Supporting Information

MOF-derived porous hollow Co_3O_4 parallelepipeds building high-performance Li-ion batteries

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Part I: Experimental Details

Synthesis of the hollow Co_3O_4 parallelepipeds: The parallelepiped Co-MOF ($[Co_3(HCOO)_6]\cdot DMF$) crystal was conveniently synthesized. Typically, cobalt (II) nitrate hexahydrate (3.405 g, 11.7 mmol) and formic acid (0.45 mL, 88%, 11.7 mmol) were dissolved in 10 mL DMF under stirring for several minites. The mixture was incubated in an oven at 100 °C for 24 h. The resultant light pink Co-MOF crystalline precipitate was filtered, rinsed with DMF for several times and dried under vacuum overnight. To obtain Co_3O_4, the as-made Co-MOF crystals were placed in a tube furnace and heated in air at 400 ºC for 3 h at a heating rate of 5 ºC min^{-1}. For comparison, the Co_3O_4 particles were prepared by thermal decomposition of commercial $CoCO_3$ in Air.

Characterization of materials: The structure and morphology of the obtained samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance with Cu Kα radiation), scanning electron microscopy (SEM, Hitachi SU8010) and transmission electron microscopy (TEM, FEI Tecnai G^2 F20). The porous structural

feature was determined using a nitrogen adsorption-desorption measurement (Quantachrome Quadrasorb SI). And the pore size distribution was analyzed using the density functional theory (DFT) method from the adsorption branch. Thermogravimetric analysis (TGA) was carried out on a METTLER TGA-DSC 1 apparatus with a heating rate of 10 °C min^{-1} under air.

Electrochemical measurement: The working electrode was fabricated by casting slurry containing Co_3O_4, acetylene black (Super-P) and polyvinylidene fluoride (PVDF) (at a weight ratio of 8:1:1) on Cu foil followed by drying at 120 °C in vacuum for 12 h and being cut into disks with diameter of 12 mm. The mass loading of each integrated electrode was about 3 mg. Electrochemical measurements were carried out via CR2032 coin-type cells assembled in an Ar-filled glove-box. Li foil and Celgard 2400 membrane were employed as the counter/reference electrode and the separator, respectively. And the electrolyte was 1 M $LiPF_6$ in ethylene carbonate/ethyl methyl carbonate/dimethyl carbonate (1:1:1 v/v/v). The galvanostatic charge-discharge tests were performed at different current densities of 100-1000 mA g^{-1} with the range of 0.01-3.00 V (vs Li^+/Li) using LAND CT2001A battery tester.

Part II: Supplementary Figures

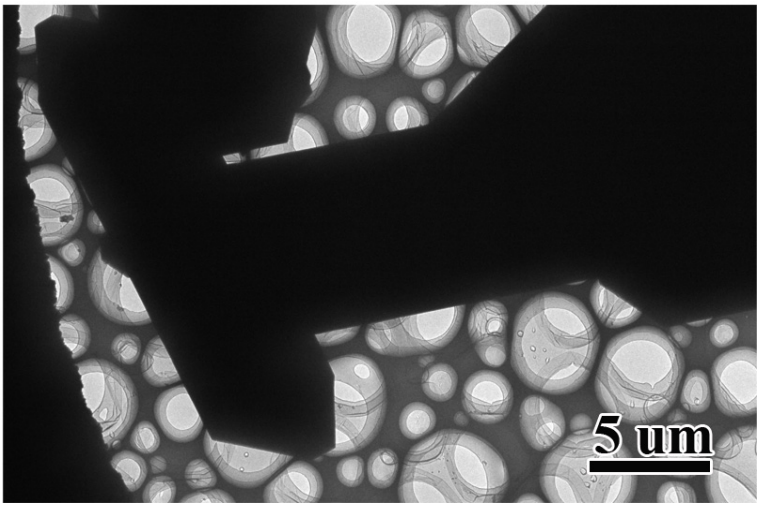

Fig. S1 TEM image of the Co-MOF precursor.

