Supporting Information

Construction of a Hierarchical $NiCo_2S_4@PPy$ Core-Shell Heterostructure Nanotube Array on Ni Foam for a High-Performance Asymmetric Supercapacitor

Minglei Yan,[†] Yadong Yao,^{*,†} Jiqiu Wen,[‡] Lu Long,[†] Menglai Kong,[†] Guanggao Zhang,[†] Xiaoming Liao,[†] Guangfu Yin,[†] and Zhongbing Huang[†]

[†]College of Materials Science and Engineering and [‡]Analytical and Test Center, Sichuan University, Chengdu 610065, china

*Corresponding Author, E-mail: yaoyd523@163.com Tel./fax: +86 28 85413003.

Calculation formulas:

(1) Single electrode

The area specific capacitances of the samples are calculated from the CV curves using the following formula ¹:

$$Cs = \frac{1}{sv(v_a - v_c)} \int_{v_a}^{v_c} I(V) dV$$
 (Formula S1)

Where the Cs (F/cm²) is the area specific capacitance, I is the response current (A), s is the area of activate materials loaded on the Ni foam, v is the rate (mV/s) and Vc and Va are the high and low potential limits of the CV tests.

The area and mass specific capacitances of the samples are calculated from the GCD curves using the following formula 2 :

$$Cs = \frac{I \times \Delta t}{s \times \Delta V}$$
 (Formula S2)
$$Cm = \frac{I \times \Delta t}{m \times \Delta V}$$
 (Formula S3)

Where the **Cs** (F/cm²) is the area specific capacitance, the **Cm** (F/g) is the mass specific capacitance, I is the response current (A), s is the area of activate materials loaded on the Ni foam, m is the mass of activate materials loaded on the Ni foam, Δt is the discharge time, ΔV is potential window of the discharge process.

(2) Supercapacitor device

The area and mass specific capacitances of the supercapacitor device calculated from the GCD curves is similar to those of single electrode.

The mass loading of activated carbon was determined by balancing the charges stored in each electrode. Its specific mass was calculated by the following formula ³:

$$C_{s+}\Delta V_{+}S = C_{m-}\Delta V_{-}m_{-} \qquad (Formula S4)$$

Where m is the mass loading, C_{s+} and C_m represent the specific capacitance of positive electrode (F/cm²⁾ and negative electrode (F/g) respectively. ΔV is the potential window of positive (+) and negative (-) electrode. S is the area of Ni foam supported NiCo₂S₄@PPy-50. m. is the mass of negative electrode.

The energy density (E) and power density (P) are obtained according to the following formulas ⁴:

$$E = \frac{1}{2}C\Delta V^{2}$$
 (Formula S5)
$$P = \frac{E}{\Delta t}$$
 (Formula S6)

Where E (Wh/kg) is the energy density, C (F/g) is the mass specific capacitance, ΔV (V) is the voltage window, P (W/kg) refers to the power density and Δt (s) is the discharge time.

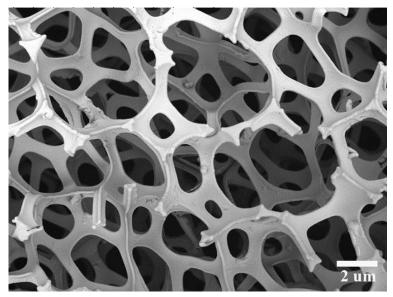


Figure S1 SEM image of Ni foam.

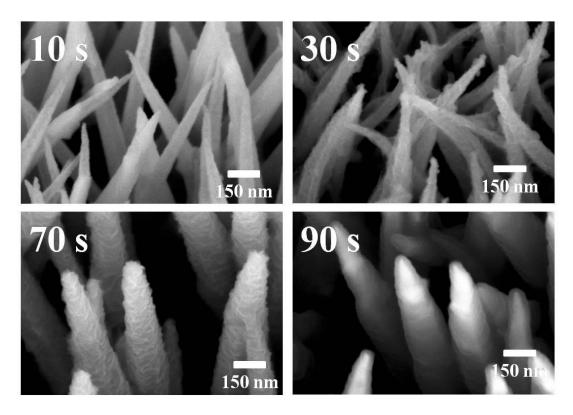


Figure S2 SEM images of $NiCo_2S_4@PPy$ NTA/NF by using different electrodeposition time.

