Electronic Supplementary Information for

A Novel Bath Lily-Like Graphene Sheets-Wrapped Nano-Si Composite as a High Performance Anode Material for Li-ion Batteries †

Yu-Shi He,[a] Pengfei Gao,[a] Jun Chen,[b] Xiaowei Yang,[a] Xiao-zhen Liao,[a] Jun Yang*[a] and Zi-Feng Ma*[a]

[a] *Institute of Electrochemical and Energy Technology, Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China. Fax: +86-21-5474 7667; Tel: +86-21-5474 7667; E-mail: yangj723@sjtu.edu.cn, zfma@sjtu.edu.cn*

[b] *Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, Australian Institute of Innovative Materials, Innovation Campus, University of Wollongong, Wollongong, NSW 2522, Australia.*

Experimental details

Preparation of GS-Si composite:

Nano-size silicon (50~200 nm) was supported by Nanjing Emperor Nano Material Co., Ltd. (Nanjing, China). Graphite oxide was synthesized from natural graphite powder (Grade 230, Asbury Carbons) using the modified Hummers method.[1] The obtained graphite oxide was exfoliated into deionized water by ultrasonication to form graphene oxide (GO) suspension. Thereafter, a certain amount of nano-silicon powder was added into the GO suspension. The mixture was sonicated for 45 min and then spray-dried at 200 ^{o}C to form a GO-Si composite using a B-290 mini spray drier (Buchi, Swiss). The obtained composite was load into a quartz tube in a flow of 20% H_2 in Ar at 700 ^{o}C for 3 h to form the graphene sheets-wrapped nano-Si (GS-Si) composite. Pure GS samples were also prepared by the same procedure and then mixed with pure Si powder to obtain GS/Si mixture for comparison.

Structural and morphological characterization:

XRD measurements were carried out using a Rigaku D/MAX-2200/PC X-ray diffractometer at 40kV and 20mA, with a Cu Kα radiation source. Raman spectroscopy was used to identify the surface characteristics of the samples using a BRUKER optic SENTERRA (R-200L) Raman spectrometer using a laser with a wavelength of 633 nm at room temperature. Thermogravimetric analysis (TGA) was performed using a STA 449F3 analyzer (NETZSCH Co., Germany) to evaluate the residual level of GS-Si composite after calcination.The morphology and microstructure of the samples were monitored using a FEI Nova SEM 230 ultra-high resolution Field Emission Scanning Electron Microscopy (FESEM) equipped with energy dispersive X-ray spectroscopy (EDS, INCA X-Max 80, Oxford Instruments) and a JEM-2100F Transmission Election Microscopy (TEM) (JEOL Ltd., Japan). EDS was obtained at four different locations for each sample. The above obtained oxygen content is a mean value.

Electrochemical characterization:

Electrode preparation:

The electrochemical performances of GS-Si composite and GS/Si mixture were evaluated under the same conditions using coin-type half cells. The working electrodes were prepared by pasting a mixture of active material, Super P conductive carbon black (40 nm, Timical) and styrene butadiene rubber/sodium carboxymethyl cellulose (SBR/SCMC, 1:1 by weight) as binder at a weight ratio of 75:15:10. After coating the mixture onto pure Cu foil, the electrodes were dried, cut to Φ14 mm sheets, pressed at 3 MPa, and finally dried at 80 °C in vacuum for 4 h. The active materials loaded on the electrode were about 1.5 mg cm^{-2}.

Cell assembly and electrochemical tests:

CR2016 coin cells were assembled in an argon-filled glove box with lithium metal as counter electrode and UP3025 separator (provided by UBE Industries, Ltd., Japan). The electrolyte contained 1 M $LiPF_6$ in dimethyl carbonate (DMC) and ethylene carbonate (EC) mixed solvent of 1:1 (LP30 from EM Industries, Inc.). Charge–discharge cycles of the half-cells were evaluated between 0.01 and 1.2 V vs Li^+/Li at room temperature using LAND CT2001A model battery test system (Wuhan Jinnuo Electronics, Ltd.) under constant current condition. The charge-discharge capacities were calculated according to the weight of GS-Si (or GS/Si) material in the electrode. For AC electrochemical impedance spectra (EIS) tests, the cells with GS-Si and GS/Si electrodes were cycled twice at 200 mA g^{-1} and then brought to a standstill for five hours. The open circuit voltage (OCV) vs Li^+/Li of both cells stabilized at about 0.9 V, indicating the same lithiation level. Finally, the EIS of the cells were measured by a Solartron FRA 1250 frequency responses analyzer combined with a Solartron SI 1287 Electrochemical Interface with an amplitude of 10 mV over a frequency range from 100 kHz to 0.1 Hz.

