

ELECTRONIC SUPPLEMENTARY INFORMATION

A one-pot microwave-assisted non-aqueous sol-gel approach to metal oxide/graphene nanocomposites for Li-ion batteries

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Experimental Section

Chemicals

Tin(IV) chloride(99.995%), iron(III) acetylacetonate ($\geq 99.9\%$ trace metals basis), benzyl alcohol ($\geq 99\%$, reagentplus), graphite (powder, $<20\ \mu\text{m}$, synthetic), phosphorus pentoxide (99%, reagentplus) were purchased from Sigma-Aldrich. NaNO_3 , H_2SO_4 , KMnO_4 , H_2O_2 and HCl were purchased from Samchun Chemical. All the chemicals were used as received.

Preparation of graphene oxide

Graphene oxide (GO) was produced from graphite powder following a modified Hummer's methods^{1 2}. Briefly, 1 g of graphite powder was added to a mixture of 20 mL of concentrated H_2SO_4 , $\text{K}_2\text{S}_2\text{O}_8$ (2.5 g) and P_2O_5 (2.5 g). Then the solution was heated to $80\ ^\circ\text{C}$ under stirring. After 5 hr, the mixture was filtered with DI water and dried at $70\ ^\circ\text{C}$ leading to pre-oxidized graphite. Afterward, 1 g of the pre-oxidized graphite, 1 g of NaNO_3 and 46 mL of H_2SO_4 were stirred together in an ice bath for 2 hours. Then, 6 g of KMnO_4 were slowly added and reacted for 2 hours. After the mixture was stirred vigorously for 5 days at room temperature, 250 mL DI water was added. The solution was then slowly heated to $98\ ^\circ\text{C}$ and maintained at this temperature for 1 hour. 6 mL of H_2O_2 (30 wt%) were slowly added and the solution was filtered and washed with 1:10 HCl aqueous solution (250 mL) to remove metal ions, followed by repeated washings with water. Finally the solid was separated by centrifugation and dried at $60\ ^\circ\text{C}$ overnight.

Reduced graphene oxide or graphene nano-sheets (GNS) were either obtained by reduction of GO by a hydrothermal assisted treatment in presence of hydrazine (GNS1) or in benzyl alcohol under microwave irradiation at $185\ ^\circ\text{C}$ for 10 min (GNS2).

Non-aqueous synthesis and graphene-composite synthesis

Under inert atmosphere, SnCl_4 or $\text{Fe}(\text{acac})_3$ were added to 20 mL of benzyl alcohol in a vial of total capacity of 35 mL, sealed with a Teflon cap and taken out of a glovebox. For the synthesis graphene/metal oxide composites, graphene oxide was also added to the

¹ W. S. Hummers et al., *J. Am. Chem. Soc.*, 1958, 80, 1339-1339

² Kovtyukhova et al., *Chem. Mater.* 1999, 11, 771-778

reaction mixtures. The solutions were homogenized by vigorous stirring for 30 seconds and sonication for 30 minutes. The solutions were then heated in a microwave (CEM Discovery SP). The experimental details of the different samples are summarized in Table 1. The resulting white (pure SnO₂) or black suspensions were centrifuged and the precipitate redispersed and washed with ethanol (once) and dichloromethane (twice). Subsequently, the powders were dried under vacuum for 1 hour.

Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained on a JEOL EM-2010 and on a Tecnai F20 microscope at an accelerating voltage of 200 kV. Field Emission-Scanning Electron Microscopy (FE-SEM) investigations were carried out using a JEOL JSM-6701F. The powder X-ray diffraction (XRD) measurement was performed using a Rigaku D/Max-3C diffractometer (Cu K α radiation, $\lambda = 0.15418$ nm). The XPS experiments were performed in an UHV multipurpose surface analysis system (SIGMA PROBE, ThermoFisher Scientific, UK) operating at base pressures $<10^{-10}$ mbar. Fourier-transform IR (FT-IR) spectra were carried out through a Nicolet 6700 (Thermo Scientific, USA) in the infrared domain 400-4000 cm⁻¹ by a KBr matrix. For TGA measurements, a TA Instruments Simultaneous DTA/TGA analyser Q600 model was used with a heating rate 10 °C/min in air.

