Morphology-controllable synthesis of rod-shaped CuO@Co₃O₄ derived from CuCo-MOF-74 for

supercapacitors

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Fabrication of asymmetrical supercapacitor (ASC)

A two-electrode asymmetrical supercapacitor (ASC) was assembled in 2 M KOH using the CuO@Co₃O₄ and commercial reduced graphene oxide (RGO) as positive and negative electrodes, respectively. The negative electrode was prepared as follow: reduced graphene oxide (RGO), acetylene black and polyvinylidene fluoride (PVDF) were dispersed by a mass ratio of 8: 1: 1 in N-methyl pyrrolidone (NMP) into the homogenous slurry. Then the slurry was coated on bare Ni foam ($1 \times 2 \text{ cm}^2$), dried in a vacuum and pressed under the pressure of 10 MPa.

The charge balance principle (equations 1 and 2) was used to determine the mass ratio of active materials between the two electrodes.

$$Q^+ = Q^- \tag{S1}$$

$$\frac{m^+}{m^-} = \frac{I_m^- \times \Delta t}{I_m^+ \times \Delta t} \tag{S2}$$

Where both Q^+ and Q^- are stored charges in positive and negative electrodes (C) respectively; I_m^+ and I_m^- are discharge current of positive and negative electrodes; m^+ and m^- refer to their loadings of active substances (g).

The energy density (E (Wh kg⁻¹)) and power density (P (W kg⁻¹)) are calculated by following formulas:

$$E = \frac{\int Q \, dv}{3.6} = \frac{\int_{t_1}^{t_2} IV dt}{3.6}$$
(S3)

$$P = \frac{E}{t} \times 3600 \tag{S4}$$

All of the discharge time ($t_{discharge}$) and discharge voltages ($V_{(t)}$) are taken into account for the calculation after the initial IR drop. In Formula 2, t_1 is the time after the initial IR drop, t_2 is the moment for the discharge, and I is the constant current densities applied to the supercapacitor.

The details of electrochemical measurement

In the three-electrode system, 2 M KOH was used as the aqueous electrolyte, and $CuO@Co_3O_4$ were employed as the working electrode, where, both platinum plate and the saturated calomel electrode (SCE) were used as the counter and reference electrodes. The loadings for the positive and negative electrodes were 2.5 mg and 2 mg, respectively. The calculation of specific capacity ($C_g(C g^{-1})$) based on GCD curves by following equation:

$$C_g = \frac{lt}{m} \tag{S5}$$

Where I (A), t (s), m (g), represent discharge current density, discharge time and loading mass, respectively.



Fig. S1 XRD pattern of CuCo-MOF-74



Fig. S2 SEM image of CuCo-MOF-74



Fig. S3 Equivalent circuit for three-electrode configuration cell



Fig. S4 Raman spectra of CuO@Co₃O₄





The GCD curves of CuO@Co₃O₄ (400 °C) are shown in Fig. S6a, with specific capacitances of 409.1, 393.3, 388.6, 374.8, 354.3, and 332.1 F g⁻¹ at current densities of 1, 2, 3, 5, 8, and 10 A g⁻¹, respectively. The GCD curves of CuO@Co₃O₄ (600 °C) are shown in Fig. S6b, with specific capacitances of 423.5, 415.9, 393.6, 385.8, 376.3, and 355.1 F g⁻¹ at current densities of 1, 2, 3, 5, 8, and 10 A g⁻¹, respectively.



Fig. S6 (a) GCD curves of CuO@Co₃O₄ (400 °C), (b) GCD curves of CuO@Co₃O₄ (600 °C)



Fig. S7 Nitrogen adsorption-desorption isotherms of the CuO@Co₃O₄ (500 °C) sample and the inset is pore size distribution curve



Fig. S8 EIS curves of CuO@Co₃O₄ (500 °C)//RGO