

Electronic Supplementary Information for

A Swelling-Suppressed Si/SiO<sub>x</sub> Nanosphere Lithium  
Storage Material Fabricated by Graphene Envelopment

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## Methods

### *Material preparation.*

To prepare the SiO<sub>x</sub> nanospheres, 10 mL of triethoxysilane ((C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>SiH, Aldrich, 99.8%) was slowly dropped into a 0.1 M HCl solution (500 mL) under continuous stirring at 800 rpm. The solution was filtered and washed with deionized water repeatedly. The precipitates were collected and dried in a convection oven at 80 °C to eliminate residual moisture. After fine grinding, the obtained powder was heated at 1000 °C under a 4% H<sub>2</sub>/Ar atmosphere with a flow rate of 0.5 L min<sup>-1</sup>. The heating rate and time were fixed at 20 °C min<sup>-1</sup> and 1 h, respectively.

For the graphene-enveloped SiO<sub>x</sub>, graphene oxide (GO) was prepared by a modified Hummers' Method and purified according to methods that have been reported previously.<sup>1,2</sup> 1 mg mL<sup>-1</sup> of GO and 1 mg mL<sup>-1</sup> of the as-recovered SiO<sub>x</sub> nanospheres were mixed in water and nebulized by a commercial mini spray dryer (CMSD, B290, Buchi). The CMSD had a two-fluid nozzle in which the precursor solution and dispersion air were introduced into the inner and outer tubes, respectively.<sup>3</sup> Precursor droplets were formed from a continuous flow of the precursor solution at the nozzle tip. For the CMSD, the solution flow rate and the temperature were fixed at 6 L min<sup>-1</sup> and 200 °C, respectively. The product was collected by a cyclone and a bag filter, connected in series at the exhaust, and then further annealed at 900 °C under an Ar atmosphere for 30 min.

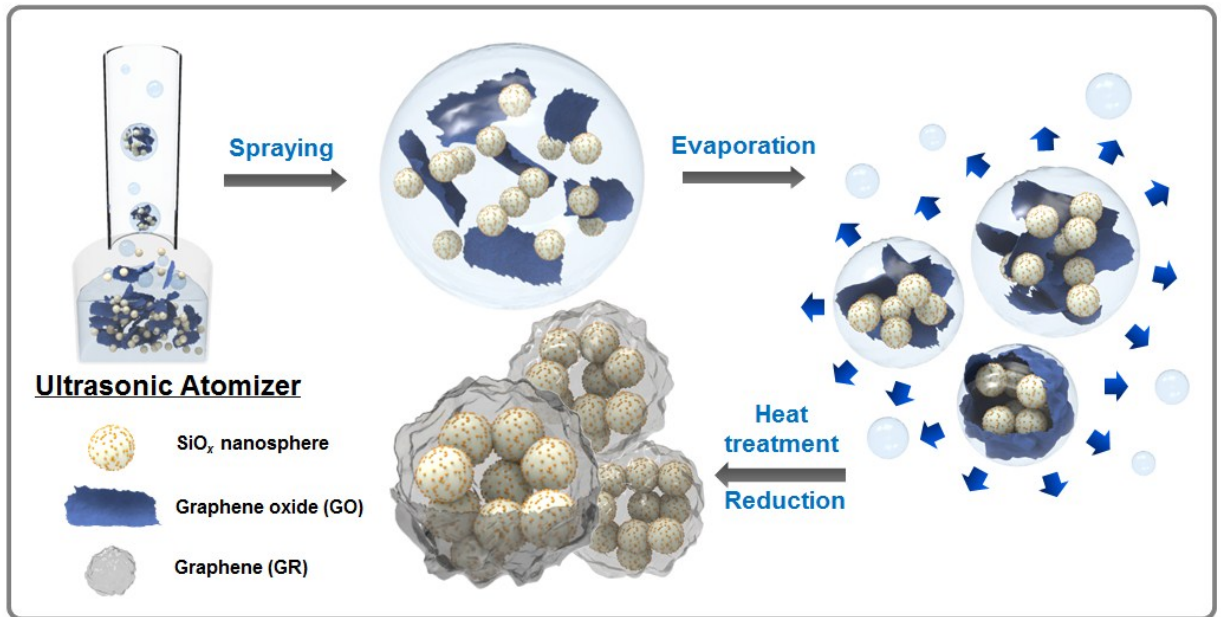
### *Material characterization.*

The morphology and microstructure of the as-prepared graphene-enveloped SiO<sub>x</sub> nanospheres were characterized using field-emission scanning electronic microscopy (FESEM; JEOL JSM-

