Supporting Information

A synchronous approach for facile production of Ge/carbon hybrid nanoparticles for high-performance lithium batteries

Xiaona Li, Jianwen Liang, Zhiguo Hou, Yongchun Zhu* Yan Wang, and Yitai Qian

Experimental Section

All chemicals were of analytical grade and purchased from Shanghai Chemical Industrial Corp. and used as received without further purification. A typical synthesis process was as follows.

***Preparation of benzfluorenone-germanium chelate complex (BGe)*:** In a typical synthesis, 0.29 g of GeO_2 was first dissolved in 50 mL HCl (33 - 37%) at room temperature under magnetic stirring. Then 125 mL of 0.5 M benzfluorenone-dissolved acidified alcohol solution was added dropwise to the above solution to form a complex, and then adjusted to pH =2.5, by using NH_4OH. The resulting mixture was stirred at room temperature for 12 h, then the complex precursor was collected by filtration, washed with distilled water and ethanol.

***Preparation of final Ge/carbon hybrid nanoparticles*:** The BGe precursor was firstly heated to 800 ^{0}C at the heating rate of 5 min^{-1} under Ar/H_2 (95:5 v/v%) atmosphere and then kept at that temperature for 5 h to obtain carbonized BGe (CBGe) sample. For the further activition process, the CBGe was heated in air at different temperature and time, and the corresponding samples were named as CBGe-T-t (T for temperature and t for time during activation). The carbon content of CBGe-460-6 sample is about 8.9 wt% based on elemental analysis (CBGe-450-8 and CBGe-470-4 sample is about 19.8 wt% and 30 wt%, respectively).

***Preparation of tannic-induced Ge/carbon hybrid nanoparticles*:** The synthesis procedure is same as the CBGe-T-t samples, except that benzfluorenone-dissolved acidified alcohol solution is changed to tannic solution with different solvent (water and ethonal).

Material Characterization: XRD patterns were collected using a Philips X' Pert Super diffract meter with Cu Kα radiation (λ=1.54178 Å). The morphology of the products was characterized by a field-emission scanning electron microscope (SEM, JEOL-JSM-6700F). TEM and HRTEM images were recorded by Hitachi H7650 and HRTEM, JEOL 2010 microscope. TG analysis was performed with a TGA-2050 (TA Corp.) apparatus at a heating rate of 10 °C min^{-1} in flowing air and N_2. Raman spectra were collected on an EA (Vario EL-III) using a 514.5 nm laser. Nitrogen adsorption/desorption measurements were carried out on a VELSORP-mini II (BEL Japan, Inc.) at 473 K in the relative pressure range of P/P_0 from 0 to 1 to determine the Brunauer–Emmett–Teller (BET) surface areas and pore size distribution. Fourier transfer infrared (FTIR) spectra were measured using an IFS-85 (Bruker) spectrometer.

Electrochemical Measurement: The lithium-storage properties were investigated by assembling 2016 coin cells under an argon-filled glove box (H_2O, O_2 < 1 ppm). The aqueous slurry containing 70% active material, 15% Super P carbon black, and 15% sodium carboxymethylcellulose (CMC) binder was spread on a piece of copper foil. After drying in vacuum at 80 °C for 12 h, it was cut into small pieces with a diameter of 12 mm. The cells were assembled in a glovebox filled with Ar atmosphere, using metallic lithium metal as counter electrode, Celgard 2300 membrane as the separator, and 1 M $LiPF_6$ dissolved in ethylene carbonate (EC)–dimethyl carbonate (DMC)–diethyl carbonate (DEC) mixture (1 : 1 : 1, by Volume; Merck) as the electrolyte. The cycling and rate performances were recorded on a Land battery measurement system (Wuhan, China) with a cut-off voltage of 0.005 – 1.50 V vs. Li^+/Li (1 C = 1600 mA h g^{-1}). The tests were firstly conducted in parallel to the pure Ge nanoparticles in order to disclose the important role of buffering carbon layer.

