-30 μm thick. They were placed directly on stainless steel plungers in the Swagelok-type cells. For the crushed samples, the working electrode was prepared with mixtures of 90.0 wt% active materials and 10.0 wt% poly(vinylidene fluoride) (PVDF, binder, Sigma-Aldrich) using a 5.0 wt% PVDF solution in *N*-methyl-2-pyrollidone (NMP, 99.5%, anhydrous, Sigma-Aldrich) exclusive of any conductive additive. The working electrode mixture was pasted onto a Cu foil (99.999%, 0.025 mm thick, Alfa-Aesar). Subsequently, the coated electrodes were dried in a vacuum oven at 75°C overnight. The typical active material loading of the electrode was 1~3 mg/cm^2 and its thickness was 30~50μm. A 1.0M $LiPF_6$ in EC/DMC 1/1(v/v) solution soaked on a microporous membrane (Celgard 2325) separator was used as the electrolyte, and lithium foil (99.9%, 0.75 mm thick, Alfa-Aesar) was used as the counter electrode. The cell was assembled in an argon-filled glove box.

For electrochemical cycling, two different cycling procedures were used. In one method, the sample was galvanostatically cycled with a cut-off voltage range of 0.02 – 2.0V while maintaining a constant current of 100 mA/g. The second cycling method was the constant current-constant voltage (CCCV) method. In this method, during lithiation, the current was held at 1000 mA/g until the potential dropped to 5 mV. After reaching 5 mV, the potential was held constant while the current was decreased from 1000 mA/g to 80 mA/g. During delithiation, the current was held at 1000 mA/g while the potential increased to 1.5V, at which point the potential was held at 1.5V until the current decreased to 80 mA/g. Additionally, CCCV tests were also performed using cut-off voltages of 1.5V – 20 mV, and current from 1000 mA/g – 50 mA/g. All electrochemical experiments were performed on a BT2000 Potentiostat/Galvanostat system (Arbin Instruments).

Sample Characterizations

X-ray Diffraction (XRD)

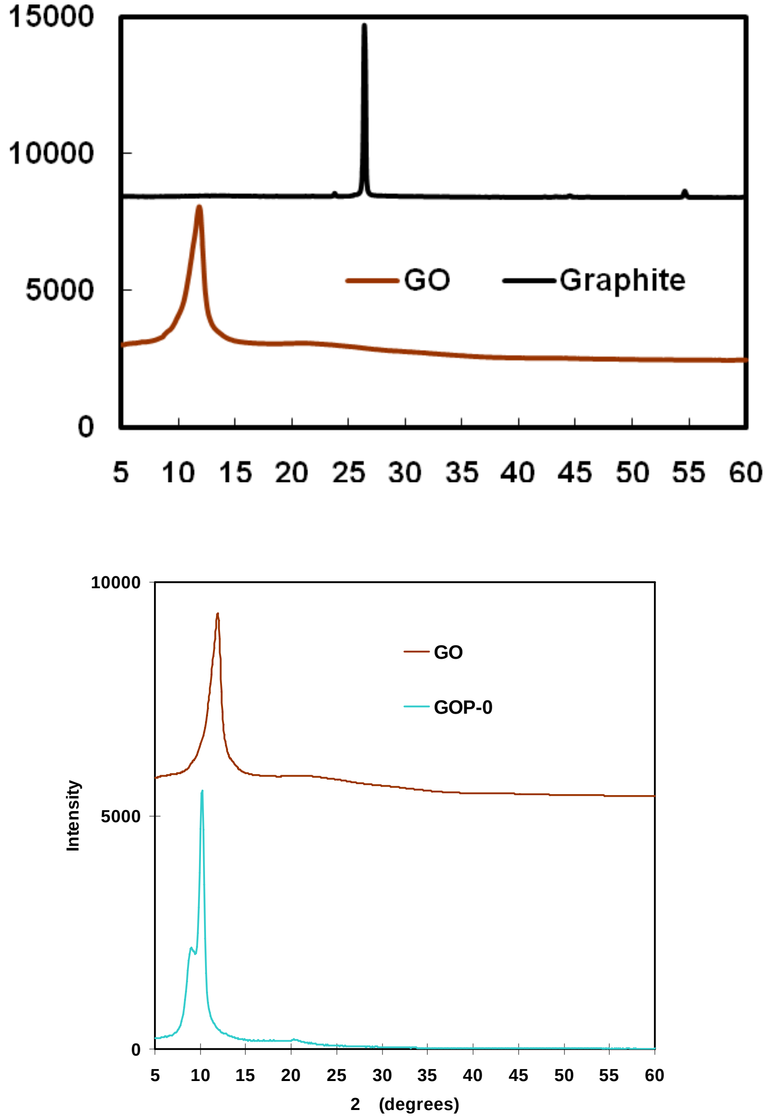


Figure S1. XRD patterns of graphite flake, graphene oxide (GO), and graphene oxide paper (GOP-0).

