Electronic Supplementary Information for

PEO-assisted electrospun silicon/graphene composite as an anode material for lithium-ion batteries

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Experimental Section

Synthesis of graphite oxide: The graphite oxide was prepared from natural graphite flake (Alfa Aesar, 325 mesh) by using a modified Hummers method.[1]

Synthesis of Si nanoparticle-graphene-carbon nanodot composite (Si-G-C): 3.0 mL of graphite oxide aqueous suspension (10.0 mg mL^{-1}) was first dispersed in 13.5 mL of deionized (DI) water under sonication, followed by addition of 0.45 g of polyethylene oxide (PEO). The mixture was continuously stirred to form a homogeneous suspension. Then 0.2 g of silicon nanoparticles was added to the above suspension, followed by vigorous stirring. After 1 h sonication, a homogeneous yellow mixture was obtained. The resulting mixture was inhaled into a 10 mL syringe with a 17-gauge blunt tip needle. The flow rate of the mixture was 1 mL h^{-1} controlled by a syringe pump (KD Scientific, KDS-100, USA). A voltage of 20 kV (Spellman, SL50P, USA) was applied between the needle and the aluminium foil of approximately 15 cm×15 cm, which was grounded and employed to collect the electrospun nanofibers. The as-collected electrospun nanofibers was heated at 1000 ^{o}C in argon atmosphere for 1 h to reduce the graphene oxide and decompose the PEO. The heating rate for the reduction and decomposition were 10 ^{o}C min^{-1}. After being naturally cooled to room temperature, the black product was mixed with 10% HF water/ethanol (1/3 v/v) solution for 30 min to remove the SiO_x on the surface of Si nanoparticles to finally obtain Si-G-C.[2]

Synthesis of graphene-carbon nanodot composite (G-C): G-C was produced using the same procedure as for Si-G-C except that Si nanoparticles were not added.

Synthesis of graphene (G): 3.0 mL of graphite oxide aqueous suspension (10.0 mg mL^{-1}) was first dispersed in 13.5 mL of deionized (DI) water under sonication, followed by freeze-drying. The resulting brown powder was heated at 1000 ^{o}C in argon atmosphere for 1 h to achieve G.

Characterization and Electrochemical measurements: SEM measurements were conducted on a Hitachi S-4800 field emission scanning electron microscope operated at 15 kV. TEM and HRTEM characterizations were carried out on a Tecnai G2 F20 U-TWIN field emission transmission electron microscope operated at 200 kV. Thermogravimetric (TG) analysis was performed on TA-Q50 and NETZSCH STA 409 PC/PG instruments. XRD patterns were recorded on a Rigaku D/max2500 diffractometer using Cu Kα radiation. XPS spectra were determined on an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al Kα radiation. Nitrogen adsorption and desorption isotherms at 77.3 K were obtained with a Nova 2000e surface area-pore size analyzer. Electrochemical experiments were carried out using Swagelok-type cells. To make working electrodes, Si-G-C composite, Super-P carbon black, and sodium alginate binder (MP Biomedicals LLC, USA) with mass ratio of 65:20:15 were added to water, and mixed into homogeneous slurry with mortar and pestle. The resulting slurry was pasted onto pure Cu foil. The electrolyte was 1 M $LiPF_6$ in EC/DMC (1:1 v/v) (Novolyte Technologies) with 2% vinylene carbonate (VC, Aldrich) as the electrolyte additive. Glass fibers (GF/D) from Whatman were used as separators and pure lithium metal foil was used as the counter electrode. The Swagelok-type cells were assembled in an argon-filled glove box. Cyclic voltammetry was investigated with an Autolab PG302N electrochemical workstation at a scan rate of 0.1 mV s^{-1}. The charge and discharge measurements of the batteries were recorded on an Arbin BT2000 system in the fixed voltage window between 5 mV and 1 V vs. Li^{+}/Li under ambient temperature. Electrochemical impedance spectral measurements were determined on a PARSTAT 2273 advanced electrochemical system over the frequency range from 100 kHz to 10 mHz.

References

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. X. Zhou, Y.-X. Yin, L.-J. Wan and Y.-G. Guo, *Adv. Energy Mater.*, 2012, **2**, 1086.