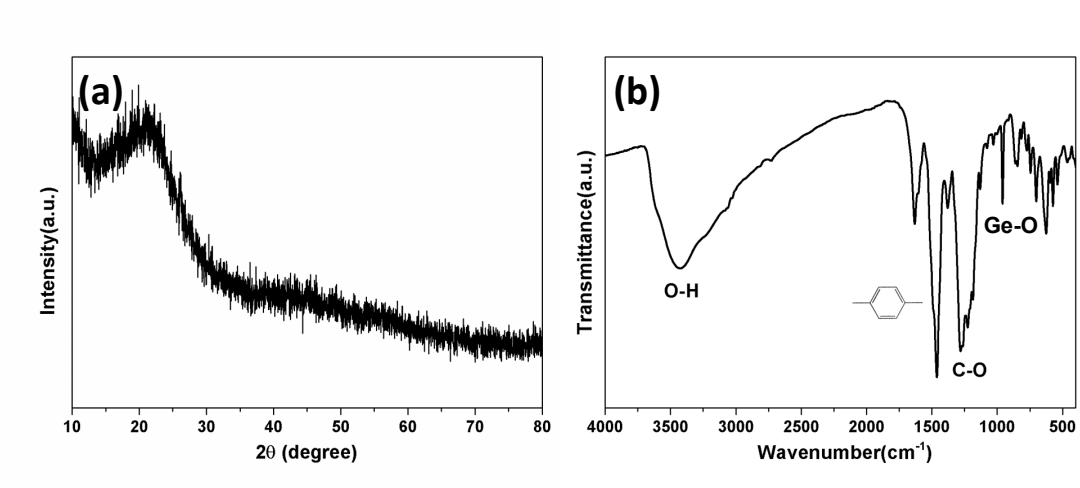

Figure S1. (a) XRD pattern and (b) FTIR spectra of benzfluorenone-germanium chelate complex (BGe) precursor.

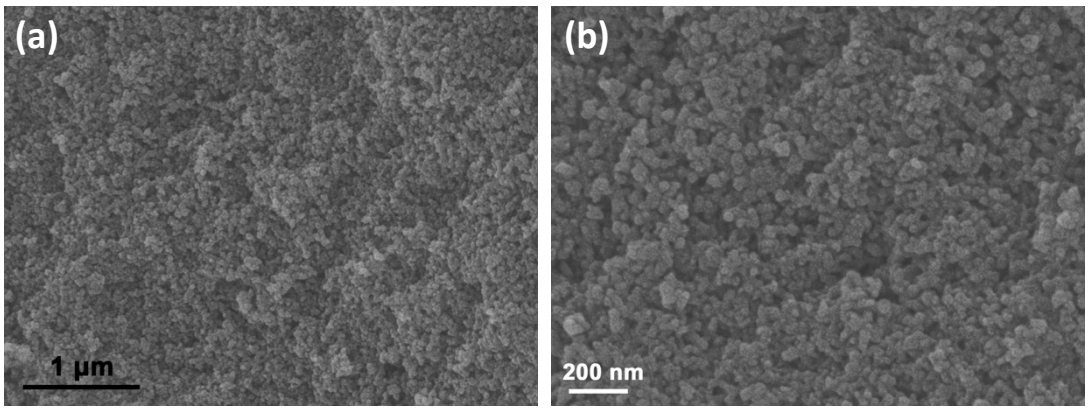

Figure S2. (a,b) SEM images of BGe precursor.

