Electronic Supplementary Information (ESI)

Hierarchical CuCo₂S₄ hollow nanoneedle arrays as novel binder-free electrodes for high-performance asymmetric supercapacitors

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Experimental details

Synthesis of the hierarchical CuCo₂S₄ hollow nanoneedle arrays on Ni foam:

Before the synthesis, five pieces of Ni foam $(1 \text{ cm} \times 1 \text{ cm})$ were carefully cleaned with 3 M HCl in an ultrasound bath for 20 min to remove the oxide layer, and then washed thoroughly with DI water and absolute ethanol, and weighted after drying in an oven at 40 °C. The $CuCo_2S_4$ –HNN electrodes were synthesized by a facile two-step hydrothermal route. In the first step of the procedure, 0.213 g of CuCl₂·2H₂O, 0.595 g of CoCl₂·6H₂O and 0.676 g of urea were added to 30 ml deionized water (DI) under vigorous stirring to obtain homogeneous apparent solution. The result pink solution was then transferred into a 40 mL Teflon-lined stainless-steel autoclave, and the weighted Ni foams were added into it. Then, the autoclave was sealed and maintained at 120 °C for 6 h. After cooling down to room temperature, the as-synthesized precursor-loaded Ni foams were washed with DI water and ethanol. In the second step, 42.6 mg of CuCl₂·2H₂O, 0.119 g of CoCl₂·6H₂O, 0.3 g of urea and 0.226 g thioacetamide (TAA) were dissolved in a 30 ml DI water, followed by addition of the precursor-loaded Ni foams in 40 mL Teflon container. The autoclave was heated to 90 °C for 4 h to completely decomposition of urea, and then maintained at 140 °C for 6 h. After cooling down to room temperature, the CuCo₂S₄ nanoneedle arrays on Ni foams were taken out and washed with DI water and ethanol, and dried in a vacuum at 50 $^{\circ}$ C for 4 h. The mass loading on the nickel foams were 3 \pm 0.03 mg cm⁻².

Characterization

Structurally characterizations were performed using X-ray powder diffraction (XRD, Philips X'pert diffractometer with Cu K_a radiation (λ = 0.154 nm) generated at 40 kV and 30 mA with a step size of 0.04° s⁻¹). X-ray photoelectron spectroscopy (XPS) analyze was conducted on a VG ESCALAB MKII spectrometer using an Mg K_a X-ray source (1253.6 eV, 120 W) at a constant analyzer. Nitrogen adsorption/desorption, specific surface area and pore size distributions were carried out using a Micromeritics ASAP-2010 apparatus at 77 K. The morphologies and structural investigations were done by a Zeiss field-emission scanning electron microscope (FESEM) and a Philips EM 208

transmission electron microscope (TEM). Electrochemical measurements were performed on a CHI 660D electrochemical workstation (CH Instruments, USA).

Electrochemical measurements

All electrochemical measurements were performed in aqueous 3 M KOH solution as the electrolyte. In three-electrode cell configuration, the as-synthesized CuCo₂S₄–HNN electrode was directly used as the working electrode, while an Hg/HgO electrode and a platinum foil were used as the reference and counter electrodes, respectively. In two-electrode cell configuration (asymmetric device), the as-synthesized CuCo₂S₄–HNN and AC electrodes were used as the positive and negative electrodes, respectively. For the preparation of the AC electrode, a mixture of the AC powder, carbon black and polytetrafluoroethylene (PTFE) in the weight ratio 85:10:5 was pressed onto a nickel foam and dried at 120 °C for 2 h. According to the specific capacitance of AC electrode (177 F g⁻¹), and in order to achieve the maximum operating potential window and performance, the optimal mass ratio between the positive and negative electrodes (m⁺/m⁻) was calculated to be around 0.143 based on the charge balance theory (q⁺ = q⁻). So, the total mass of the two electrode materials was 24 mg cm⁻².

The specific capacitances (C_{sp}), energy densities (ED, Wh kg⁻¹) and power densities (PD, W kg⁻¹) were calculated from the discharge curves using the following equations:

$$C_{sp} = \frac{I\Delta t}{m\Delta V}$$
(1)

$$ED = \frac{C_{sp}\Delta V^2}{2}$$
(2)

$$PD = \frac{ED}{\Delta t}$$
(3)

where I is the discharge current (A), Δt is the discharge time (s), ΔV is the potential window (V), and m is the mass loading (g).