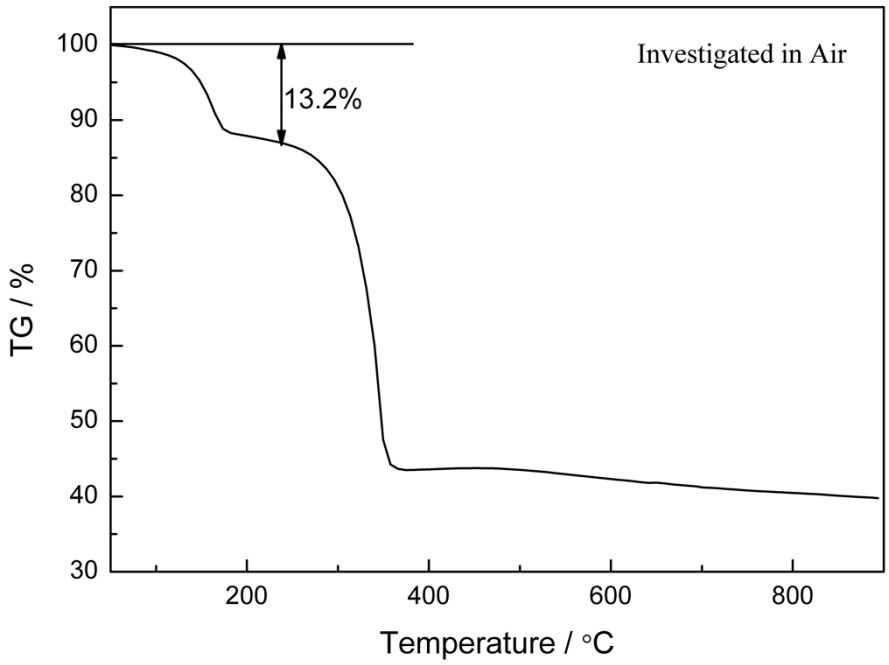

Fig. S2 TGA curve of the Co-MOF precursor.

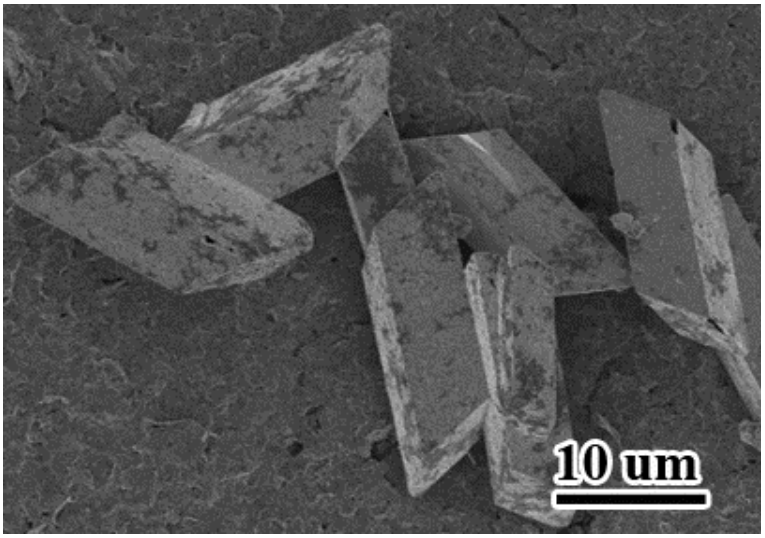

Fig. S3 Low magnification SEM image of Co_3O_4 parallelepipeds.

