

Electronic Supplementary Information

Rational synthesis of carbon-coated hollow Ge nanocrystals with enhanced lithium-storage properties

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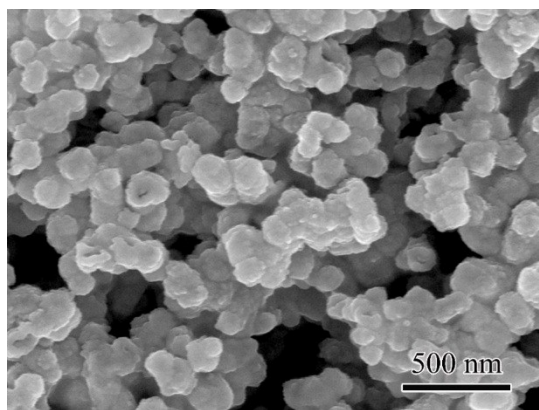


Fig. S1 FE-SEM image of solid Ge particles prepared at the absence of THF.

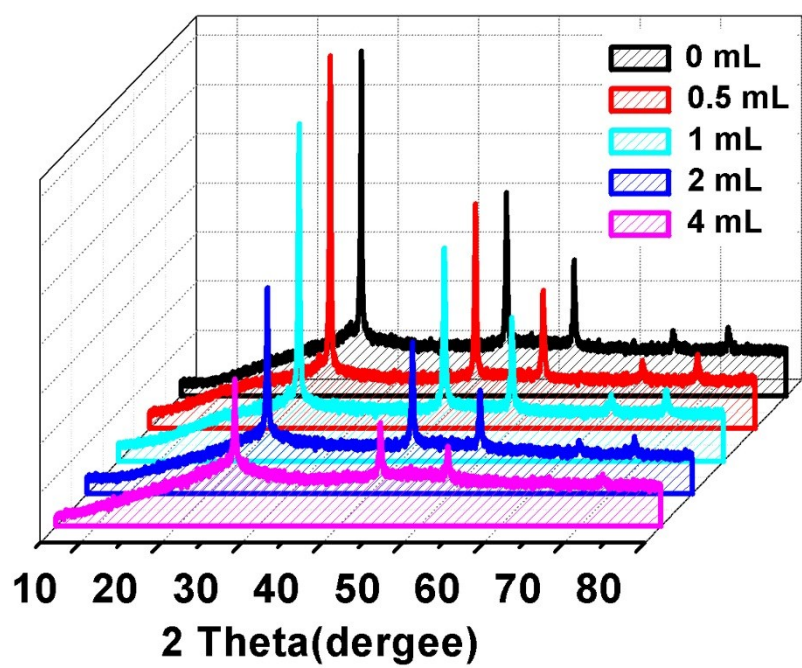


Fig. S2 XRD patterns for the Ge products prepared in the presence of different amounts of THF (0, 0.5, 1, 2, and 4 mL).

