Supporting Information

Facile synthesis of hierarchical porous $ZnCo_2O_4$ microspheres towards high-performances supercapacitors

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Experimental

Synthesis of hierarchical porous *$ZnCo_2O_4$ microspheres*

All chemicals were of analytical grade and used without further purification. The formation process of the hierarchical porous $ZnCo_2O_4$ microspheres is based on a solvothermal methods followed by an annealing process. In a typical procedure, 1 mmol of $Zn(NO_3)_2 \cdot 6H_2O$, 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 15 mmol of urea were added together into 35 mL of absolute ethanol to form a solution. Then the solution was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 50 mL, heated in an oven at 140 ℃ for 24 h, and then allowed to cool to room temperature naturally. The precursor was collected by centrifugation and washed with water and ethanol for several times, before drying at 60 ℃ for 12 h. Finally, after annealing the above precursors in air at 400 ℃ for 2 h, hierarchical porous $ZnCo_2O_4$ microspheres were obtained.

Materials characterization

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The crystallographic information of samples was gathered by powder X-ray diffraction (XRD) on a Rigaku D/Max-2500 powder diffractometer (Cu Kα radiation, λ=0.15418 nm). The morphologies were characterized by field emission scanning electron microscopy (FESEM; JEOL JSM-6700F), transmission electron microscope (TEM), high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED) pattern (Tecnai G2 F20). The specific surface areas and porous nature of the as-prepared samples were further investigated by nitrogen adsorption-desorption measurements on an ASAP 2020/Tristar 3000.

Electrochemical measurements

The working electrodes were fabricated by mixing the active material, acetylene black and Polyvinylidene Fluoride (PVDF) binder in a weight ratio of 80:10:10 to obtain a viscous slurry. The slurry was screen printed onto a piece of nickel foam (1.0 cm×1.0 cm), and dried under vacuum at 100 °C for 10 h. Electrochemical measurements were conducted in a three-electrode arrangement in 2 M KOH electrolyte. A bright Pt plate and Hg/HgO electrode were used as the counter electrode and the reference electrode, respectively. Cyclic voltammetry (CV) was conducted with a Zahner IM6e electrochemical workstation with voltage scan rates of 5, 10, 20 and 50 mV s^{-1}. The galvanostatic charge-discharge tests were conducted on a LAND battery system at the current densities of 1, 2, 5 and 10 A g^{-1}. The specific capacitance is calculated according to the following equation:

$$C = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where C (F g^{-1}) is the specific capacitance, I (A) represents the discharge current, and m (g), ΔV (V) and Δt (s) designate mass of active materials, potential drop during

discharge and total discharge time, respectively.

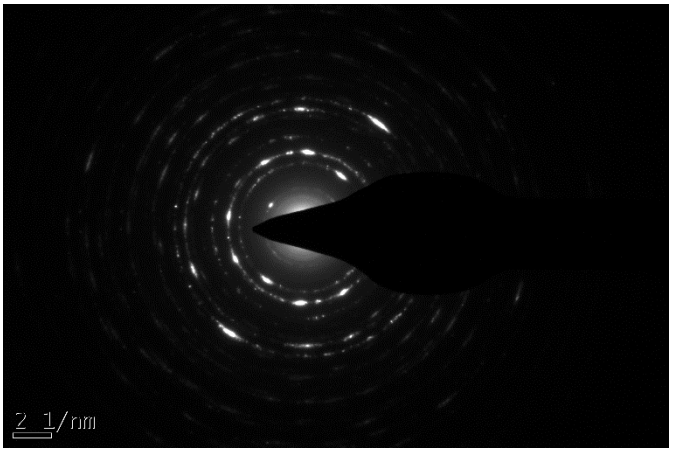

Fig. S1 SAED pattern of the as-prepared hierarchical porous $ZnCo_2O_4$ microspheres.

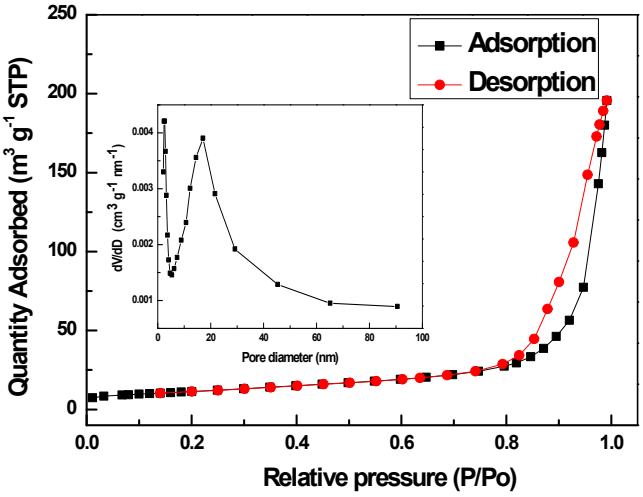

Fig. S2 Nitrogen adsorption-desorption isotherm and the corresponding pore size distribution (insert of Fig. S2) of the hierarchical porous $ZnCo_2O_4$ microspheres.