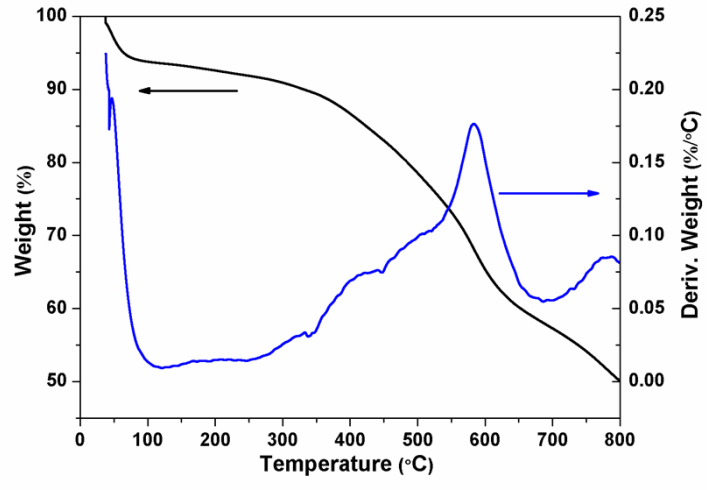

Figure S3. TGA curve of the as-synthesized BGe precursor in N_2 atmosphere.

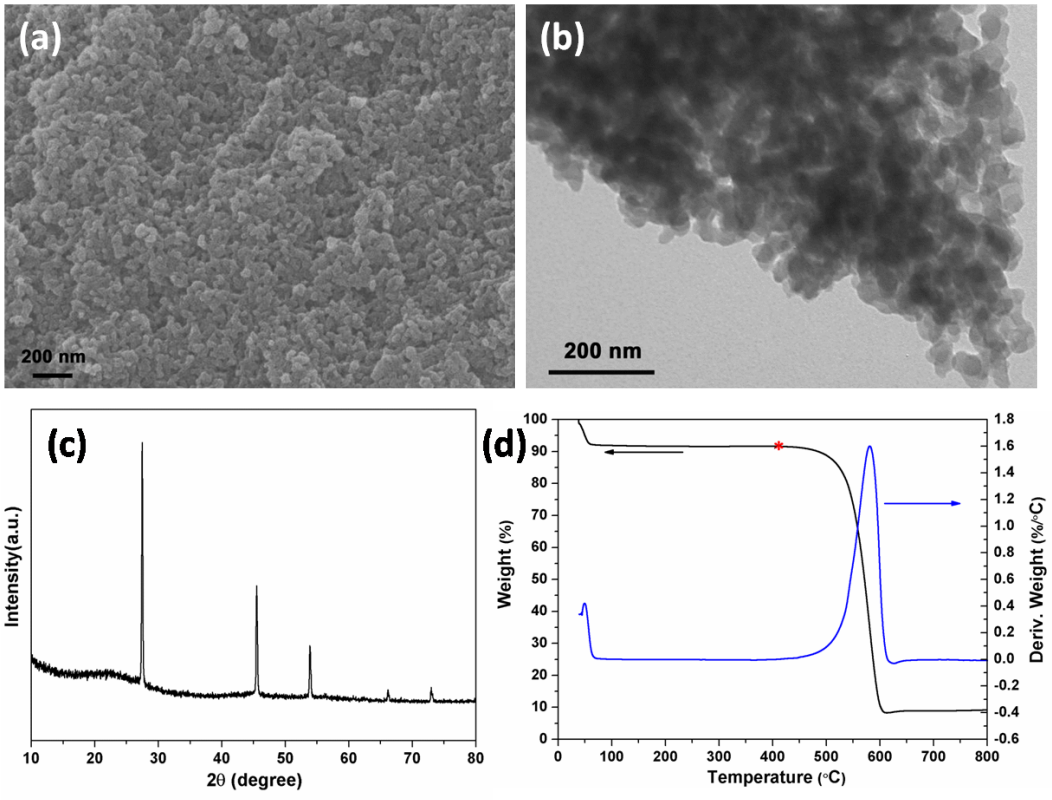

Figure S4. (a) SEM image, (b) TEM image, (c) XRD pattern and (d) TGA curve in air atmosphere of carbonized BGe precursor after Ar/H_2 (CBGe).

From the TGA curve (Figure S4d), one can see that the weight loss due to the loss of carbon in the composite is starting slowly from 408 °C (*), and the main reaction temperature is much higher than 500 °C. Since the carbon content of CBGe precursor is as high as about ~ 70%, the carbon content can still retain high ratio in the CBGe-470-4 sample.

