Electronic supplementary information (ESI)

Three dimensional hierarchical pompon-like Co_3O_4 porous spheres for high-performance lithium-ion batteries

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Experimental

1. Preparation of 3D hierarchical Co_3O_4 structures

All of the chemicals were analytical grade and were used without further purification. Three kinds of Co_3O_4 with different morphologies were prepared through a hydrothermal method. In a typical experiment, Cobalt nitrate hexahydrate ($Co(NO_3)_2$•$6H_2O$) and urea ($CO(NH_2)_2$) (Molar Ratio = 4:1) were dissolved in deionized water (40 mL) under vigorous stirring for 1 h. The mixed solution was transferred into a 50 mL polytetrafluoroethylene (PTFE) Teflon-lined autoclave, sealed, and maintained at 160 ℃ for 6-12 h in an electric oven. After cooling to room temperature, the precipitates were centrifuged, washed with distilled water and ethanol for more than 3 times. Finally, the red powders of the precursor were calcined in a muffle furnace at 300 ℃ for 2 h in air at a ramping rate of 1 ℃•min^{-1}, and then cooled down to room temperature in air gradually. The as-obtained products show 3D pompon-like sphere structures. To prepare the Co_3O_4 nanoparticles, the molar ratio of Cobalt nitrate hexahydrate to urea was 1:5. For the Co_3O_4 nanowires, the molar ratio was 6:5, other than that, the experimental conditions of the two morphologies are similar with that of pompon-like sphere.

2. Characterization

The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Focus X-ray diffractometer with Ni-filtered Cu-Kα radiation (λ = 0.15406 nm). The scanned 2θ range was between 10 ° and 80 ° at room temperature. The morphologies and microstructures of the samples were characterized by scanning electron microscope (SEM) at 10.0 kV on a JEOL JSM-7001F microscope. Transmission electron microscopy (TEM) observations and selected area electron diffraction (SAED) measurements were performed by using a JEOL JEM-2100 microscope operating at 200 kV. The specific surface area and pore volume of the samples were performed by the N_2 adsorption and desorption isotherm method at -196 ℃ on a Quadrasorb SI-MP analyzer, respectively. Prior to measurement, all of the samples were degassed in a vacuum at 4 mmHg and 150 ℃ for 7 hours.

3. Electrochemical measurements

The electrochemical experiments were performed using CR2032 type coin cells assembled in a dry argon-filled glovebox. The working electrode was fabricated by mixing the Co_3O_4, acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 70:20:10, followed by pasting the mixture onto copper foil and dried at 80 ℃ in vacuum oven for 12 h. Lithium foil was used as the counter electrode and they were separated by a Celgard 2400 membrane. The electrolyte used in this experiment was $LiPF_6$ (1M) /EC+DEC+DMC (1:1:1, weight). The galvanostatic charge/discharge tests were carried out on a LAND battery testing system in the voltage range of 0.01-3.2 V with different current density at room temperature. Electrochemical impedance spectroscopy (EIS) measurements tests were carried out on a ACM Gill-AC-4 electrochemical station.