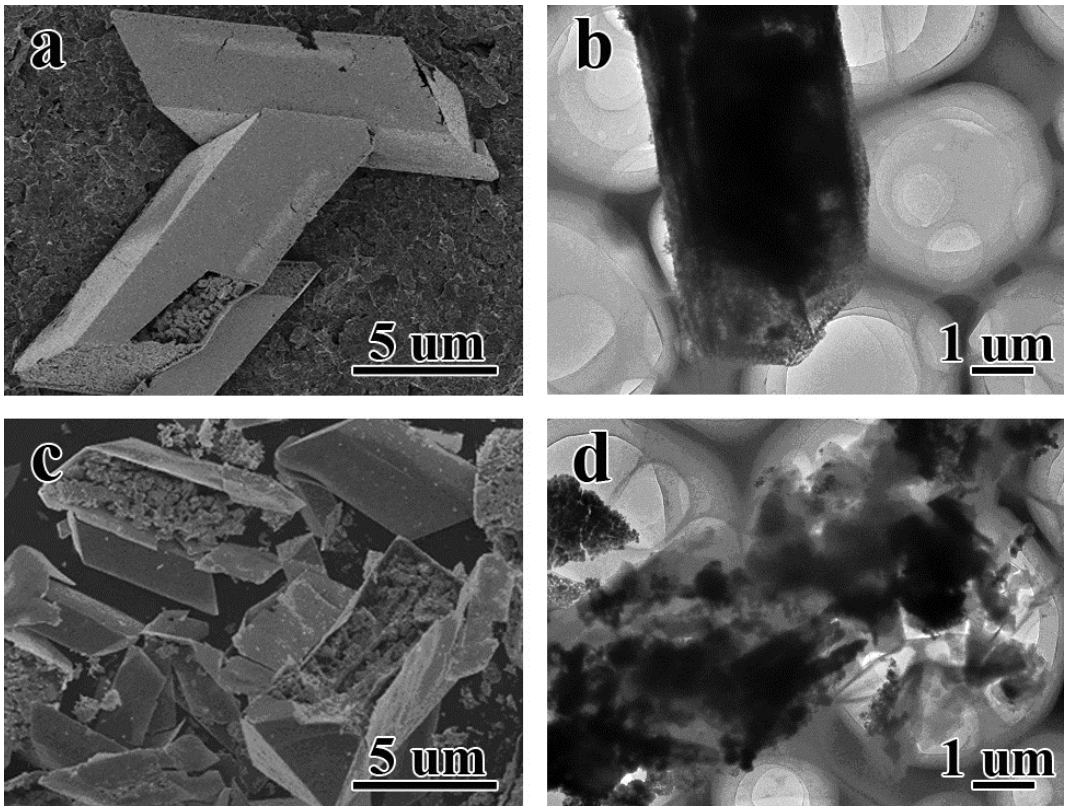

Fig. S4 SEM and TEM images of samples formed by the thermal decomposition of Co-MOF precursor in air at (a, b) 300 ºC and (c, d) 500 ºC.

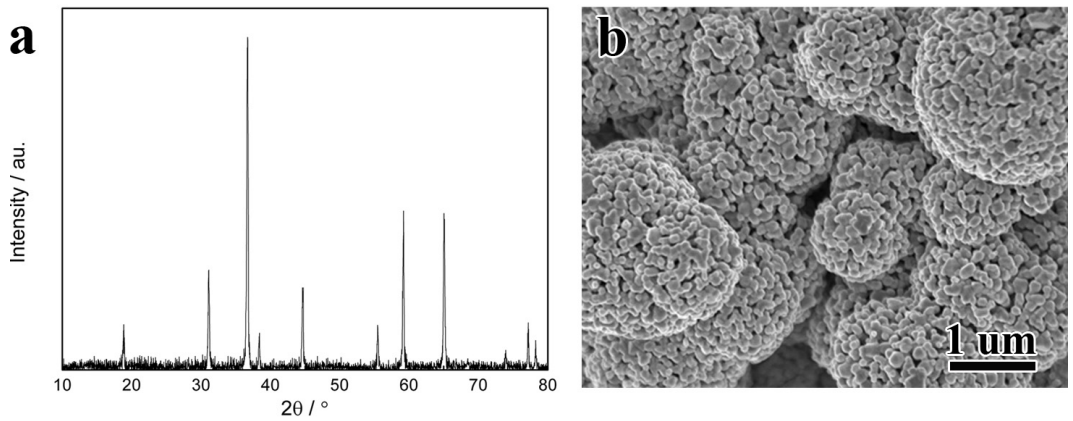

Fig. S5 (a) XRD pattern and (b) SEM image of the Co_3O_4 particles.