

Supporting Information

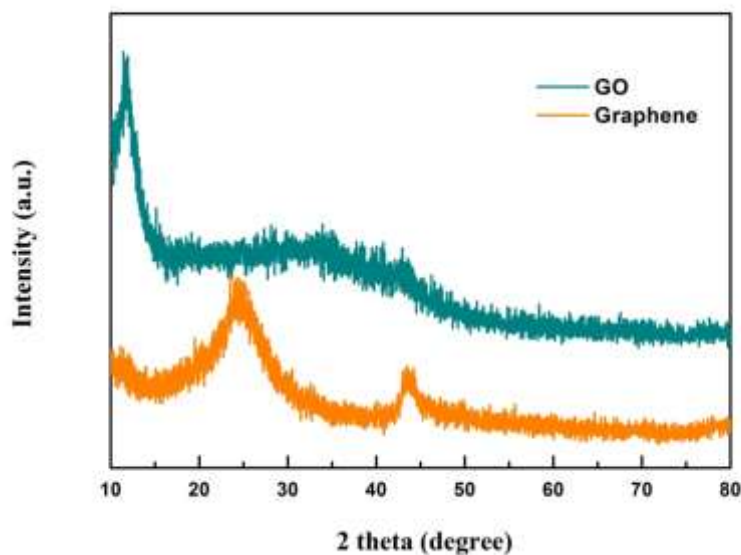


Figure S1. Powder X-ray diffraction patterns of graphene oxide and graphene.

A pure graphene sample was also prepared for comparison, and the experimental steps were the same as for the synthesis of GeO₂/graphene composite, but without the GeCl₄/ethanol solution. The characteristic (002) peak shifted from 11.4° for GO to 24.1° for graphene, which indicates that the GO can be reduced during the in situ solvothermal reaction. The interplanar spacing corresponding to the (002) peak of graphene (0.38 nm) is larger than that of standard graphite (0.34 nm),⁴⁴ giving evidence that oxygen-containing functional groups have been generated, providing additional intercalation sites for accommodation of lithium ions and therefore promoting enhanced electrochemical performance.^{45, 46}

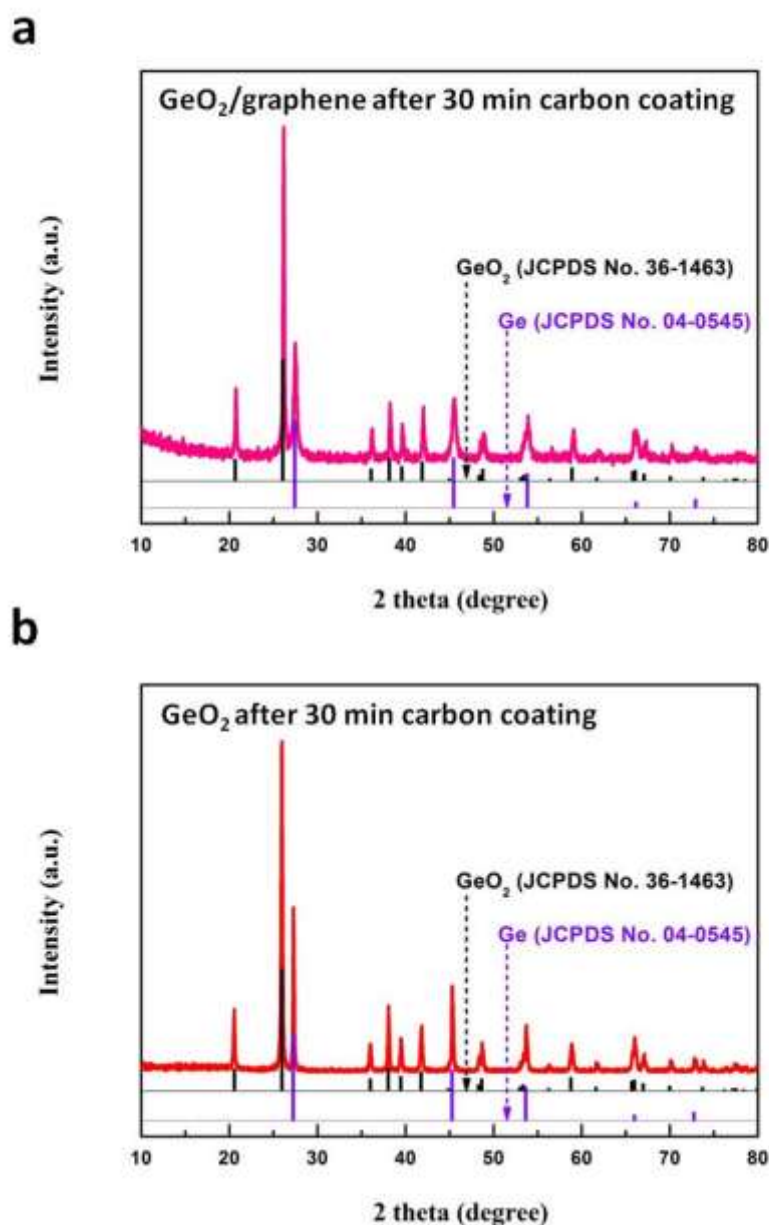


Figure S2. Powder X-ray diffraction patterns of (a) GeO₂/graphene and (b) GeO₂ after 30 minute carbon coating.

