Supporting Information

The Catalytic Role of Ge for Enhancing Electrochemical Performance of SnO$_2$(GeO$_2$)$_{0.13}$/G Anodes in Lithium Ion batteries

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Experimental section

Preparation of SnO$_2$/GeO$_2$, SnO$_2$/G and SnO$_2$(GeO$_2$)$_{0.13}$/G nanocomposites

Graphene oxide (GO) was synthesized via a modified Hummer's method. [1,2] The as-prepared GO (43 mg) was ultrasonically dispersed in 60 mL of deionized (DI) water for 5 h and then 0.02 g GeO$_2$ (1.60 mmol) and 0.1 g SnCl$_2$ (1.44$\times$10^{-2} mmol) was added into the solution. After magnetic stirring and sonication for 1 h and 20 min respectively, 0.76 mL HCl was added and stirred for 10 min. Then the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated in a normal lab oven at 180 ^{o}C for 24 h. After cooling naturally, the black precipitate was collected by centrifugation and washed with deionized water and ethanol for several times to remove the unreacted chemicals and residue, followed by drying in vacuum oven at 60 ^{o}C for 24 h. For the control samples, SnO$_2$/G was prepared by the same method without the addition of GeO$_2$, and SnO$_2$/GeO$_2$ was prepared by mixing the commercial SnO$_2$ (0.08 g) and GeO$_2$ (0.02 g) powder through the mechanical mixing method.
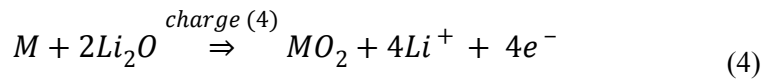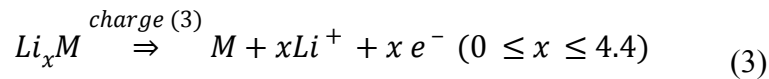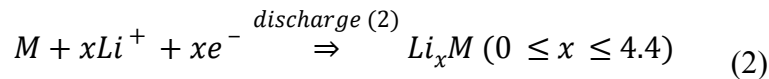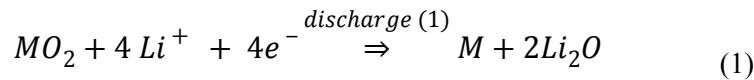
Materials Characterization

The crystal structures of the as-prepared samples were characterized by X-ray diffraction (XRD) using a Siemens D5005 powder diffractometer equipped with Cu Kα radiation ($\lambda \approx$ 1.54Å). The microstructures were investigated by field-emission scanning electron microscopy (FESEM, JEOL JSM-7600F) and transmission electron microscopy (TEM JEM2100F). Raman spectra were carried out by a WITec Instruments Raman system (Germany) with a 514.5 nm Ar$^+$ laser excitation. The elemental composition of samples was characterized by an X-ray photoelectron spectrometer (SPECS, mode XP-50) with a monochromatic Al Kα radiation (hv = 1486.6 eV).

Electrochemical measurement

The electrode slurry was made by mixing 75 wt% active materials (i.e., SnO_2/GeO_2, SnO_2/G, or $SnO_2(GeO_2)_{0.13}/G$), 15 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP) with magnetic stirring for 5 h. The slurry was then coated onto nickel foam and dried at 110 °C in vacuum furnace for 12 h. The coin-type cells (CR 2032) were assembled in an argon filled glovebox with the slurry as the active electrodes, Li metal as the counter/reference electrode, and polypropylene micro-porous film (Celgard 2300) as the separator. The electrolyte was 1 M LiPF6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1:1 in volume). The cells were galvanostatically charged and discharged at 50–2000 mA/g in the voltage range of 0.01–3.0 V vs Li/Li^+ on a NEWARE battery tester. Cyclic voltammetry (CV) measurements were carried out at 0.1 mV/s between 0.01 and 3.0 V using an electrochemical work station (VMP3, Bio-logic). The electrochemical impedance spectra (EIS) measurements were measured by applying a sinusoidal wave with amplitude of 5 mV in the frequency range of 10^5 to 0.01 Hz. All of the electrochemical measurements were conducted at room temperature.

