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Electronic Supplementary Information

Hollow Carbon Spheres with Encapsulated Germanium as an Anode Material for Lithium Ion Batteries

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Experimental

Synthesis of SiO_2 spheres: SiO_2 spheres were synthesized by a slightly modified Stöber process.[16] In a typical synthesis, 0.6 mL tetraethyl orthosilicate (TEOS) was added into a mixture of 63.3 mL isopropyl alcohol, 23.5 mL deionized water, and 13.0 mL ammonium aqueous solution (30%), and then vigorous stirred at room temperature for 1 h. Then, 5 mL TEOS was added dropwise into the solution at 35 ^{o}C for 2 h. Then, the SiO_2 spheres were centrifugally separated from the suspension and washed with ethanol and deionized water several times before drying in a vacuum oven at 70 ^{o}C overnight.

Synthesis of SiO_2@RF core-shell spheres: 1 g of the obtained SiO_2 spheres was homogeneously dispersed in a solution of deionized water (70 mL) and ethanol (28 mL) by ultrasonication for 30 min, followed by the addition of 2.3 g hexadecyl trimethyl ammonium bromide (CTAB), 0.35 g resorcinol, and 0.1 mL ammonium aqueous solution, and then stirring at room temperature. The mixed solution was homogenized for 30 min to form a uniform dispersion. Then, 0.5 mL formaldehyde solution was added to the dispersion with continuous stirring for 8 h at 35 ^{o}C. After that, the products, the SiO_2@RF core-shell spheres, were collected by centrifugation and washed with ethanol and deionized water several times before drying in a vacuum oven at 70 ^{o}C overnight.

Synthesis of hollow carbon spheres (HCS): The as-prepared SiO_2@RF core-shell spheres were carbonized under argon atmosphere at 350 ^{o}C for 1.5 h, followed by a further annealing treatment at 900 ^{o}C for 3 h with a heating rate of 1 ^{o}C min^{-1}. Finally, the furnace was left to cool down to room temperature before the obtained SiO_2@C spheres were removed from the tube furnace. After soaking and washing in 3 M NaOH aqueous solution at 70 ^oC for 48 h, the as-synthesized SiO_2@C core-shell spheres were converted into HCS.

Synthesis of GeO_2@hollow carbon spheres (GeO_2@HCS): 0.5 g HCS was sealed in a two-neck flask, which was then subjected to vacuum for 30 min. Then, 1.5 g germanium ethoxide was injected into the evacuated flask, stirred for 48 h, and washed with ethanol several times to remove extra germanium ethoxide before drying in a vacuum oven at 70 ^oC overnight.

Synthesis of Ge@hollow carbon spheres (Ge@HCS): The as-prepared GeO_2@HCS sample was reduced to Ge@HCS under 5% hydrogen/argon gas at 650 ^oC for 10 h with a heating rate of 5 ^oC min^{-1}.

Synthesis of GeO_2 bulks, GeO_2@carbon bulks (GeO_2@C bulks), and Ge@carbon particles (Ge@C particles): GeO_2 bulks were obtained by the natural hydrolysis of germanium ethoxide in a sealed vial for 48 h. Then, the obtained GeO_2 bulks were coated with a carbon layer through carbonization in ethanol vapour in nitrogen at 650 ^oC for 3 h with a heating rate of 5 ^oC min^{-1} to obtain the GeO_2@C bulks. The Ge@C particles were synthesized by reducing the as-prepared GeO_2@C bulks under 5% hydrogen/argon gas at 650 ^oC for 10 h with a heating rate of 5 ^oC min^{-1}.

Characterization: The crystalline phases of the resultant materials were analysed by powder X-ray diffraction (XRD, MMA GBC, Australia), which was carried out using Cu Kα radiation (λ = 1.54056 Å) from 2θ. = 10° to 80°. Thermogravimetric analysis

(TGA) was carried out to determine the carbon content with a TGA/differential scanning calorimetry (DSC) type instrument (METTLER TOLEDO, Switzerland) at a heating rate of 10 °C min^{-1} from room temperature to 650 °C in air. The morphologies and structures of the samples were characterized by field-emission scanning electron microscopy (SEM, JSM-7500FA, JEOL, Japan), and transmission electron microscopy (TEM) investigations were performed using a JEOL 2011F analytical electron microscope (JEOL, Japan) operating at 200 keV. Raman spectroscopy was used to characterize the germanium and carbon using 514 nm laser excitation.