In order to confirm the results of the thermal carbon decomposition, XRD testing was conducted on the precursors of the carbon-coated GeO₂/graphene and GeO₂, which were prepared by the same experimental steps as for C/Ge/graphene and Ge/C, but with no reduction treatment by hydrogen gas. The results showed that both precursors

were mixtures of germanium and GeO₂, indicating that GeO₂ was partially reduced by the acetylene gas in the carbonization process.

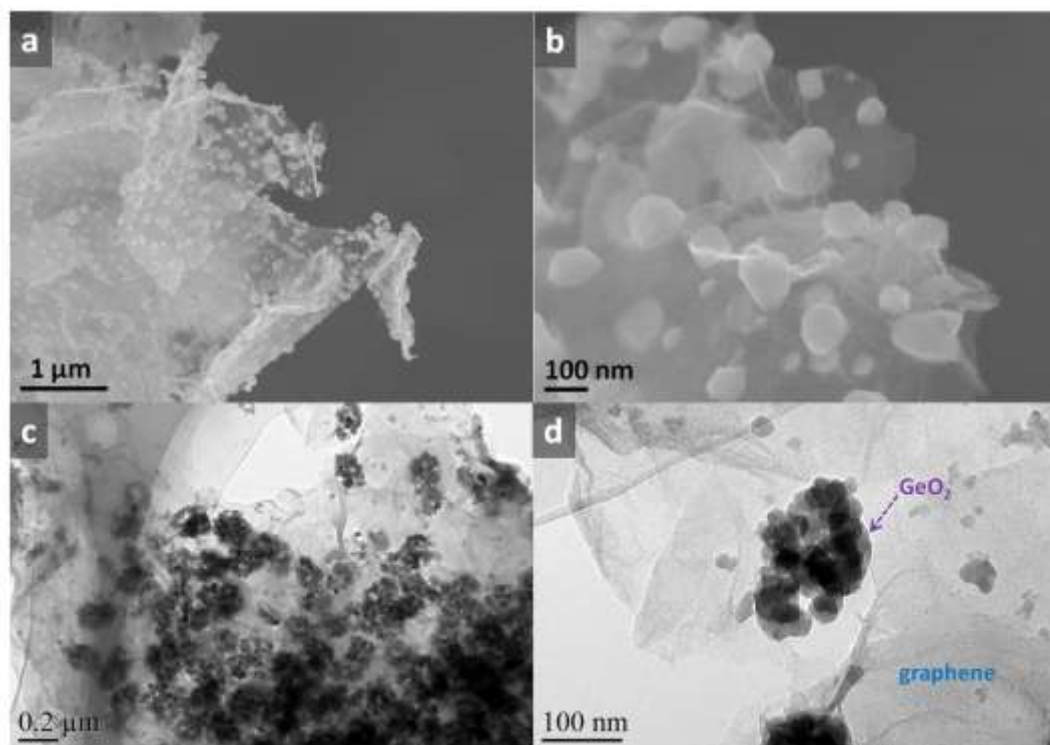


Figure S3. (a) and (b) SEM images, and (c) and (d) TEM images of GeO₂/graphene composite. The purple arrow in (d) indicates the GeO₂ nanoparticles.

