Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Self-supported Co_3O_4 wire-penetrated-cage hybrid arrays with enhanced supercapacitance properties

Junqi Li,[a, b] Xiao Wang,*[a] Shuyan Song,[a] Shu'na Zhao,[a, b] Fan Wang,[a, b] Jing Pan,[a, d, c] Jing Feng,[a] and Hongjie Zhang*[a]

[a.] *State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, Jilin, P. R. China. E-mail: skybyyn@ciac.ac.cn; hongjie@ciac.ac.cn*

[b.] *University of Chinese Academy of Sciences, 19 A Yuquan Road, Beijing 100049, Beijing, P. R. China*

[c.] *Department of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, Jilin, P. R. China*

Experimental Section

Synthesis of Co(OH)F/Ni foam arrays: Ni foam (1×3 cm) is first washed with HCl, water and ethanol in turn to clean the surface and well dried. The growth process is according to the recent report.[S1] In a typical synthesis, 0.291 g $Co(NO_3)_2$, 0.093 g NH_4F and 0.3 g urea are dissolved in 20 mL water to form a transparent solution. Then, the pre-treated Ni foam is put in the mixture, following by a hydrothermal treatment at 120 °C for 6 hours. After cooling down to room temperature, the Ni foam is taken out and washed with water *via* ultra-sound treatment for several times. Finally, the as-obtained Co(OH)F/Ni foam is dried for further use.

Synthesis of Co_3O_4/Ni foam arrays: The Co_3O_4/Ni foam arrays are obtained by annealing the as-obtained Co(OH)F/Ni foam precursors in air at 400 °C (at a heating rate of 3 °C/min) for 1 hour.

Surface modification process: 60 mg PAA molecule is first dissolved in 20 mL water. Then, Co_3O_4/Ni form is put in. After heating at 80 °C for four hours, the produces are separated, washed with water for three times and dried at 60 °C for further use.

Synthesis of Co_3O_4–ZIF-67/Ni foam precursors: 1.5 mmol $Co(NO_3)_2$ is dissolved in 10 mL methanol, then the surface modified Co_3O_4/Ni form is put in and stew for 30 min. Another 10 mL methanol containing 4 mmol MeIm is added. The reaction is finished after 24 hours. The Ni foam is carefully washed with methanol to remove the un-reacted ions.

Synthesis of Co_3O_4 self-penetrated arrays/Ni foam arrays: The final product is prepared by annealing the Co_3O_4–ZIF-67/Ni foam precursors in air at 400 °C (at a heating rate of 3 °C/min) for 1 hour.

Characterization: The X-ray diffraction patterns of the products were collected on a Rigaku-*D*/max 2500 V X-ray diffractometer with Cu-K_α radiation (λ=1.5418 Å), with an operation voltage and current maintained at 40 kV and 40 mA. Transmission electron microscopic (TEM) images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. The catalytic performances of the catalysts were monitored on-line by mass spectrogram.

Electrochemical Measurements: The pseudocapacitive performances are investigated by using a three-electrode system with a Pt foil as the counter electrode and a SCE as the reference electrode in 2.0 M KOH aqueous electrolyte. CHI 660E workstation has been used. The areal specific capacitance of the electrodes was calculated from the CP curves based on equation:

$$AC=I\Delta t/C\Delta V,$$

where C, I, t and ΔV are the SC (F/cm^2) of the electroactive materials, the discharging current density (A/cm^2), the discharging time (s), and the discharging potential range (V), respectively.

S1 J. Tian, Q. Liu, A. Asiri and X. Sun, *J. Am. Chem. Soc.*, 2014, **136**, 7587–7590.

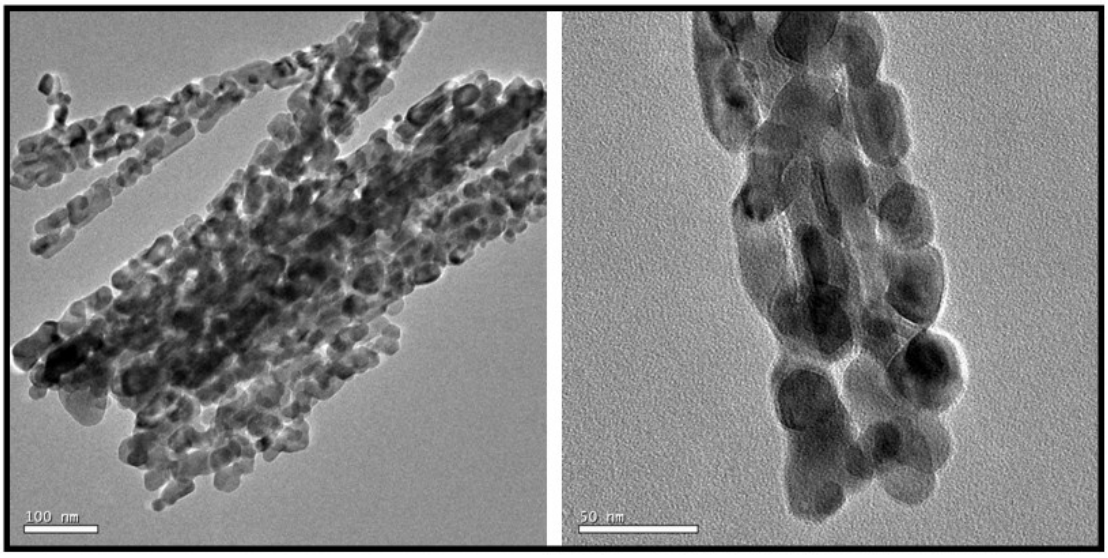

Figure S1. TEM images of bare Co_3O_4 nanowires on Ni foam.