Fig. S1 (a) CV of the current collector (bare Ni foam) and the as-prepared $CuCo_2S_4$ -HNN electrode in aqueous 3 M KOH electrolyte at a scan rate of 5 mV s⁻¹, (b) CD curves of the $CuCo_2S_4$ -HNN electrode at various current densities.



Fig. S2 CV curves of $CuCo_2S_4$ -HNN and AC electrodes at a scan rate of 10 mV s⁻¹ in a three-electrode system.

Fig. S3 (a) CVs of the $CuCo_2S_4$ -HNN//AC asymmetric supercapacitor at different potential windows at 20 mV s⁻¹, (b) CD curves of the device at different potential windows at a fixed current density of 48 mA cm⁻².

Fig. S4 the rate capability of the asymmetric supercapacitor at various current densities.



Fig. S5 EIS plot of the device before and after cycling. In order to further electrochemical investigation of the device, EIS experiments were performed before and after cycling. As shown, nearly identical Nyquist plots before and after cycling further confirm the excellent long-term cycling stability of the device. In addition, the facile pseudocapacitance feature of the device was verified by the small charge transfer resistance at high frequencies, whereas its excellent capacitor characteristics can be found from the linear part observed at low frequencies. Moreover, the very low internal resistance of the device was confirmed from the intercept of the Nyquist curves on the real axis before (0.18 Ω) and after (0.32 Ω) cycling.

Table S1. Comparison of the electrochemical performance of $CuCo_2S_4$ -HNN electrodes in three- and two-electrode systems with other previously reported binder-free electrodes.

Morphology/Composition	Synthesis method	Capacitance @current density	Cell (Config)	Cycles	Retention	ED (Wh/kg)	Electrolyte	ΔV (V)	Reference (year)
CuCo ₂ O ₄ nanograsses	Hydrothermal	796 F/g at 2 A/g	3E	5000	94.7% at 2 A/g	-	КОН	0.6	S1(2015)
CuCo ₂ O ₄ nanobelts	Hydrothermal	809 F/g at 2 mA/cm ²	3E	1800	127% at 26 mA/cm ²	-	КОН	0.45	S2(2015)
CuCo ₂ O ₄ nanowires	Electrospinning	0.44 F/cm ² at 1 mA/cm ²	3E	1500	90% at 1 mA/cm ²	-	КОН	0.45	S3(2015)
		0.47 F/cm ² at 10 mV/s	2E (vs. AC)	3000	82% at 2 mA/cm ²	38	КОН	1.5	
CuCo₂O₄@MnO₂ nanoflakes	Hydrothermal	416 F/g at 1 A/g	3E	4200	92% at 8 A/g	-	Na_2SO_4	1	S4(2015)
		78 F/g at 1 A/g	2E (vs. AG)	-	-	43.3	Na ₂ SO ₄	2	
CuCo₂O₄ @MnO₂ on carbon fibers	Hydrothermal	327 F/g at 1.25 A/g	3E	5000	90% at 6.25 A/g	-	КОН	0.5	S5(2014)
		0.71 F/cm ² at 1 mA/cm ²	2E (Symm)	-	-	-	ΡVΑ/ΚΟΗ	1	
CuCo ₂ O ₄ nanowire @NiCo ₂ O ₄ nanosheet	Hydrothermal- electrodeposition	2.6 F/cm ² at 10 mA/cm ²	3E	4500	80% at 10 mA/cm ²	-	КОН	0.42	S6 (2015)
NiCo ₂ S ₄ nanosheets	Solution-based chemical growth	4 F/cm ² at 2.3 mA/cm ²	3E	3000	81% at 30 A/g	-	КОН	0.5	S7 (2016)
Core-shell NiCo ₂ S ₄	Hydrothermal	2 F/cm ² at 1 mA/cm ²	3E	5000	94% at 2 mA/cm ²	-	КОН	0.5	S8 (2015)
		0.34 F/cm ² at 1 mA/cm ²	2E (vs. PC)	5000	77% at 5 mA/cm ²	22.8	КОН	1.5	
NiCo ₂ S ₄ Nanotube	Hydrothermal	738 F/g at 4 A/g	3E	4000	93.4% at 4 A/g	-	КОН	0.5	S9 (2014)
NiCo₂S₄@CoS _x core/shell	Hydrothermal- electrodeposition	4.74 F/cm ² at 5 mA/cm ²	3E	1500	76.1% at 50 mA/cm ²	-	КОН	0.45	S10 (2015)
NiCo ₂ S ₄ @NiCo ₂ S ₄ nanosheets	Hydrothermal	4.38 F/cm ² at 5 mA/cm ²	3E	5000	82% at 30 mA/cm ²	-	КОН	0.55	S11 (2015)
		75 F/g at 5 mA/cm ²	2E (vs.RGO)	5000	81% at 20 mA/cm ²	24.9	КОН	1.55	
NiCo₂S₄@Ni-Mn LDH/GS	Hydrothermal	1.74 F/cm ² at 1 mA/cm ²	3E	1000	88.3 % at 5 mA/cm ²	-	КОН	0.5	S12 (2015)
		0.5 F/cm ² at 5 mA/cm ²	2E (vs. VN)	5000	84.5 % at 20 mA/cm ²	-	КОН	1.5	
NiCo ₂ S ₄ @MnO ₂ core/shell	Hydrothermal	2.6 F/cm ² at 3 mA/cm ²	3E	5000	104 % at 50 mV/s	-	КОН	0.55	S13 (2015)
NiCo₂S₄@MnO₂ heterostructures	Hydrothermal	1338 F/g at 2 A/g	3E	2000	82 % at 10 A/g	-	КОН	0.45	S14 (2015)