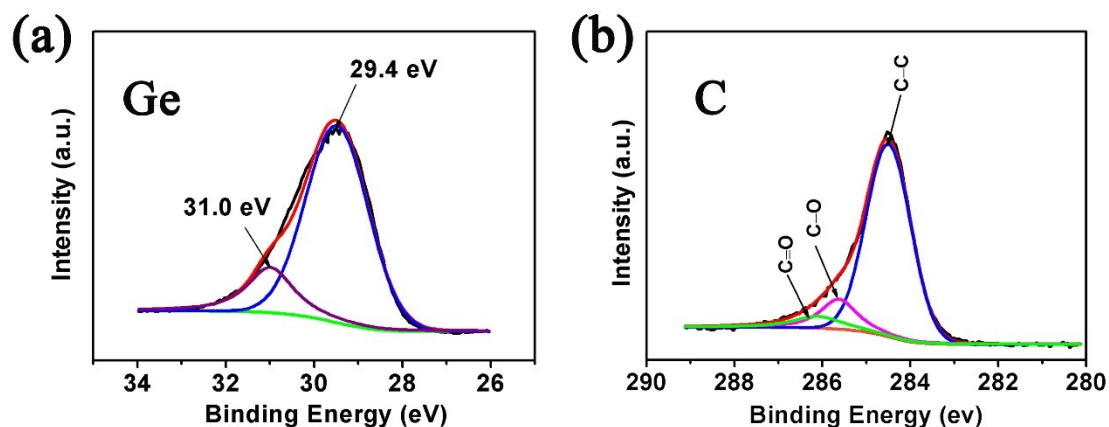


Fig. S3 XPS spectra of the hollow Ge@C hybrid: (a) high-resolution spectrum of Ge 3d and (b) C 1s. The binding energy at 29.4 eV is assigned to Ge (0) and a trace of Ge (II) at 31.0 eV appears. The Ge (IV) signal at 32.6 eV was not found.^[1] The existence of Ge (II) may be resulted from the partially oxidized Ge in air. Both the Ge 3d and C 1s XPS spectra suggest that the Ge@C product is mainly made of Ge⁰ and carbon with a negligible content of Ge (II).

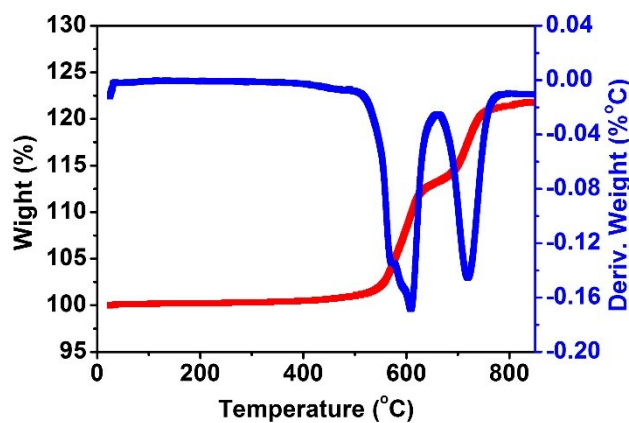


Fig. S4 TG curves of the hollow Ge@C composite obtained at a heating rate of 5 °C min⁻¹. The composite contains 84.5 wt% Ge and 15.5 wt% C, based on the weight loss upon carbon combustion and complete oxidation of Ge into GeO₂ in air.

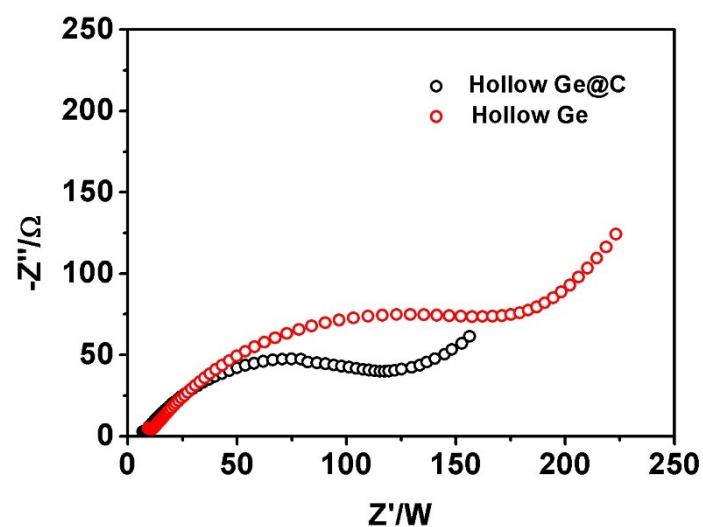


Fig. S5 Electrochemical impedance spectra of the hollow Ge and hollow Ge@C electrodes.