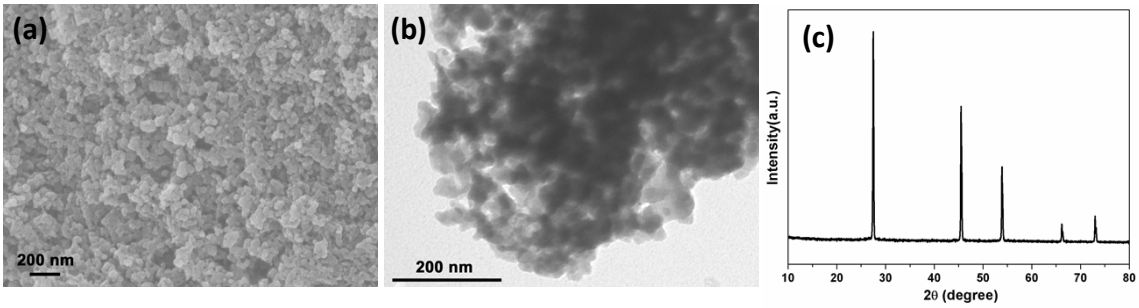

Figure S5. (a) SEM image, (b) TEM image and (c) XRD pattern of as-prepared CBGe-450-8 sample.

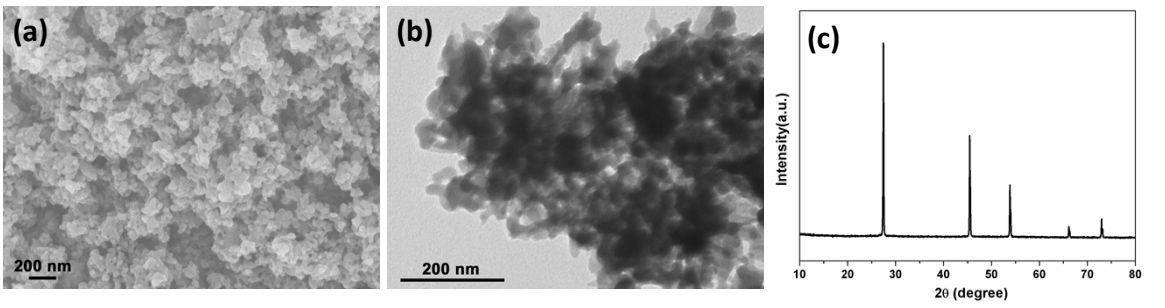

Figure S6. (a) SEM image, (b) TEM image and (c) XRD pattern of as-prepared CBGe-470-4 sample.

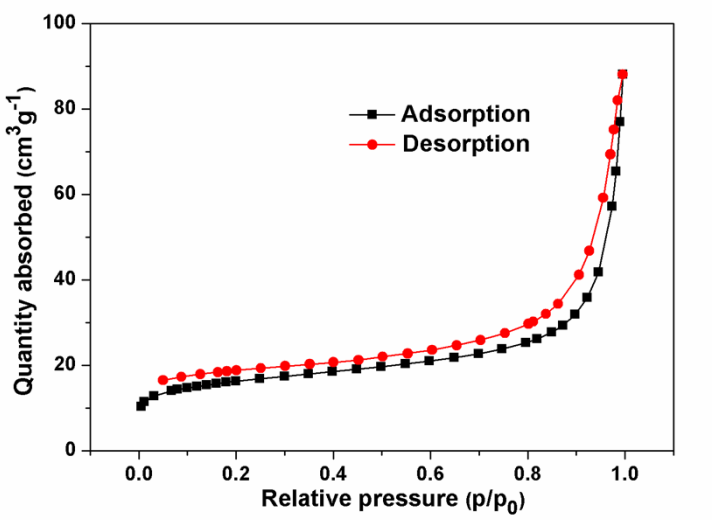

Figure S7. Nitrogen adsorption and desorption isotherms of CBGe-460-6.