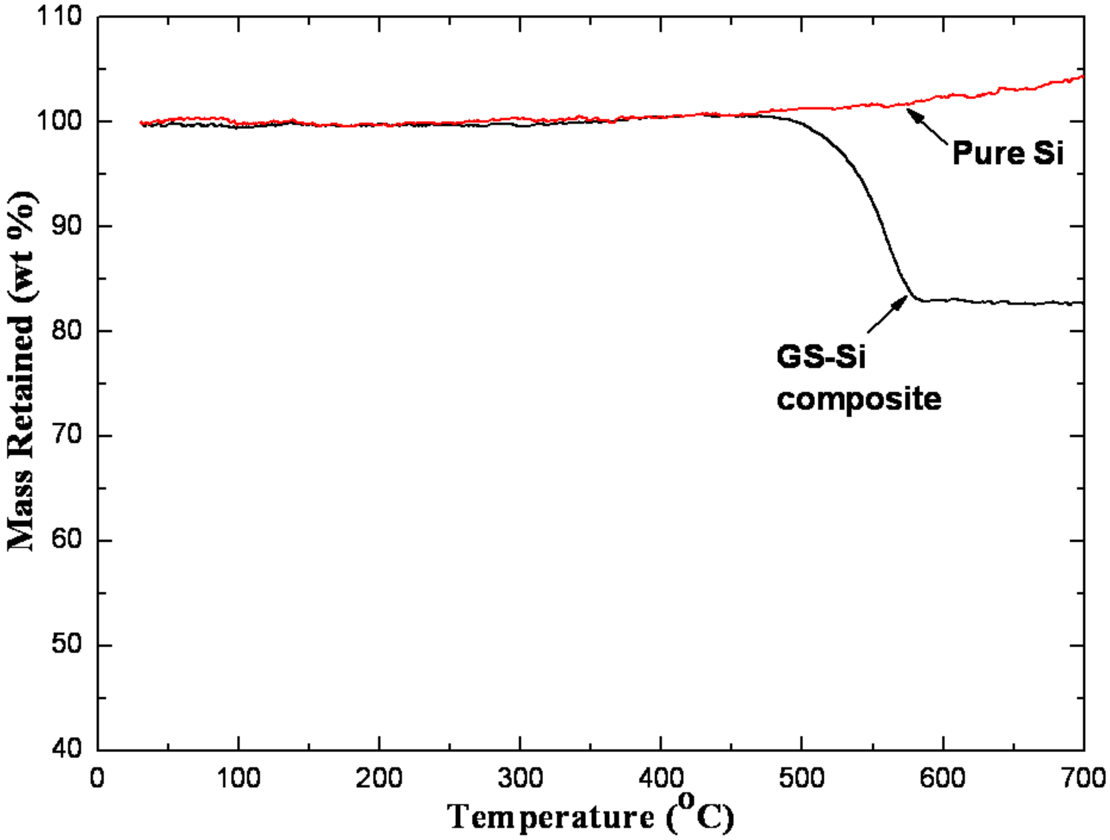

Fig. S1 TGA curves of pure Si and GS-Si composite.