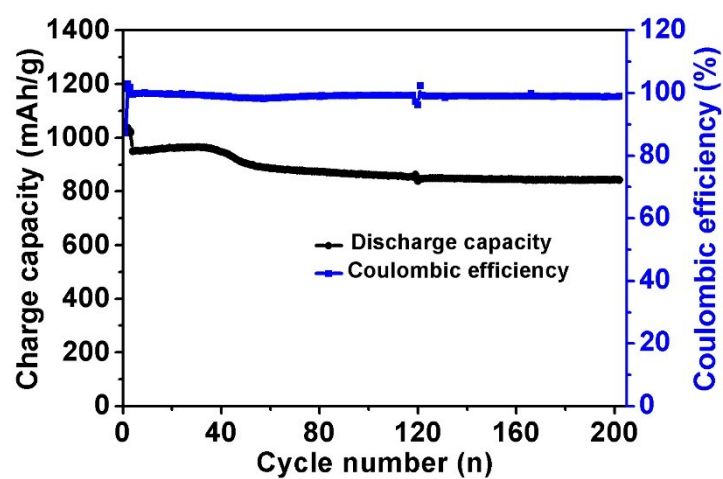


Fig. S6 Cycling performance and coulombic efficiency of the hollow Ge@C electrode at 500 mA g^{-1} in a potential window of 0.01–3.0 V.

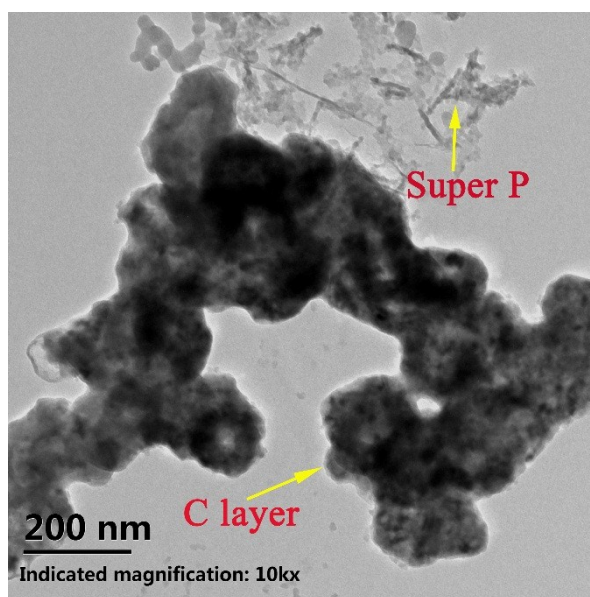


Fig. S7 TEM image of hollow Ge@C electrode after 200 charge/discharge cycles at 500 mA g⁻¹.