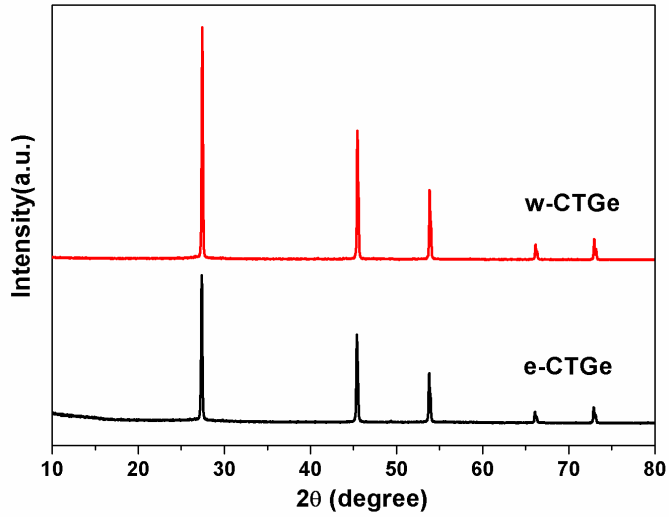

Figure S8. XRD patterns of w-CTGe and e-CTGe samples.

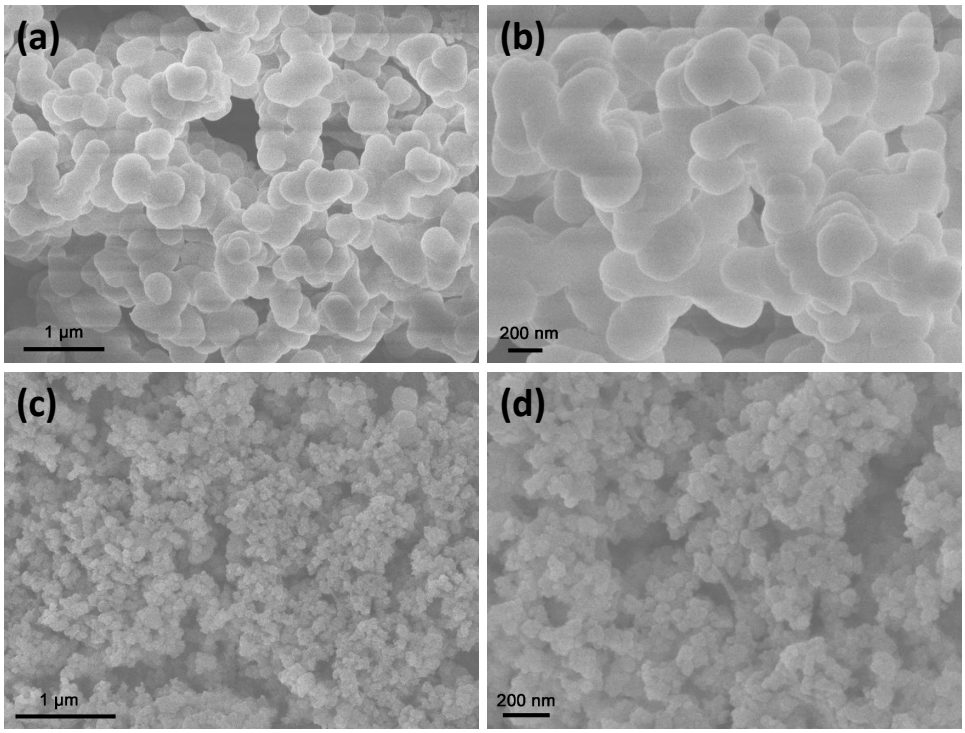

Figure S9. SEM images of as-prepared (a,b) TGe precursor with tannin dissolved in water and (c,d) TGe precursor with tannin dissolved in ethanol.

