Electronic Supplementary Information for

Facile synthesis of silicon nanoparticles inserted in graphene sheets as improved anode materials for lithium-ion batteries

Xiaosi Zhou, Ya-Xia Yin, Li-Jun Wan and Yu-Guo Guo*

Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, P. R. China E-mail: ygguo@iccas.ac.cn

Experimental Section

Preparation of graphite oxide (GO): The graphite oxide was synthesized from natural graphite flake by a modified Hummers method.¹ In the experiment, concentrated H₂SO₄ (15 mL) was mixed with K₂S₂O₈ (3.0 g) and P₂O₅ (3.0 g) at 90 °C in a 150 mL beaker, and then the mixture was cooled to 80 °C. 3.6 g of natural graphite flake was slowly added to the above solution with stirring. The mixture was kept at 80 °C for 4.5 h. Afterwards, the mixture was diluted with 600 mL double distilled water and left to stand for 12 h. Then the mixture was filtered and washed with excess double distilled water using a 0.2 micron Nylon Millipore filter until the pH of the filtrate was neutral. The solid product was dried in air for one day. Then, the pretreated graphite flake was added to cold (3 °C) concentrated H₂SO₄ (140 mL). While keeping the reaction temperature less than 10 °C, KMnO₄ (18.0 g) was added slowly until completely dissolved. This mixture was stirred at 35 °C for 2 h. 300 mL double distilled water was added to the mixture slowly and the reaction temperature was kept less than 50 °C using an ice bath. Then the mixture was stirred for 2 h followed by adding additional 800 mL double distilled water. Successively, 20 mL 30% H₂O₂ was added to the mixture, resulting in a brilliant yellow color along with bubbling. The mixture was deposited overnight and then the clear supernatant was decanted. The remaining mixture was centrifugated and washed with 1500 mL of 10% HCl solution and 2000 mL double distilled water. The resulting graphite oxide was then diluted into a 400 mL brown dispersion, which was subjected to dialysis to completely remove residual salts and acids. Finally, 1.0% w/w dispersion was obtained by dialysis for three weeks, and the dispersion was used to prepare all the following dispersions.

Fabrication of silicon/thermally reduced graphene (Si/TRG) composites: In a typical synthesis of Si/TRG composites, 200 mg silicon nanoparticles (<300 nm, Top Vendor Science & Technology Co., Ltd.) were dispersed in 200 mL water by sonication in a water bath (KQ3200DE, 40 kHz). After the as-prepared GO aqueous dispersion (10.0 mg mL⁻¹) was diluted to 1.0 mg mL⁻¹ with double distilled water, the

exfoliation of GO aqueous dispersion was achieved by sonicating the dispersion. The obtained brown dispersion was centrifugated at 4000 rpm for 30 min to remove any unexfoliated GO. Then, 50 mL of graphene oxide aqueous dispersion was mixed with 200 mL of silicon aqueous dispersion in a flask and sonicated for several minutes. The resulting homogeneous aqueous dispersion was lyophilized, followed by reduction in a crucible in a tube furnace at 700 °C for 2 h under H₂ (5 vol%)/Ar (95 vol%) atmosphere to achieve Si/TRG composites (heating rate 2 °C min⁻¹). It has been reported that the possible existence of SiO_x on the surface of Si nanoparticles could limit the lithium electroactivity of Si.² Therefore, both Si/TRG composites and silicon particles were treated with 20 % HF water/ethanol solution to etch away the layer of SiO_x (ca. 2-3 nm, Fig. S1) on the surface of Si nanoparticles, and were followed by drying under vacuum at 70 °C before mixing with Super-P carbon black and PVDF.

Structural and electrochemical characterization: XRD measurements were conducted on a Philips PW 3710 diffractometer using CuKa radiation. XPS analysis was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlKa radiation. SEM was carried out with a JEOL 6701 scanning electron microscope operated at 10 keV. TEM and HRTEM were performed using a JEOL 1011 and Tecnai T20 transmission electron microscope operated at 100 and 200 kV, respectively. EDX analysis was conducted on an EDAX system attached to a Tecnai T20 microscope. TG analysis was carried out with a TA Q50 instrument. 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 prepare working electrodes, Si/TRG composites or Si nanoparticles after HF treatment, Super-P carbon black, and poly(vinylidene fluoride) (PVDF) with mass ratio of 70:20:10 were mixed into a homogeneous slurry with mortar and pestle, and then the obtained slurry was pasted onto pure Cu foil (99.9 %, Goodfellow). The electrolyte was 1 M LiPF₆ in EC/DMC (1:1 v/v) plus 2 wt% vinylene carbonate (VC) provided by Tianjing Jinniu Power Sources Material Co. Ltd. The VC additive has been confirmed to improve the cycling performance of the $Si@SiO_x/C$ nanocomposites electrode.² Glass fibers (GF/D) from Whatman were utilized as separators and pure lithium metal foil was used as counter electrode. The Swagelok-type cells were assembled in an argon-filled glove box. The discharge and charge measurements of the batteries were performed on an Arbin BT2000 system in the fixed voltage window between 0.05 and 1 V at room temperature. The specific capacity of the Si/TRG composites was calculated using the total mass of silicon and graphene. Electrochemical impedance spectral measurements were recorded on a PARSTAT 2273 advanced electrochemical system over the frequency range from 100 kHz to 100 mHz. Cyclic voltammetry was carried out on a Voltalab 80 electrochemical workstation at a scan rate of 0.1 mV s⁻¹.