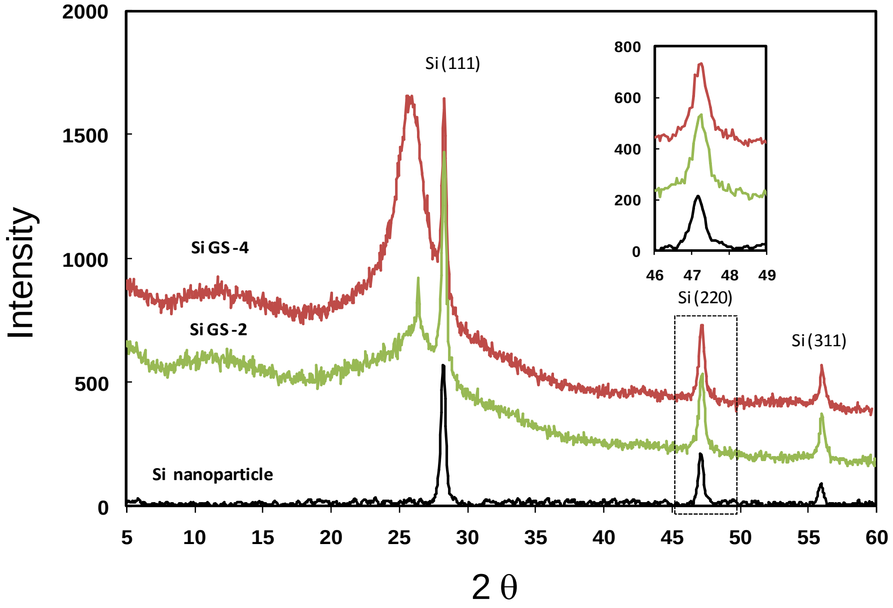


Figure S2. XRD patterns of Si nanoparticles and two different reduced SG composites (green and red curves). Inset shows Si (220) diffractions. Intensities were displaced for clarity.

