

Supplementary materials for Journal of Materials Chemistry

This journal is © The Royal Society of Chemistry 2012

Electronic Supplementary Information (ESI)

Facile template-free synthesis of ultralayered mesoporous nickel cobaltite nanowires towards high-performance electrochemical capacitors

**Changzhou Yuan ^{*a}, Jiaoyang Li ^a, Linrui Hou ^a, Long Yang ^a, Laifa Shen ^b, Xiaogang
Zhang ^{*b}**

^a *Anhui Key Laboratory of Metals and processing, School of Materials Science and Engineering,*

Anhui University of Technology, Ma`anshan, 243002, P.R. China.

^b *College of Material Science and Engineering, Nanjing University of Aeronautics and*

Astronautics, Nanjing, 210016, P.R. China.

E-mail: ayuancz@163.com; azhangxg@163.com

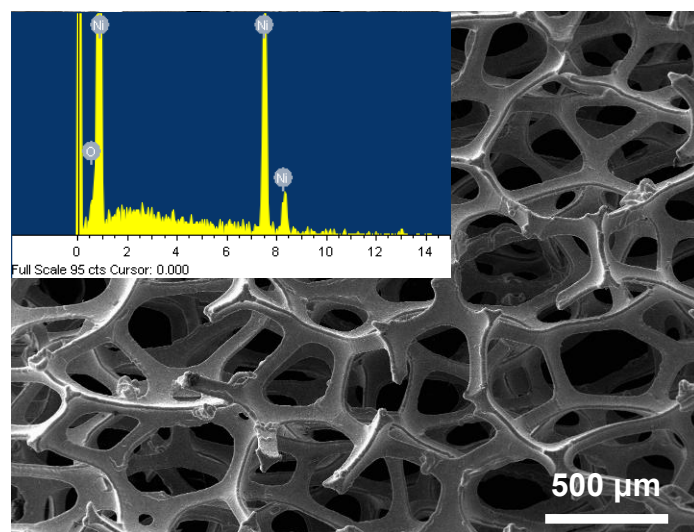


Fig. S1 FESEM images and EDAX (the inset) of the pretreated nickel foam

As seen in the Fig. S1, a three dimensional (3 D) grid structure and hierarchical porosity can be seen for the Ni foam itself. Moreover, the high purity of the Ni foam can be seen from the EDAX data (the inset in Fig. S1).

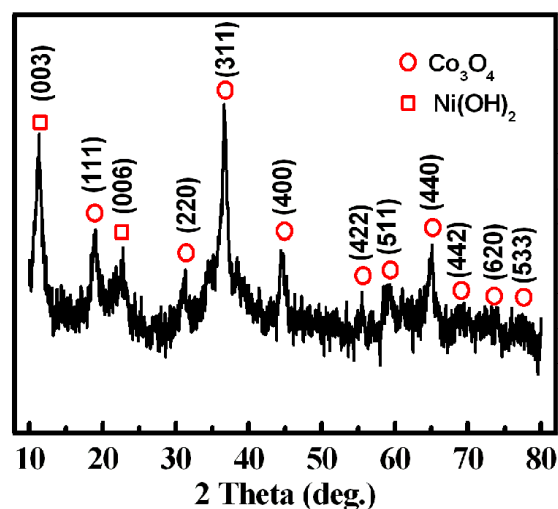
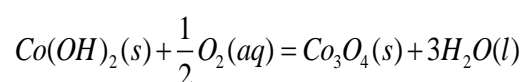


Fig. S2 XRD pattern of the uncalcinated precursor of the NiCo_2O_4 NWs

Of note, Co^{2+} and Ni^{2+} ions have similar coordination capability with other ions. Here, the added NH_4NO_3 makes the bivalent Co^{2+} and Ni^{2+} ions fully coordinated with NH_4^+ to form $\text{M}(\text{NH}_3)_x^{2+}$ ions,^[1] which will result in a relatively constant ratio of Co^{2+} to Ni^{2+} ions.^[1-4] Additionally, Co^{2+} and Ni^{2+} ions have similar affinity towards OH^- ions according to their solubility constants.^[1-4] The difference between Ni^{2+} and Co^{2+} ions may be reduced by forming complex with NH_4^+ , which leads to a similar nucleation and grown rate of $\text{Co}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$. Then during the following stirring and refluxing process, the Co_3O_4 comes from the solid-state reaction between the formed $\text{Co}(\text{OH})_2$ and the dissolved oxygen in the solution following the reactions as reported before^[5, 6]:



As seen from the Fig. S2, clearly, the uncalcinated precursor can be well indexed as a mixed phase including the $\text{Ni}(\text{OH})_2$ (JCPDS card no. 38-0715) and cubic Co_3O_4 (JCPDS card no. 43-1007).

