

Experimental

Hydrothermal of urchin-like $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ 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 $\text{Cu K}\alpha$ source ($\lambda = 0.15406$ 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.

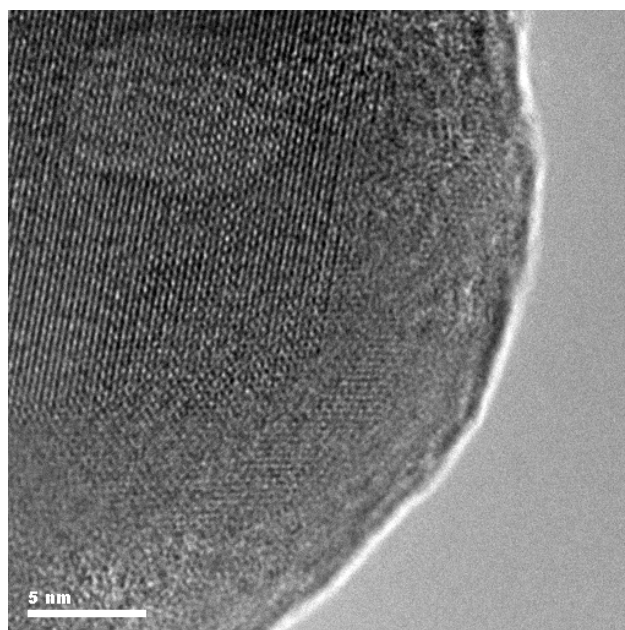


Fig. S1 HRTEM image of UHS-1.

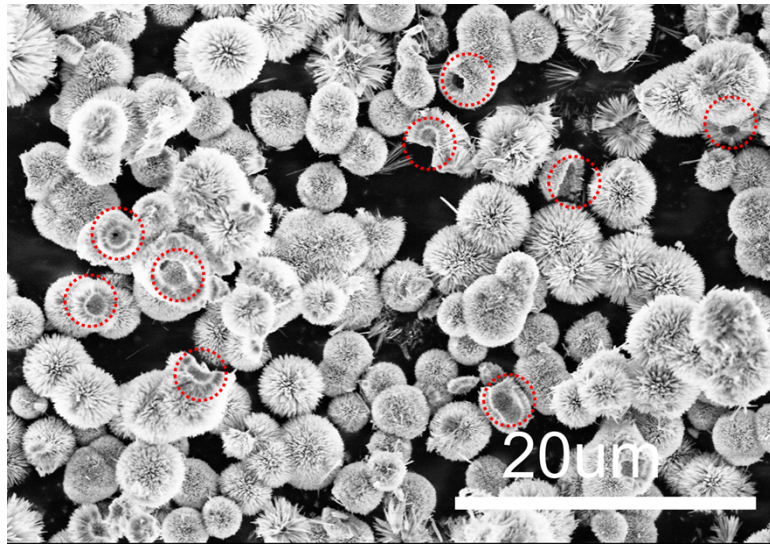


Fig. S2 SEM images of UHS-2.

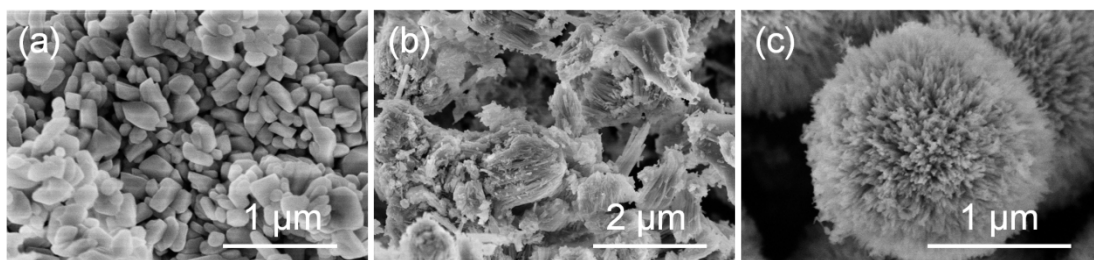


Fig. S3 SEM images of UHS-1 at different times: (a) 10 min, (b) 20 min, and (c) 30 min.