Dynamic light scattering (DLS) of GO dispersion in water

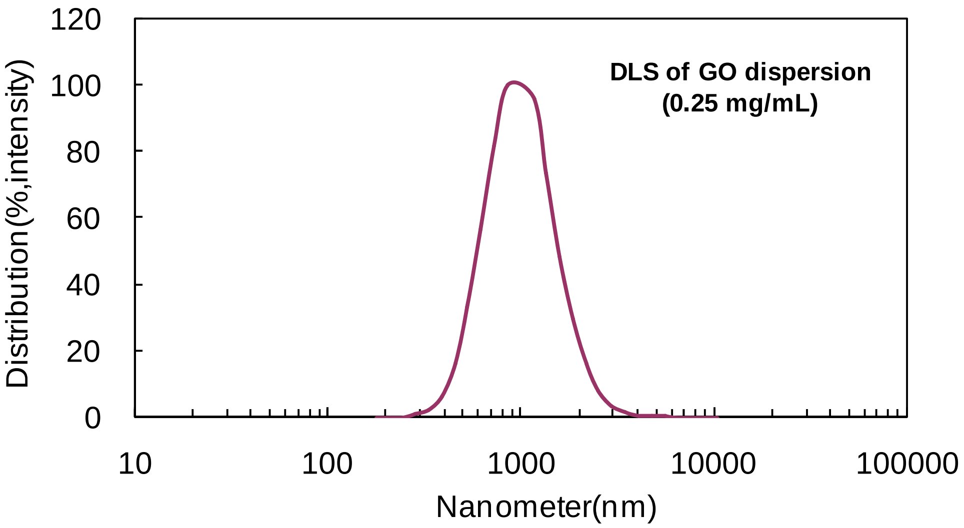
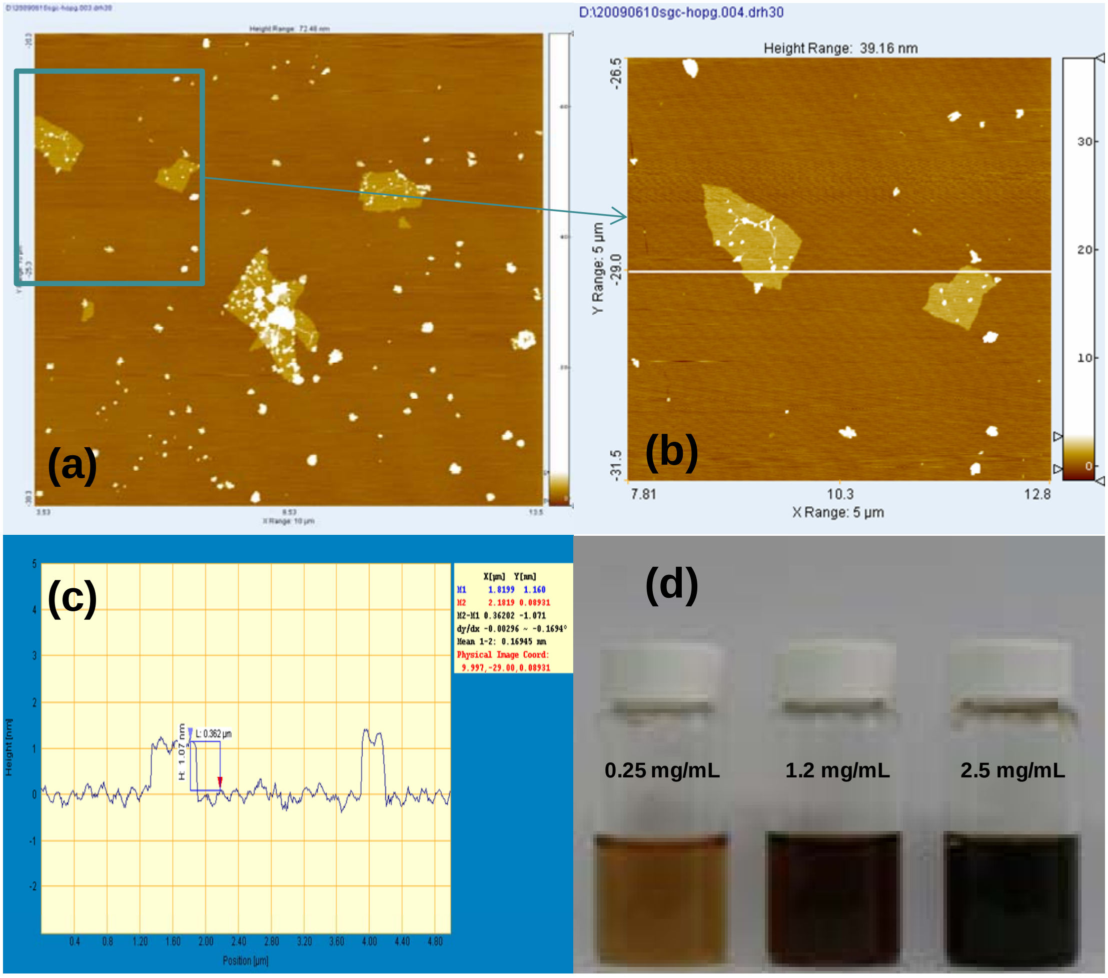


Figure S3. Hydrodynamic size distribution of GO by dynamic light scattering (DLS).

