Electronic Supplementary Information (ESI)

Growth of ultrathin mesoporous Co₃O₄ nanosheet arrays on Ni foam for

high-performance electrochemical capacitors

Changzhou Yuan,^{a, b} Long Yang,^a Linrui Hou,^a Laifa Shen,^c Xiaogang Zhang, *^c and Xiong Wen (David) Lou*^b

^a Anhui Key Laboratory of Metals and processing, School of Materials Science and Engineering, Anhui University of Technology, Maanshan, 243002, P.R. China.
^b School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, 637457, Singapore E-mail:XWLou@ntu.edu.sg
^c College of Material Science & Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016, P.R. China E-mail:azhangxg@nuaa.edu.cn

Experimental

1. Materials synthesis

Nickel foam (approximately 1 cm × 4 cm) was carefully cleaned with 6 M HCl solution in an ultrasound bath for 30 min in order to remove the NiO layer on the surface, and then rinsed with deionized water and absolute ethanol, respectively. The electrodeposition was performed in a standard three-electrode glass cell consisting of the clean Ni foam working electrode, a platinum plate counter electrode and a saturated calomel reference electrode (SCE) at room temperature of 25 \pm 1 °C. The Co(OH)₂ was electrodeposited upon Ni foam in a 0.05 M Co(NO₃)₂·6H₂O aqueous electrolyte using an IVIUM Electrochemical Workstation (the Netherlands). The electrodeposition potential is -1.0 V (vs. SCE). After electrodeposition for 20 min, the green Ni foam was carefully rinsed several times with deionized water and absolute ethanol with the assistance of ultrasonication, and finally dried in air. Then, the sample was put in a quartz tube and calcined at 250 °C for 2 h with a ramping rate of 1 °C min⁻¹ to transform into ultrathin mesoporous Co₃O₄ nanosheets. In average, about 1.4 mg of Co₃O₄ nanosheets was grown on the 1 cm² Ni foam, carefully weighted after calcination. For comparison, another heating rate of 10 °C min⁻¹ is also used.

2. Sample characterization

The morphologies and structures of the samples were characterized by scanning electron microscopy (SEM, LEO 1430VP, Germany), transmission electron microscope (TEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) (JEOL JEM 2100 system operating at 200 kV), powder X-ray diffraction (XRD) (Max 18 XCE, Japan) using a Cu Ka source ($\lambda = 0.1542$ nm) at a scanning rate of 3 ° min⁻¹ over a 2 θ range of 10 - 80°, and N₂ adsorption-desorption measurements using an ASAP-2010 surface area analyzer. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area of samples. The pore size distributions (PSD) were derived from the desorption branch of the isotherm with the Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analysis was performed on a TG instrument (NETZSCH STA 409 PC) with a heating rate of 10 °C min⁻¹ from 30 to 600 °C under ambient atmosphere.

3. Electrochemical characterizations

The ultrathin mesoporous Co_3O_4 nanosheet arrays supported on Ni foam were directly used as the working electrode. A platinum plate (1 cm²) and a SCE were used as the counter and reference electrodes, respectively, for following electrochemical tests by cyclic voltammetry (CV) and chronopotentiometry (CP) performed with an IVIUM Electrochemical Workstation (the Netherlands). The electrolyte was a 2 M KOH aqueous solution. The specific capacitance of ultrathin mesoporous Co_3O_4 nanosheets grown on Ni foam was calculated from the CP curves based the following equation:

$$C = \frac{It}{\Delta V}$$

where *C*, *I*, *t* and ΔV are the SC (F g⁻¹), the discharging current density (A g⁻¹), the discharging time (s) and the discharging potential range (V), respectively.



Fig. S1. XRD pattern and an optical image of the Co(OH)₂/Ni foam.

From Figure S1, except the three peaks ($2\theta = 44.3^{\circ}$, 51.7° and 76.1°) ascribed to the Ni foam, other five obvious diffraction peaks of the as-synthesized green Co(OH)₂/Ni foam (the inset in Figure S1) can be easily identified for α -Co(OH)₂ crystalline structure,¹ which is consistent with the previous reports.

(a) J. Yang, H.W. Liu, W.N. Martens and R.L. Frost, *J. Phys. Chem. C*, 2010, **114**, 111; (b)
 J.R.S. Brownson and C.L. Clément, *Electrochim. Acta*, 2009, **54**, 6637; (c) T. Zhao, H. Jiang and J.
 Ma, *J. Power Sources*, 2011, **196**, 860; (d) Z.A. Hu, Y.L. Xie, Y.X. Wang, L.J. Xie, G.R. Fu, X.Q.
 Jin, Z.Y. Zhang, Y.Y. Yang and H.Y. Wu, *J. Phys. Chem. C*, 2009, **113**, 12502.