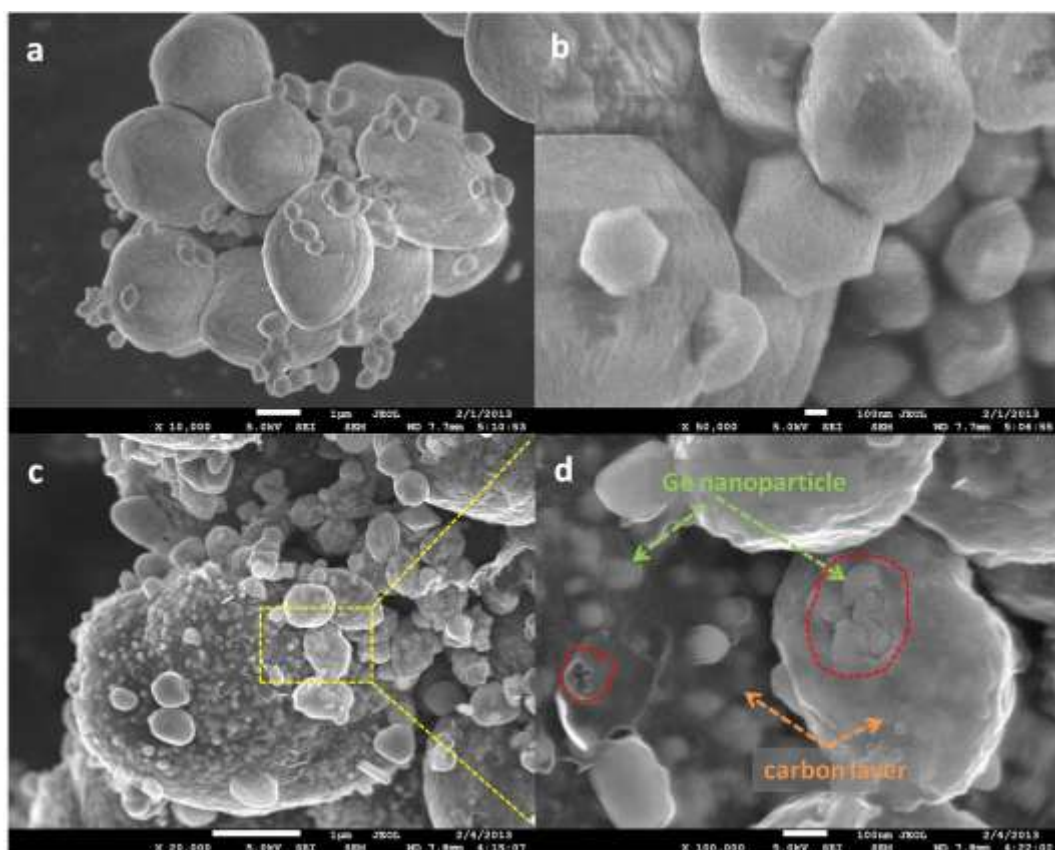


Figure S4. SEM images of (a) and (b) GeO₂; (c) and (d) Ge/C. (d) is an enlarged image of the indicated area of (c). The green and orange arrows, and the red circles in (d) indicate the germanium nanoparticles, the carbon layers, and the holes in the carbon layer, respectively.

Without the participation of graphene, GeO₂ particles are prone to further grow and agglomerate during the synthesis process. From the SEM images, it can be found that the obtained GeO₂ sample has bigger hexagonal-like particles about 2 μm in size, with several small GeO₂ particles (300-500 nm in size) attached to their surfaces. The particles are significantly bigger than those in the GeO₂/graphene sample (where the particle size is 20-30 nm). The globular structure of the particles is maintained after the carbonization and reduction treatments, as is shown in Figure S4(c) and (d). Note that there are several holes in the carbon layer, however, which stem from the

relatively large amount of oxygen released from the agglomerated GeO_2 precursor during the reduction treatment. Under the carbon layer, the germanium nanoparticles are 70-100 nm in size, which is much bigger than for the germanium particles in the C/Ge/graphene composite.

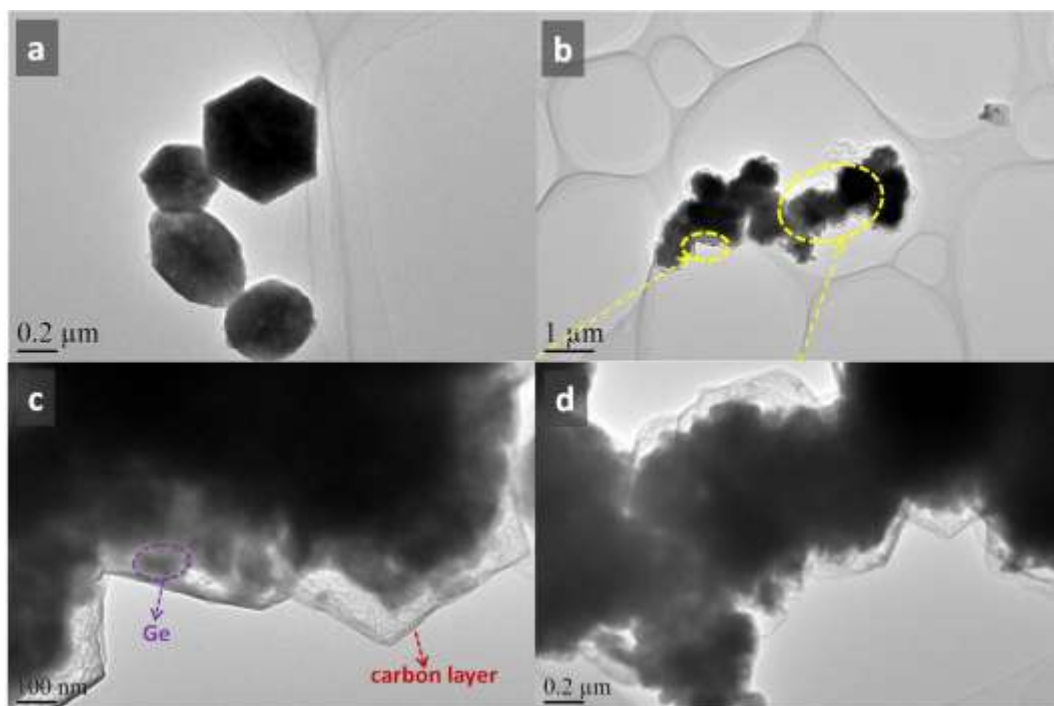


Figure S5. TEM images of (a) GeO₂; (b), (c), and (d) Ge/C. (c) and (d) are enlarged images of the indicated areas of (b). The purple and red arrows in (c) indicate the germanium nanoparticles and the carbon layer, respectively.