Electrochemical Measurements: To prepare the working electrode for electrochemical testing, an electrode slurry of Ge@HCS was prepared by thoroughly mixing the active material, sodium carboxymethyl cellulose, polyacrylic acid, and acetylene black in a weight ratio of 80:5:5:10 in de-ionized water. For the Ge@C particle sample, the slurry was made up in a weight ratio of 83.2:4.2:4.2:8.4 in order to keep the same carbon content as in the Ge@HCS electrode. The resultant slurry was then spread onto copper foil substrates and dried in a vacuum oven at 150 °C for 3 h. The electrochemical tests were carried out with CR2032 coin type cells. The cells were constructed of lithium foil as anode, the prepared active material on copper as cathode, microporous polyethylene (Celgard 2400) as the separator, and 1.15 M $LiPF_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) (3:4:3 by volume) as the electrolyte. The whole assembly process was carried out in an argon-filled glove box (Mbraun, Unilab, Germany). The charge/discharge cycling was performed within the voltage range of 0.01-1.5 V *vs.*

Li^+/Li on a battery test instrument (CT2001A, KINGNUO, China) at ambient temperature. The loading amount of active material for all electrodes was at least 0.9 mg cm^{-2}. The specific capacities were calculated based on the weight of the composites.

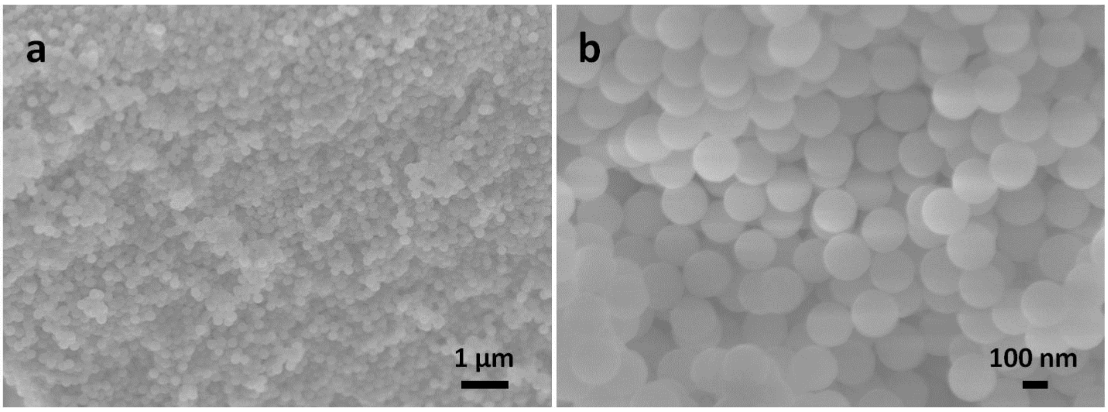

Fig. S1. SEM images of as-prepared SiO_2 spheres.