NiCo ₂ S ₄ Nanotube on carbon fiber paper	Hydrothermal	2.86 F/cm ² at 4 mA/cm ²	3E	2000	96 % at 10 mA/cm ²	-	КОН	0.5	S15 (2014)
Al@Ni@MnO _x nanospike	Anodization- electrodeposition	942 F/g at 50 mV/s	3E	-	-	-	Na_2SO_4	0.8	S16 (2015)
		59 F/g at 10 mV/s	2E(vs. CCG)	10000	96.3 % at 2 A/g	23.02	PVA/Na_2SO_4	1.8	
Carbon fiber paper@ NiCo₂O₄ nanowires	Hydrothermal	680 F/g at 0.5 A/g	3E	-	-	-	КОН	0.45	S17 (2015)
		97.5 F/g at 1 A/g	2E (vs. GF)	10000	92.2 % at 2 A/g	34.5	КОН	1.6	
$ZnCo_2O_4$ nanowire	Hydrothermal	1625 F/g at 5 A/g	3E	5000	94 % at 20 A/g	-	КОН	0.5	S18 (2014)
		0.34 F/cm ² at 1 mA/cm ²	2E (Symm)	-	-	12.5	КОН	0.8	
ZnCo ₂ O ₄ nanoflakes	Hydrothermal	1220 F/g at 2 A/g	3E	5000	94.2 % at 2 A/g	-	КОН	0.6	S19 (2015)
ZnCo ₂ O ₄ nanoflowers on CNT/N-doped graphene	Hydrothermal	1802 F/g at 1 A/g	3E	4000	100 % at 10 A/g	-	КОН	0.5	S20 (2015)
		119 F/g at 0.5 A/g	2E (vs. CNT)	-	-	37.2	КОН	1.5	
ZnCo₂O₄@MnO₂ core- shell	Hydrothermal	2.4 F/cm ² at 6 mA/cm ²	3E	5000	90% at 24 mA/cm ²	-	КОН	0.5	S21 (2015)
		0.4 F/cm ² at 2.5 mA/cm ²	2E (Fe ₂ O ₃)	5000	91% at 5 mA/cm ²	37.8	КОН	1.3	
ZnCo ₂ O ₄ nanowires on carbon textile	Hydrothermal	1283 F/g at 1 A/g	3E	5000	Negligible at 8 A/g	-	КОН	0.4	S22 (2014)
Zn-Ni-Co ternary oxide nanowire	Hydrothermal	4.2 F/cm ² at 1.7 mA/cm ²	3E	6000	80.9 % at 10 A/g	-	КОН	0.5	S23 (2015)
		114 F/g at 1 A/g	2E (vs. AC)	6000	71.2 % at 3 A/g	35.6	КОН	1.5	
NiCo₂O₄@NiMoO₄ nanowires	Hydrothermal	1067 F/g at 10 mA/cm ²	3E	5000	84 % at 10 mA/cm ²	-	КОН	0.5	S24 (2015)
		-	2E (vs. AC)	5000	87 % at 10 mA/cm ²	-	КОН	1.4	
nickel copper oxide nanowires	Hydrothermal	2.24 F/cm ² at 10 mA	3E	1000	90 % at 10 A/g	-	КОН	0.5	S25 (2014)
		126 F/g at 2 mA/cm ²	2E (vs. AC)	5000	87 % at 20 mA/cm ²	30	КОН	1.3	
nickel cobalt oxide nanowires	Hydrothermal	1479 F/g at 1 A/g	3E	-	-	-	КОН	0.5	S26 (2014)
		105 F/g at 3.6 mA/cm ²	2E (vs. AC)	3000	83 % at 20 mV/s	37.4	КОН	1.6	
Co₃O₄@PPy@MnO₂ nanowires	Hydrothermal- polymerization- soaking	629 F/g at 1.2 mA/cm ²	ЗE	-	-	-	NaOH	0.8	S27 (2014)
		96.5 F/g at 0.1 A/g	2E (vs. AC)	1100	100 % at 3 A/g	34.3	NaOH	1.6	
CuCo ₂ S ₄ -HNN	Hydrothermal	2163 F/g (6.5 F/cm ²) at 6 mA/cm ²	3E	3000	96.3 % at 15 mA/cm ²	-	КОН	0.6	This work
		124 F/g (3 F/cm ²) at 24 mA/cm ²	2E (vs. AC)	6000	94.1 % at 48 mA/cm ²	44.1	кон	1.6	