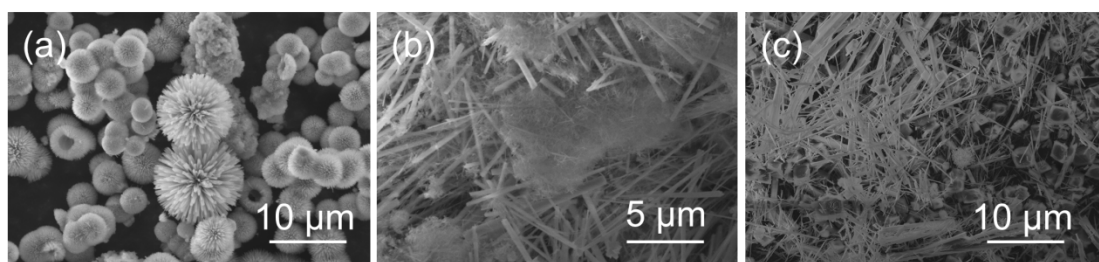


Fig. S4 (a-c) SEM images of samples synthesized under different conditions.

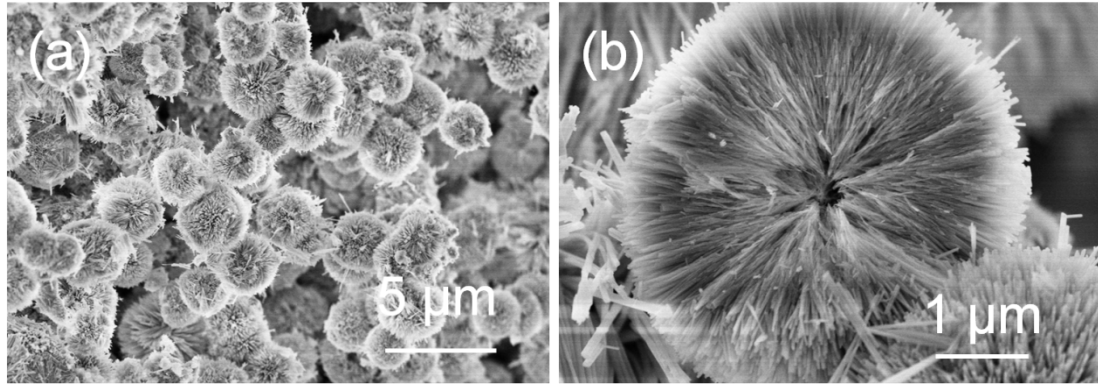


Fig. S5 (a and b) SEM images of the sample synthesized with urea.

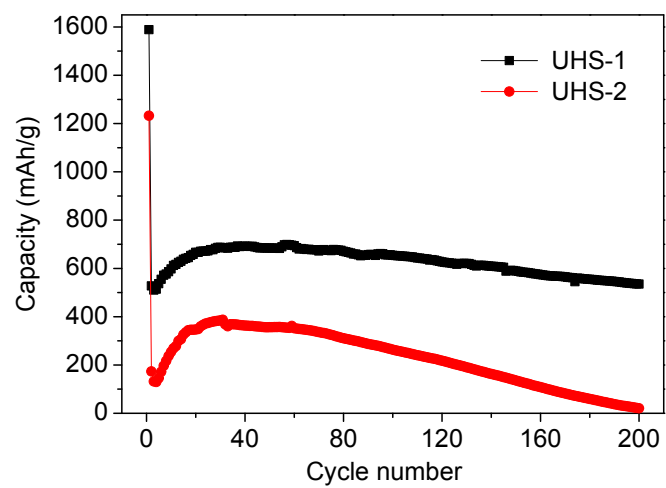


Fig. S6 The cycle performances of UHS-1 and UHS-2 after calcining at a current density of 1 A/g.

