Supporting information

Hierarchical bilayered hybrid nanostructural arrays of NiCo₂O₄ microurchins and nanowires as free-standing electrode with high loading for high-performance lithium-ion batteries

Yu Wang,^{a,c} Pengcheng Liu,^{b*} Kongjun Zhu,^{a*} Jing Wang,^a Jinsong

Liu^{a,c}

^a State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

^b School of Mechanical and Electric Engineering, Guangzhou University, Guangzhou 510006

^c China College of Materials Science and Engineering , Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

Corresponding Author: kjzhu@nuaa.edu.cn (K. Zhu); pch060710111@hotmail.com (P. Liu)



Figure S1. SEM images and the corresponding XRD images of these products prepared in pH=3, pH=5, pH=7 under hydrothermal condition, respectively.



Figure S2 TG measurement of NiCo-precursor HNAs at a temperature range of 0-800 $^{\circ}$ C and the heating rate 10 $^{\circ}$ C /min

To further confirm the calcination temperature during annealing, we conduct the TG measurement of NiCo-precursor HNAs at a temperature range of 0-800 °C with a heating rate of 10 °C /min, and the TG data is shown in Figure R1. The XRD pattern of the Ni-Co precursors, which may be mixture of $Co_2(CO_3)(OH)_2 \cdot 0.11H_2O$ and $Ni_2(CO_3)(OH)_2 \cdot 4H_2O$, is shown in Figure R2. In Figure R1, the initial 1 % mass loss between 50 and 200 °C is due to the evaporation of moisture. The large mass loss of about 3 % between 200 and 300 °C can be observed, which is attributed to the release of CO₂ and hydrolysis during the transformation from $Co_2(CO_3)(OH)_2 \cdot 0.11H_2O$ and $Ni_2(CO_3)$ (OH)₂·4H₂O to NiCo₂O₄. The mass have a slight increase during the following temperature rise, which may be caused by the oxidation of metallic Ni. Thus, selecting 300 °C as the annealing temperature can not only ensure the complete transformation from $Co_2(CO_3)(OH)_2 \cdot 0.11H_2O$ to $NiCo_2O_4$, but also avoid the excessive oxidation of nickel foam. In addition, our dense NiCo₂O₄ HNAs on NF can have an effect to prevent the oxidation of NF during annealing. So, the calcination temperature was finally set as 300 °C.



Figure S3 Raman spectra of NiCo₂O₄ HNAs.



Figure S4 The SEM images of $NiCo_2O_4$ HNAs before and after ultrasonic treatment.



Figure S5 Nitrogen adsorption/desorption isotherms and pore-size distribution curves for $NiCo_2O_4$ HNAs.

Type of materials	Capacity	Rate performance	Cycling stability	loading (mg/cm ²)	Reference
NiCo ₂ O ₄ HNAs/NF	1094 mAh g ⁻¹ (at 500mA g ⁻¹)	875 mAh g ⁻¹ (at 1000 mA g ⁻¹)	90 % (After 100 cycles at 500 mA g ⁻¹)	7	This work
NiCo ₂ O ₄ NWAs/ CT	1012 mAh g ⁻¹ (at 500mA g ⁻¹)	589 mAh g ⁻¹ (at 3000 mA g ⁻¹)	84 % (After 100 cycles at 500 mA g ⁻¹)	1.2	1
NiCo ₂ O ₄ @ NiCo ₂ O ₄ Nanocactus/NF	925 mAh g ⁻¹ (at 120 mA g ⁻¹)	407 mAh g ⁻¹ (at 960 mA g ⁻¹)	90% (After 100 cycles at 120 mA g ⁻¹)	3.0	2
NiCo ₂ O ₄ complex hollow spheres	1401 mAh g ⁻¹ (at 150 mA g ⁻¹)	533 mAh g ⁻¹ (at 2000 mA g ⁻¹)	78% (After 100 cycles at 200 mA g ⁻¹)	-	3

NiCo ₂ O ₄ /C nanocomposites	1154 mAh g ⁻¹ (at 40 mA g ⁻¹)		$\begin{array}{ccc} 78.3\% \\ (After & 50 \\ cycles at & 40 \\ mA & g^{-1} \end{array}$	-	4
flower-like NiCo ₂ O ₄	~1280 mAh g^{-1} (at 150 mA g^{-1})	420 mAh g ⁻¹ (at 2000 mA g ⁻¹)	$\sim 55\%$ (After 60 cycles at 500 mA g ⁻¹)	-	5
NiCo ₂ O ₄ microspheres	~1680 mAh g^{-1} (at 100 mA g^{-1})	393 mAh g ⁻¹ (at 1600 mA g ⁻¹)	$\sim 53\%$ (After 70 cycles at 800 mA g ⁻¹)	-	6
NiCo ₂ O ₄ –RGO composite	1351 mAh g ⁻¹ (at 100 mA g ⁻¹)	396 mAh g ⁻¹ (at 800 mA g ⁻¹	80.1% (After 70 cycles)	-	7

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