Electrochemical characterization

Working electrodes were prepared from all the samples (cf. Table 1), Super P (as a conducting agent) and polyvinylidene fluoride (PVDF, as a binder) (70:15:15 in weight ratio) in n-methyl-2-pyrrolidinone. The slurry was coated onto a copper foil current collector via doctor blade processing and then pressed for use as the working electrode. Electrochemical test cells were assembled in an argon-filled glove box using coin-type half-cells (2016 type) with lithium foil as a counter electrode. The organic electrolyte was composed of 1.0 M LiPF₆ in ethylene carbonate and diethyl carbonate (1:1 vol.%). The cells were galvanostatically charged and discharged in the voltage range from 2.0 to 0.01 V vs. Li⁺/Li in the SnO₂/graphene case and from 3.0 to 0.01 V for the Fe₃O₄/graphene.

Electrochemical measurements were made with a WBCS3000 cycler (WonA Tech, Korea) at room temperature.

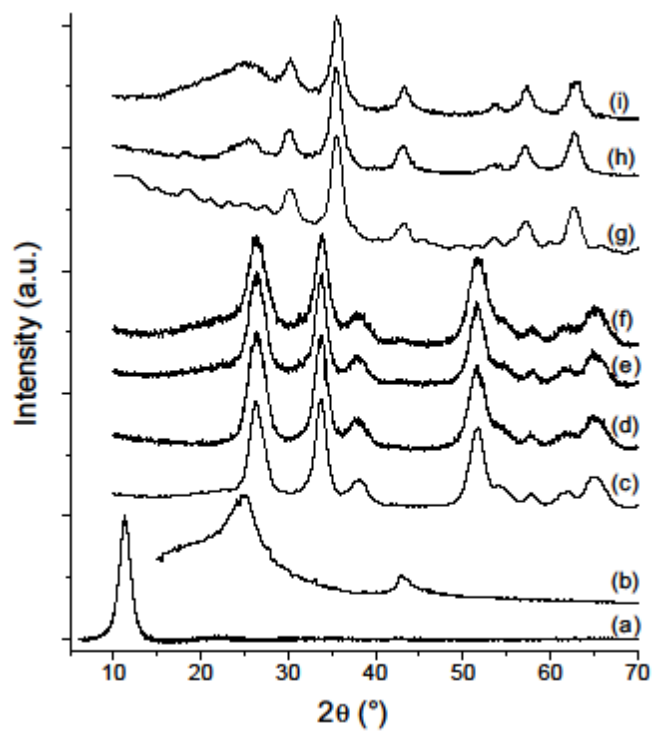


Fig S11. XRD patterns of the various samples. a) GO, b) GNS2, c) Pure SnO_2 , d) TGC1, e) TGC2, f) TGC3, g) Pure Fe_3O_4 , h) IGC1 and i) IGC2.