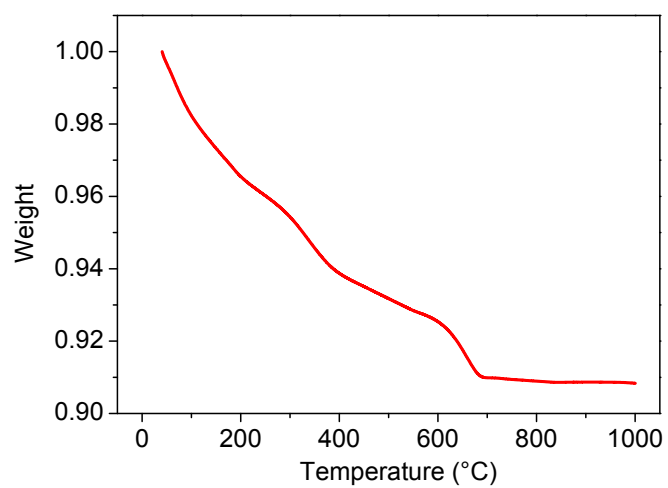


Fig. S7 The thermogravimetric (TG) analysis of UHS-1.

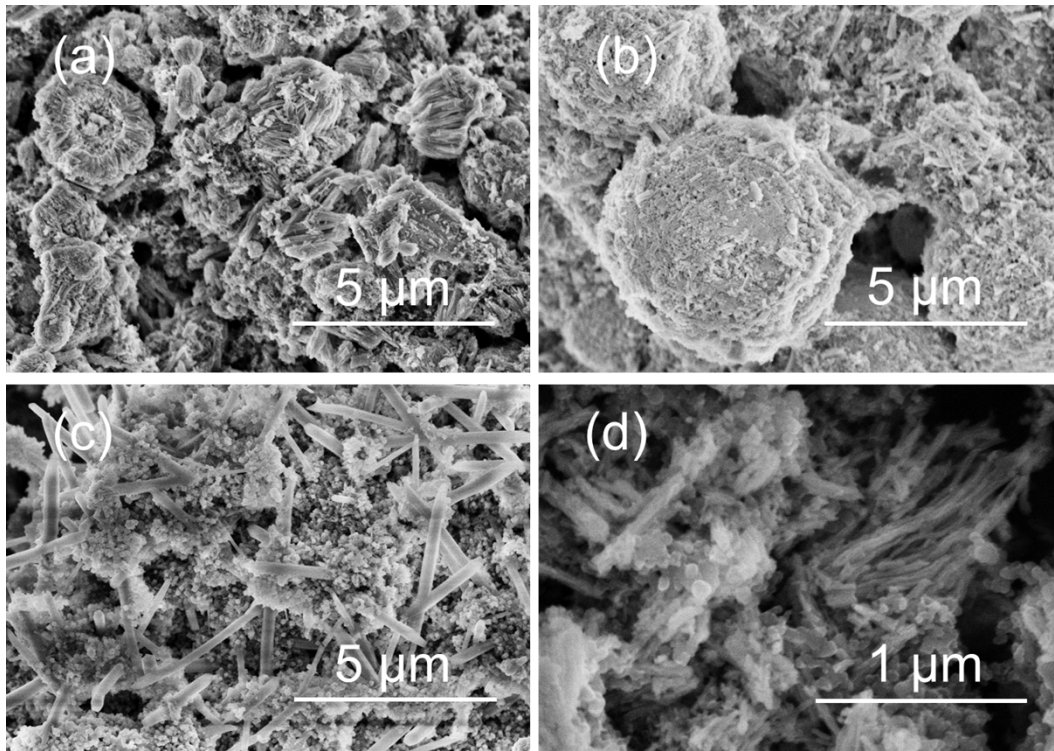


Fig. S8 SEM images of the $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ anodes, (a) UHS-1 anode before cycling, (b) UHS-2 anode before cycling, (c) UHS-1 anode after 200 cycles, (d) UHS-2 anode after 200 cycles.