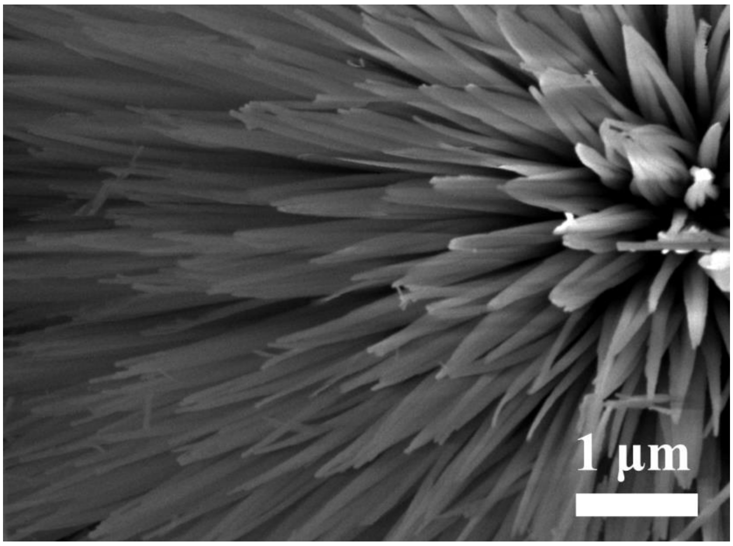

Fig. S1 Specific SEM image of 3D pompon-like Co_3O_4

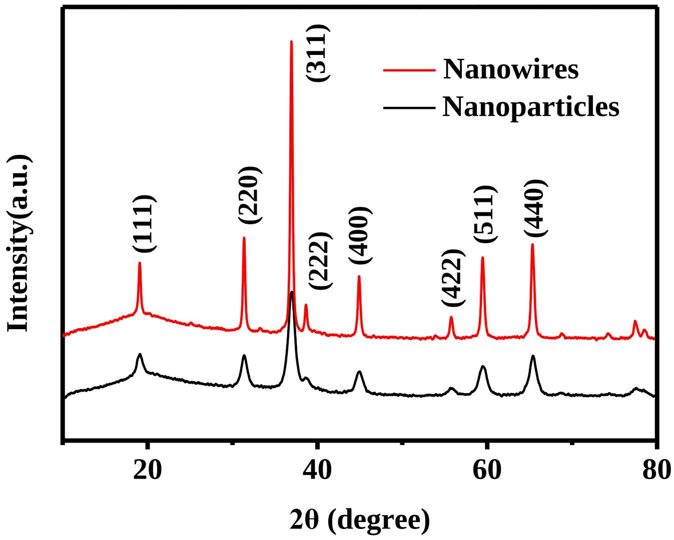

Fig. S2 XRD pattern of other two different kinds of Co_3O_4 morphologies

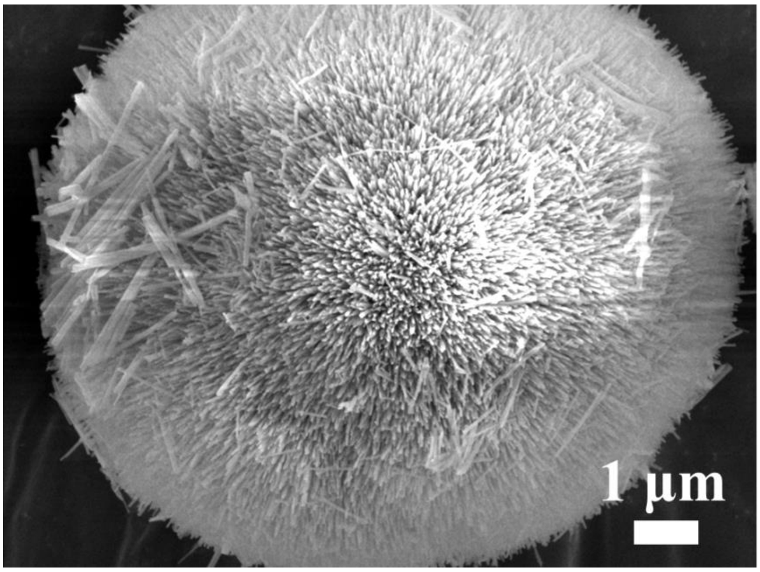

Fig. S3 SEM image of 3D pompon-like Co_3O_4 after calcination

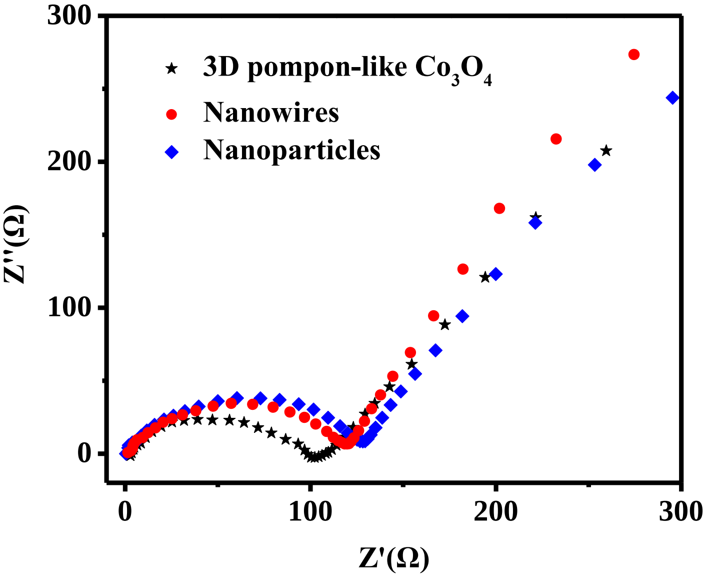

Fig. S4 Impedance spectra of three kinds of Co_3O_4 before cycling

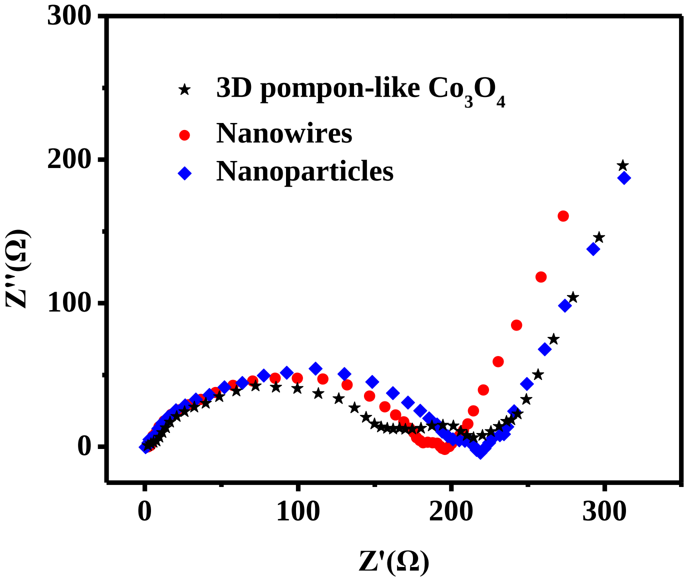

Fig. S5 Impedance spectra of three kinds of Co_3O_4 at the 5th cycle.