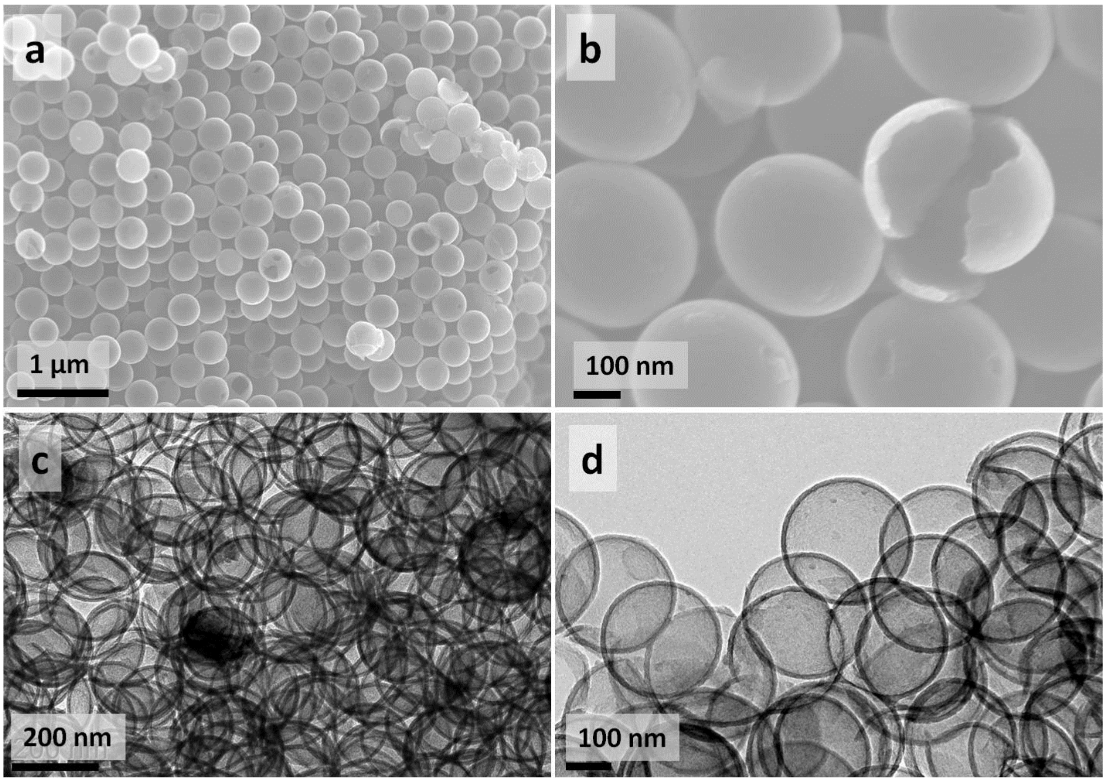

Fig. S2. (a, b) SEM images, (c, d) TEM images of as-prepared hollow carbon spheres.

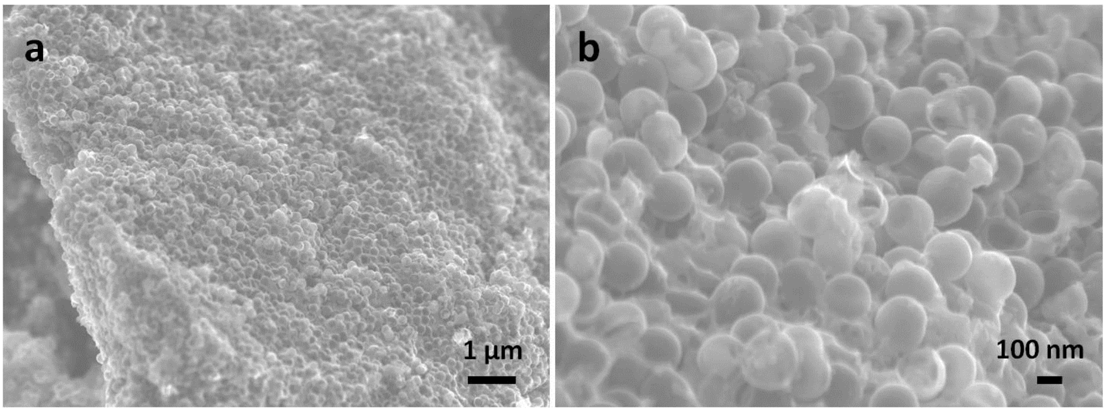

Fig. S3. SEM images of GeO_2@HCS.