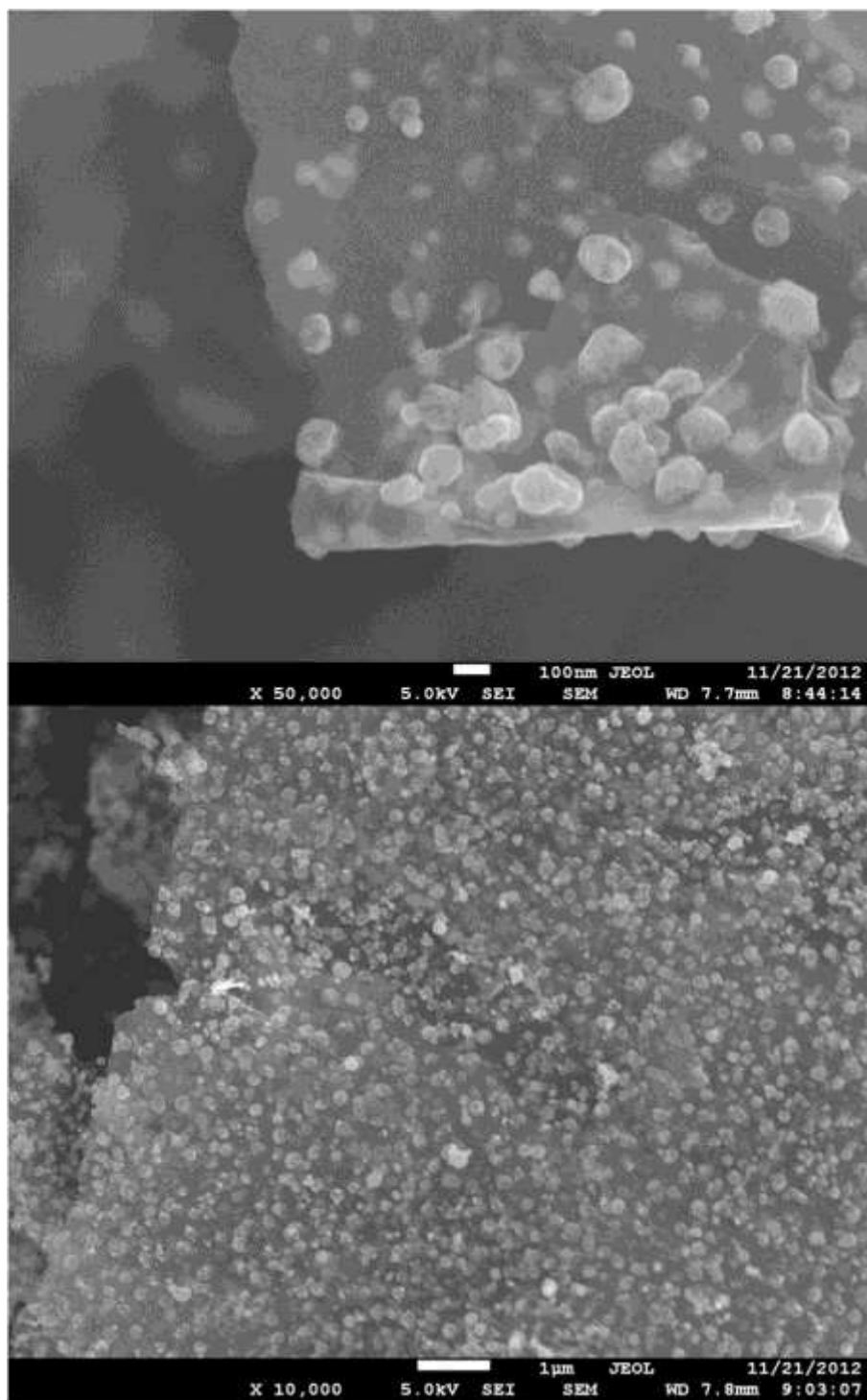


Figure S6. SEM images at different magnifications of C/Ge/graphene composite.

