Facile synthesis and superior supercapacitor performances of three-dimensional cobalt sulfide hierarchitectures

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Experimental

Synthesis

All chemicals were of analytical grade and used as received. In a typical synthesis of flower-like $CoS_{1.097}$ architectures, 2.5 mmol $CoCl_2 \cdot 6H_2O$ was dissolved in 65 mL ethanol, then 10 mL carbon bisulfide was added under continuous stir to form a homogenous blue solution. Then the solution was transferred into 100 mL teflon–lined stainless steel autoclave and maintained at 220 ^oC for 24 h. Subsequently, the reactor was cooled to room temperature naturally. The resulting samples were collected and washed with de-ionized water and ethanol for several times, and dried at 60 ℃ in vaccum. The controlled experiments were conducted following a similar procedure by adjusting experimental parameters, such as temperature, concentration and reaction time.

Characterization

The crystal structures of samples were characterized by powder X-ray diffraction (XRD) on a Rigaku D/Max-2500 powder diffractometer (Cu Kα radiation, λ=0.15418 nm). The morphologies were detected by scanning electron microscopy (SEM) on a JEOL JSM-6700F (Field Emission) scanning electron microscope, transmission

electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) on a Tecnai G2 F20 TEM.

The working electrodes were fabricated by mixing the as-prepared $CoS_{1.097}$ powder, graphite, acetylene black and polytetrafluoroethylene (PTFE) binder in a weight ratio of 70:10:10:10. The first three components were mixed together in an agate mortar until homogeneous black powder was achieved. PTFE was then added to the mixture with a few drops of ethanol. The synthesized paste was pressed at 20 MPa to a piece of nickel foam (1.0 cm×1.0 cm), and dried under vacuum at 40 ^{o}C for 10 h. Electrochemical measurements were conducted in a three-electrode arrangement in 2 M KOH electrolyte. A nickel foil and a saturated calomel electrode (SCE) electrode were used as a counter electrode and reference electrode, respectively. Cyclic voltammetry (CV) was conducted by a Zahner IM6e electrochemical workstation with voltage scan rates of 5 mV s^{-1}, 10 mV s^{-1}, 20 mV s^{-1} and 50 mV s^{-1}. The galvanostatic charge-discharge tests were conducted on a LAND battery system at the current of 5 mA cm^{-2}, 10 mA cm^{-2}, 20 mA cm^{-2} and 50 mA cm^{-2} and 100 mA cm^{-2}. 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 specific capacitance, I (A) represents discharge current, and m (g), ΔV (V) and Δt (s) designate mass of active materials, potential drop during discharge and total discharge time, respectively.

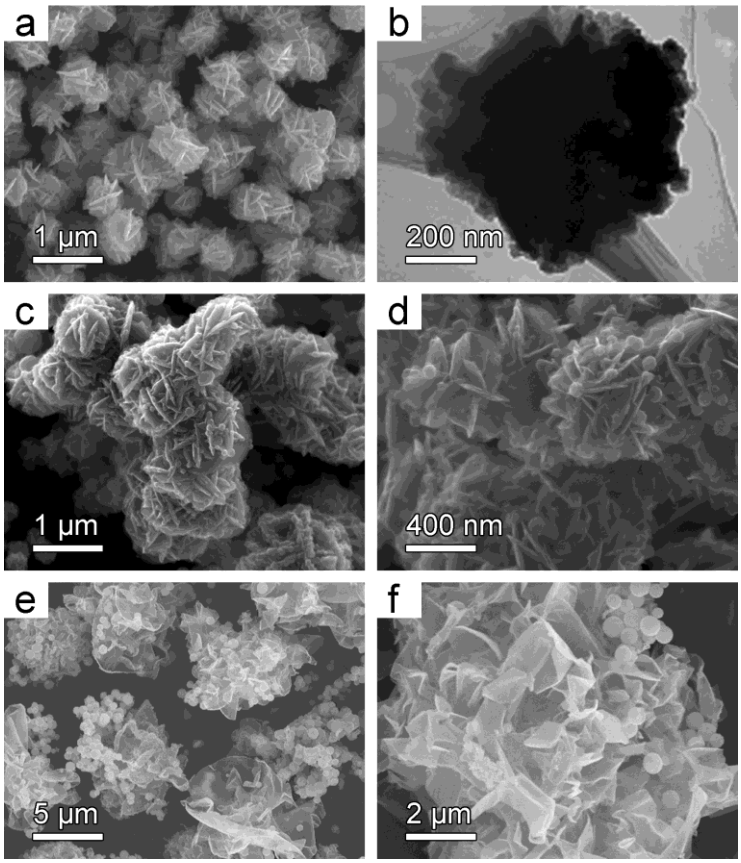

Fig. S1 SEM and TEM images of the samples obtained at different temperature for 24 h: (a, b) 200 ℃, (c, d) 180 ℃ and (e, f) 160 ℃.