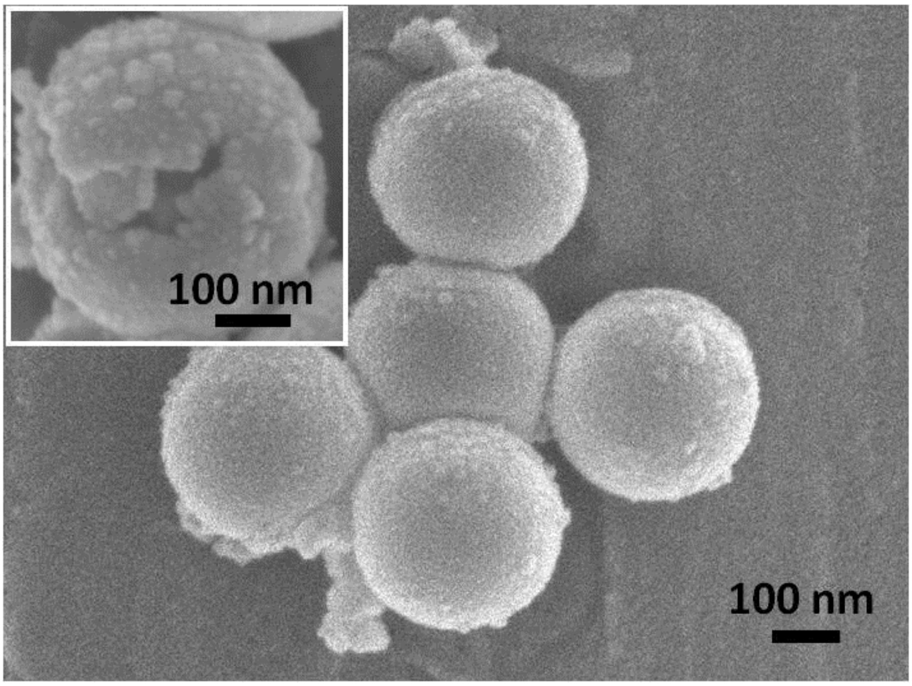

Fig. S4. SEM images of Ge@HCS. The inset is an enlarged Ge@HCS sphere.

In order to observe the germanium particles, the inset SEM image was taken after a long sonication to break the carbon sphere.

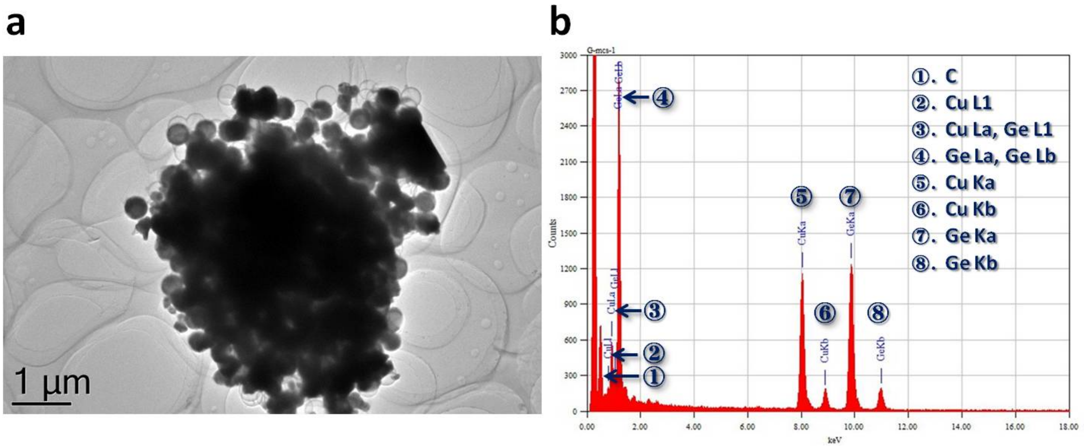

Fig. S5 (a) Low magnification TEM image of Ge@HCS. (b) Energy dispersive spectroscopy analysis of the Ge@HCS sample (Cu is from the copper grid).

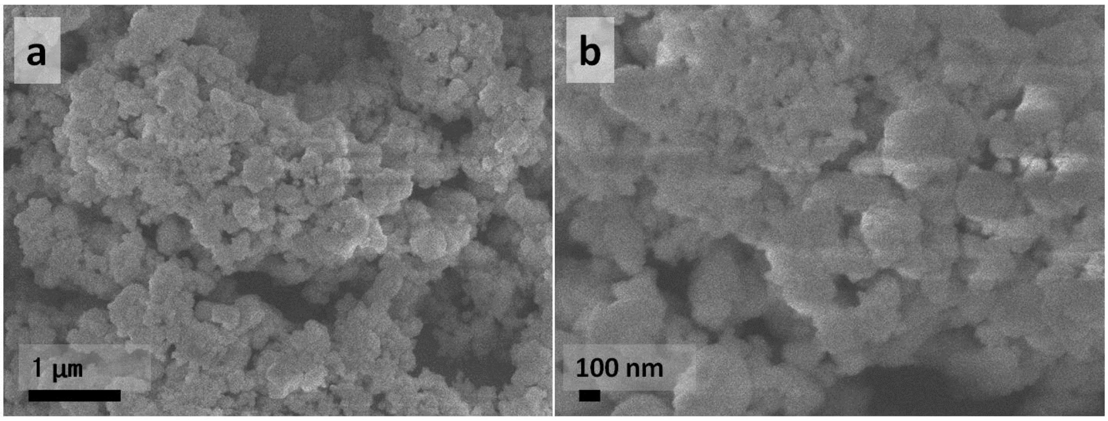

Fig. S6. SEM images of as-prepared GeO_2 particles.