Fig. S6 Electrochemical performance of $CuCo_2S_4$ –HNN electrode in polysulfide electrolyte. (a) CD curves of the $CuCo_2S_4$ –HNN electrode at different current densities, (b) a comparison between the specific capacitance and rate capability of the $CuCo_2S_4$ –HNN electrode with previously reported $CuCo_2S_4$ electrode (ref. 8), (c) long-term cycling stability of the $CuCo_2S_4$ –HNN electrode at a current density of 70 A g⁻¹. For comparing the electrochemical performance of our electrodes with previously reported $CuCo_2S_4$ electrode (Ref. 8), we performed electrochemical tests in polysulfide electrolyte (1 M KOH/1 M Na₂S·9H₂O/1 M Sulfur powders). As shown, our electrodes have better electrochemical performance including higher specific capacitances in various current densities, better rate capability (38 % retention vs. 27 % retention for ref. 8) and more cycling stability (10.7 % loss vs. 20.5 % loss for ref.8). In addition, the present work has more advantages such as: binder-free and conductive-agent-free electrodes with a unique hierarchical hollow nanoporous nanoneedle array structures directly grown on Ni foam. Symmetric and asymmetric devices based on $CuCo_2S_4$ –HNN electrodes are the other novelties of this work.



Fig. S7 Electrochemical performance of $CuCo_2S_4$ –HNN//CuCo_2S_4–HNN symmetric supercapacitor. (a) CD curves at various current densities, (b) rate capability, and (c) Ragone plot of the symmetric and asymmetric devices. We assembled two as-prepared $CuCo_2S_4$ –HNN electrodes with a cellulosic paper as the separator to make a symmetric device for comparing its overall performance with the $CuCo_2S_4$ –HNN//AC asymmetric device. Fig. S7 shows the CD curves (a) and the specific capacitances of the symmetric device (b); also the overall performance comparison between the symmetric device and the asymmetric device was performed in the Ragone plot (c). As shown, the asymmetric device has a much more energy densities than symmetric device.

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