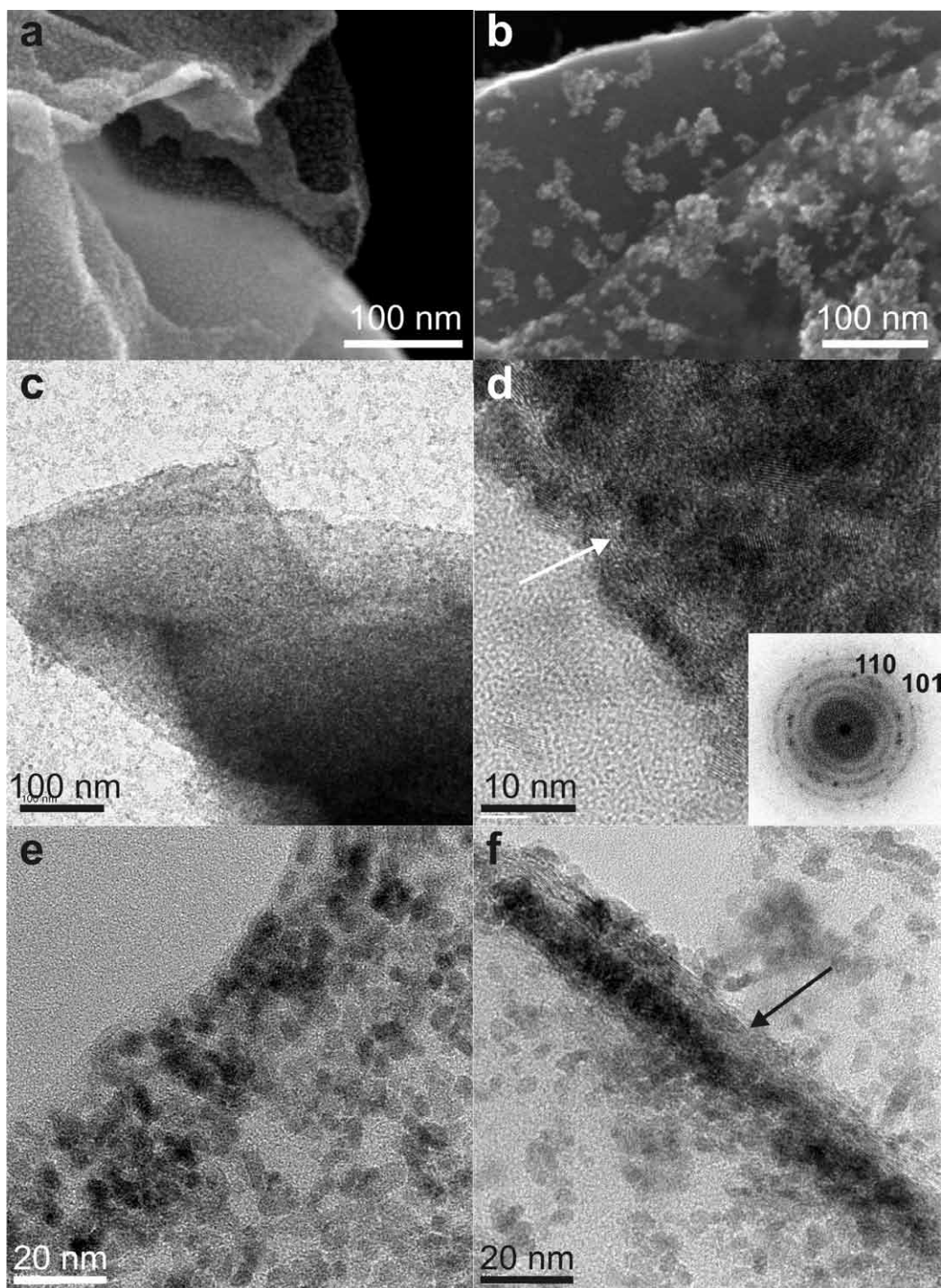


Figure SI2. Electron microscopy studies of tin oxide/graphene nanocomposites. a,b) FE-SEM image of TGC1 and TGC2 c,d) Overview and high resolution TEM images of TGC1, inset shows the power spectrum. e,f) High resolution TEM images of TGC2 and TGC3. In d) and f) the arrows point out the stacking of GNS.

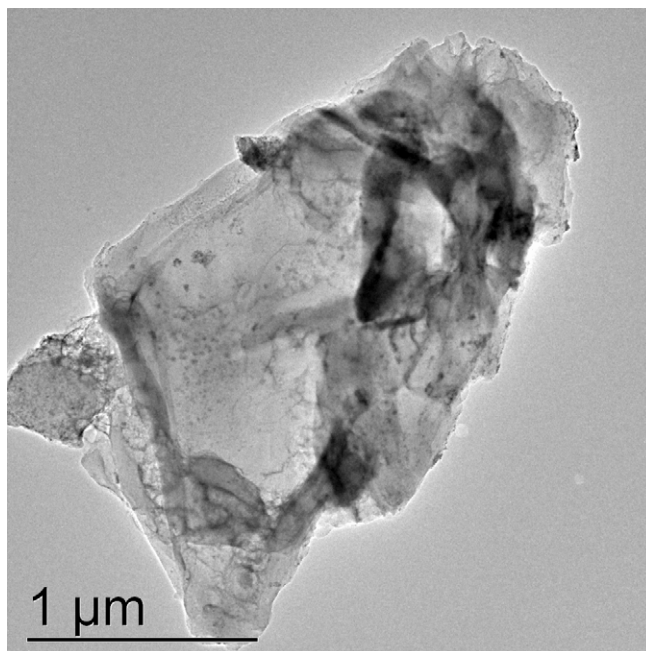


Figure SI3. Transmission electron microscopy images of tin oxide/graphene nanocomposites synthesized by traditional heating, showing the lower particle density and the non-homogeneous coating of the GO as compared to microwave heating.

