

## Supplemental Information

### Tailoring Nanostructures in Micrometer Germanium Particles to Improve their Performance as an Anode for Lithium Ion Batteries

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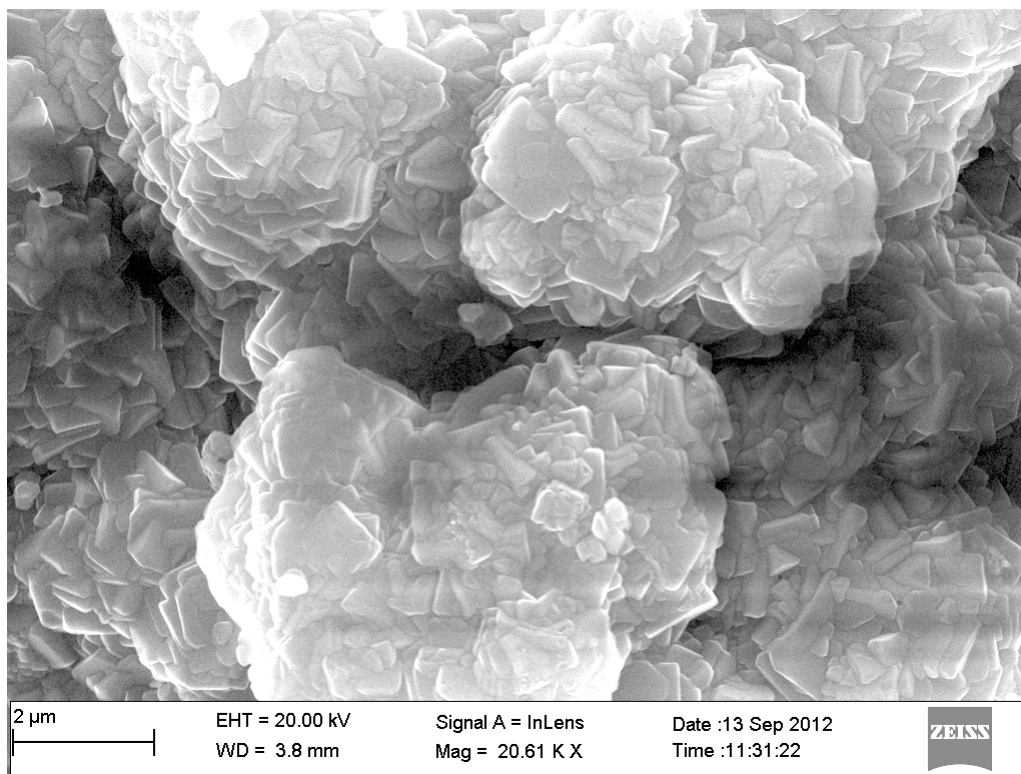
### Experimental

**Materials preparation:** Commercial GeO<sub>2</sub> powders were obtained from Alfa Aesar to produce semiconducting Ge. Porous Ge particles were synthesized by a thermal reduction approach in a tube furnace with flowing hydrogen at 300 – 600°C for 10 hours. The pressure of hydrogen was approximately 1 bar.

**Materials Characterization:** The in-situ X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Kratos AXIS 165 high-performance electron spectrometer. The morphology and phase of the as-synthesized samples were characterized by X-ray diffraction (XRD, Rigaku X-ray diffractometer, Cu-K $\alpha$  radiation) and scanning electron microscopy (SEM; Carl ZEISS Microscopy).

**Electrochemical Measurements:** The electrodes were prepared by spreading a mixture of 80 wt% Ge particles (or Ge particles), 10 wt% Na-alginate with medium viscosity as a binder, and 10 wt% EC600JD carbon black on to a copper foil. The as-prepared electrodes were dried at 80°C in a vacuum oven for 12 hours and then pressed under 10 MPa. Electrochemical properties of the electrodes were measured by assembling them into coin cells (type CR2015) in an argon-filled glove box with water and oxygen contents less than 0.1 ppm. The Li metal foil was used as counter electrode and Celgard 2400 separator as the separator. The electrolyte consists of a solution of LiPF<sub>6</sub> (1 M) in a mixture of ethylene carbonate (EC) / dimethyl carbonate (DMC) / diethyl carbonate (DEC) 1:1:1 (vol %) containing 2 wt% vinylene carbonate (VC). The cells were galvanostatically discharged and charged on a battery test system (Arbin BT2000) between 0.02 and 2.0 V at room temperature.

