Experimental

*Hydrothermal of urchin-like Ca$_2$Ge$_7$O$_{16}$ hollow spheres*  In a typical synthesis, 0.35 mmol GeO$_2$, 0.1 mmol CaCl$_2$ and 1 g N-methyl urea was dispersed to 35 ml distilled water, then stirring for 30 min. The mixture was then transferred to an autoclave of 50 mL which was heated to 240 °C for 12 h. The white precipitation was centrifuged, filtered, and rinsed with alcohol and distilled water for three times. Finally, the product was dried at 80 °C for 24 h in oven.

*Characterization* The X-ray diffraction (XRD) patterns of the products were recorded with Rigaku D/max Diffraction System using a Cu Kα source (λ = 0.15406 nm). The scanning electron microscopy (SEM) images were taken with a JEOLJSM-6700F field emission scanning electron microscope (15 kV). The transmission electron microscopy (HR-TEM) images were taken on a JEOL 2010 high-resolution transmission electron microscope performed at 200 kV. The specimen of HR-TEM measurement was prepared via spreading a droplet of ethanol suspension onto a copper grid, coated with a thin layer of amorphous carbon film, and allowed to dry in air.

*Electrochemical Test* The electrochemical Li intercalation performance was investigated in Li test cells. Typically, the electrode consisted of 80 wt% active material, 10 wt% conductivity agents (acetylene black), and 10 wt% binder (carboxyl methyl cellulose). After ethanol was evaporated, the mixture was rolled into a sheet and cut into circular strips of 12 mm diameter. The strips were then dried at 120 °C.
for 10 h in air. Lithium metal was used as the counter and reference electrodes. The electrolyte consisted of a solution of 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1, in weight percent). The above three parts were assembled into test cells in an argon-filled dry glovebox, and then the cells were measured at different current densities within a voltage range of 0.01-3.0 V with a Land CT 2001 battery tester.
Fig. S1 HRTEM image of UHS-1.
Fig. S2 SEM images of UHS-2.
Fig. S3 SEM images of UHS-1 at different times: (a) 10 min, (b) 20 min, and (c) 30 min.
Fig. S4 (a-c) SEM images of samples synthesized under different conditions.
Fig. S5 (a and b) SEM images of the sample synthesized with urea.
Fig. S6 The cycle performances of UHS-1 and UHS-2 after calcining at a current density of 1 A/g.
Fig. S7  The thermogravimetric (TG) analysis of UHS-1.
Fig. S8 SEM images of the Ca$_2$Ge$_2$O$_{16}$ anodes. (a) UHS-1 anode before cycling, (b) UHS-2 anode before cycling, (c) UHS-1 anode after 200 cycles, (d) UHS-2 anode after 200 cycles.