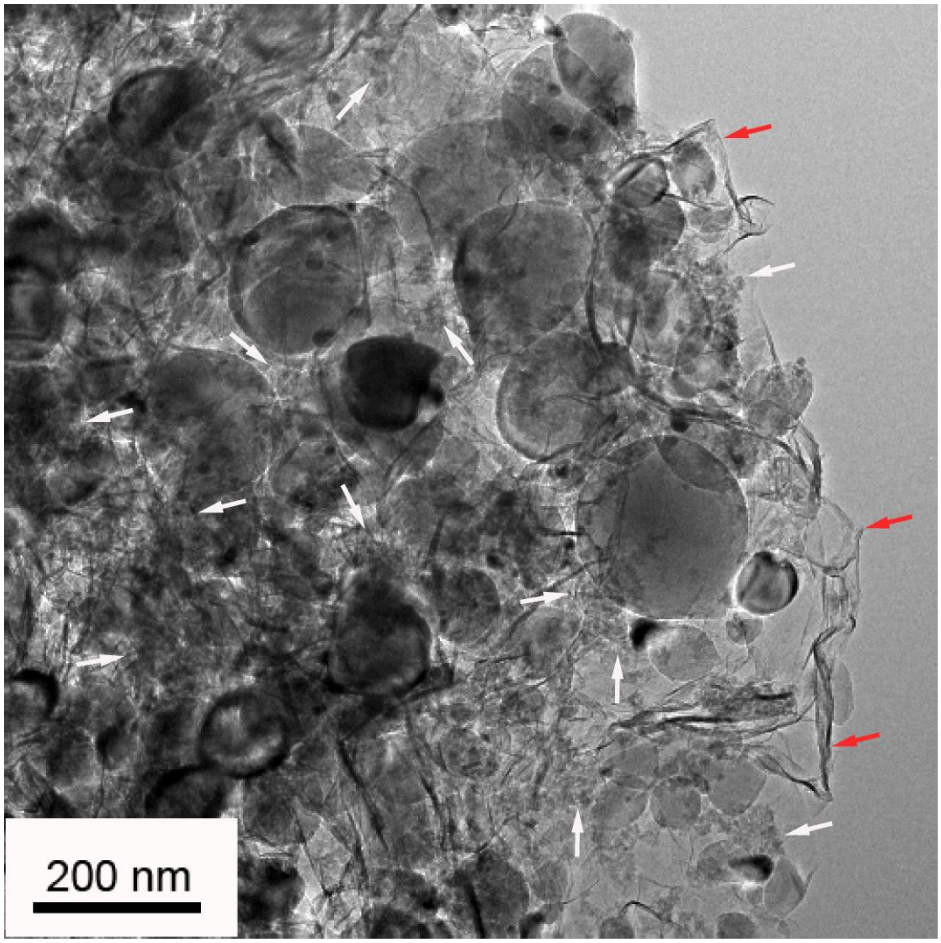


Figure S1. TEM image of Si-G-C. The graphene sheets and carbon nanodots are marked with red and white arrows, respectively.

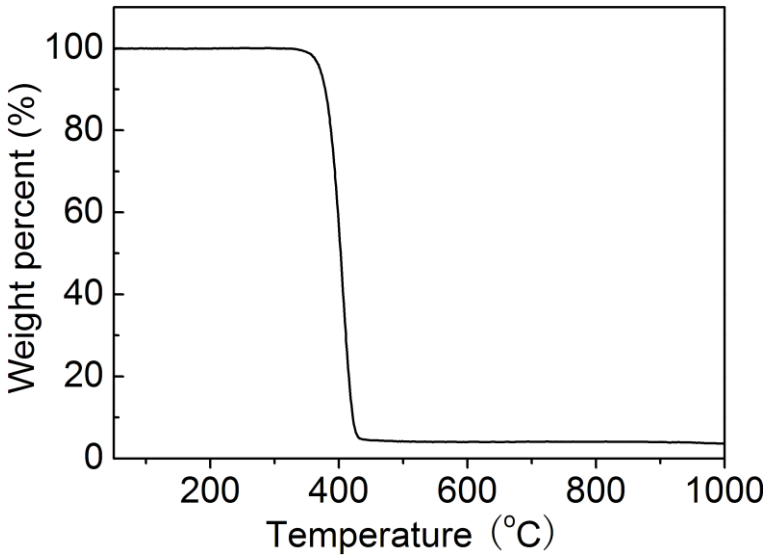


Figure S2. TG analysis curve of polyethylene oxide (PEO) under nitrogen atmosphere at a heating rate of 10 ^{o}C min^{-1}. The residual weight percent of PEO at 1000 ^{o}C is about 3.5 wt%.