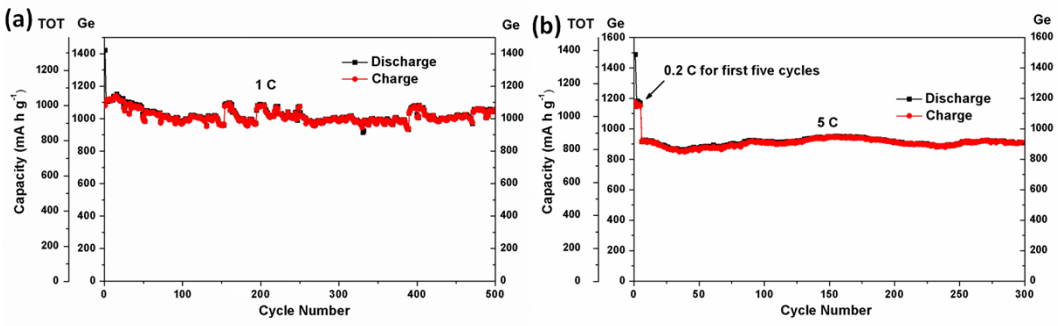

Figure S10. Cycling performance of CBGe-460-6 electrode at 1 C and 5 C. Specific capacity values are referred to the active material amount of both the pure germanium (i.e., Ge) and the total weight including Ge and carbon (i.e., TOT = Ge + carbon)