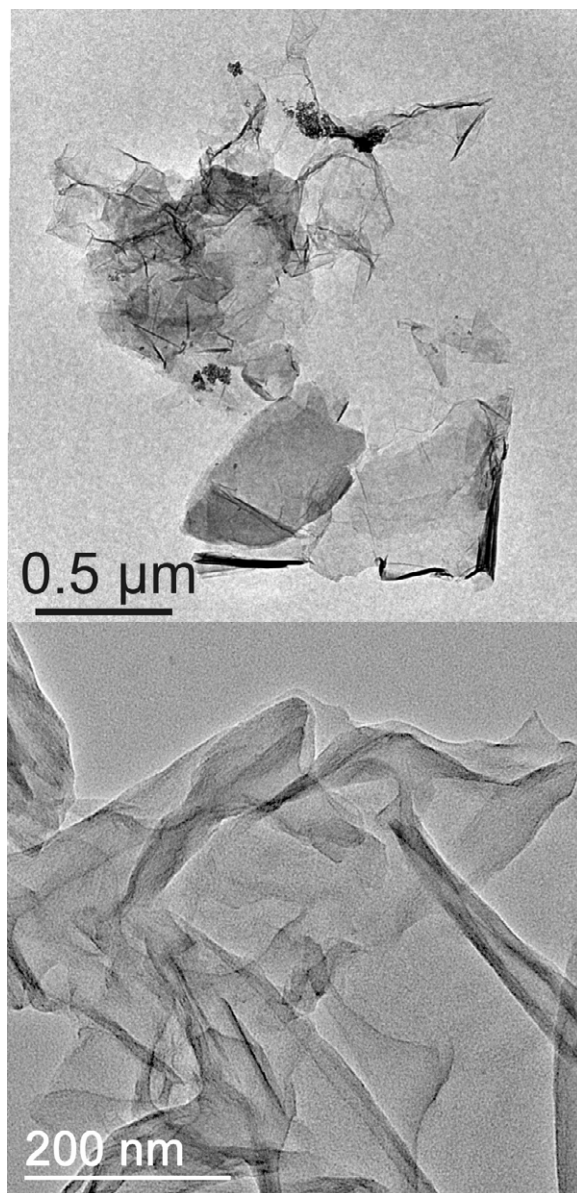


Figure SI4. Transmission electron microscopy images of GNS1 (top) and GNS2 (bottom)