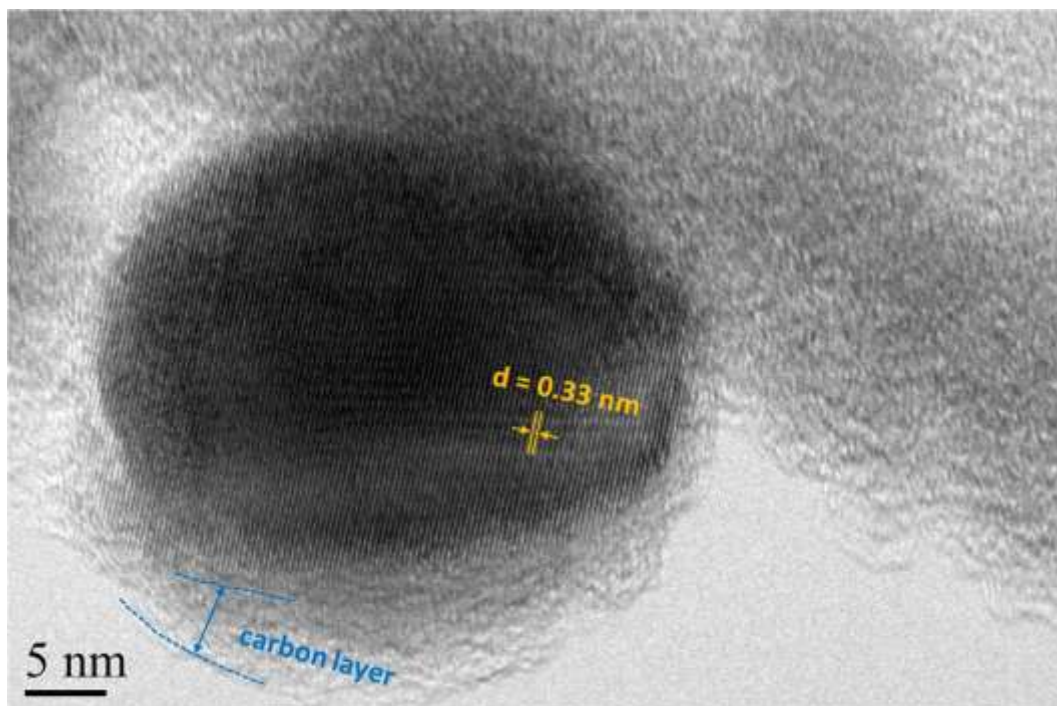


Figure S7. High-resolution TEM image of C/Ge/graphene composite, indicating the strongly crystalline nature of a germanium nanoparticle attached on a graphene sheet. The carbon layer around the germanium particle can be clearly observed to be 3-5 nm in thickness.

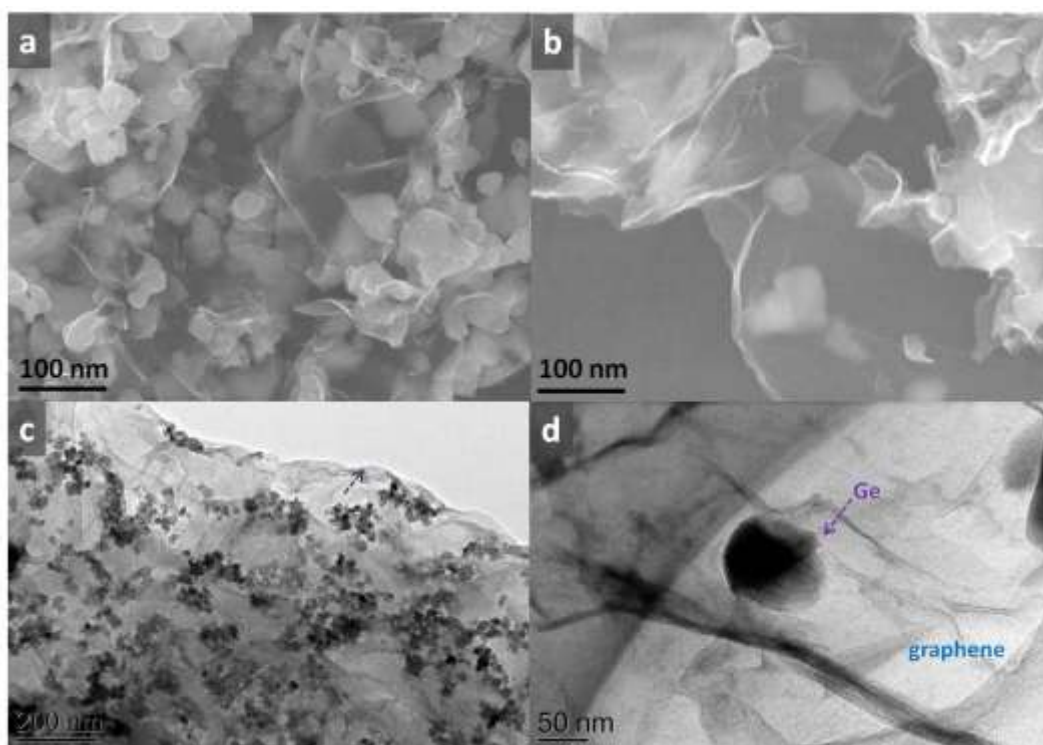


Figure S8. (a) and (b) SEM images, (c) and (d) TEM images of Ge/graphene composite. The purple arrow in (d) indicates the Ge nanoparticles.