Fig. S2. Thermogravimetric data of the α -Co(OH)₂ precursor.

As seen from Fig. S2, the Co(OH)₂ obtained by electrodeposition undergoes a two step weight loss due to dehydration and deposition, rather than a single step weight loss for the β -Co(OH)₂.^{2,3} Specifically, the weight loss below 155 °C is attributed to the removal of the absorbed water and the evaporation of the intercalated water molecules.³ And the weight loss above 155 °C is associated with the loss of water produced by the decomposition and dehydroxylation of Co(OH)₂.³ After thermally oxidative transformation into Co₃O₄, the net weight loss observed is *ca*. 23%, much larger than that of 13.6% of the β -Co(OH)₂.² These data further indicates the formed precursor is α -Co(OH)₂ phase rather than β -Co(OH)₂.

2 R.S. Jayashree and P. Vishnu Kamath, J. Mater. Chem., 1999, 9, 961.

3 J.H. Zhou, A.L. Wang, G.R. Li, J.W. Wang, Y.N. Ou and Y.X. Tong, *J. Mater. Chem.*, 2012, **22**, 5656.



Fig. S3. XRD patterns of the pure Ni foam and Co₃O₄/Ni foam.



Fig. S4. TEM image of the Co_3O_4 nanosheets scratched down from the Ni foam.



Fig. S5. FESEM images of the precursor $Co(OH)_2/Ni$ foam.



Fig. S6. FESEM images of the Co_3O_4/Ni foam obtained by calcination with a ramping rate of 10 °C min⁻¹.

Electrode structure	Specific capacitance
Ultrathin mesoporous Co ₃ O ₄ nanosheet arrays/Ni	2735 F g^{-1} at 2 A g^{-1}
foam (this study)	
Co ₃ O ₄ nanosheets@nanowire arrays/Ni foam (ref. 4)	715 F g ⁻¹ at <i>ca</i> . 0.67 A g ⁻¹
Hollow Co ₃ O ₄ nanowire arrays/Ni foam (ref. 5)	599 F g^{-1} at 2 A g^{-1}
Mesoporous Co ₃ O ₄ nanowire arrays (ref. 6)	1160 F g^{-1} at 2 A g^{-1}
Co ₃ O ₄ nanowire arrays/Ni foam (ref. 7)	754 F g^{-1} at 2 A g^{-1}
Porous nanowall Co ₃ O ₄ film/Ni foam (ref. 8)	$325 \text{ F g}^{-1} \text{ at } 2 \text{ A g}^{-1}$
Co ₃ O ₄ nanoflowers/Ni foam (ref. 9)	1309.7 F g^{-1} at 3 A g^{-1}
Co ₃ O ₄ nanowire arrays/Ni foam (ref. 10)	746 F g ⁻¹ at <i>ca.</i> 0.31 A g ⁻¹
Net-like Co ₃ O ₄ nanostructures/Ni foam (ref. 11)	1090 F g ⁻¹ at 10 mV s ⁻¹

Table S1. Specific capacitances and area loading of the Co_3O_4 /nickel foam in this study, compared with some other Co_3O_4 /nickel foam electrodes reported in previous literature.

- 4 Q. Yang, Z.Y. Lu, Z. Chang, W. Zhu, J.Q. Sun, J.F. Liu, X.M. Sun and X. Duan, *RSC Adv.*, 2012, **2**, 1663.
- 5 X.H. Xia, J.P. Tu, Y.J. Mai, X.L. Wang, C.D. Gu and X.B. Zhao, *J. Mater. Chem.*, 2011, **21**, 9319.
- 6 F. Zhang, C.Z. Yuan, X.J. Lu, L.J. Zhang, Q. Che and X.G. Zhang, J. Power Sources, 2012, 203, 250.
- 7 X.H. Xia, J.P. Tu, Y.Q. Zhang, Y.J. Mai, X.L. Wang, C.D. Gu and X.B. Zhao, *RSC Adv.*, 2012, **2**,1835.
- 8 J.B. Wu, Y. Lin, X.H. Xia, J.Y. Xu and Q.Y. Shi, *Electrochim. Acta*, 2011, 56, 7163.
- 9 X.X. Qing, S.Q. Liu, K.L. Huang, K.Z. Lv, Y.P. Yang, Z.G. Lu, D. Fang and X.X. Liang, *Electrochim. Acta*, 2011, **56**, 4985.
- 10 Y.Y. Gao, S.L. Chen, D.X. Cao, G.L. Wang and J.L. Yin, J. Power Sources, 2010, 195, 1757.
- 11 H.T. Wang, L. Zhang, X.H. Tan, C.M.B. Holt, B. Zahiri, B.C. Olsen and D. Mitlin, J. Phys. Chem. C, 2011, 115,17599