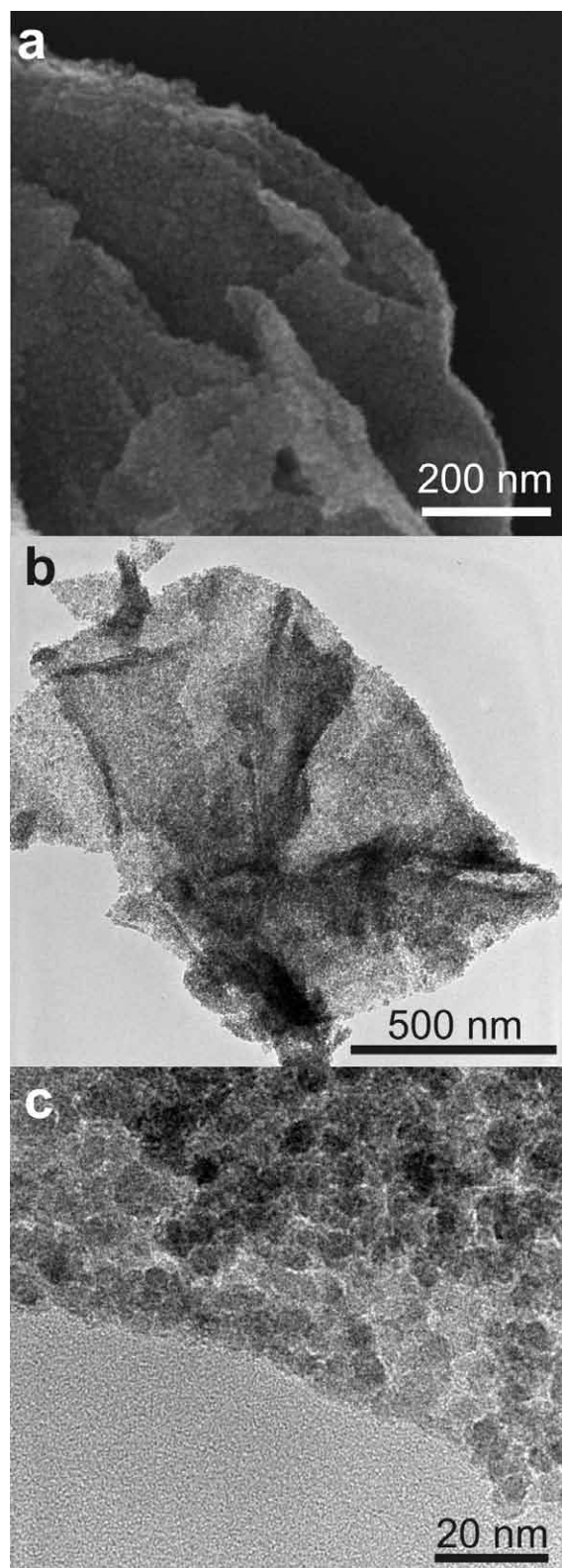


Figure SI5. Electron microscopy images of magnetite/graphene nanocomposites. a) FE-SEM, b) TEM and c) HRTEM of IGC1.

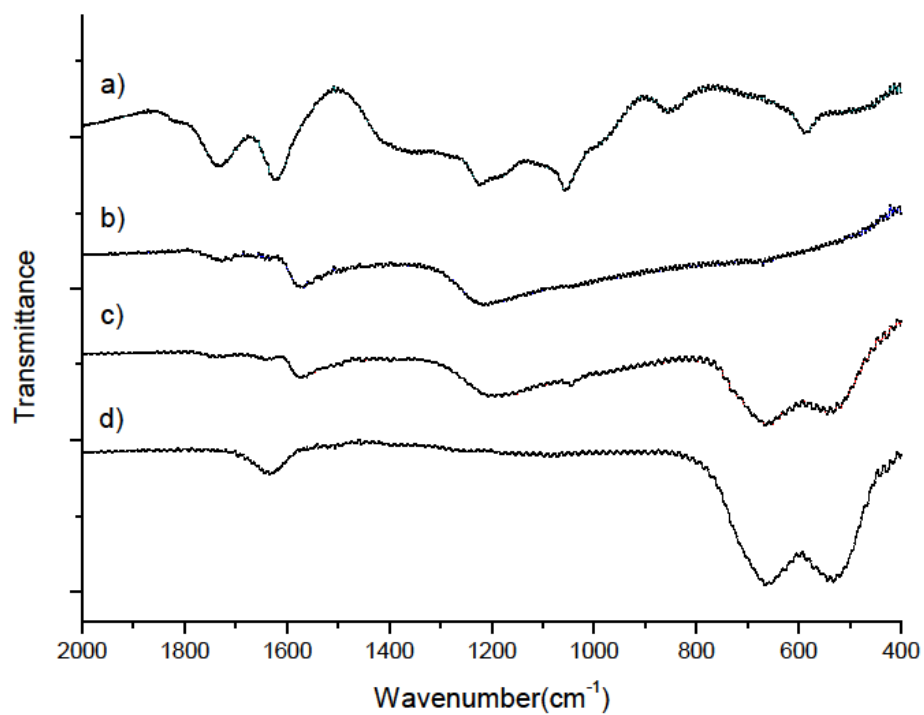


Figure SI6. FT-IR. a) GO, b) GNS1 c) TGC2, d) Pure SnO₂.