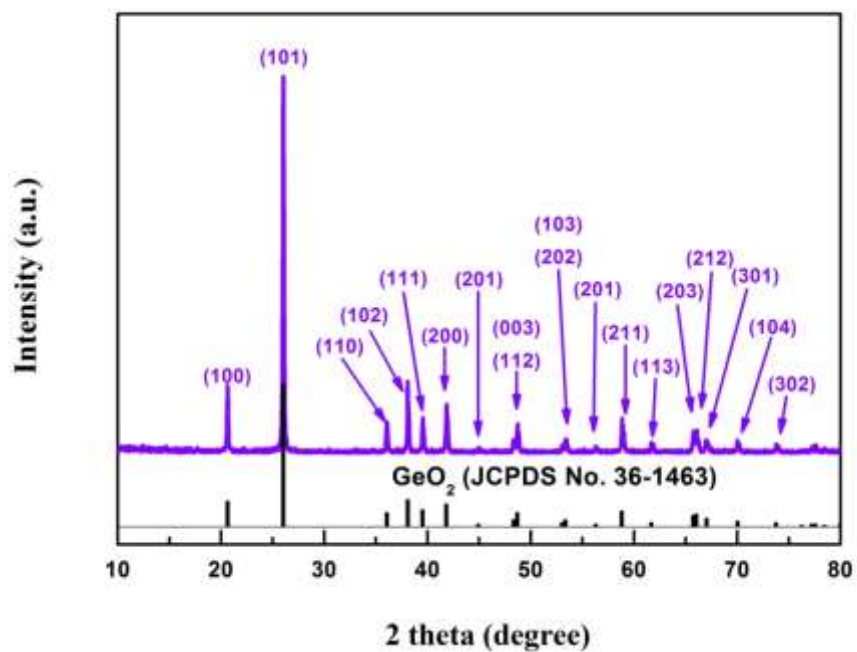


Figure S9. Powder X-ray diffraction pattern of GeO₂ precursor.

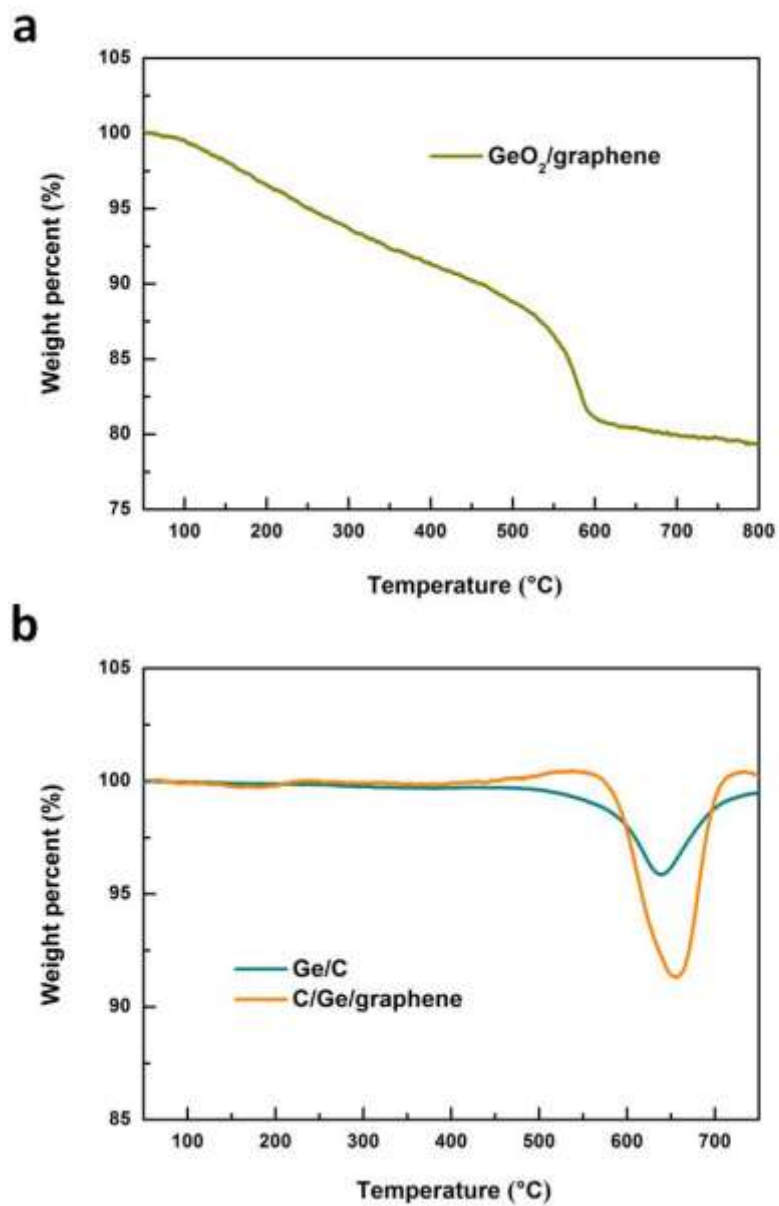


Figure S10. TGA curves of (a) GeO₂/graphene composite, (b) C/Ge/graphene and Ge/C composites.