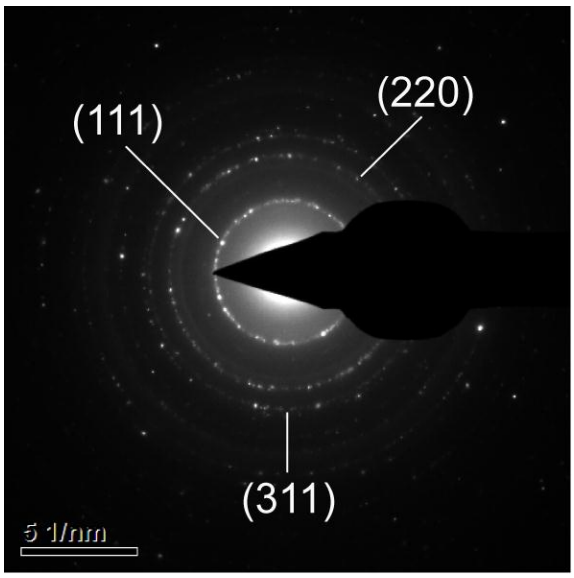


Figure S3. SAED pattern of Si-G-C.

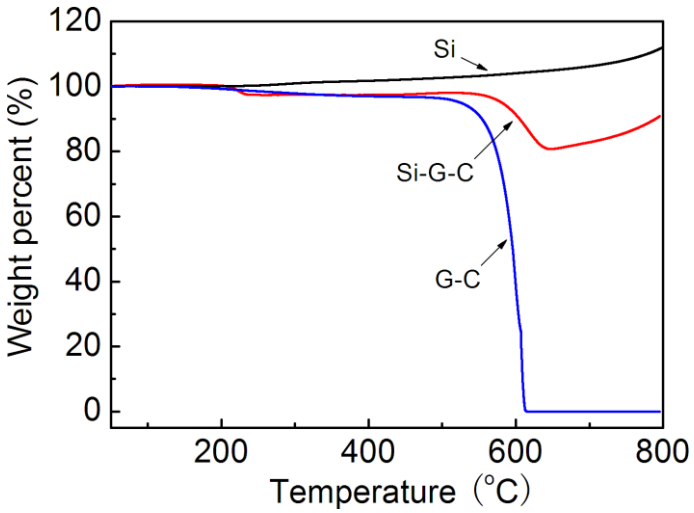


Figure S4. TG analysis curves of Si nanoparticles, G-C, and Si-G-C under air atmosphere at a heating rate of 10 ^{o}C min^{-1}. We could calculate the contents of Si in Si-G-C composite based on the equation $W_{Si} * X_{Si} + W_{G-C} * (1-X_{Si}) = W_{Si-G-C}$, where W_{Si}, W_{G-C}, and W_{Si-G-C} are residual weight percent of Si, G-C, and Si-G-C at 700 ^{o}C, and X_{Si} is the content of Si in Si-G-C. The contents of Si in the composite is approximately 78.0 wt%.

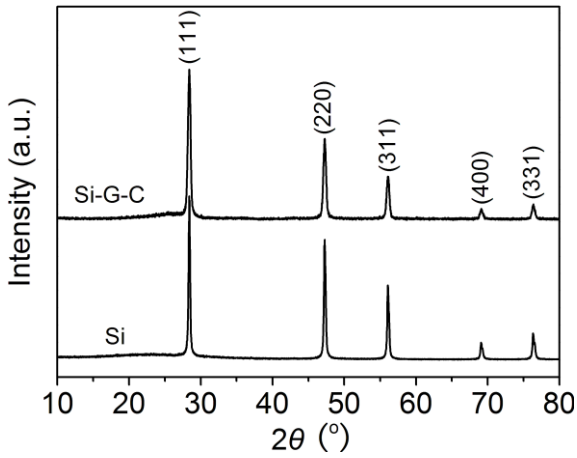


Figure S5. a) XRD patterns of Si nanoparticles (Si) and Si-G-C.