AFM images and pictures of GO dispersions in water



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       X[µm]  Y[nm]
M1     1.8199  1.160
M2     2.1819 0.08931
M2-M1 0.36202 -1.071
dy/dx -0.00296 ~ -0.1694°
Mean 1-2: 0.16945 nm
Physical Image Coord:
 9.997,-29.00,0.08931
```

Figure S4. **AFM images of GO sheets of a large area (a) and a selected area (b), AFM height scanned (c), pictures of GO dispersions in water at different GO concentrations (d). (*White particles in AFM images are Mn oxide species remained due to incomplete washing after graphite oxidation. For SG paper sample preparation, GO samples were further washed with DI water until Mn concentration in the supernatant was below 0.1 ppm by AAS.*)**

HRTEM pictures of SG composites

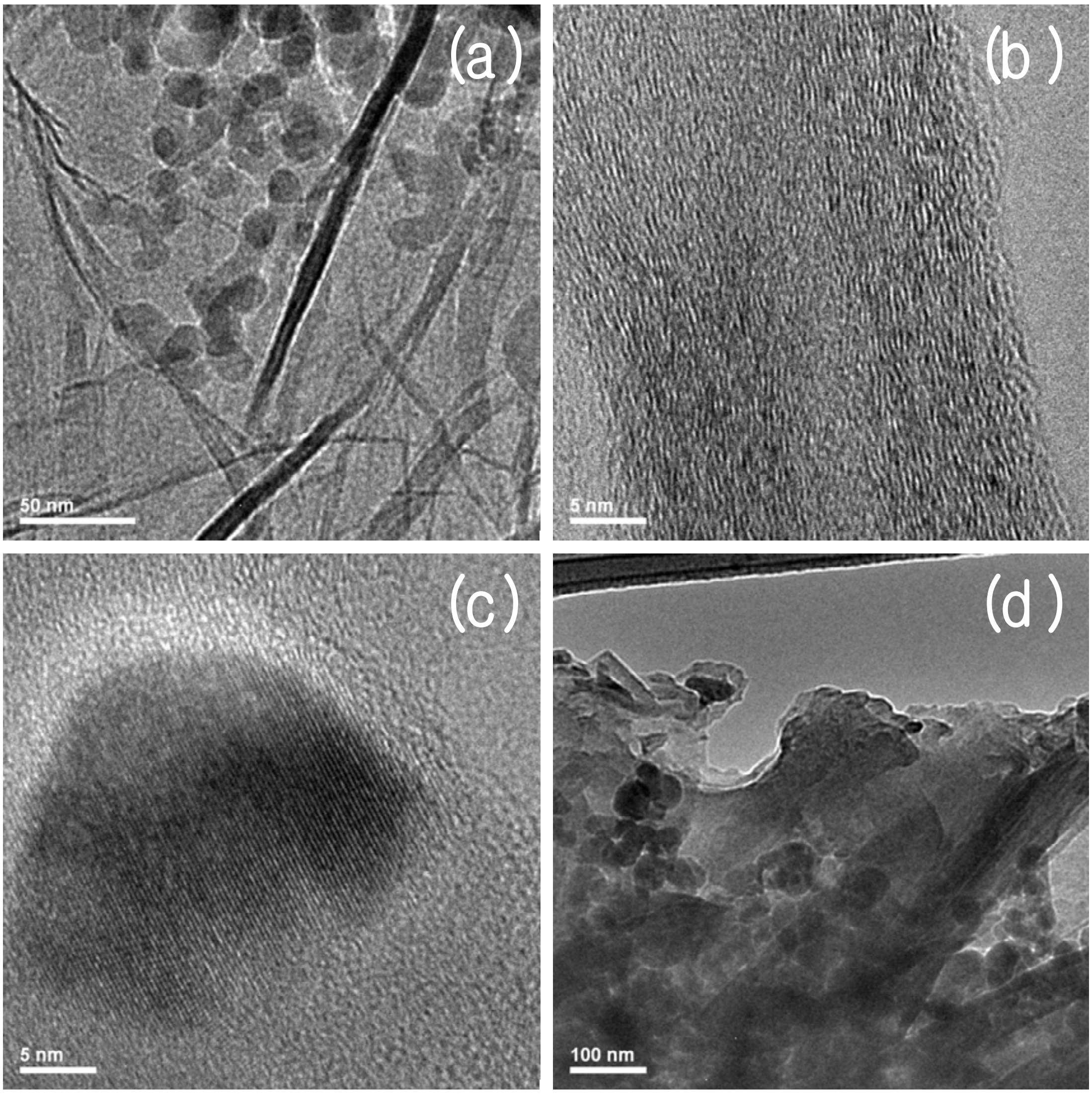

Figure S5. HRTEM pictures of SG composites: (a) Si nanoparticles of 20 – 25 nm in size are distributed in the graphene sheets, (a) and (b) the reassembled graphite phase composed of 5-13 layers of graphene is clearly observed, (c) a crystalline Si nanoparticle showing atomic lattice, (d) edge view of a crushed SG composite fragment showing layered structure of graphene and Si nanoparticles.