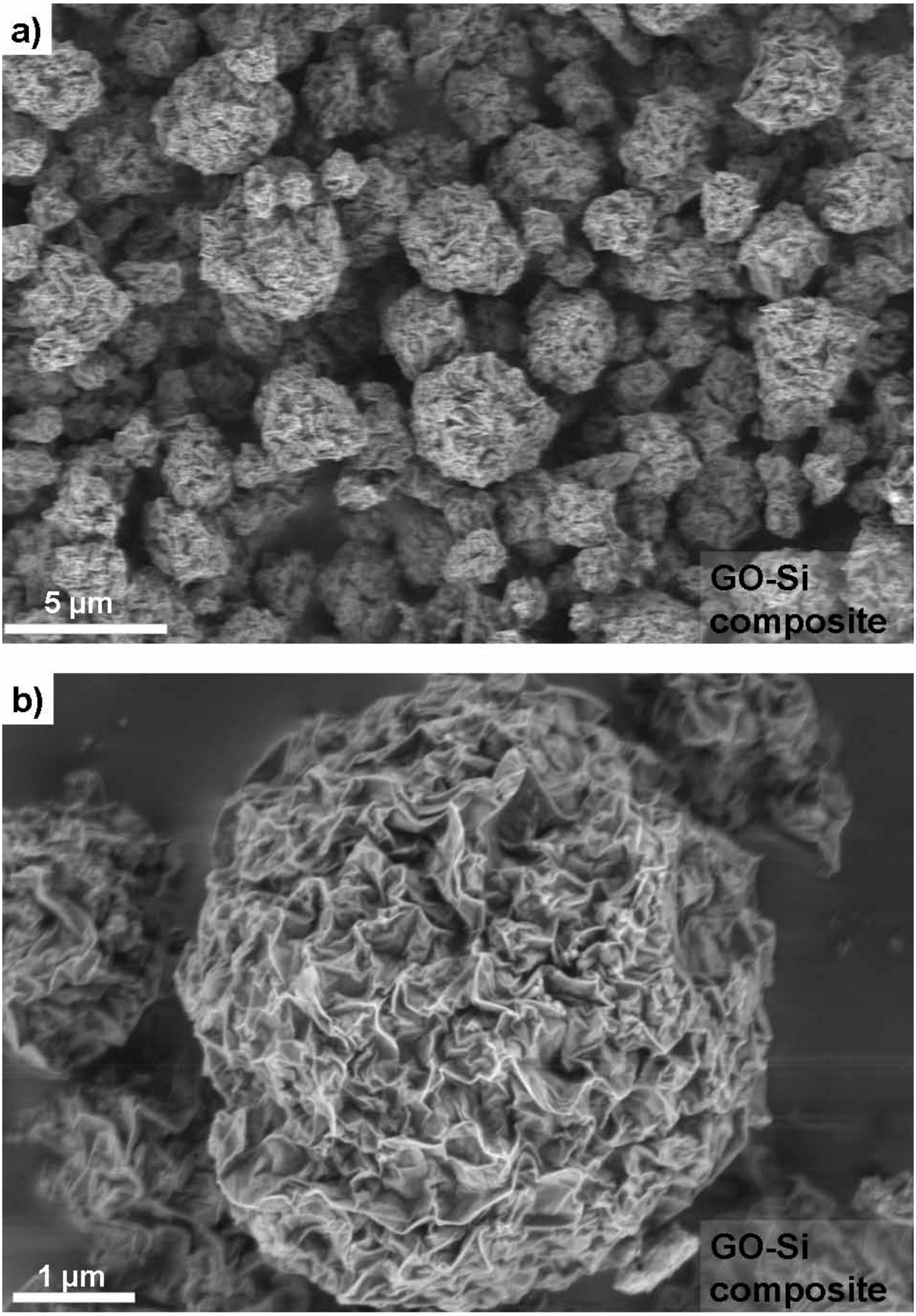

Fig. S2 SEM images of GO-Si composite.

