

Experimental Section

Synthesis: All the chemicals were of analytical grade and used without further purification. In a typical procedure to synthesize the urchin-like hollow $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ nanospheres, equal volumes of 4 mol/L aqueous solution of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 6 mol/L aqueous solution of NH_4HCO_3 were mixed together and stirred at room temperature for 10 h. The resulting product was then collected by filtration, washed several times with distilled water and absolute ethanol, and dried at 60 °C in air for 4 h. After annealing the urchin-like hollow $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ spheres in air at 300 °C for 4 h, Co_3O_4 hollow spheres could be obtained.

Characterization: The samples were characterized with a Phillips X-ray diffractometer with Cu $K\alpha$ radiation, Hitachi S-5500 STEM, and JEOL 2010 TEM operating at 300 kV. The specimen for TEM characterization was prepared by spreading a droplet of ethanol suspension containing the sample onto a copper grid coated with a thin layer of amorphous carbon film and allowing it to dry in air. Thermogravimetric analysis (TGA) was carried out with a Perkin Elmer TGA7 in flowing air.

Electrochemical measurements: The electrodes for the electrochemical evaluation were prepared by mixing 75 wt. % active material (Co_3O_4) powder, 10 wt. % carbon black (Super P), and 15 wt. % poly(vinylidene fluoride) (PVDF) in N-methylpyrrolidone (NMP) to form a slurry. The slurry was spread onto a copper foil and dried at 120 °C for 2 h under vacuum. The electrodes were then assembled into CR2032 coin cells in an Ar-filled glove box with Celgard polypropylene separator, lithium foil as the counter electrode, and 1 M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by v/v) electrolyte. The discharge-charge experiments were performed galvanostatically at a constant current density of 89 mA/g of active material within the voltage range of 0.01 – 3.0 V vs Li/Li^+ .

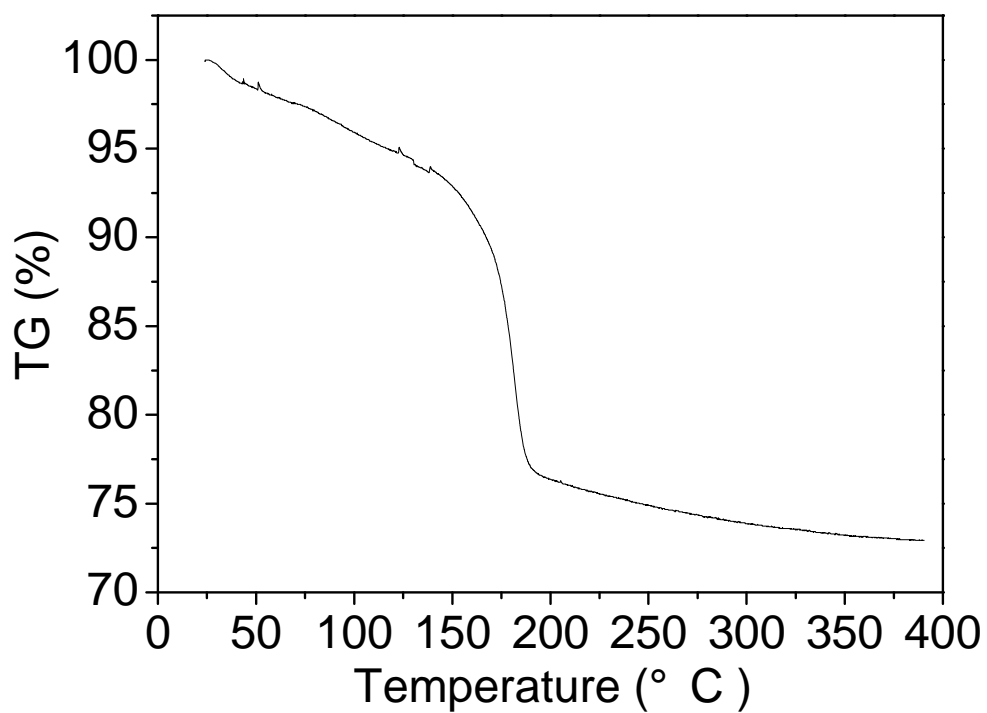


Fig. S1 TGA curve of the urchin-like hollow $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ nanospheres.

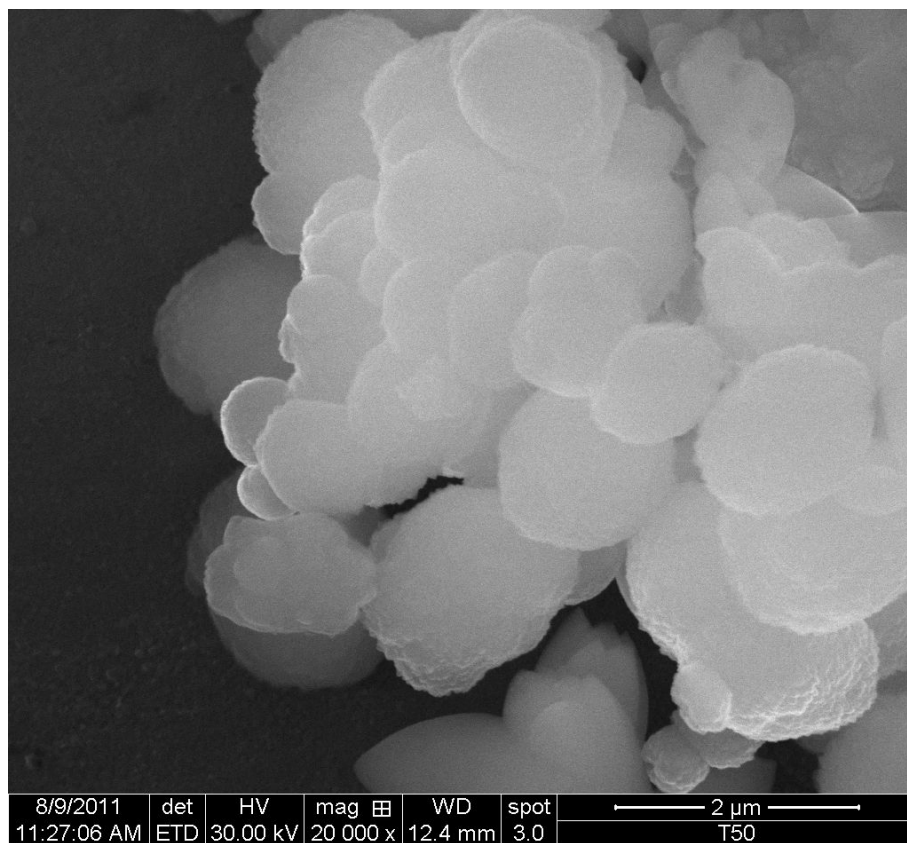


Fig. S2 SEM image of the $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ sample synthesized for 3 h.