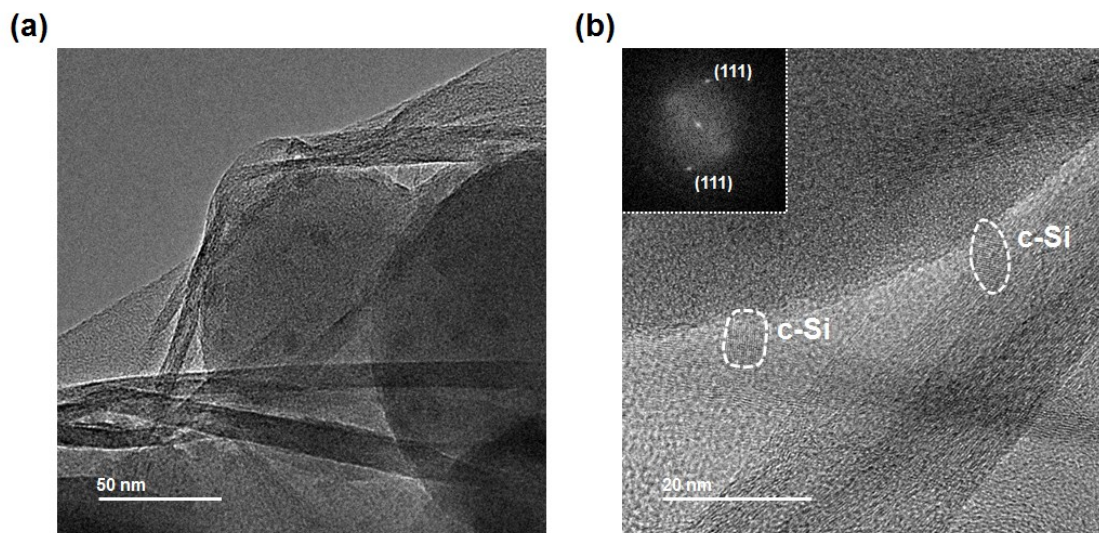
7000F), high-resolution transmission electron microscopy (HRTEM; JEOL 2100F), and scanning transmission electron microscopy (STEM; JEOL 2100F). The microstructure was further identified by conducting X-ray diffraction (XRD) with an X-ray diffractometer (RTP 300 RC, Rigaku) and a Raman spectrometer (Dimension-P1 Raman, Lamda Solutions Inc.) with an Ar-ion continuous-wave laser at a wavelength of 514 nm. The amount of C in the graphene-enveloped SiO<sub>x</sub> nanospheres was confirmed by thermogravimetric analysis (TGA; DTG-60H, Shimadzu).

### ***Electrochemical characterization.***

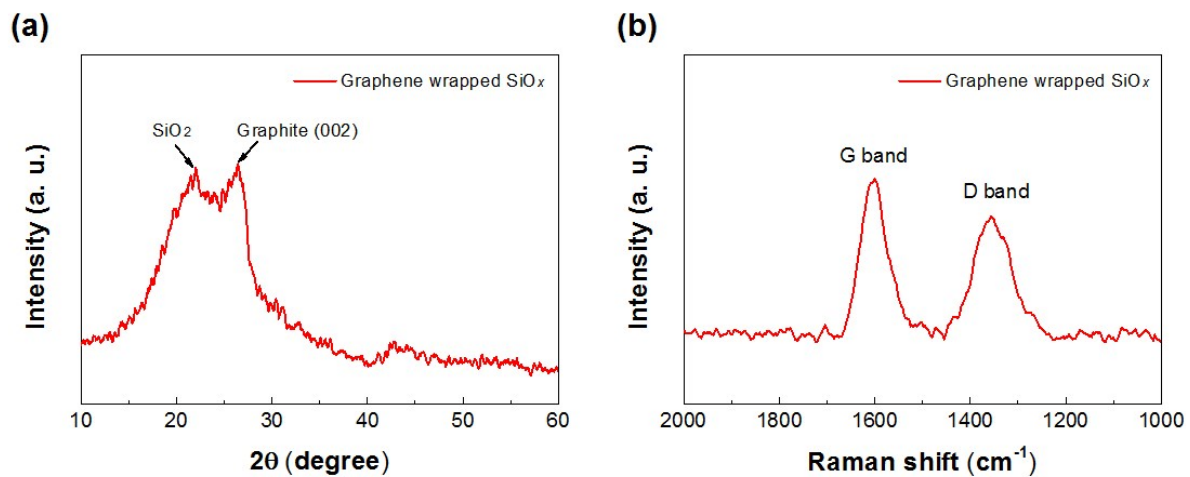
The electrodes were prepared by coating slurries consisting of the graphene-enveloped SiO<sub>x</sub> nanospheres (70 wt%, as the active materials), a conducting agent (Super-P, 15 wt%), and a polyamide-imide binder (PAI, 15 wt%) dissolved in n-methyl-2-pyrrolidone (NMP, Sigma Aldrich) onto Cu foil with a mass loading of 1.0 mg cm<sup>-2</sup>. The electrodes were dried at 200 °C for 2 h in a vacuum oven and were pressed under a pressure of 200 kg cm<sup>-2</sup>. The electrochemical performance was examined by assembling CR2032 coin-type half cells in an Ar-filled glove box. These cells were assembled with a polyethylene (PE) membrane as the separator and Li metal as the counter and reference electrodes. 1 M LiPF<sub>6</sub> was dissolved in a mixed solvent of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (1:2 v/v, Panax Etec Co. Ltd.) with 2.0 wt% fluoroethylene carbonate (FEC); this was employed as the electrolyte. The cells were tested in constant current (CC) mode in a voltage window of 0.01–2.0 V vs. Li/Li<sup>+</sup> at room temperature.