## Figures



**Figure S1.** An SEM image of as-received GeO<sub>2</sub>.

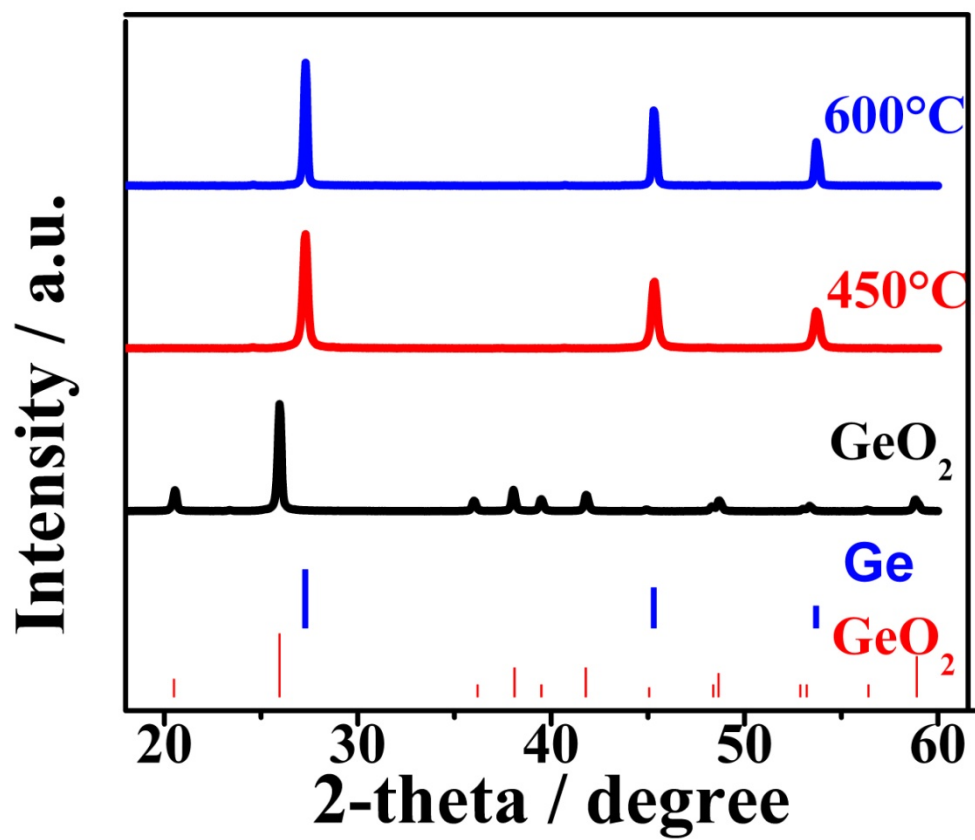
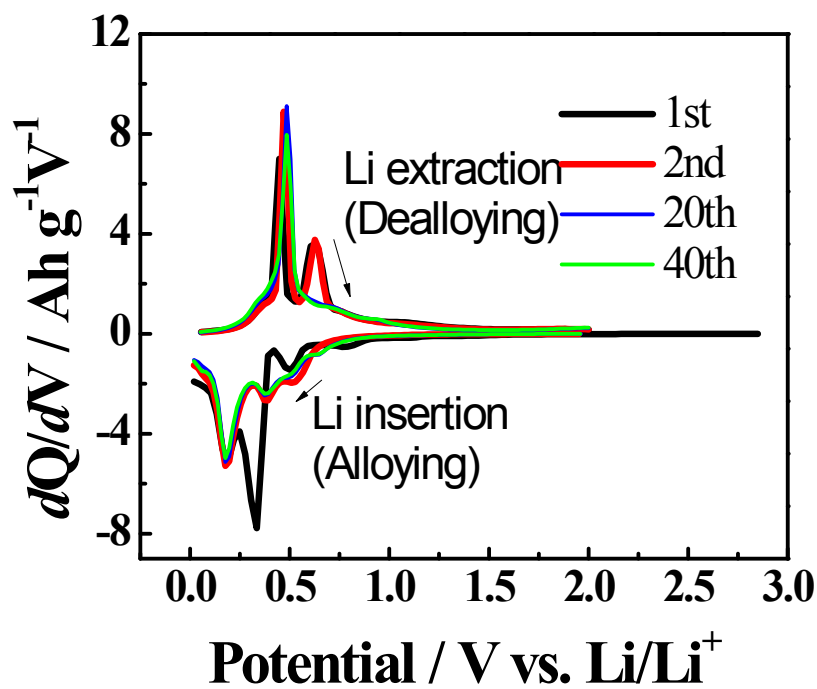
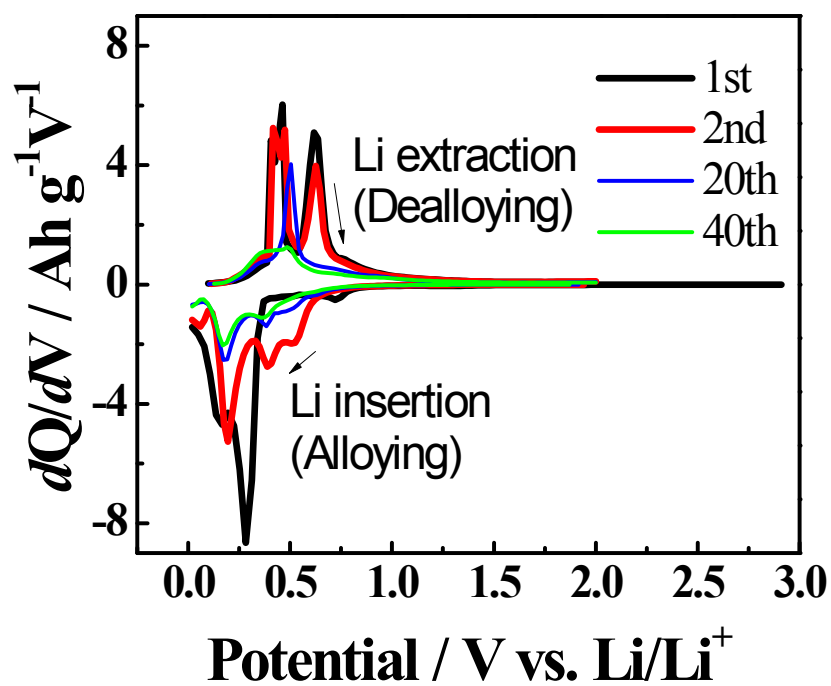