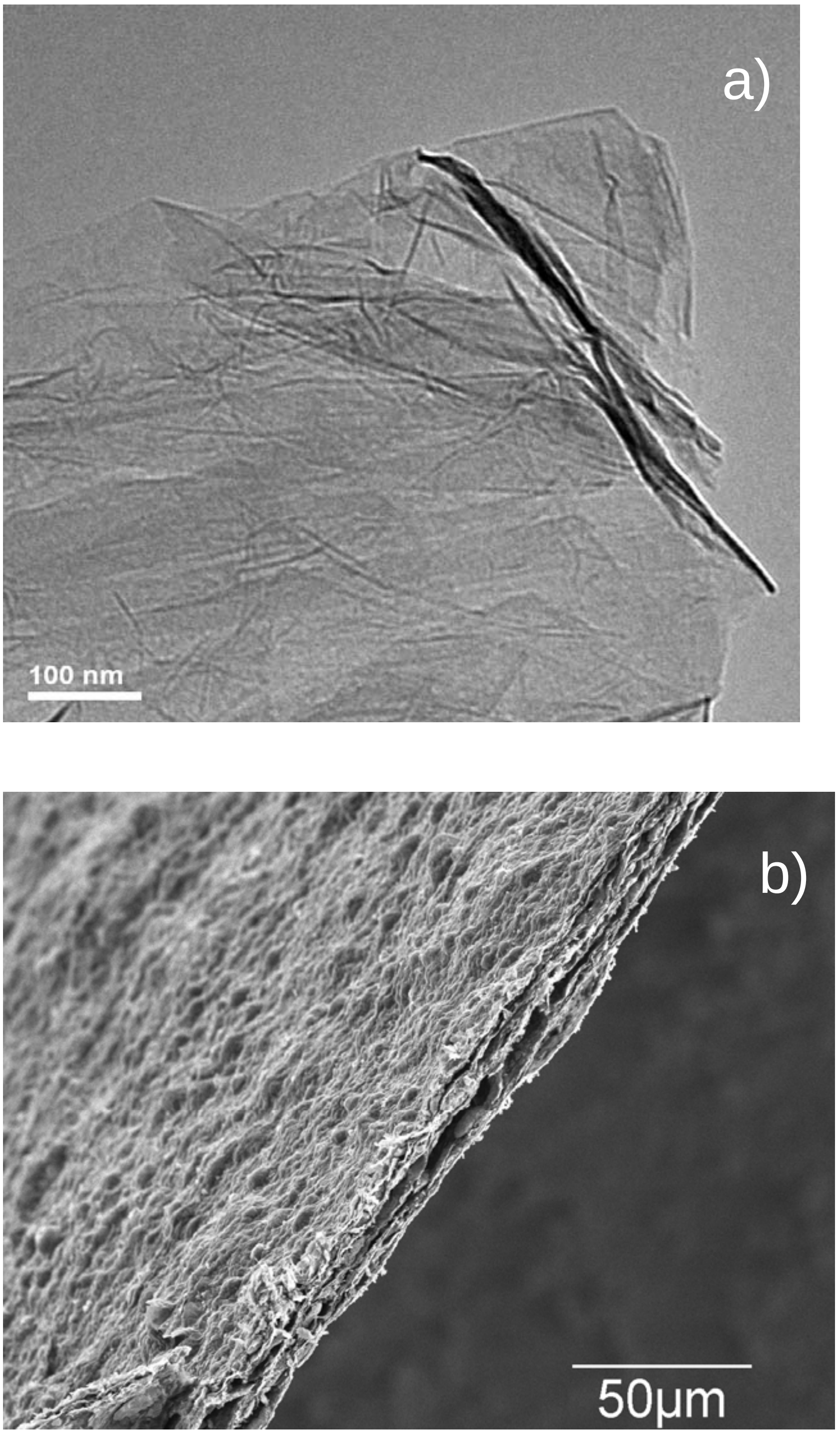

Figure S6: a) TEM image of graphene sheets. b) SEM image of reduced SG composite surface and thickness.