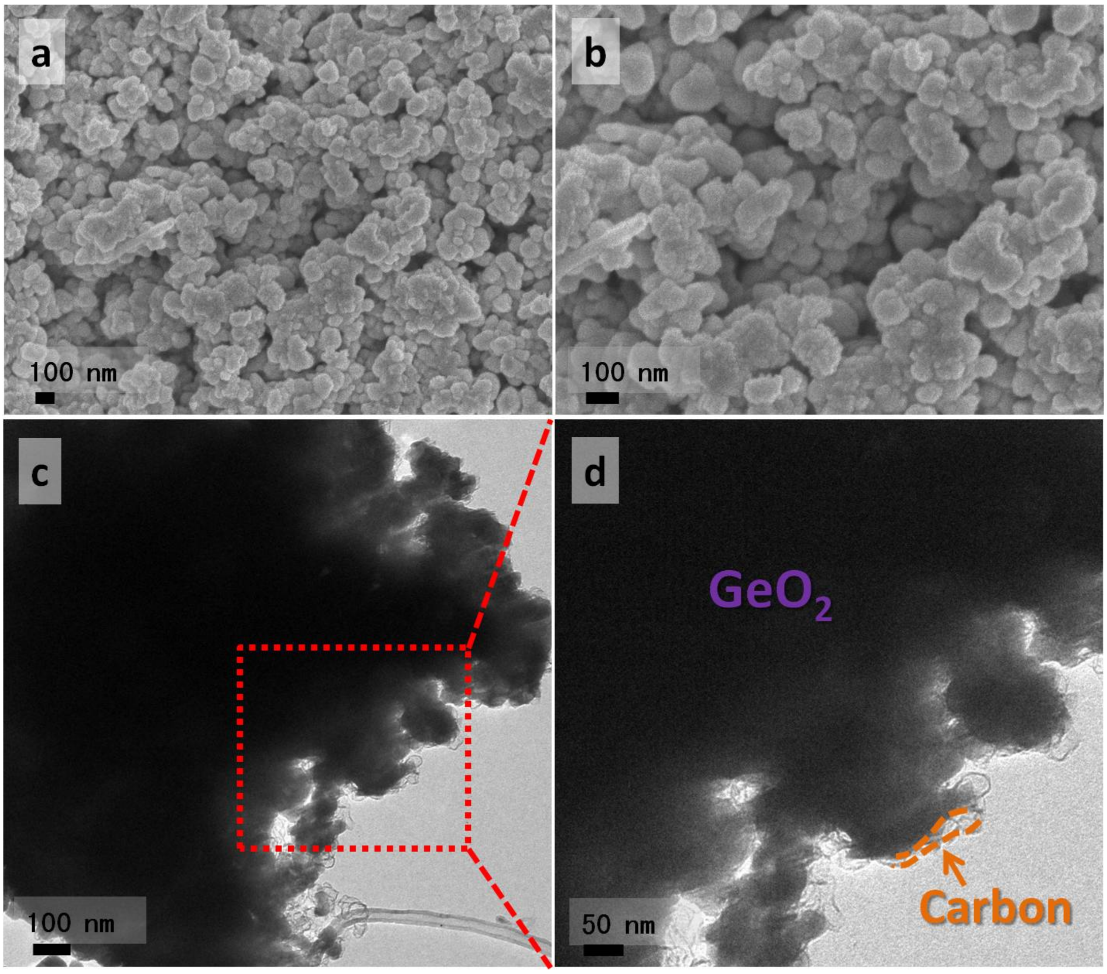

Fig. S7. (a, b) SEM images, (c, d) TEM images of GeO_2@C bulks. (d) is an enlarged image of the indicated red dashed square of (c). The orange arrow in (d) indicates the carbon layer on the surface of the GeO_2 bulks.