$$Si + x Li^+ + x e^- \longrightarrow Li_xSi$$

Scheme S1. Alloying/dealloying reaction of Si with Li.



Figure S1. HRTEM image of a silicon nanoparticle before HF etching.



Figure S2. TEM images of (a) silicon nanoparticles after HF treatment and (b) a graphene sheet.



Figure S3. (a) XPS survey scan of Si/TRG composites. XPS C 1s spectra of (b) GO, (c) TRG, and (d) Si/TRG composites. The Si/C ratio obtained by XPS is 0.12, which is lower than the result of TGA because the existence of adventitious carbon in the XPS chamber and the detection depth of XPS is usually less than 10 nm, i.e. the carbon layer on the sample surface mainly contributes to the XPS signals. Furthermore, in Figure S3b-d the main peaks center at 284.8 eV corresponding to extensively delocalized sp²-hybridized carbon atoms, and the independent peaks with binding energies of 286.5, 287.8, 289.1, and 291.0 eV are attributed to carbon atoms in C-O, C=O, O-C=O, and the shakeup of C=C, respectively. The oxygen functionalities of the graphite oxide are severely decreased during the thermal reduction process, which could be observed by comparing the XPS C1s spectra of GO, TRG, and Si/TRG composites.



Figure S4. EDX spectrum of the Si/TRG composites. The copper signals are from the Cu grids.



Figure S5. Low-magnification TEM image of Si/TRG composites.



Figure S6. (a) Bright-field TEM image of Si/TRG composites. (b) HRTEM image taken from the site marked with red cycle in (a) exhibiting multi-layer structure of TRG.



Figure S7. TGA curves of TRG, Si nanoparticles, and Si/TRG composites under air atmosphere at a heating rate of 10 °C min⁻¹. The residual weight percents of TRG, Si nanoparticles, and Si/TRG composites at 700 °C, 800 °C, and 850 °C are collected to calculate the mass ratios of TRG to Si in Si/TRG composites. The weight of Si nanoparticles increased during the heat treatment in air due to the formation of SiO_x, and the weight of TRG decreased during the heat treatment due to the decomposition of graphene. Thus, we could calculate the content of Si and TRG in the Si/TRG composites basing on the equation $W_{TRG} * X_{TRG} + W_{Si} * (1-X_{TRG}) = W_{Si/TRG}$, where W_{TRG} , W_{Si} , and W_{TRG} is residual weight percent of TRG, Si, and Si/TRG at different temperature and X_{TRG} is the content of TRG in the Si/TRG composites. The results are summarized in the following table. Which reveals that the average content of Si and TRG in the Si/TRG composites is 82.1 wt% and 17.9 wt%, respectively.

	TRG (wt %)	Si (wt %)	Si/TRG (wt %)	TRG:Si (mass ratio)
700 °C	9.19	106.2	87.16	19.6:80.4
800 °C	9.13	112.1	94.17	17.4:82.6
850 °C	8.87	120.0	101.4	16.7:83.3



Figure S8. (a) Nitrogen adsorption and desorption isotherms of Si/TRG composites, (b) pore-size distribution plot calculated by the BJH formula with the desorption isotherm.



Figure S9. Nyquist plots of Si/TRG composite electrode (empty circles) and silicon particles electrode (solid squares), (a) before cycling, (b) and (c) after 100 cycles. As shown in Figure S9a, both Nyquist plots contain one depressed semicircle at high frequencies and a straight line at low frequencies. The semicircle should be related to properties of the SEI layer because the resistance of electrode and electrolyte are negligible. It demonstrates that the diameter of the semicircle of the Si/TRG composite (14.2 Ω) is much smaller than that of Si (31.0 Ω). Figure S9b and S9c exhibit the diameter of the semicircle of Si (101.3 Ω). These results indicate that a thicker and/or denser SEI layer is formed on the surface of Si nanoparticles than that of Si/TRG composites.



Figure S10. TEM images of Si/TRG composites after 100 cycles under a current density of 200 mA g^{-1} , showing the integrity of the structure.

References:

- 1. W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc. 1958, 80, 1339.
- 2. Y. -S. Hu, R. Demir-Cakan, M. -M. Titirici, J. -O. Müller, R. Schlögl, M. Antonietti, J. Maier, *Angew. Chem. Int. Ed.* 2008, 47, 1645.