Highly uniform Platanus fruit-like CuCo$_2$S$_4$ microsphere as electrode material for high performance lithium-ion batteries and supercapacitors

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1. Synthesis of CuCo$_2$O$_4$ precursor

1 mmol Cu(NO$_3$)$_2$·3H$_2$O, 2 mmol Co(NO$_3$)$_2$·6H$_2$O, 6 mmol NH$_4$F and 10 mmol urea were totally dissolved in 70 mL deionized water under vigorous stirring to produce a uniform solution. The resulting solution was sealed in a 100 mL Teflon-lined stainless-steel autoclave and kept at 120 °C for 12 h. After the autoclave cooled down to room temperature, the Cu-Co precursor precipitate was collected by centrifuged and washed with ethanol several times and then dried in an oven at 70°C for 12 h. The

precursors were subsequently annealed at 350℃ for 2 h to obtain the $CuCo_2O_4$.

2. Synthesis of $CuCo_2S_4$ Microsphere

The above $CuCo_2O_4$ was re-dispersed in 70 mL distill water with excessive concentration of $Na_2S\cdot9H_2O$ aqueous solution and stirring for 1 h to form a black suspension. Then the mixture was transferred into a Teflon-lined stainless-steel autoclave and kept at 180 °C for 12 h. After filtered and washed with ethanol for several times, the $CuCo_2S_4$ platanus fruit-like microsphere were obtained.

3. Materials Characterization

The crystal structure, morphology and microstructure of $CuCo_2S_4$ powders were characterized by X-ray diffraction (XRD, RIGAKU), field-emission scanning electron microscopy (FE-SEM, ZEISS) and high-resolution transmission electron microscopy (HR-TEM, JEM 2100F), respectively. The specific surface area of the samples was characterized by Brunauer-Emmett-Teller measurements (BET, Micromeritics, ASAP 2020). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Escalab 250Xi) was performed to characterize the composition and valence of the materials.

4. Electrochemical measurements

For Li ion batteries, the CR2025 coin-type half-cells were assembled in an argon-filled glovebox (Mikrouna, China), where the moisture and oxygen levels were less than 0.01 ppm. The working electrodes were prepared by dissolved active material ($CuCo_2S_4$ microsphere), binder (polyvinylidene fluoride PVDF) and conductive agent (acetylene black) with weight ratios of 7:2:1 in N-methyl-2-pyrrolidone (NMP) solvent, after keep stirring for 8h to generate the homogeneous slurry. Subsequently, the slurry

was uniformly coated on the surface of Cu foil and dried in a vacuum oven at 80 °C for 12 h. Finally, the foil was punched into a circular pellet with a diameter of 1.4 cm, Lithium foil was used as counter electrode and a piece of polypropylene films (Celgard 2400) was served as separator. The electrolyte contained 1 M $LiPF_6$ dissolved in ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) with volume ratios of 1:1:1. The loading mass of active material is about 0.4 mg cm^{-2}.

The galvanostatic charge-discharge (GCD) measurements were carried out with Neware battery test systems (Neware, China) in a voltage range of 0.01−3.0 V (vs. Li/Li$^+$) at various current rates. Cyclic voltammetry (CV) curves were tested using CHI1000C (Chenhua, China) electrochemistry workstation at a scanning rate of 0.5 mV s^{-1} between 0.01 V and 3.0 V. Electrochemical impedance spectra (EIS) were determined on Zahner (Zahner, Germany) electrochemistry workstation in the range of 100 kHz and 0.01 Hz frequency.

For supercapacitor, all electrochemical tests were conducted in a LAND CT2001A system (LANHE, China). Cyclic voltammetry (CV) curves and electrochemical impedance spectra (EIS) were determined on Zahner (Germany) electrochemistry workstation. CV curves were obtained at a potential window of 0–0.5 V with a scan rate ranging from 5 to 80 mV s^{-1}. The maximum voltage of GCDs was 0.5 V and the current density was from 1 to 8 A g^{-1}. The EIS test was conducted using an open circuit voltage with an amplitude of 5 mV over the frequency range of 0.01–100k Hz.