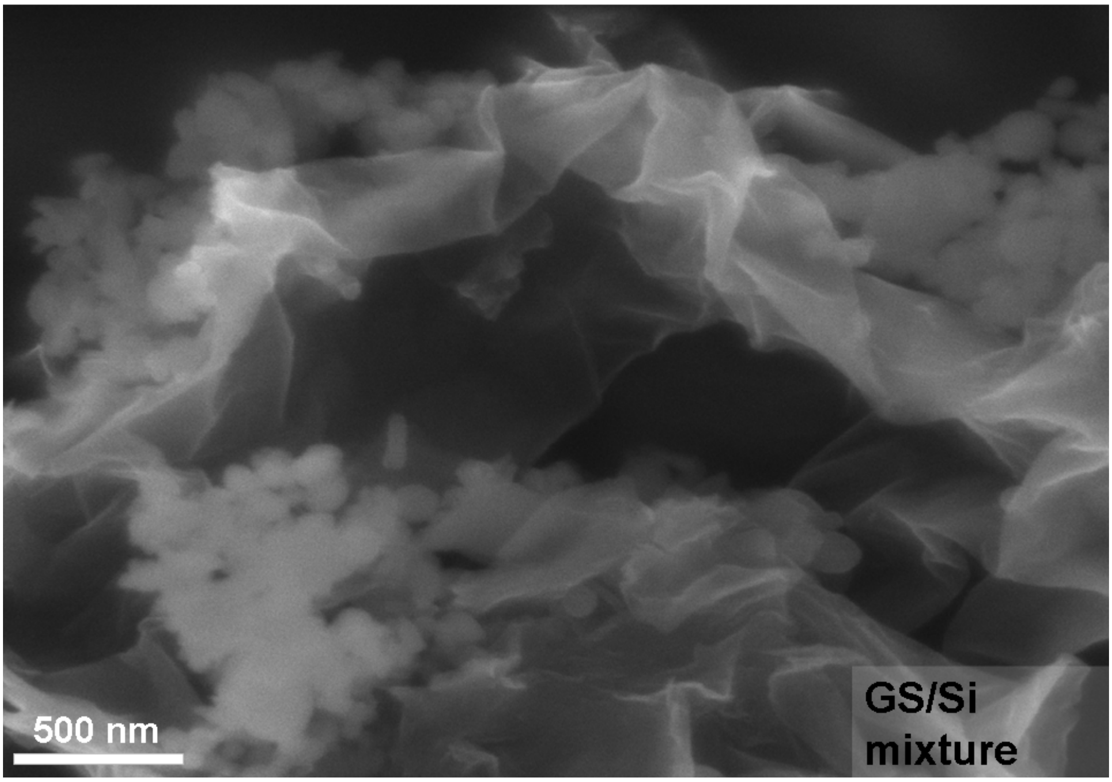

Fig. S3 SEM images of GO/Si mixture.

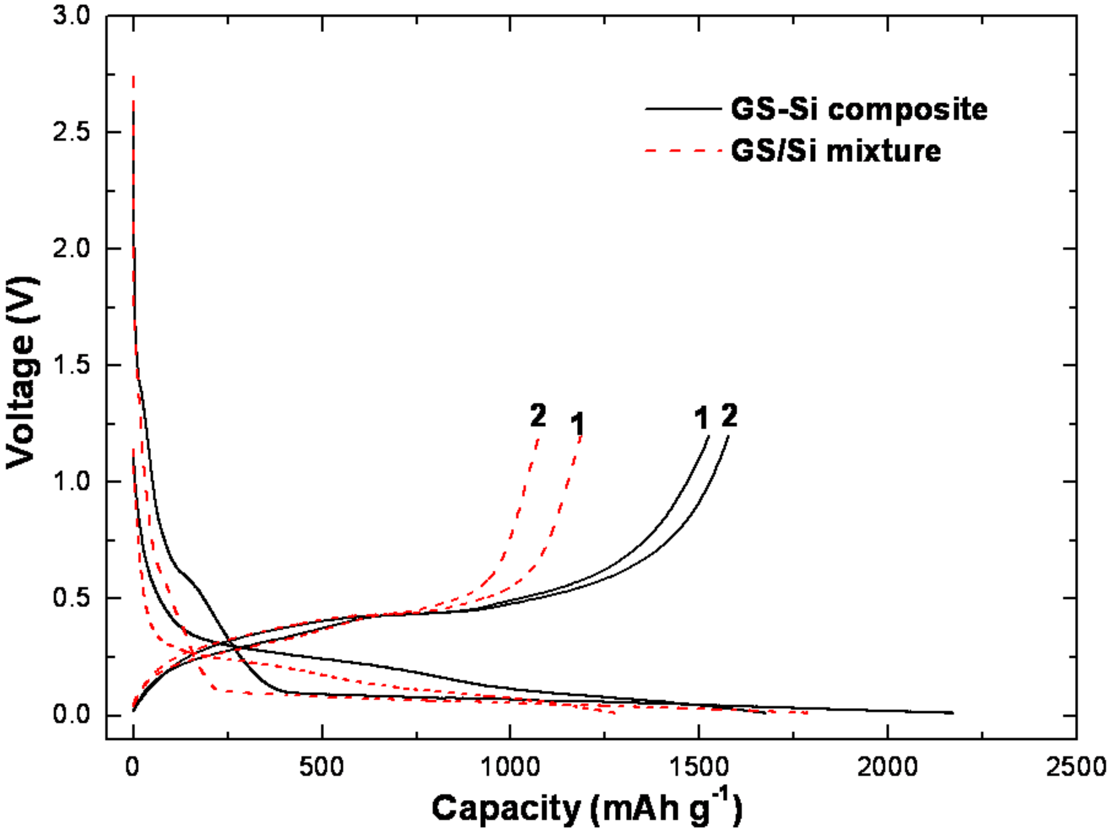

Fig. S4 The initial two charge-discharge profiles of GS-Si composite and GS/Si mixture at a current density of 100 mA g^{-1}.

References

1. D. Li, M. B. Muller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101.