## Electronic Supplementary Information(EIS)

## Synthesis of hollow GeO<sub>2</sub> nanostructures, transformation into Ge@C, and lithium storage properties

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Fig. S1. FE-SEM images of GeO<sub>2</sub> precursors synthesized at different reaction times: (a, b) 5, (c, d) 30, (e, f) 50, (g, h) 90, (i, j) 120 min.



Fig. S2. X-ray diffraction patterns of GeO<sub>2</sub> precursors at different reaction times.







Fig. S3. EDS spectra of  $GeO_2$  precursors at different reaction times with corresponding FE-SEM images.



Fig. S4. X-ray diffraction patterns of Ge@C ellipsoids (Ge@C-1, Ge@C-2, Ge@C-3).







(b)

Fig. S5. Raman spectra of (a)  $\text{GeO}_2$  precursors and (b) Ge@C.



Fig. S6. FTIR spectra of GeO<sub>2</sub> precursors and Ge@C.

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Fig. S7. TGA curves of Ge@C and pure Ge.



Fig. S8. Nitrogen adsorption-desorption isotherms and Barrett-Joyner-Hallenda (BJH) pore size distribution plots (inset) of hollow Ge@C ellipsoids.



Fig. S9. FE-SEM images of (a, d) Ge@C-1, (b, e) Ge@C-2, and (c, f) Ge@C-3 samples at different resolutions.



Fig. S10. FE-SEM image of pure Ge after reduction in  $H_2/Ar$ .



Fig. S11. Voltage profiles of (a) Ge@C-1 and (b) Ge@C-3 at 2<sup>nd</sup>, 10<sup>th</sup>, and 50<sup>th</sup> cycles at 0.2 C in the range of 0.01 V to 1.5 V.



Fig. S12. Cyclic voltammograms for Ge@C-1 sample for the first 5 cycles at the scan rate of 0.1 mV/s from 0.01 V to 1.5 V.



Fig. S13. Voltage profiles of (a) Ge@C-1 and (b) Ge@C-3 at different rates, (c) cycling performance of Ge@C-1 and Ge@C-3 at the 0.1 C/0.1 C charging/discharging rate for the first 5 cycles, then at the 5 C/0.5 C charging/discharging rate for the rest of the cycling.



Fig. S14. Rate performance of Ge@C-4 at increasing rates from 1 to 25 C, with the discharging rate fixed at 0.5 C.

The Ge@C-4 sample was synthesized under the same conditions as Ge@C-3, except for the reaction temperature of 750 °C. From Fig. S14, we can observe that at low rates, the capacity retention is increased compared to Ge@C-3, but when the rate is increased to 20 C and 25 C, the capacity is still lower than that of Ge@C-1. This demonstrates that the enhanced electrochemical performance of Ge as anode material for LIBs is not only attributable to the amount of carbon shell, but also related to the hollow and porous structure.