A conventional three-electrode system containing a 3 M aqueous KOH solution as the electrolyte was used to evaluate electrochemical properties. The standard calomel

electrode (SCE) and the 20 mm × 20 mm platinum plate worked as the reference and the counter electrodes, respectively. The work electrodes were prepared by mixing active material, PTFE binder (75 wt% aqueous dispersion), and acetylene black with a weight ratio of 80, 10 and 10 wt.% to form a homogeneous slurry. Then, the obtained slurry was uniformly coated on a pre-cleaned Ni foam (NF) of 1 cm × 1.5 cm (a square area with coating area of 1 cm × 1 cm) and dried at 80 °C overnight in a vacuum oven. At last, the work electrodes were obtained by pressing the coated nickel foams at 10 MPa pressure for 20 s. The mass loading of active materials was about 4 mg, prior to testing, the electrodes were immersed in 3M KOH electrolyte for 5 h.

The specific capacitances of the electrode materials were calculated from the GCD curves according to the following formula (1):

$$C_s = \frac{I \times \Delta t}{m \times \Delta t}$$

(1)

Where C_s is the specific capacitance (F g^{-1}), I is the discharge current (mA), Δt is the discharge time (s), ΔV is the potential window (V) and m is the mass of the active electrode material (mg).

Asymmetric supercapacitor devices were further assembled, in which the as-prepared $CuCo_2S_4$ were used as the positive electrode and the CTP as the negative electrode. The KOH/PVA gel electrolyte was prepared according to the following procedure: 3 g PVA (Mw=89 000) were dissolved in 30 mL DI water and stirred vigorously at 95°C for 1 h. Subsequently, 3 g KOH were dissolved in 5 mL DI water and drop in the above solution. Both positive and negative electrodes were soaked in the electrolyte for 10 min and then allowed to solidify at room temperature for 10 h.

The mass ratio between the positive and negative materials was calculated based on the charge balance relationship (q+ = q−) [34], according to the equation (2):

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+}$$
(2)

From Eq. (2) the mass loading of CTP is considering the value of specific capacitance of $CuCo_2S_4$ and CTP and potential window as 0.5 and 1 V, respectively. The $CuCo_2S_4$ positive and CTP negative operating potential window was set to 1.5 V.

The specific capacitance (C, F g^{-1}), energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) were calculated, respectively, based on the following equations, respectively[35]:

$$C_s = \frac{I \times t}{m \times \Delta t}$$
(3)

$$E = \frac{1}{2 \times 3.6} C \Delta V^2$$
(4)

$$P = \frac{E \times 3600}{\Delta t}$$
(5)
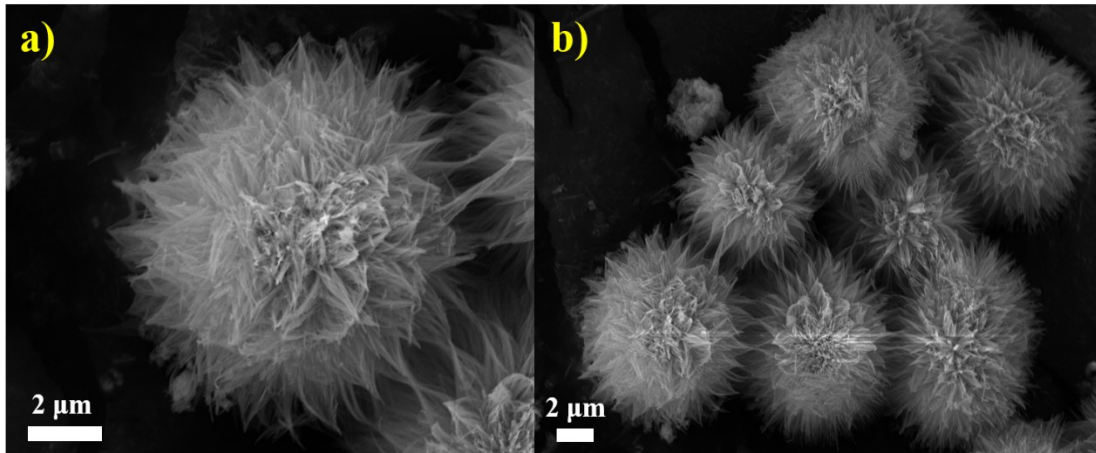
Fig. S1 (a, b) FE-SEM images of platanus fruit-like $CuCo_2S_4$ after 200 cycles.