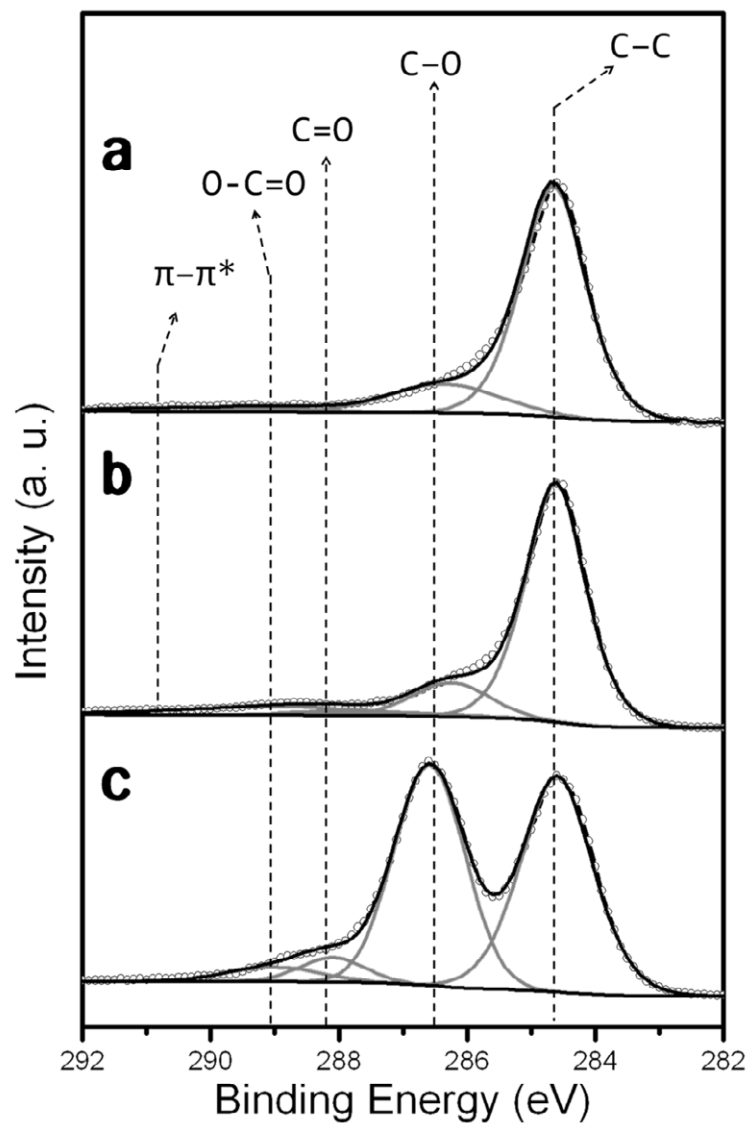


Figure SI7. XPS C1s edges of a) TGC2, b) GNS2 c) GO

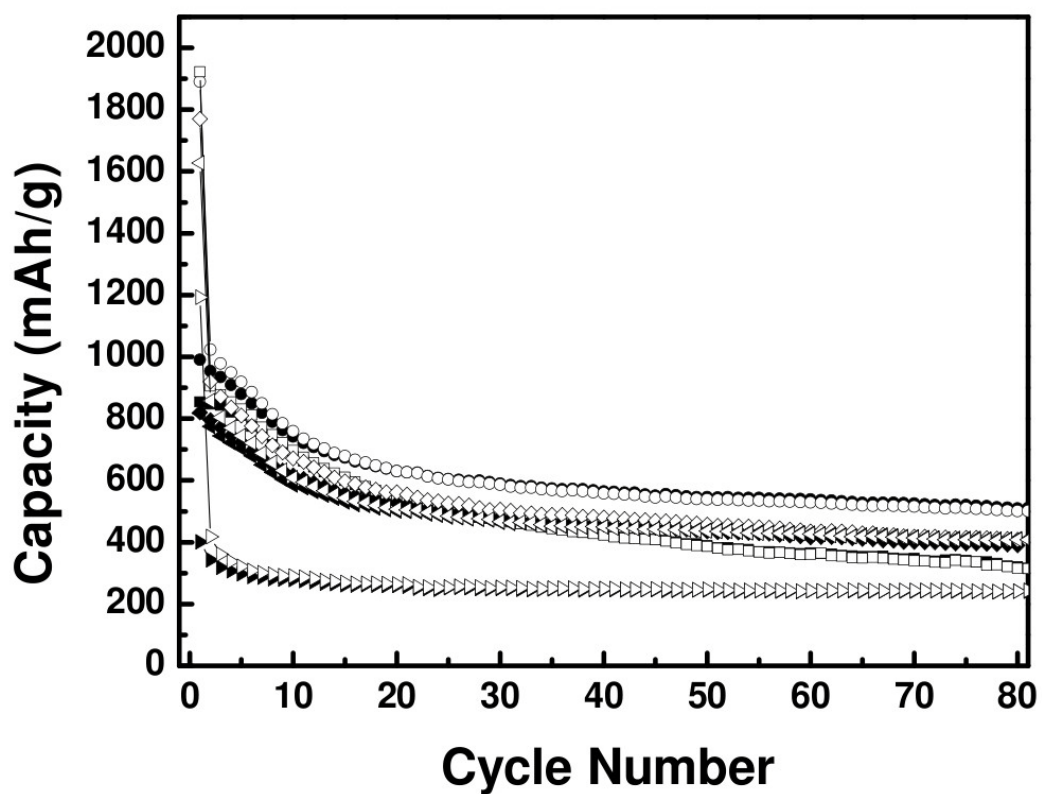


Figure SI8. Cycling performance of GNS (triangles right), SnO₂ (squares), TGC1 (circles), TGC2 (diamonds) and TGC3 (triangles left) at a current density of 100 mA/g.