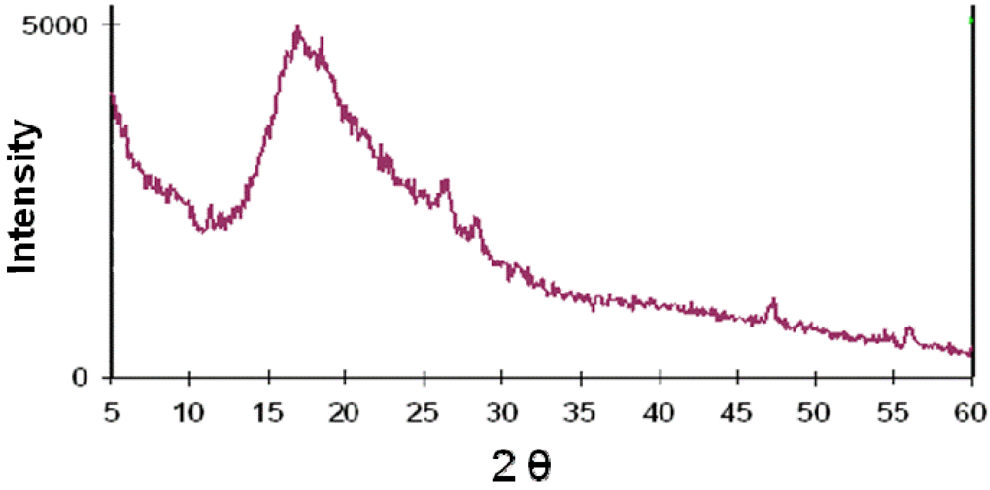

Figure S7. XRD pattern of SG sample 1.

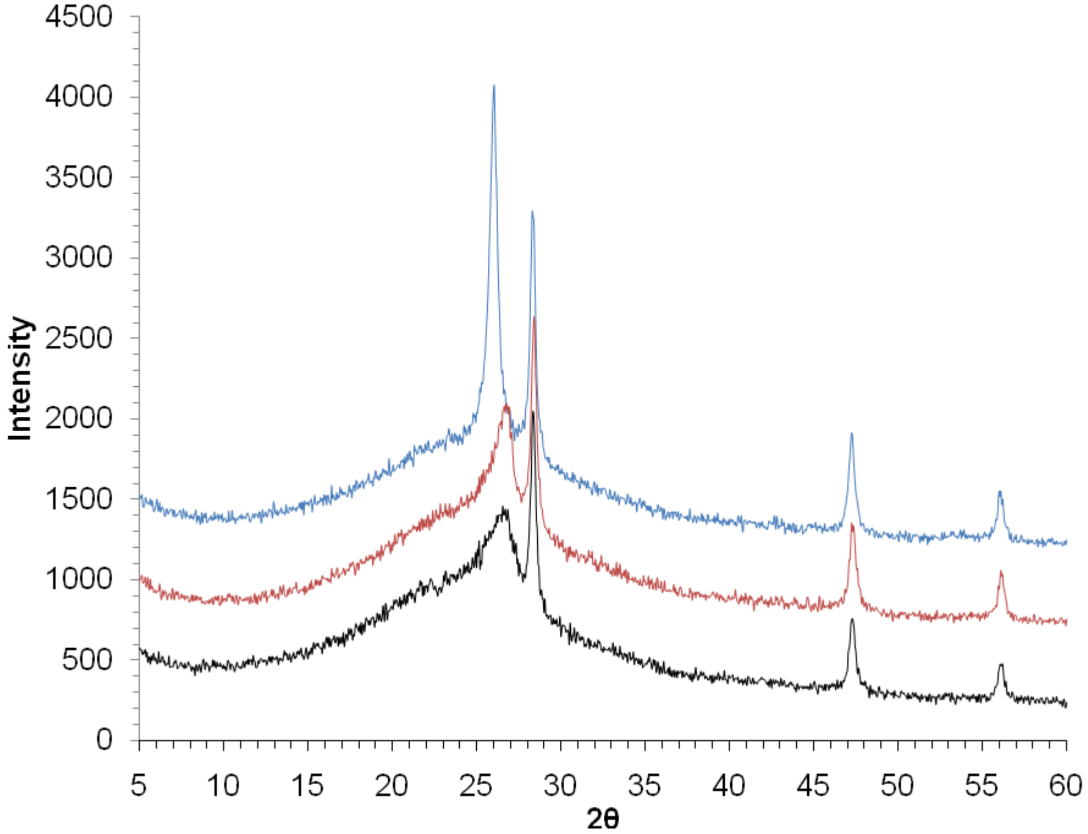

Figure S8: XRD spectra of silicon-graphene (SG) composites reduced at 550°C (blue), 700°C (red), and 850°C (black). The corresponding electrical conductivities are shown in Table S1 and Figure S9. The curves are displaced vertically for clarity. All samples contain ~60wt% silicon. Diffraction peaks are identified in the text of the article (caption for Figure 2). Electrochemical results in Figure 4.

Conductivity and Sheet Resistance Results

Table S1: Sheet resistance and conductivity values for SG samples after different thermal reduction. The unreduced SGO sample serves as reference. All SG samples contain ~60wt% silicon. The unreduced sample contains ~37.5wt% silicon, since the graphene oxide had not lost mass due to reduction.