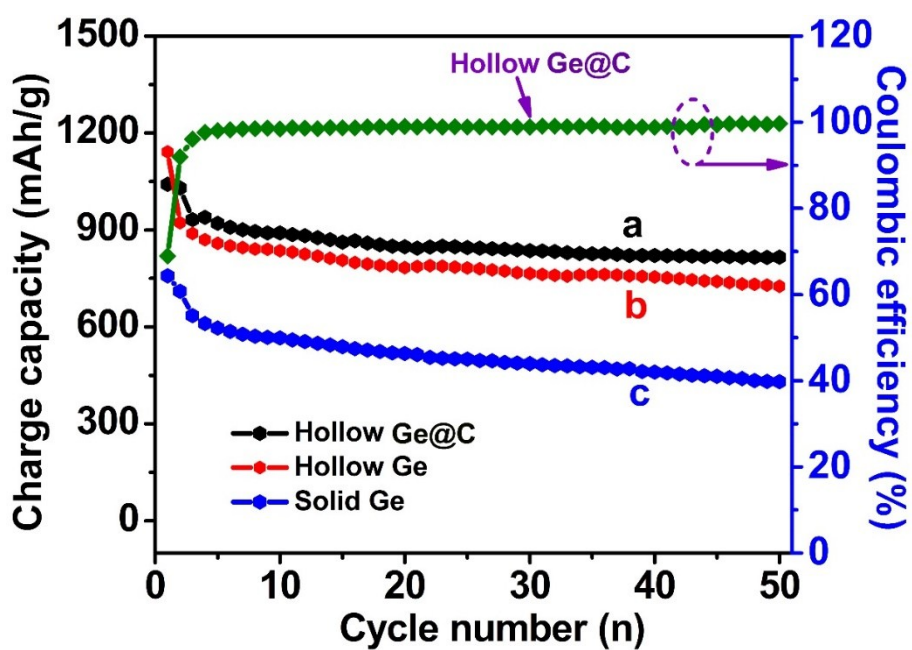


Fig. S8 Discharge/charge capacity and Coulombic efficiency versus cycle number for half-cells of made of solid Ge, hollow Ge nanospheres, and hollow Ge@C nanospheres at a current density of 1000 mA g⁻¹.

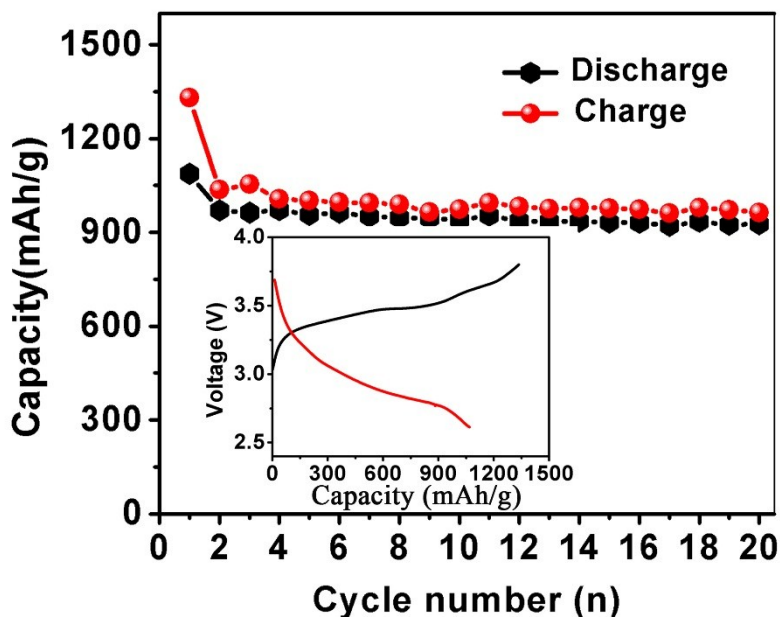


Fig. S9. Electrochemical performance of the CR-2032 coin-type full cell containing an anode made of hollow Ge@C nanospheres and a cathode made of LiCoO₂. C-rate: 100 mA g⁻¹; Inset: the first charge/discharge curve. Before assembling the Li-ion cell, the Ge@C electrode was pre-lithiated according to the previous literature to eliminate the irreversible capacity loss during the first formation cycle.^[2,3] The specific capacity of the anode/cathode was controlled at about 1:1.2 according to the mass of both active materials. To evaluate the performance of the anode material, the full cells here are anode-limited and the specific capacity was evaluated based on the anode.

References:

- [1] M. M. Bentlohner, M. Waibel, P. Zeller, K. Sarkar, P. M. Buschbaum, D. F. Rohlffing, T. F. Fässler, *Angew. Chem. Int. Ed.* 2014, **126**, 9187; *Angew. Chem.* 2014, **53**, 9041.
- [2] D. T. Ngo, H. T. T. Le, C. Kim, J. Y. Lee, J. G. Fisher, I.D. Kim, C. J. Park, *Energy Environ. Sci.*, 2015, **8**, 3577.
- [3] C. Chae, H. J. Noh, J. K. Lee, B. Scrosati, Y. K. Sun, *Adv. Funct. Mater.* 2014, **24**, 3036.