Calculation of the theoretical capacity of $SnO_2(GeO_2)_{0.13}/G$ nanocomposite

The electrochemical reactions involved for the alloying-dealloying type metals as following:

$$MO_2 + 4\,Li^+ + 4e^- \overset{discharge\ (1)}{\Rightarrow} M + 2Li_2O \qquad (1)$$

$$M + xLi^+ + xe^- \overset{discharge\ (2)}{\Rightarrow} Li_xM\ (0 \leq x \leq 4.4) \qquad (2)$$

$$Li_xM \overset{charge\ (3)}{\Rightarrow} M + xLi^+ + x\,e^-\ (0 \leq x \leq 4.4) \qquad (3)$$

$$M + 2Li_2O \overset{charge\ (4)}{\Rightarrow} MO_2 + 4Li^+ + 4e^- \qquad (4)$$

The theoretical capacity of $SnO_2(GeO_2)_{0.13}/G$ nanocomposite can be calculated according to the

above electrochemical reaction. Thus, we could divide the calculation into the following two cases:

1) The reactions (1) and (4) are irreversible.

The content of SnO_2, GeO_2, and graphene are 72.3 wt%, 6.5 wt%, and 21.2 wt%, respectively. According to the following formula: $C = n \times F/3600 \times m_a$, where C is the theoretical specific weight capacity of the active material, n is the number of transferred electrons per molecule of active material, $F = 96485$ C/mol is the Faraday constant, m_a is the molar weight of the active material. Without reaction (1) and (4), the involved electrons are 4.4. Thus, the theoretical specific weight capacity of SnO_2 and GeO_2 is 782 and 1126 mAh/g, respectively. The reversible capacity graphene obtained by the modified Hummer's method is around 300 mAh/g. [3] Therefore, the theoretical capacity of $SnO_2(GeO_2)_{0.13}$/G nanocomposite is calculated by: $782 \times 72.3\% + 1126 \times 6.5\% + 300 \times 21.2\% = 702$ mAh/g.

2) The reactions (1) and (4) are reversible.