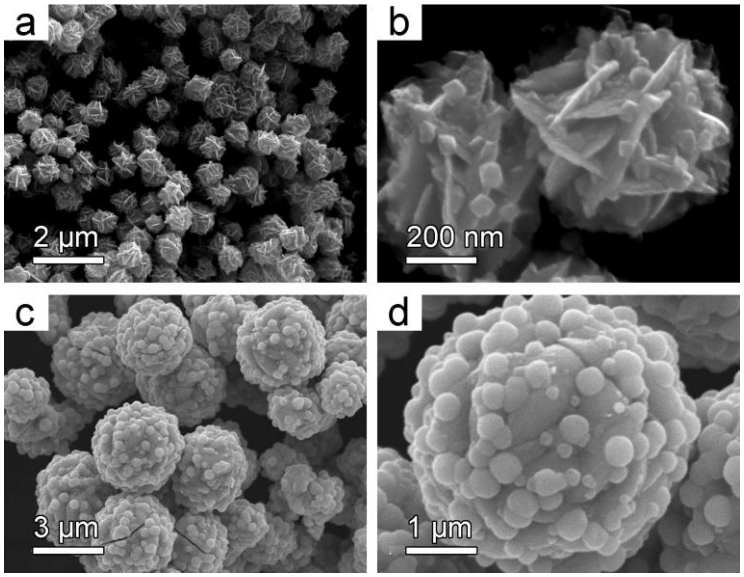

Fig. S2 SEM images of the samples obtained at 220 ℃ for 24 h with different concentrations of $CoCl_2 \cdot 6H_2O$: (a, b) 1.25 mmol and (c, d) 5 mmol.

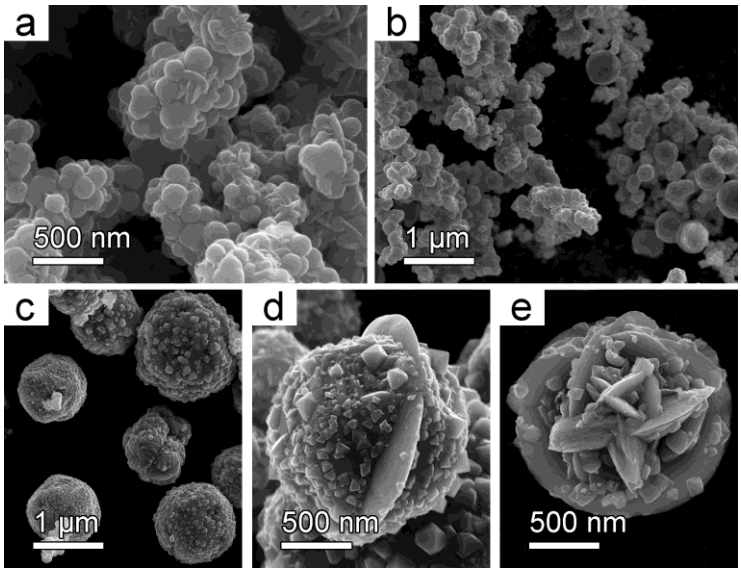

Fig. S3 SEM images of the samples synthesized at 220 ℃ for various dwell time: (a) 2 h, (b) 4 h, (c) 8 h, (d) 12 h and (e) 16 h.

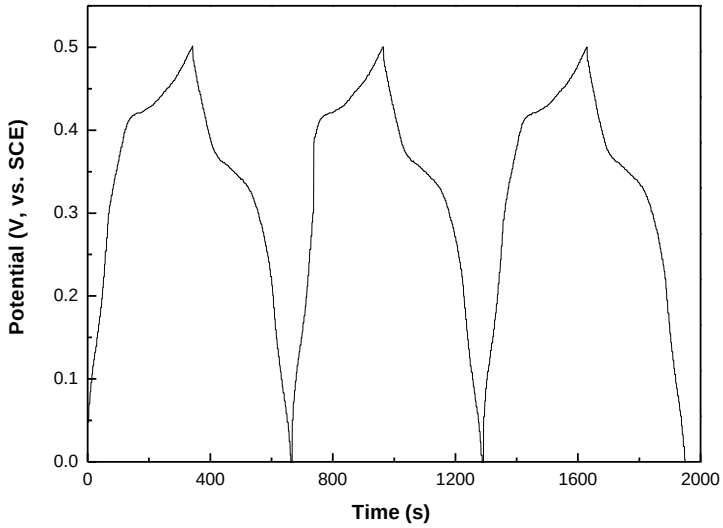

Fig. S4 Galvanostatic charge/discharge curves of the $CoS_{1.097}$ electrode, recorded at a constant current density of 5 mA cm^{-2}.

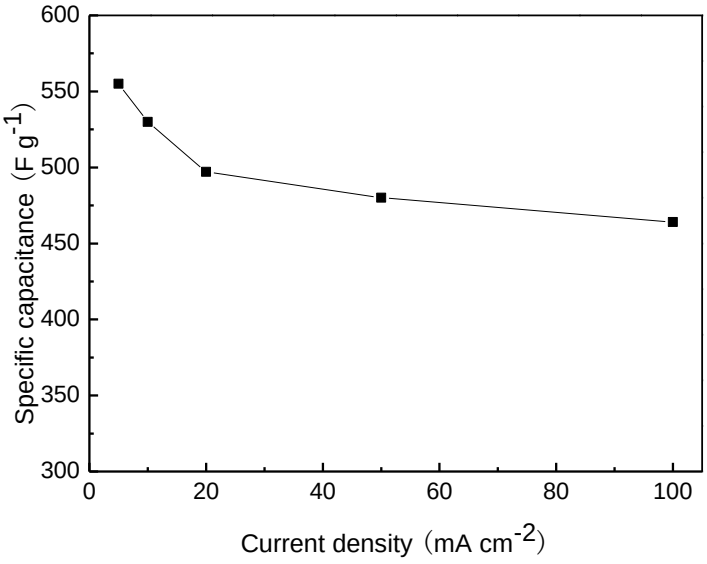

Fig. S5 Specific capacitances of the $CoS_{1.097}$ electrodes in 2 M KOH solution, recorded at various applied current densities.