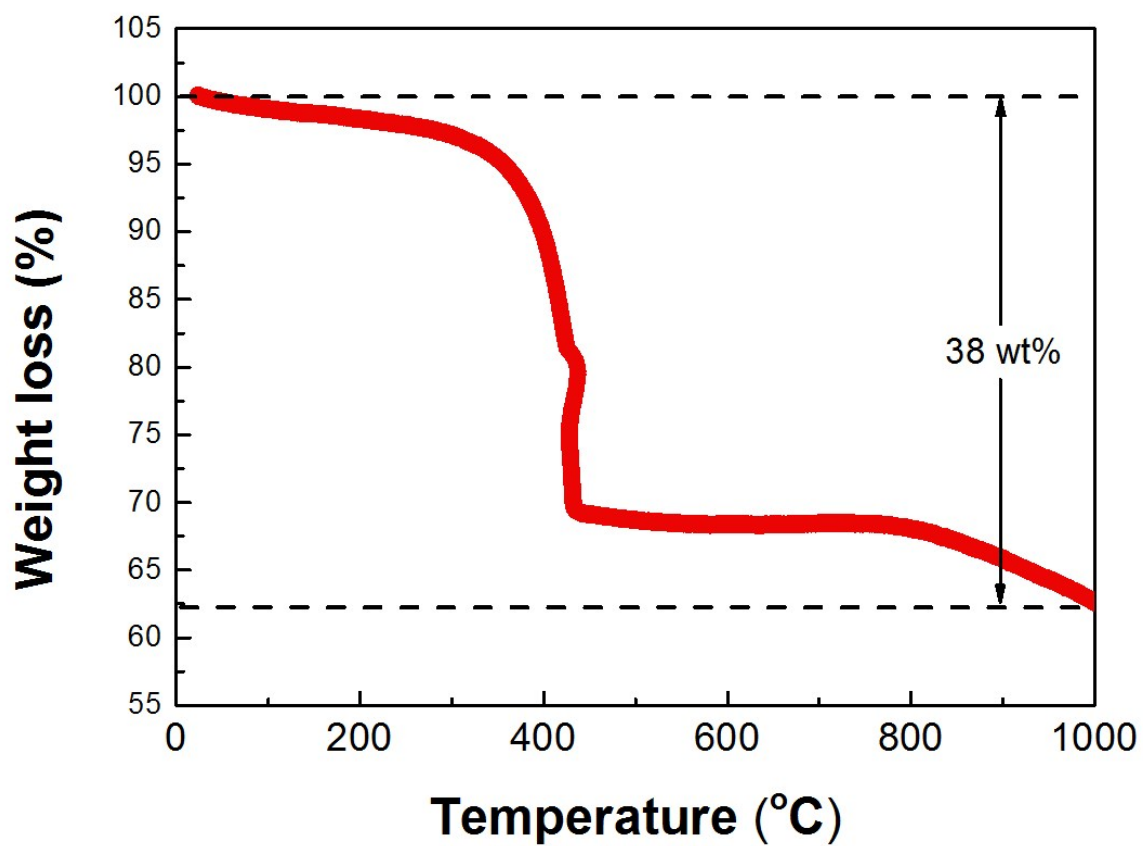
**Fig. S1** Schematic illustrations of graphene-enveloped  $\text{SiO}_x$  nanospheres fabricated by a one-step, capillary force-driven aerosol process.