If the reactions (1) and (4) are reversible, the involved electrons during the charge and discharge process are 8.4. Thus, according to the following formula: $C = n \times F/3600 \times m_a$, the theoretical capacities of SnO_2 and GeO_2 are 1493 and 2152 mAh/g, respectively. So, the theoretical capacity of $SnO_2(GeO_2)_{0.13}$/G nanocomposite is $1493 \times 72.3\% + 2152 \times 6.5\% + 300 \times 21.2\% = 1283$ mAh/g.
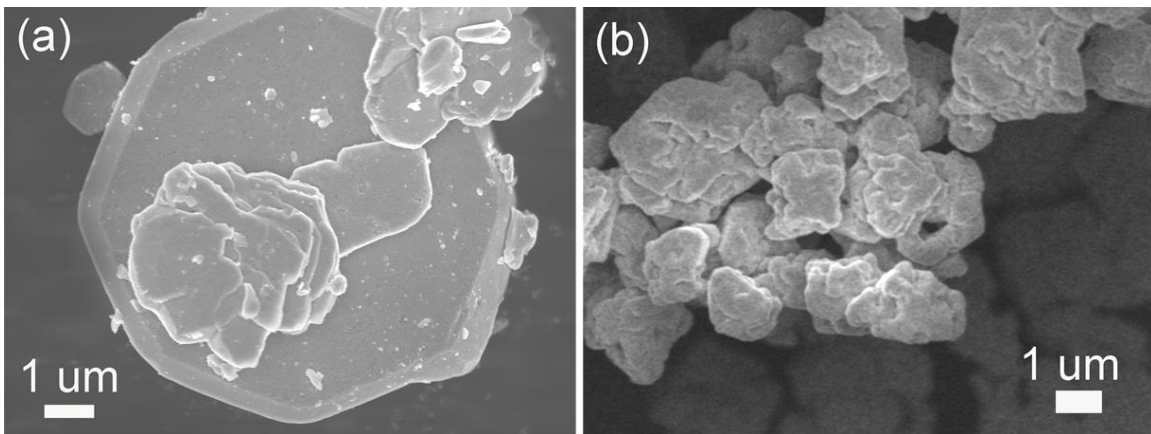
Figure S1. SEM images of the (a) commercial SnO_2 and (b) commercial GeO_2 particles.
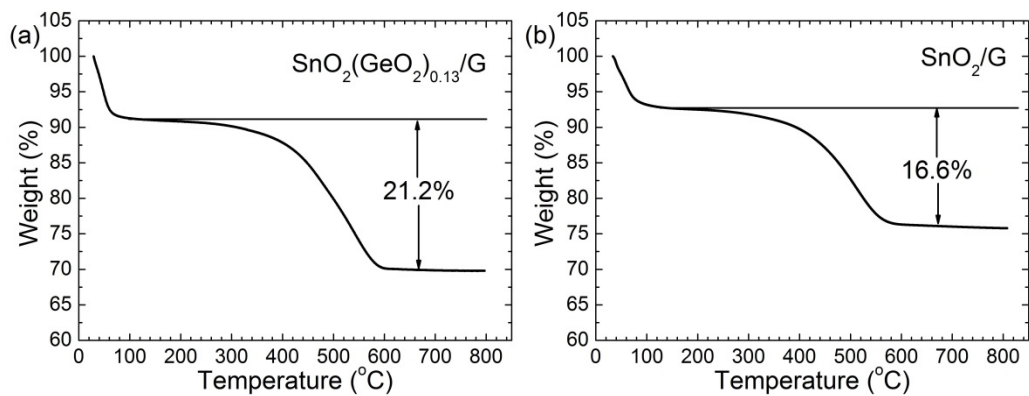
Figure S2. TGA curves of $SnO_2(GeO_2)_{0.13}/G$ (a) and SnO_2/G (b).
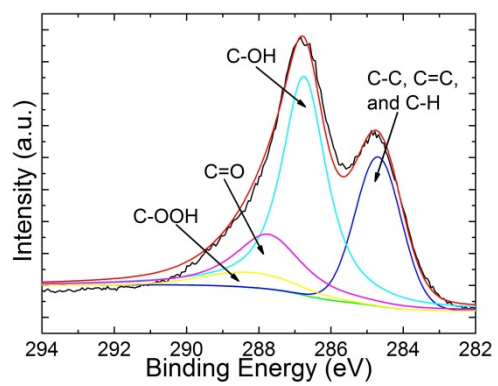
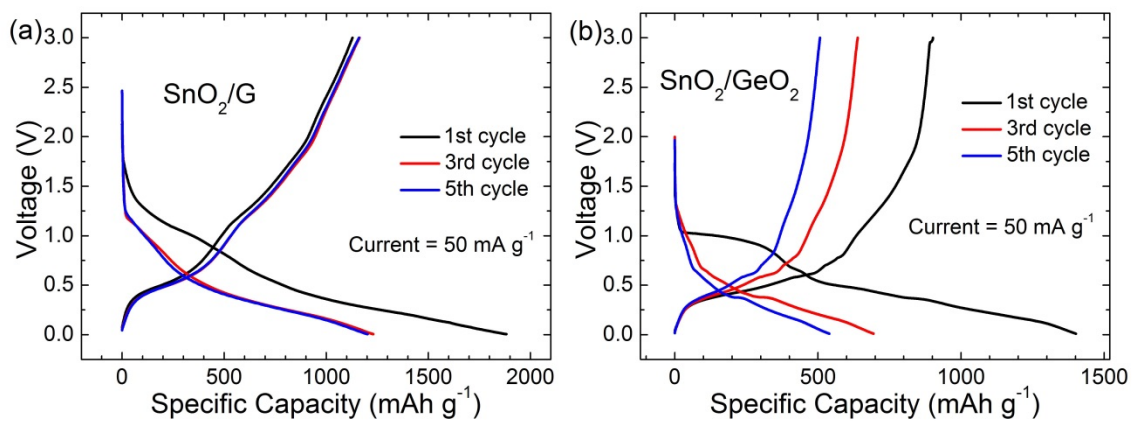**Figure S3.** XPS C 1s spectrum of reduced graphene oxide (RGO).