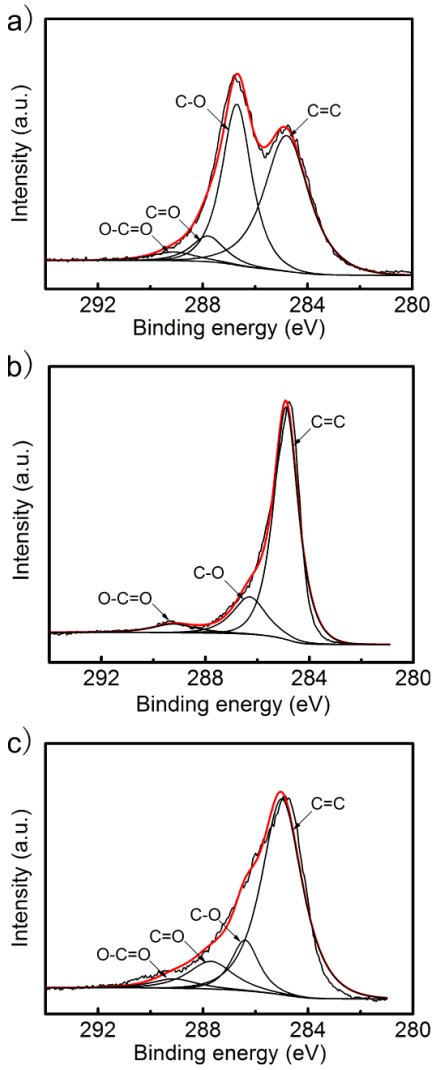
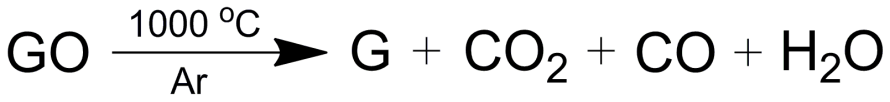


Figure S6. XPS C 1s spectra of a) GO, b) G, and b) Si-G-C. the main peaks centered at 284.9 eV corresponding to extensively delocalized sp^2-hybridized carbon atoms, and the independent peaks with binding energies of 286.4, 287.8, and 289.1 eV can be attributed to carbon atoms in C-O, C=O, and O-C=O, respectively.



Scheme S1. Reaction mechanism for reduction of graphene oxide by heat treatment at 1000 °C in argon atmosphere.

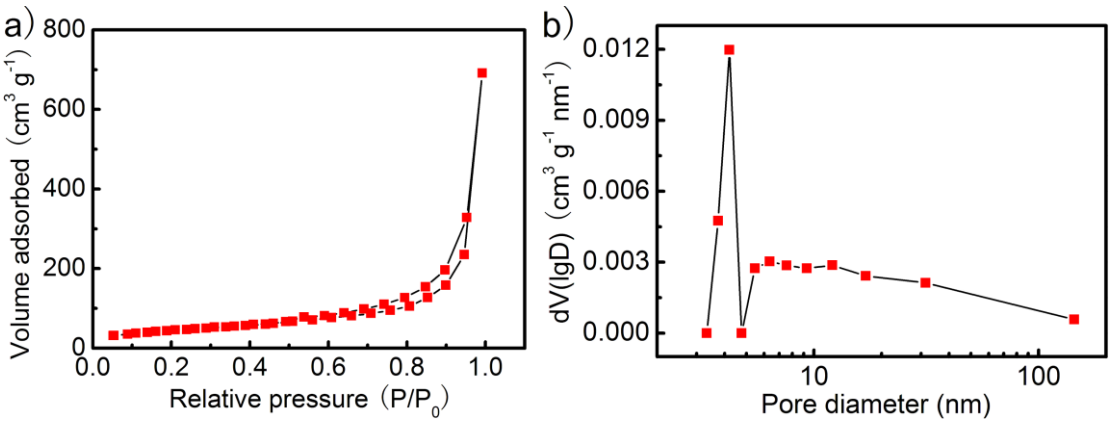


Figure S7. a) Nitrogen adsorption/desorption isotherms of Si-G-C, (b) pore-size distribution plot calculated by the BJH formula with the desorption isotherm.