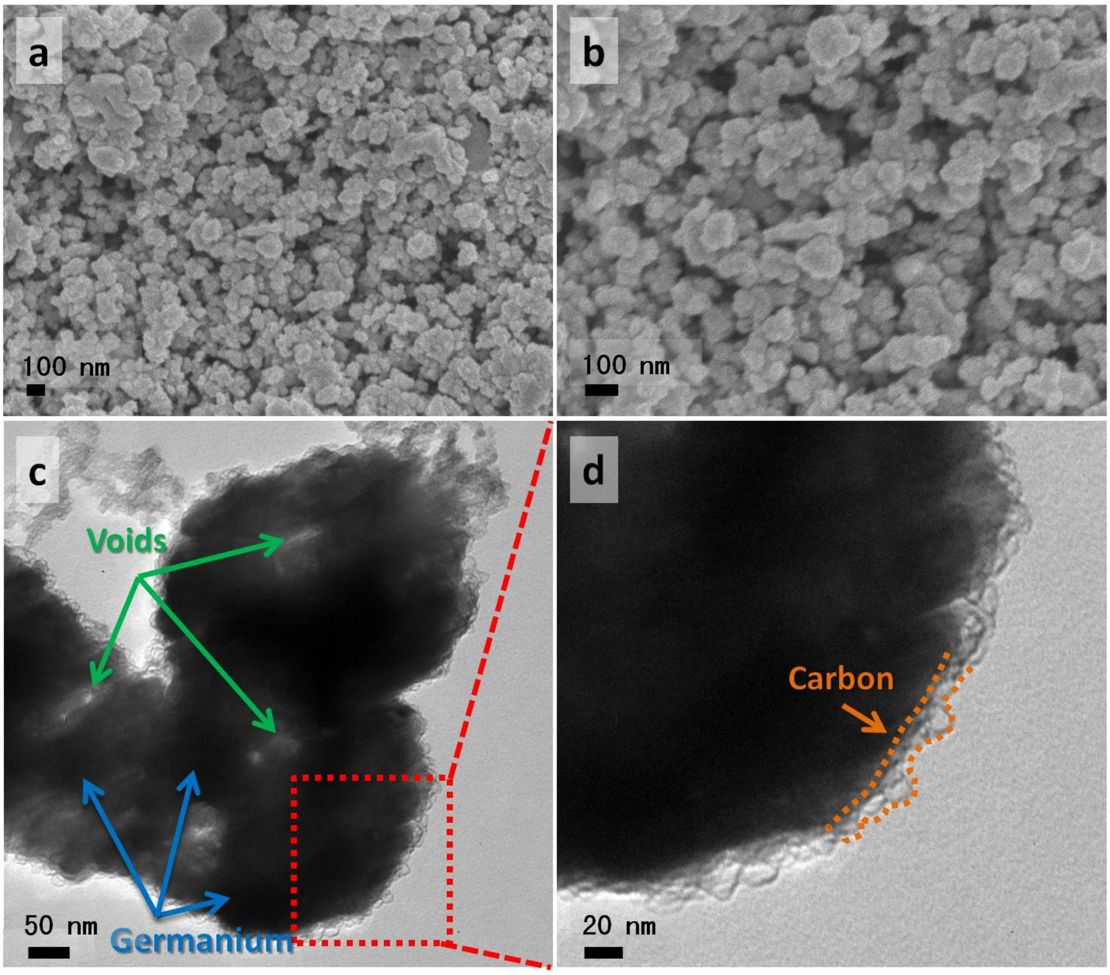

Fig. S8. (a, b) SEM images and (c, d) TEM images of Ge@C particles. (d) is an enlarged image of the indicated red dashed square in (c). The green and blue arrows in (c) indicate the voids and germanium particles, respectively. The orange arrow in (d) indicates the carbon layer on the surface of the germanium particles.