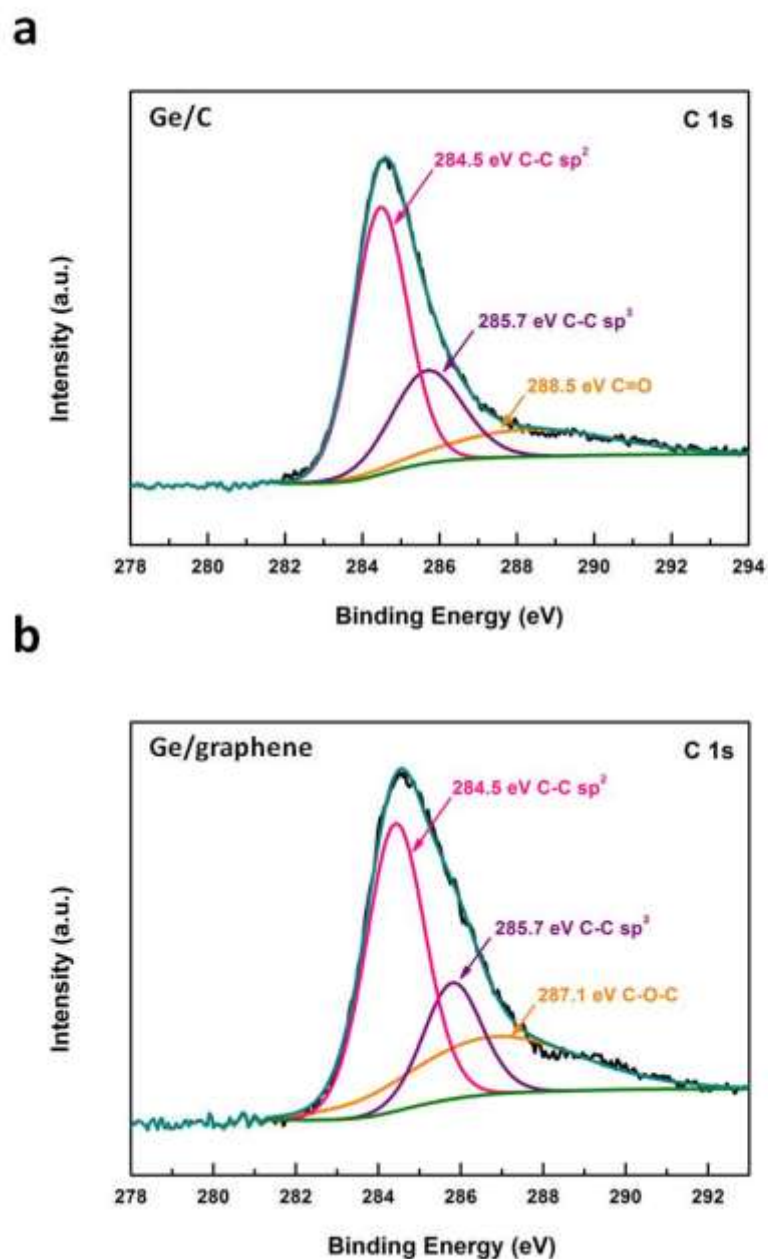


Figure S11. XPS spectra with curve fittings of C 1s spectra of (a) Ge/C and (b) Ge/graphene composites.

The C 1s XPS spectra of both Ge/C and Ge/graphene can be deconvoluted into three peaks. The main peak at 284.5 eV can be assigned to sp² hybridized C atoms in the graphene, while the higher energy peaks arise from sp³ hybridized C at 285.7 eV and C=O at 288.5 eV for Ge/C, and C-O-C at 287.1 eV for Ge/graphene.^{32, 37} The ratio of

germanium to carbon elements is 2.98 and 13.71 mol% for Ge/C and Ge/graphene, respectively. In addition, the ratio of oxidized carbon to non-oxygenated carbon is calculated to be 12.21 mol % and 33.39 mol % for Ge/C and Ge/graphene, respectively.

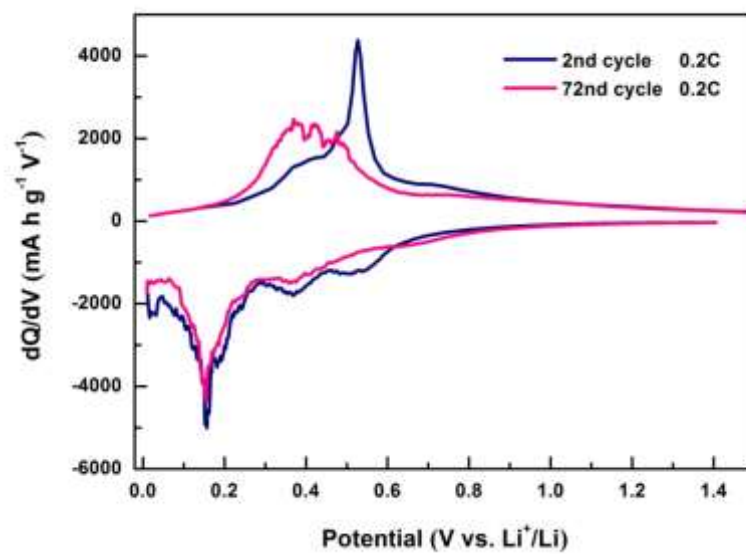


Figure S12. Differential capacity plots of C/Ge/graphene composite at the 2nd and 72nd cycle at the 0.2 C rate.