Figure S4. The galvanostatic charge/discharge curves of 1st, 3rd, and 5th cycles of (a) SnO_2/G and (b) SnO_2/GeO_2 nanocomposites at a current density of 50 mA/g.
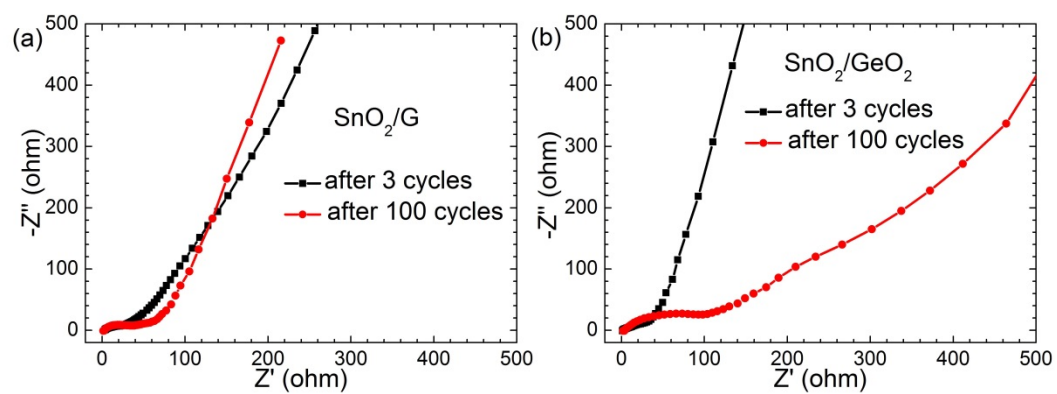
Figure S5. Electrochemical impedance spectroscopy (EIS) spectra of (a) SnO$_2$/G and (b) SnO$_2$/GeO$_2$ after 5 and 100 cycles.
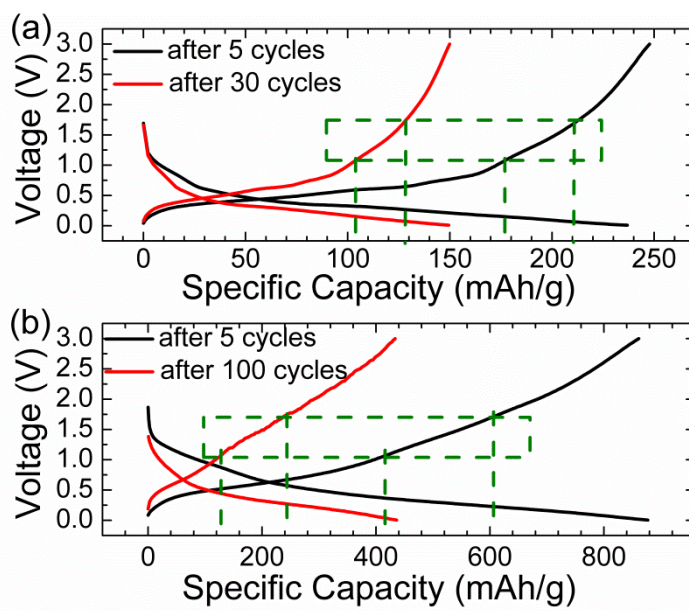
Figure S6. (a) The 5th and 30th charge and discharge curves of SnO_2/GeO_2 electrode. The retention of the plateau for the electrochemical reaction of forming SnO_2 or GeO_2 is around 70%. (b) The 5th and 30th charge and discharge curves of SnO_2/G electrode. The retention of the plateau for the electrochemical reaction of forming SnO_2 is about 60%.

References

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