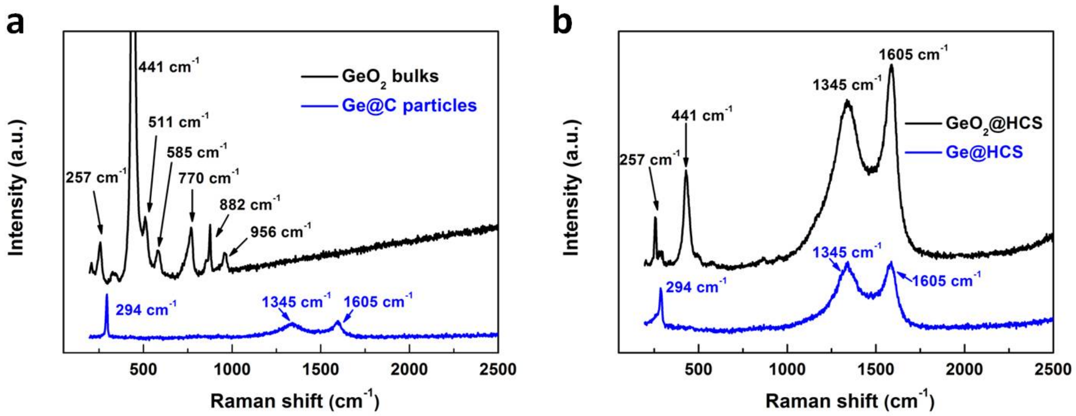

Fig. S9. Raman spectra of a) Ge@C particles and b) Ge@HCS with their corresponding GeO_2 precursors. The 294 cm^{-1} peak corresponds to the vibrations of crystalline Ge, and the peaks detected at 1345 and 1605 cm^{-1} are related to the D and G bands of carbon. All the peaks of the GeO_2 precursors can be indexed to the characteristic GeO_2 vibrations.

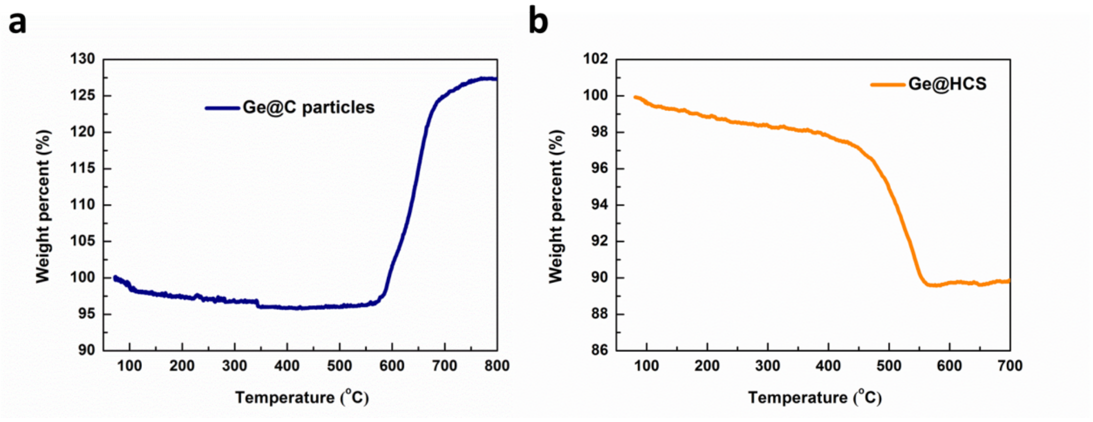

Fig. S10. TGA curves of (a) Ge@C particles, (b) Ge@HCS composite.

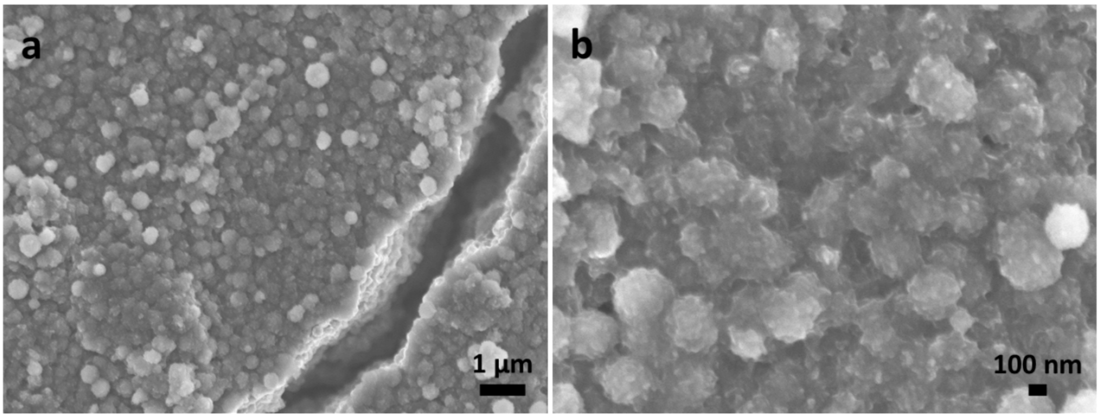

Fig. S11. SEM images of Ge@HCS composite electrode after 100 charge/discharge cycles.