Figure S2. XRD patterns of GeO<sub>2</sub> reduced under H<sub>2</sub> at different temperature



(a)



(b)

**Figure S3.** Differential discharge-charge capacity curves of (a) Ge electrode consisting of nanopores and (b) Ge electrode comprised of dense grains

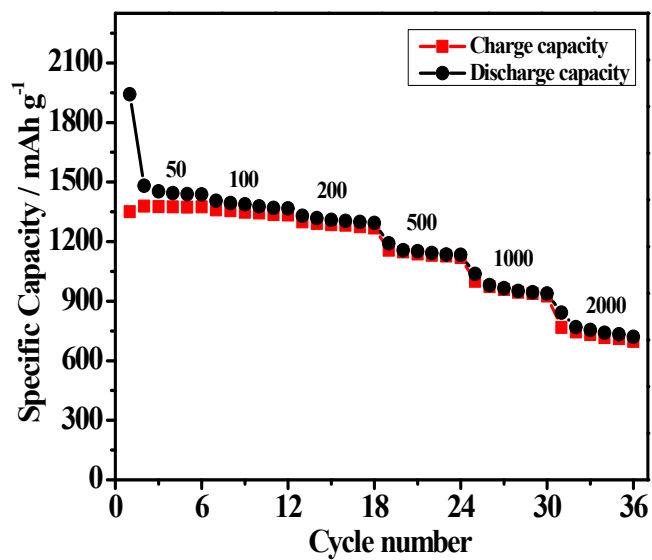


Figure S4. Rate capability of nano/microstructure Ge electrode measured at different charge/discharge rates.