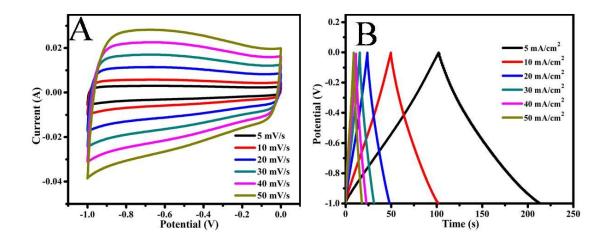


Figure S3 (A) CV curves of the AC at different scan rates; (B) GCD curves of the AC at different current densities.

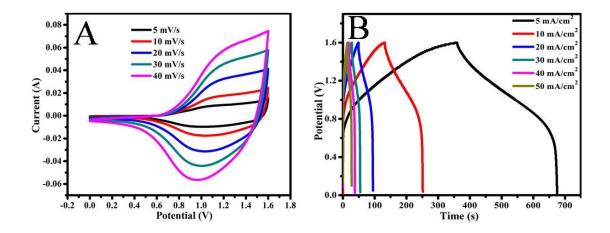


Figure S4 (A) CV curves of $NiCo_2S_4//AC$ at different scan rates; (B) GCD curves of $NiCo_2S_4//AC$ at different current densities.

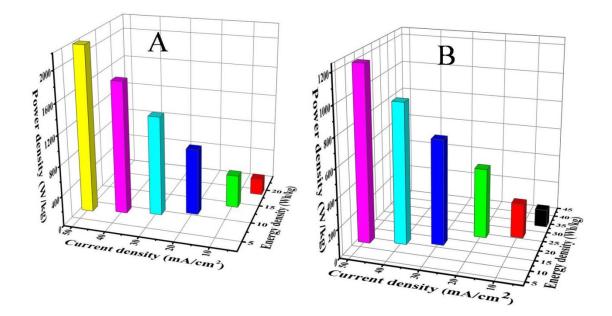


Figure S5 (A) the energy density and power density of $NiCo_2S_4//AC$ at different current densities; (B) the energy density and power density of $NiCo_2S_4@PPy-50//AC$ at different current densities.

Electrode	Method	Morphology	Specific	Capacitance	Ref.
material			capacitance	retention	
Carbon@ NiCo ₂ S ₄	hydrothermal	nanorods	1455 F/g at 1	83% after 2000	5
			A/g	cycles at 20	
				A/g	
NiCo ₂ S ₄ @ NiCo _x S _y	hydrothermal and	core-shell	3.9 F/cm^2 at	77% after 1500	6
	electrodeposition	nanotube	1 mA/cm^2	cycles at 10	
		arrays		mA/cm ²	
NiCo ₂ S ₄ @CoS _x	hydrothermal	core-shell	4.74 F/cm^2 at	76.1% after	7
		nanotube	5 mA/cm^2	1500 cycles at	
		arrays		50 mA/cm^2	
NiCo ₂ S ₄ /CFC	solvothermal	Burl-like	0.83 F/cm^2 at	75.9% after	8
			25 mA/cm^2	5000 cycles at	
				20 mA/cm^2	
CoS @ NiCo ₂ S ₄	ion exchange process	core-shell	7.62 F/cm ² at	71.7% after	9
		nanoarrays	5 mA/cm^2	3000 cycles at	
				10 mA/cm^2	
NiCo ₂ S ₄ @MnO ₂	hydrothermal	core-shell	1337.8 F/g at	82% after 2000	10
		nanotubes	2 A/g	cycles at 20	
				A/g	
CoNi ₂ S ₄	hydrothermal	mushroom-	5.71 F/cm ² at	80.91% after	11
		like	20 mA/cm^2	3000 cycles at	

Table S1 Comparison of synthesis method, morphology and electrochemicalperformance of different electrode materials