	Reduction temperature			Unreduced SGO sample
	550°C	700°C	850°C	
Sheet resistance (Ω "per square")	153	107	60	2.9×10^5
Resistivity (Ω•cm)	0.076	0.053	0.030	146
Conductivity ($S \bullet cm^{-1}$)	13.1	18.7	33.1	0.0068

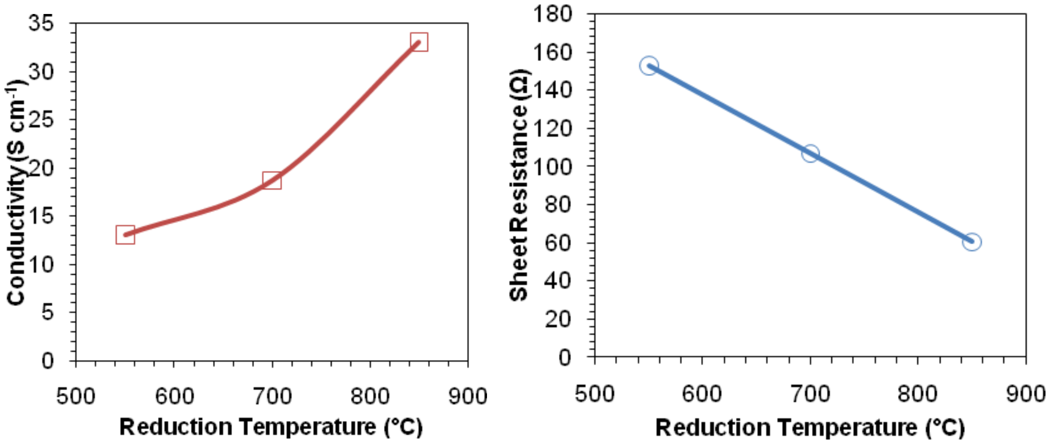

Figure S9: Conductivity and sheet resistance data derived from Table S1.

Electrochemical Results

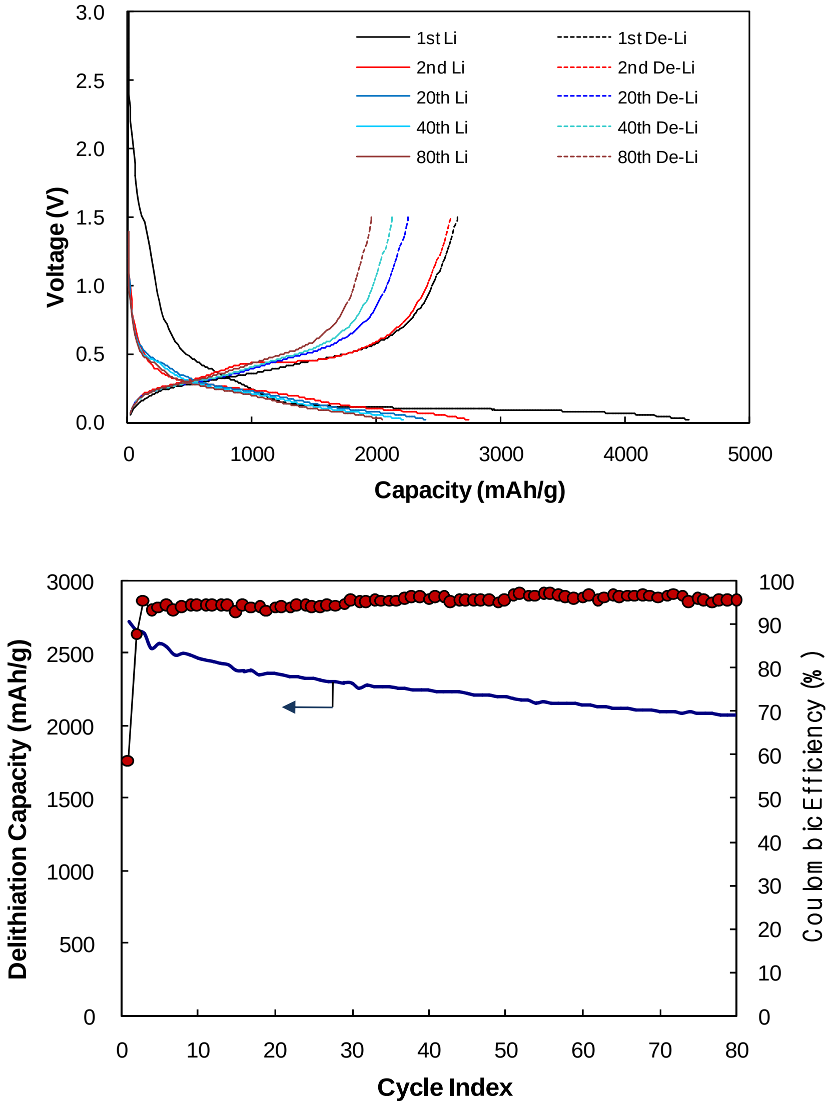

Figure S10. Charge-discharge curves (top) and Coulombic efficiency (bottom) of SG paper sample 2 of Fig. 5.