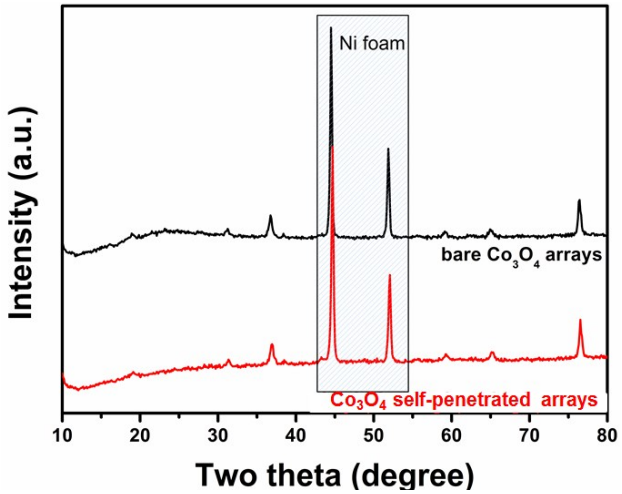

Figure S2. XRD patterns of bare Co_3O_4 (black line) and Co_3O_4 self-penetrated (red line) arrays.

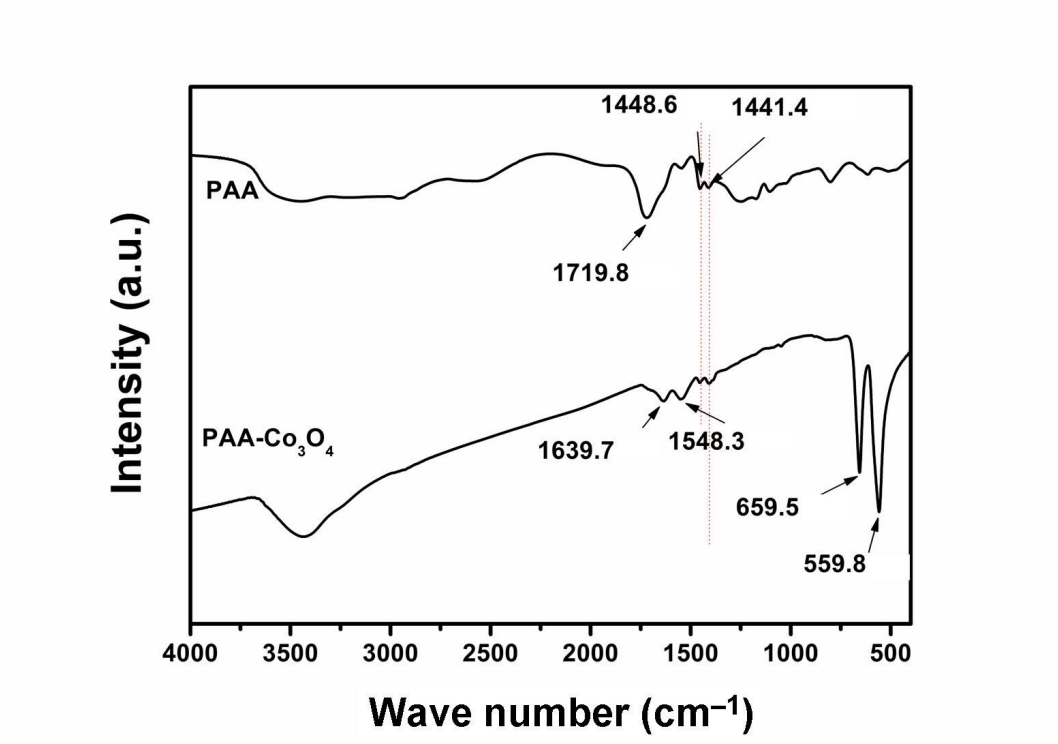

Figure S3. IR spectra of PAA and PAA modified Co_3O_4 nanowires.

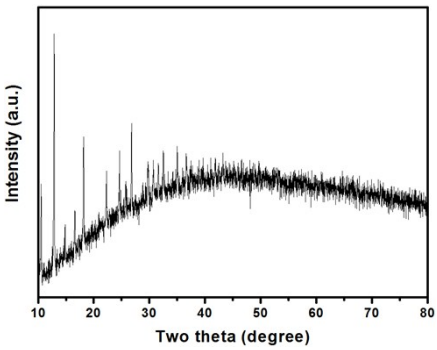

Figure S4. XRD data of Co_3O_4 nanowire-penetrated ZIF-67 precursors obtained by collected the free sample out of Ni foam after ultra-sound treatment.