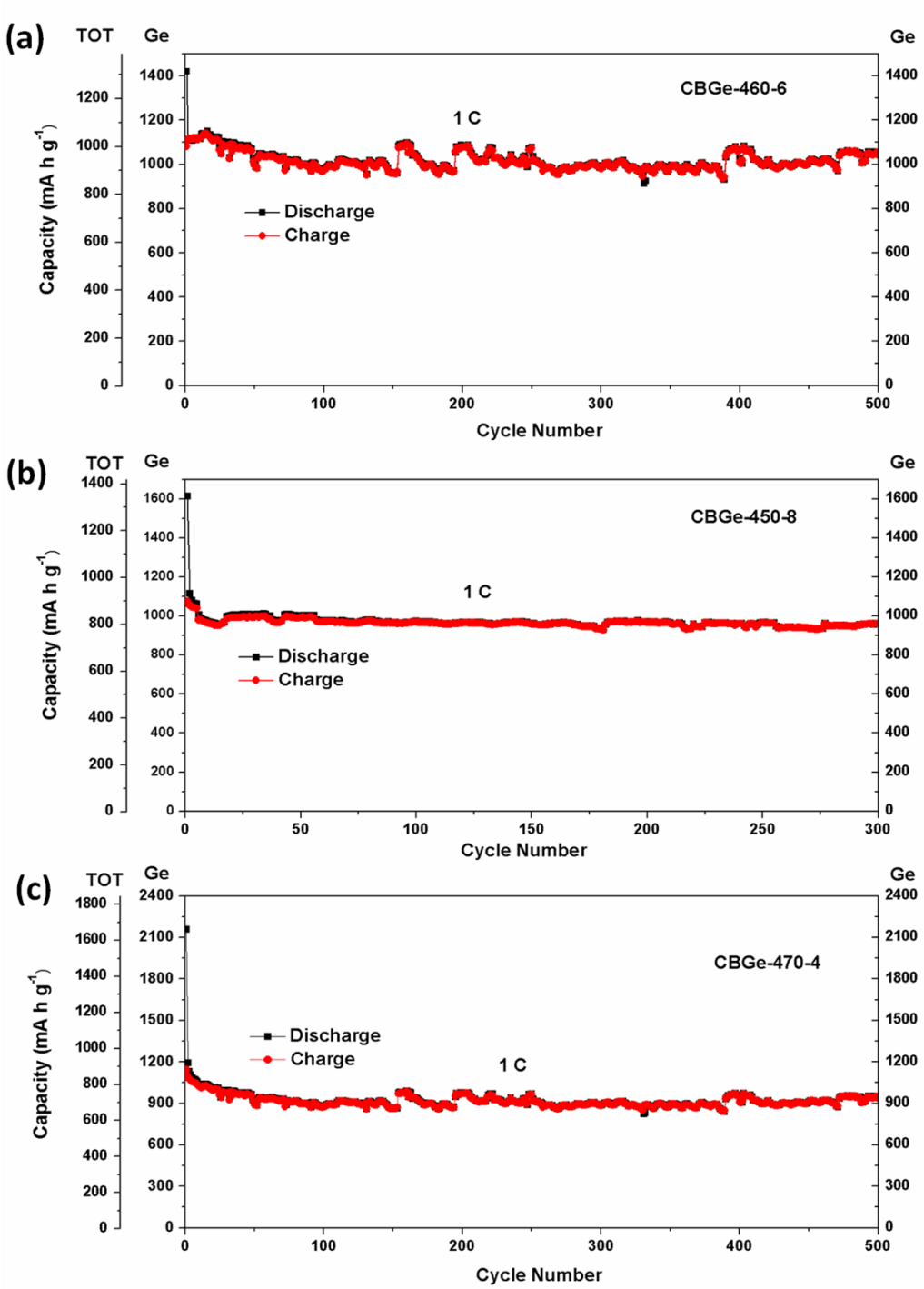

Figure S11. Cycling performance of (a) CBGe-460-6, (b) CBGe-450-8, and (c) CBGe-470-4 electrodes at 1 C. Specific capacity values are referred to the active material amount of both the pure germanium (i.e., Ge) and the total weight including Ge and carbon (i.e., TOT = Ge + carbon)

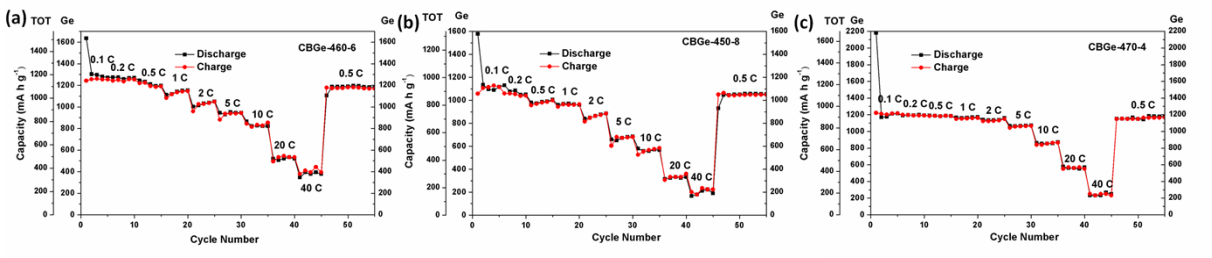

Figure S12. Rate capabilities of (a) CBGe-460-6, (b) CBGe-450-8, and (c) CBGe-470-4 electrodes from 0.1 C to 40 C. Specific capacity values are referred to the active material amount of both the pure germanium (i.e., Ge) and the total weight including Ge and carbon (i.e., TOT = Ge + carbon)