				20 mA/cm^2
NiCo ₂ S ₄ /MWCNTs	solvothermal reaction	nanotubes	2080 F/g at 1	83% after 2000 ¹²
			A/g	cycles at 8 A/g
NiCo ₂ S ₄ @PPy	hydrothermal and	core-shell	9.781 F/cm ²	72.19% after This
	electrodeposition	nanotube	(1364 F/g) at	3000 cycles at work
		arrays	5 mA/cm^2	50 mA/cm^2

Reference

(1) Mei, L.; Yang, T.; Xu, C.; Zhang, M.; Chen, L.; Li, Q.; Wang, T. Hierarchical Mushroom-Like CoNi₂S₄ Arrays as a Novel Electrode Material for Supercapacitors. *Nano Energy* **2014**, *3*, 36-45.

(2) Li, R.; Wang, S.; Huang, Z.; Lu, F.; He, T. $NiCo_2S_4@Co(OH)_2$ Core-Shell Nanotube Arrays in Situ Grown on Ni Foam for High Performances Asymmetric Supercapcitors. *J. Power. Sources* **2016**, *312*, 156-164.

(3) Chen, H.; Jiang, J.; Zhang, L.; Xia, D.; Zhao, Y.; Guo, D.; Qi, T.; Wan, H. In Situ Growth of NiCo₂S₄ Nanotube Arrays on Ni Foam for Supercapacitors: Maximizing Utilization Efficiency at High Mass Loading to Achieve Ultrahigh Areal Pseudocapacitance. *J. Power. Sources* **2014**, *254*, 249-257.

(4) Kong, W.; Lu, C.; Zhang, W.; Pu, J.; Wang, Z. Homogeneous Core–Shell NiCo₂S₄ Nanostructures Supported on Nickel Foam for Supercapacitors. *J. Mater. Chem. A* 2015, *3*, 12452-12460.

(5) Li, L.; Dai, Z.; Zhang, Y.; Yang, J.; Huang, W.; Dong, X. Carbon@NiCo₂S₄ Nanorods: An Excellent Electrode Material for Supercapacitors. *RSC Adv.* **2015**, *5*, 83408-83414.

(6) Ding, R.; Zhang, M.; Yao, Y.; Gao, H. Crystalline NiCo₂S₄ Nanotube Array Coated with Amorphous Nicoxsy for Supercapacitor Electrodes. *J. Colloid. Interface. Sci.* **2016**, *467*, 140-147.

(7) Fu, W. Cobalt Sulfide Nanosheets Coated on NiCo₂S₄ Nanotube Arrays as Electrode Materials for High-Performance Supercapacitors. *J. Mater. Chem. A* 2015, *3*, 10492-10497.

(8) Sun, M.; Tie, J.; Cheng, G.; Lin, T.; Peng, S.; Deng, F.; Ye, F.; Yu, L. In Situ Growth of Burl-Like Nickel Cobalt Sulfide on Carbon Fibers as High-Performance Supercapacitors. *J. Mater. Chem. A* **2014**, *3*, 1730-1736.

(9) Zeng, W.; Zhang, G.; Wu, X.; Zhang, K.; Zhang, H.; Hou, S.; Li, C.; Wang, T.;
Duan, H. Construction of Hierarchical CoS Nanowire@ NiCo₂S₄ Nanosheet Arrays
Via One-Step Ion Exchange for High-Performance Supercapacitors. *J. Mater. Chem.*A 2015, 3.

(10) Yang, J. Hybrid NiCo₂S₄@MnO₂ Heterostructures for High-Performance Supercapacitor Electrodes. *J. Mater. Chem. A* **2014**, *3*, 1258-1264.

(11) Mei, L.; Yang, T.; Xu, C.; Zhang, M.; Chen, L.; Li, Q.; Wang, T. Hierarchical Mushroom-Like CoNi₂S₄ Arrays as a Novel Electrode Material for Supercapacitors. *Nano Energy* **2014**, *3*, 36-45.

(12) Wen, P.; Fan, M.; Yang, D.; Wang, Y.; Cheng, H.; Wang, J. An Asymmetric Supercapacitor with Ultrahigh Energy Density Based on Nickle Cobalt Sulfide Nanocluster Anchoring Multi-Wall Carbon Nanotubes Hybrid. *J. Power. Sources* **2016**, *320*, 28-36.