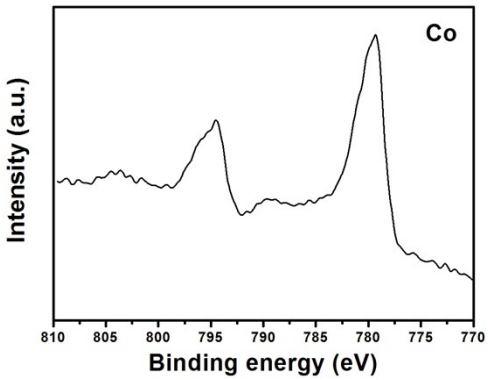

Figure S5. XPS spectra of Co element in final products.

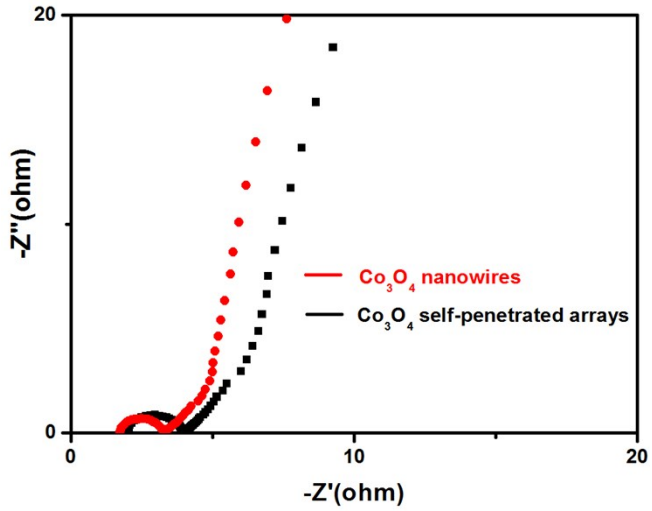

Figure S6. EIS curves of Co_3O_4 nanowires and Co_3O_4 self-penetrated arrays.

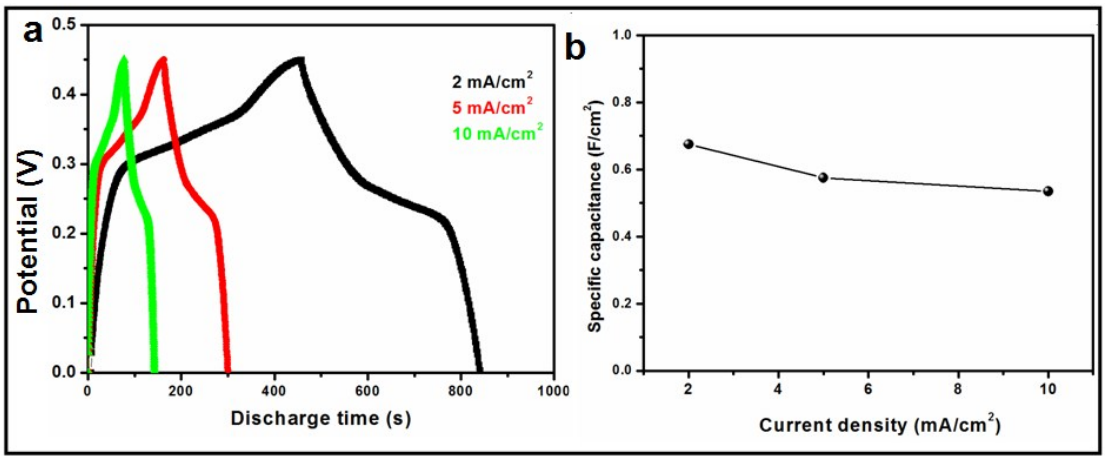

Figure S7. Two-electrodes result of the as-obtained Co_3O_4 self-penetrated arrays.

Arrays	Current density (mA/cm^2)	Areal capacitance (F/cm^2)	Ref.
Co_3O_4 self-penetrated hybrids	2	3.7	This work.
	5	3.2	This work.
	10	3.0	This work.
	20	2.8	This work.
Bare Co_3O_4 nanowires	2	1.1	This work.
Co_3O_4@$NiCo_2O_4$ core@shell nanowires	5	2.04	Ref. 17
	10	1.62	Ref. 17
	20	1.32	Ref. 17
$NiCo_2O_4$ needles	2.78	1.44	Ref. S2
	5.56	0.99	Ref. S2
	11.12	0.79	Ref. S2
	22.24	0.59	Ref. S2
Co_3O_4@$NiCo_2O_4$ nanoforest	1.6	0.89	Ref. S3

Table S1. Areal capacitances of Co_3O_4–based hybrid arrays reported in the representative literatures in aqueous electrolytes using three-electrode systems.

S2 G. Q. Zhang, H. B. Wu, H. E. Hoster, M. Chan-Park, X. W. Lou, *Energy Environ. Sci.*, 2012, **5**, 9453.
S3 Y. Li, Y. Zhang, Y. Li, Z. Wang, H. Fu, X. Zhang,Y. Chen, H. Zhang, X. Li, *Electrochimica Acta*, 2014, **145**, 177.