- [1] L.Y. Yuan, X.H. Lu, X. Xiao, T. Zhai, J.J. Dai, F.C. Zhang, B. Hu, X. Wang, L. Gong, J. Chen, C.G. Hu, Y.X. Tong, J. Zhou, Z.L. Wang, *ACS Nano*, **2012**, 6, 656-661.
- [2] X.H. Lu, D.Z. Zheng, T. Zhai, Z.Q. Liu, Y.Y. Huang, S.L. Xie, Y.X. Tong, *Energy Environ. Sci.*, **2011**, 4, 2915-2912.
- [3] D. Yuan, T.X. Zhou, S.L. Zhou, S.S. Mo, N.N. Xia, *Electrochem. Commun.*, **2011**, 13, 242-246.
- [4] X.H. Lu, X. Huang, S.L. Xie, T. Zhai, C.S. Wang, P. Zhang, M.H. Yu, W. Li, C.L. Liang, Y.X. Tong, *J. Mater. Chem.*, **2012**, DOI:10.1039/C2JM30927K.
- [5] Y.G. Li, B. Tan, Y.Y. Wu, *Nano Lett.* 2008, 8, 265-270.
- [6] Y.G. Li, B. Tan, Y.Y. W, *J. Am. Chem. Soc.* 2006, 128, 14258-14259.

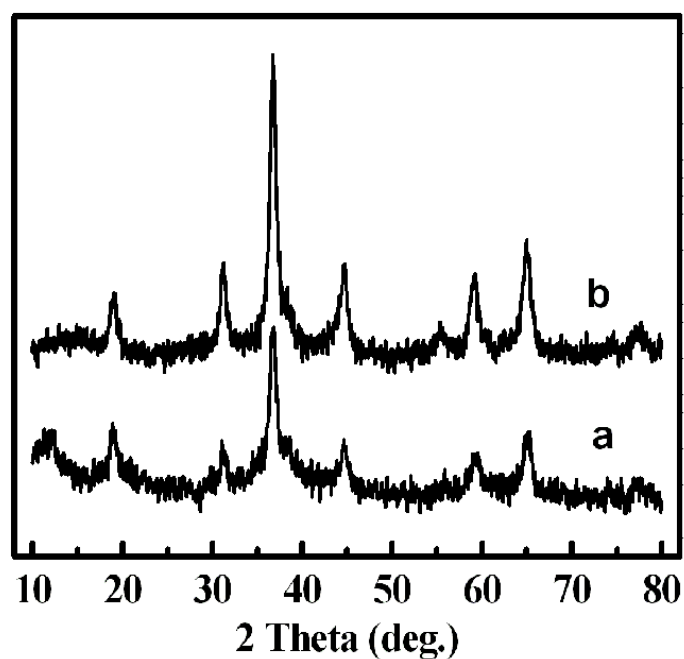


Fig. S3 XRD patterns for the precursor of the NiCo_2O_4 NWs calcinated at different temperatures. (a) 200 °C; (b) 400 °C.

As seen from the Fig. S3, after calcinated at 200 °C, the obtained sample still presents typical diffraction peaks of $\text{Ni}(\text{OH})_2$, with the comparison with the Fig. S2. And when the temperature increases up to 300 and 400 °C, the diffraction peak of $\text{Ni}(\text{OH})_2$ wholly disappears and the pure phase of NiCo_2O_4 can be found.

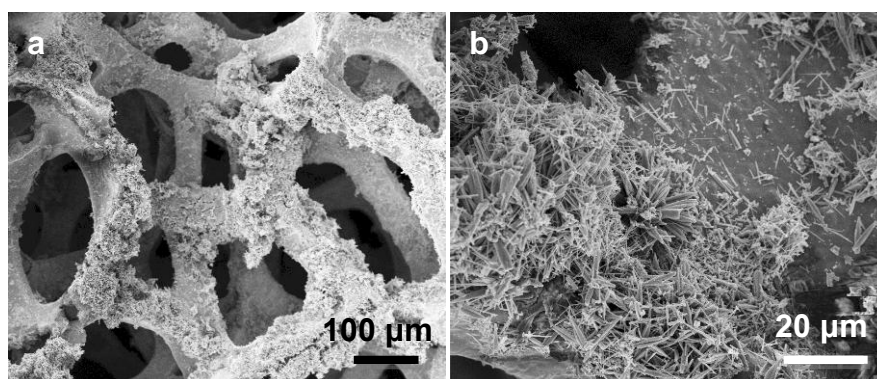


Fig. S4 FESEM images of the NiCo_2O_4 NWs/nickel foam after ultrasonication.

