Supporting Information

Template-Free Synthesis of Mesoporous Co$_3$O$_4$ with Controlled Morphologies for Lithium Ion Batteries

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Experimental Section

Sample preparation: For preparing CoCO$_3$ microspheres, 0.25 g of CoCl$_2$·6H$_2$O was added into a solution of 5 mL H$_2$O, 15 mL glycerol and 0.5 g urea at room temperature under stirring. After 1h, this solution was transformed into a Teflon-lined stainless steel autoclave and maintained at 180 °C for 12 h. After the sample was cooled to ambient temperature, the precipitates were collected after being rinsed with pure ethanol and water repeatedly and dried in vacuum at 80 °C. For preparing CoCO$_3$ microcubes, the volume ratio of H$_2$O and glycerol is 1:1.

Characterization: The microscopic features of the samples were characterized by scanning electron microscopy (SEM, JEOL-6701F) and transmission electron microscopy (TEM, JEOL JEM-2010). The powder X-ray diffraction pattern was collected using a Panalytica X'pert PRO diffractometer. The TGA measurement was carried out under air at a heating rate of 2 °C min$^{-1}$ using a TQ500 instrument. Nitrogen adsorption/desorption isotherms were measured at -196 °C using a Micromeritics ASAP 2020 system.
**Electrochemical Measurements:** The active material (70 wt.%), carbon black (20 wt.%), and poly(vinylidene fluoride) binder (10 wt.%) in N-methylpyrrolidone were mixed into a homogeneous slurry. The obtained slurry was pasted on copper foil and then dried in a vacuum oven at 80 °C for 12 h. Electrochemical test cells were assembled in an argon-filled glove box. Lithium foil was used as the counter electrode. A solution of LiPF₆ in a 1:1 vol/vol mixture of ethylene carbonate and diethyl carbonate was used as the electrolyte. Celgard 2400 film was used as separator. The cells were charged and discharged galvanostatically in a voltage range of 0.005 and 3.0 V using a Neware battery tester.

**Scheme 1** Schematic of preparation of mesoporous Co₃O₄ microspheres and microcubes.

**Fig. S1** SEM images of CoCO₃ synthesized at a ratio of H₂O and glycerol (volume:volume): (a) 20:0 (b) 15:5.
**Fig. S2** Effect of the urea concentration on the morphologies of CoCO₃ (a, b and c) microcubes and (d, e and f) microspheres: 0.1, 0.2 and 1g urea.

**Fig. S3** Nitrogen adsorption/desorption isotherms of mesoporous Co₃O₄ microspheres and microcubes. The inset is BJH pore size distribution.
Fig. S4 Discharge-charge profiles of mesoporous Co$_3$O$_4$ (a) microspheres and (b) microcubes.