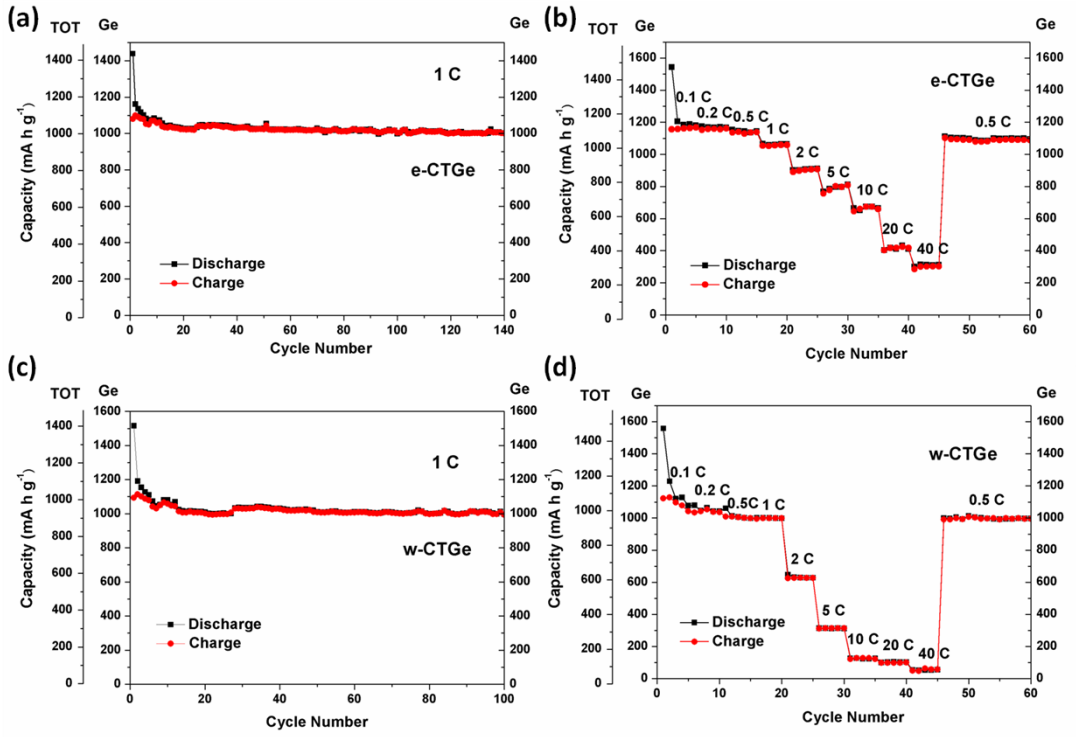

Figure S13. Cycling performance and rate capabilities of (a,b) e-CTGe and (c,d) w-CTGe electrodes, respectively. Specific capacity values are referred to the active material amount of both the pure germanium (i.e., Ge) and the total weight including Ge and carbon (i.e., TOT = Ge + carbon)

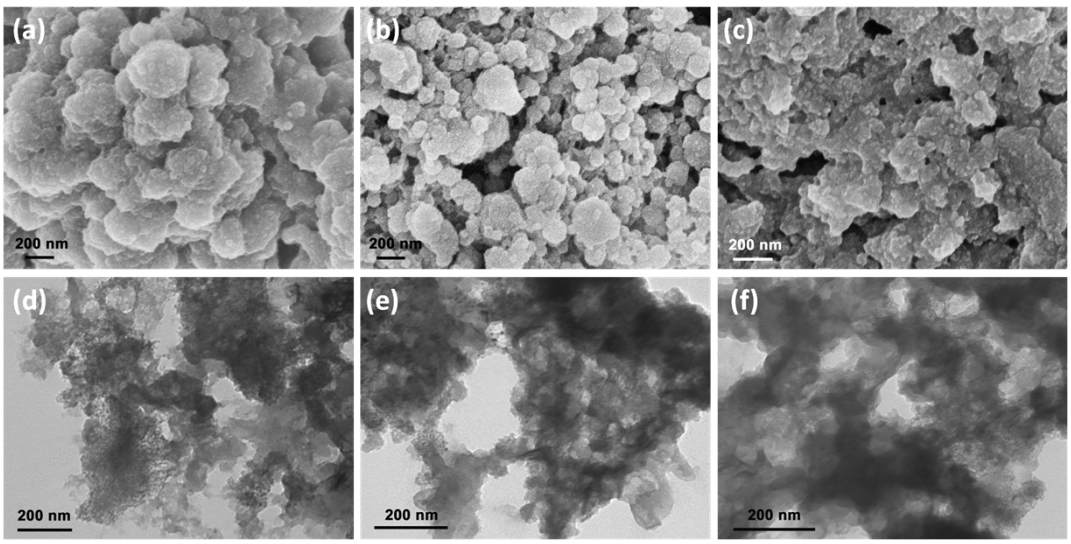

Figure S14. (a−c) SEM (d−f) TEM images of CBGe-460-6 sample after 200, 500, and 1000 cycles, respectively.