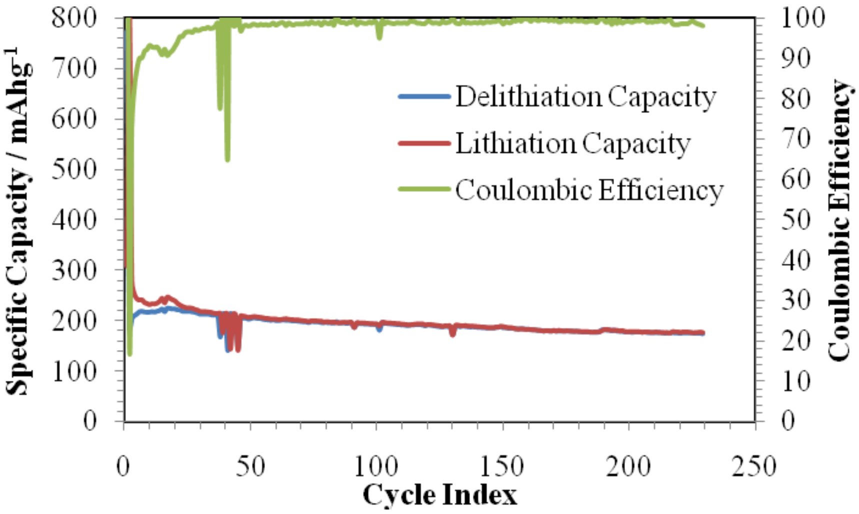

Figure S11. Graphene paper electrode (no silicon) cycled using modified CCCV mode. In the modified mode, the lower potential cut-off was 20 mV and the currrent was allowed to decrease from 1000 mA/g to 50 mA/g.

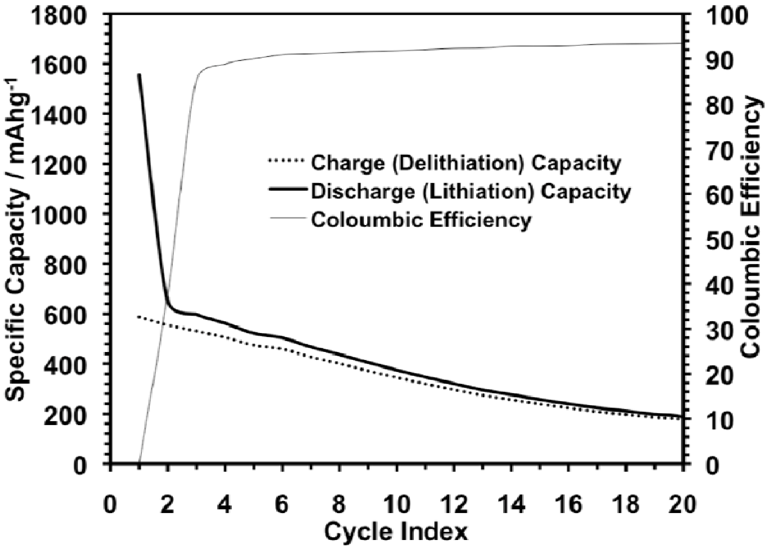

Figure S12. H-capped Si nanoparticles (~50wt%) and phenyl isocyanate-capped graphene oxide sheets (reduced with 1,1-dimethylhydrazine). Sample was dried using RotoVap, crushed and mixed with PVDF binder. Cycled at 100 mA/g between 0.02 – 2.0 V.

References

1. N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, 11, 771-778.

2. B. D. Cullity, *Elements of X-Ray Diffraction 2nd Ed.*, Addison-Wesley Publishing Company, Inc., 1978.