## **Experimental section**

## 1.1 Synthesis of the Porous Amorphous Ge/C Composites

In a typical synthetic process,  $3g \text{ GeO}_2$  was dispersed into 9g oleic acid, followed by adding ethylenediamine (en) drop by drop until the GeO<sub>2</sub> was dissolved completely. Then, the mixture was heated to 60 °C for 12 hrs for removing the en. After that, the porous amorphous Ge/C composites were obtained through annealing the above-mentioned resulting mixture from room temperature to 650 °C at a rate of 3 °C/min and then held at 650 °C for 2h in 5%H<sub>2</sub>/Ar.

## 1.2 Characterization

The microstructure of the as-prepared samples was characterized by X-ray diffraction (XRD; GBC MMA diffractometer) with Cu K $\alpha$  radiation at a scanning rate of 2°/min. Thermogravimetric analysis (TGA) of the as-prepared amorphous porous Ge/C composites was carried out with a TGA/DSC1 type instrument (METTLER TOLEDO, Switzerland) at a heating rate of 5 °C/min from 25 to 800 °C in air. The morphology of the as-prepared amorphous porous Ge/C composites was evaluated using a JEOL 7500FA field emission scanning electron microscope (FE-SEM, JEOL, Tokyo, Japan) and a JEOL JEM-ARM200F transmission electron microscope (STEM, JEOL, Tokyo, Japan). Energy dispersive X-ray spectroscopy (EDX, JEOL 7500FA) was used to confirm the C content. X-Ray photoelectron spectroscopy (XPS) experiments were carried out on a VG Scientific ESCALAB 220IXL instrument using aluminium K $\alpha$  X-ray radiation during XPS analysis.

## **1.3 Electrochemical Measurements**

The working electrodes were prepared by mixing 80 wt% as-prepared porous Ge/C composites with 10 wt% carbon amorphous black and 10 wt% carboxymethylcellulose (CMC) binder in distilled water to form homogeneous slurry, which was uniformly pasted onto copper foil. The prepared working electrodes were dried in a vacuum oven at 80 °C over 12 h and were then ready for assembly in test cells after pressing. Electrochemical cells (CR2032 coin type) using the active materials (about 1.5 mg per sheet) as working electrode, Li foil as the counter electrode and reference electrode, a microporous polypropylene film as the separator, and 1 M LiPF<sub>6</sub> in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte were assembled in an Ar-filled glove box (H<sub>2</sub>O,  $O_2 < 0.1$  ppm, Mbraun, Unilab, USA). The cells were galvanostatically charged and discharged over a voltage range of 0.01-3 V versus Li/Li<sup>+</sup> at different constant current densities based on the weight of the samples on a Land CT2001A cycler. Cyclic voltammetry (CV) was performed on an Ametek PARSTAT®2273 electrochemistry workstation.



Fig. S1 TGA curve of the porous amorphous Ge/C composites.

The Ge content of Ge/C composites is calculated from the weight change from the increase from Ge to  $\text{GeO}_2$  due to the oxidation of Ge before 250 °C, and then the carbon was lost due to the oxidization of carbon into carbon dioxide. So TGA in air, it involves the oxidation of Ge and carbon, respectively.



**Fig. S2** N<sub>2</sub>-adsorption/desorption isotherm and porous size distribution curves of the porous amorphous Ge/C composites.



Fig. S3 SEM image of commercial GeO<sub>2</sub> sample.



Fig. S4 Coulombic efficiency of the porous amorphous Ge/C composites at various current densities.