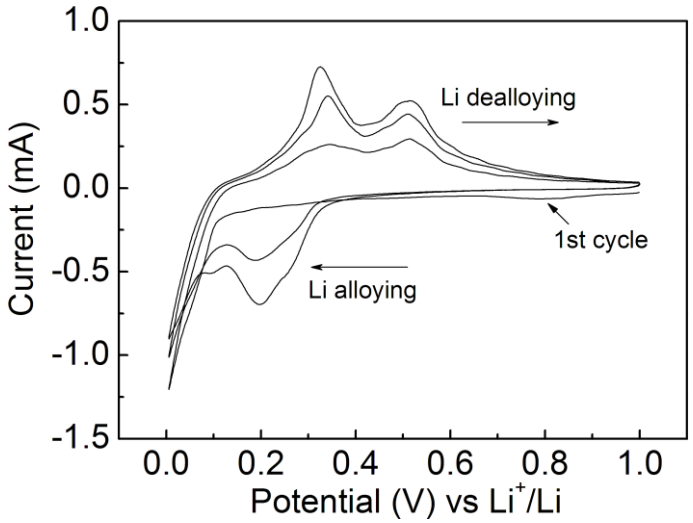


Figure S8. CV curves of the initial three cycles of Si-G-C.

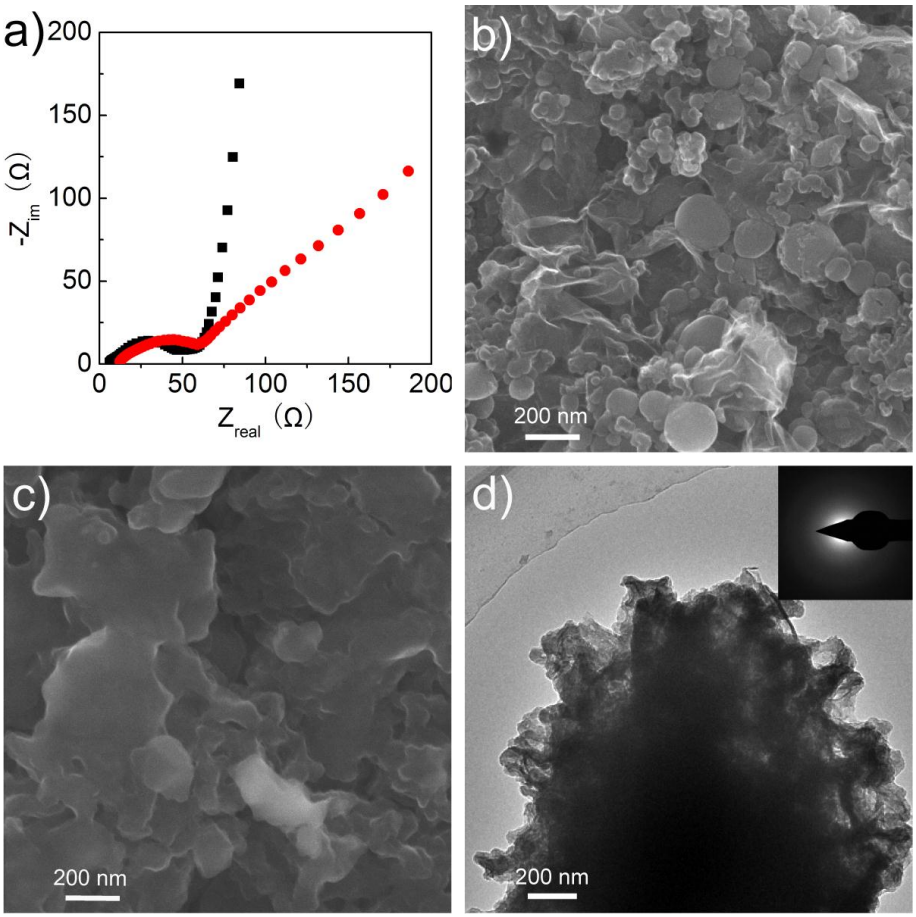


Figure S9. a) Nyquist plots of the Si-G-C electrode after 3 cycles (black aquares) and 200 cycles (red circles); b), c) SEM images of the Si-G-C electrode before and after 200 cycles; d) TEM image of the Si-G-C electrode after 200 cycles, the inset shows the corresponding SAED pattern.