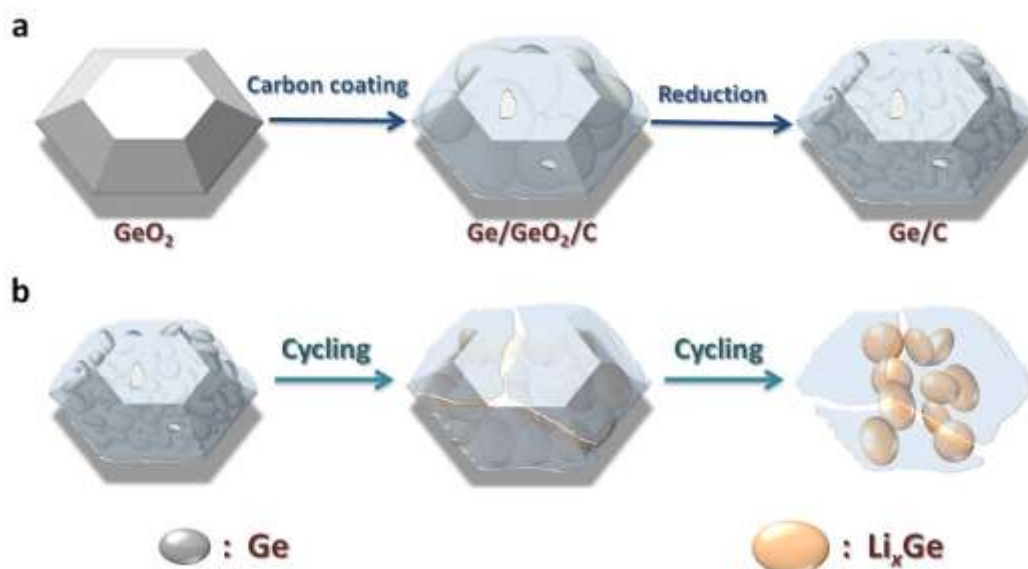


Figure S13. Schematic illustration of (a) the synthesis process for Ge/C composite, (b) the morphology of Ge/C after several cycles of lithiation and delithiation.

After carbonization and reduction treatments of GeO_2 , germanium precursor nanoparticles were covered by a carbon layer with several holes in it (Figure S4). They also aggregated away from the inner surface of the carbon shell (Figure S5), forming an extra space between the germanium nanoparticles and the carbon shell for absorbing volume expansion during lithiation. This incomplete carbon layer is not inherently robust and flexible enough, however, to accommodate the large volume changes in the germanium nanoparticles during the alloying/de-alloying process, especially for the inner nanoparticles, so that it bursts into fragmented carbon pieces. Therefore, the germanium or Li_xGe nanoparticles that are formed lose their attachment to each other, and thus are prone to peel off from the broken parts of the carbon layer as lithiation/de-lithiation processes continue, resulting in inferior electrochemical performance.

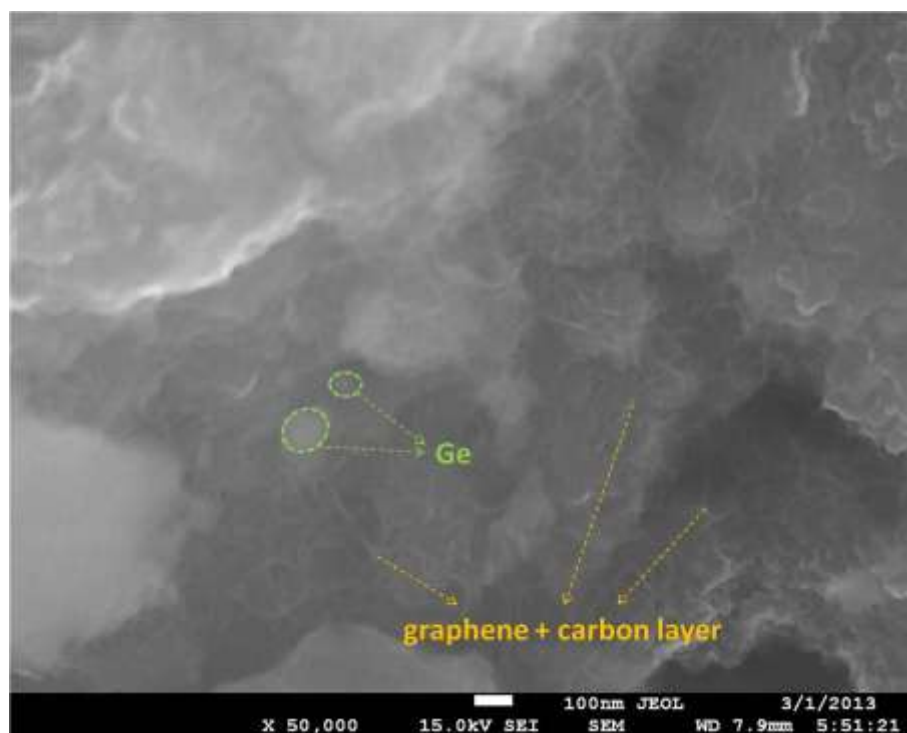


Figure S14. SEM images of C/Ge/graphene electrode after 160 charge/discharge cycles. The green and orange arrows indicate the germanium nanoparticles and carbon layer, respectively.

After charging and discharging for 160 cycles, it can be found that there is a wrinkled carbon shell (including graphene and carbon layer) on the surface of germanium nanoparticles. The highly flexible graphene and uniformly coated carbon layer are robust enough to not only accommodate the volume change during the lithium intercalation and deintercalation, but also maintain the structural integrity of the electrode.