Facile and Controllable Synthesis of Sea Urchin-like $CuCo_2O_4$ on Ni Foam for High-performance Supercapacitors

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Materials

Cobalt nitrate hexahydrate (Co $(No_3)_2 \cdot 6H_2O$), Copper nitrate trihydrate (Cu $(No_3)_2 \cdot 3H_2O$), Urea (Co $(NH_2)_2$), Ammonium fluoride (NH_4F), ethanol (ET), Potassium Hydroxide (KOH) were purchased from the official website of Aladdin Reagent (Shanghai), and all of the chemicals were analytically pure and not further purified. The deionized water used comes from local sources.

Characterization

X-ray diffraction (XRD, Bruker D8) measured the crystalline structure and phase composition with Cu Kα radiation between 10° and 80°. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was used to test the chemical composition and valence state on the surface of the samples. And scanning electron microscopy (SEM, SU8010) was applied to characterize morphology and microstructure.

Characterization

The cyclic voltammetry (CV), galvanostatic charge and discharge (GCD), and electrochemical impedance spectroscopy (EIS) tests were carried out on a CHI 660E electrochemical workstation (Shanghai ChenHua Instrument Co., Ltd) at a range of 0.01 to 100 kHz. The cyclic stability of the electrode was tested by a Land cell measurement system (Wuhan Land Electronics Co., Ltd.) at a current density of 10 A g^{-1}.

Fabrication of asymmetrical supercapacitor (ASC)

A two-electrode asymmetrical supercapacitor (ASC) was assembled in 2 M KOH using the $CuCo_2O_4$ 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 (1×2 cm^2), dried in a vacuum and pressed under the pressure of 10 MPa.

The charge balance principle (equations S1 and S2) was used to determine the mass ratio of active materials between the two electrodes.

$$Q^{+} = Q^{-} \#(S1)$$

$$\frac{m^{+}}{m^{-}} = \frac{I_m^{-} \times \Delta t}{I_m^{+} \times \Delta t} \#(S2)$$

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:

$$E = \frac{\int Qdv}{3.6} = \frac{\int_{t_1}^{t_2} IVdt}{3.6} \#(S3)$$

$$P = \frac{E}{t} \times 3600 \#(S4)$$

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 $CuCo_2O_4$ 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:

$$C_g = \frac{It}{m} \#(S5)$$

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

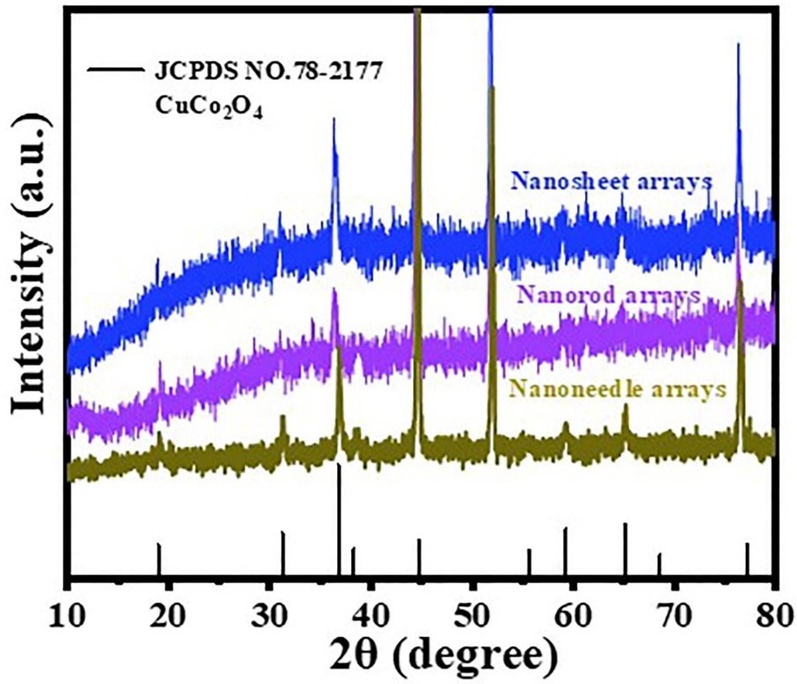

Fig. S1 XRD patterns of $CuCo_2O_4$-R, $CuCo_2O_4$-S, $CuCo_2O_4$-T

Table S1 Comparison studies of energy and power densities for various devices.

Device	Energy density (Wh kg^{-1})	Power density (W kg^{-1})	Reference
$CuCo_2O_4$@$MgMoO_4$//AC	24.9	160	[42]
$CuCo_2O_4$-NWs//AC	36.16	1,010	[25]
$CuCo_2O_4$@CuO//RGO	37.43	250	[43]
$CuCo_2O_4$/CuO NSs//RGO	38.8	1,000	[44]
$CuCo_2O_4$@CuO//AC	26.04	899.27	[45]
$CuCo_2O_4$//$BiVO_4$	26.6	4,800	[46]
NiO/$CuCo_2O_4$//AC	25.17	400	[47]
$CuCo_2O_4$//RGO	59.6	802.3	This work
	43.1	8,026.5	