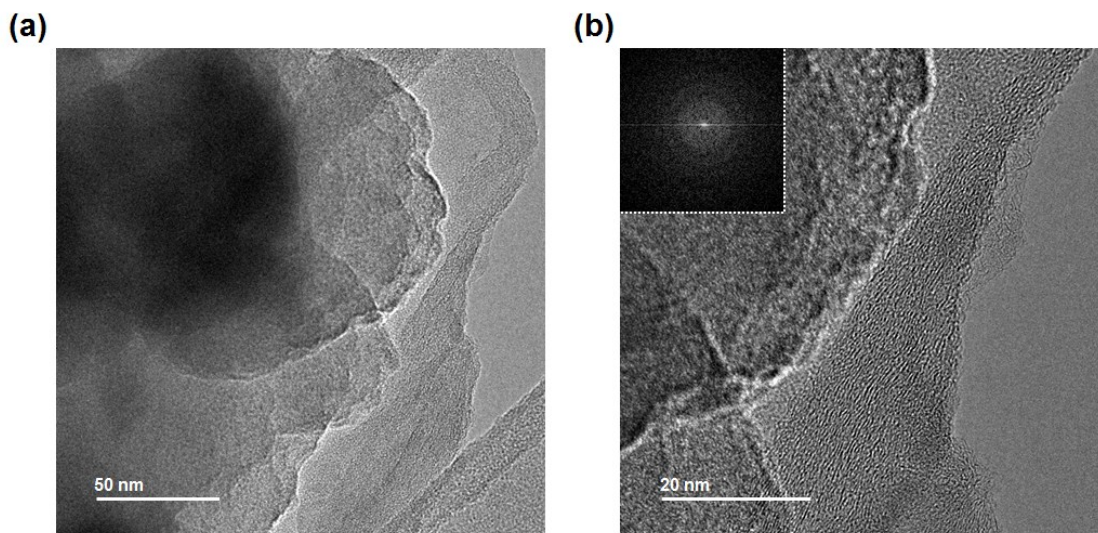
**Fig. S2** HRTEM images of graphene-enveloped  $\text{SiO}_x$  nanosphere (pristine, before cycling): (a) low-magnification image and (b) high-magnification image with the corresponding selected area diffraction pattern (SADP, inset).



**Fig. S3** (a) XRD pattern and (b) Raman spectrum collected from graphene-enveloped  $\text{SiO}_x$  nanospheres.

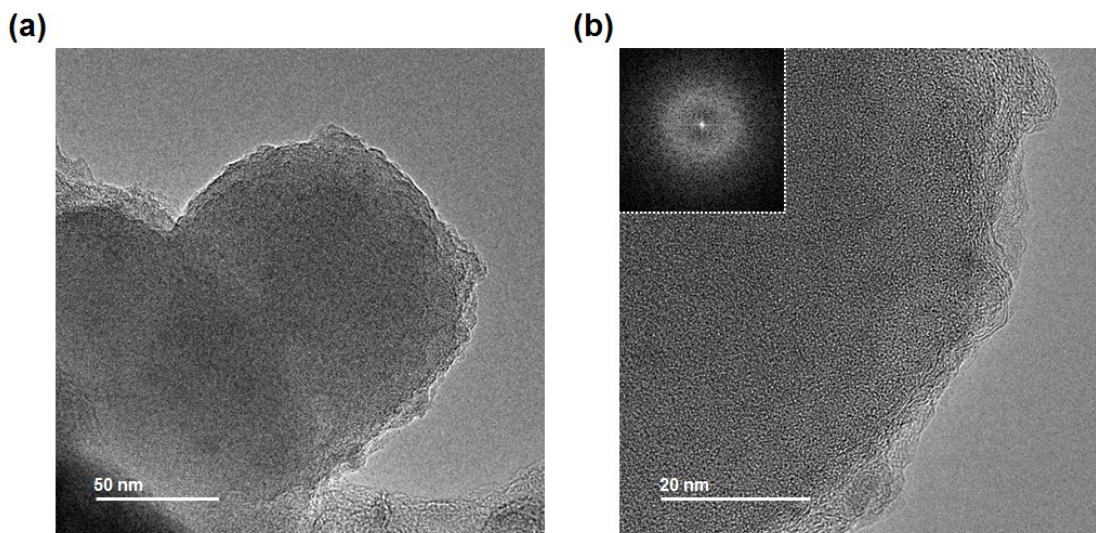


**Fig. S4** TGA curve of graphene-enveloped SiO<sub>x</sub> nanospheres.



**Fig. S5** HRTEM images of graphene-enveloped  $\text{SiO}_x$  nanosphere after the first charge to 10 mV vs.  $\text{Li/Li}^+$ : (a) low-magnification image and (b) high-magnification image with the corresponding selected area diffraction pattern (SADP, inset).





**Fig. S6** HRTEM images of graphene-enveloped  $\text{SiO}_x$  nanosphere after the first discharge to 2.0 V vs.  $\text{Li/Li}^+$ : (a) low-magnification image and (b) high-magnification image with the corresponding selected area diffraction pattern (SADP, inset).

## Reference

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