After ultrasonication for 1h in ethanol, the NiCo_2O_4 NWs/nickel foam still demonstrates black color and the ethanol solution turns out to dark black. As seen from Fig. S4, some NiCo_2O_4 NWs still can be found randomly dispersed on the surface of the Ni foam after ultrasonication, demonstrating a disordered NWs structure. Therefore, it is easy to conclude that the adherence of NiCo_2O_4 NWs to the Ni foam is relatively strong.

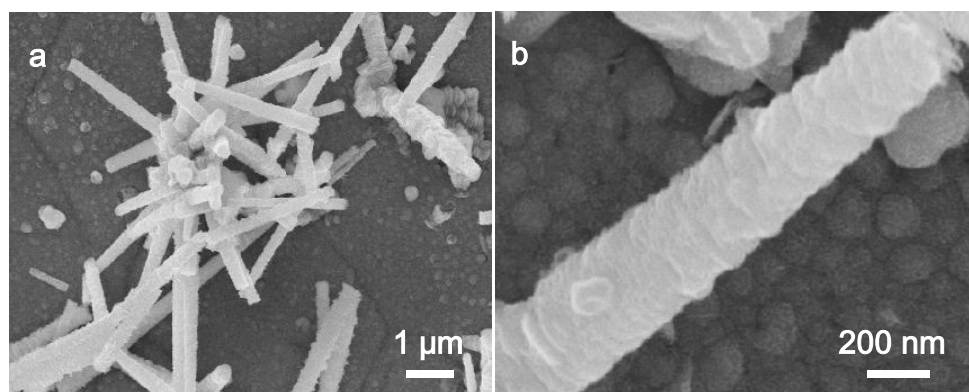


Fig. S5 FESEM images of the precursor for the NiCo_2O_4 NWs

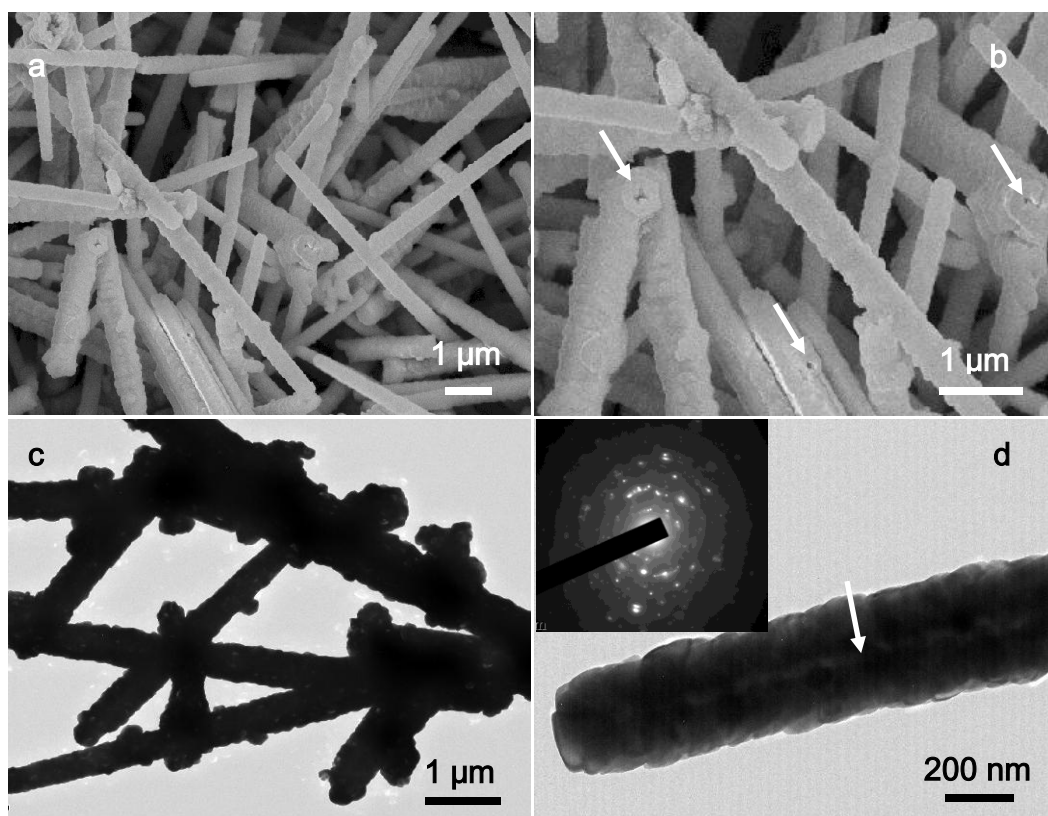


Fig. S6 FESEM (a, b), TEM (c, d) images and SAED pattern (the inset in d) of the Co_3O_4 NWs. The white arrays indicate their hollow nature

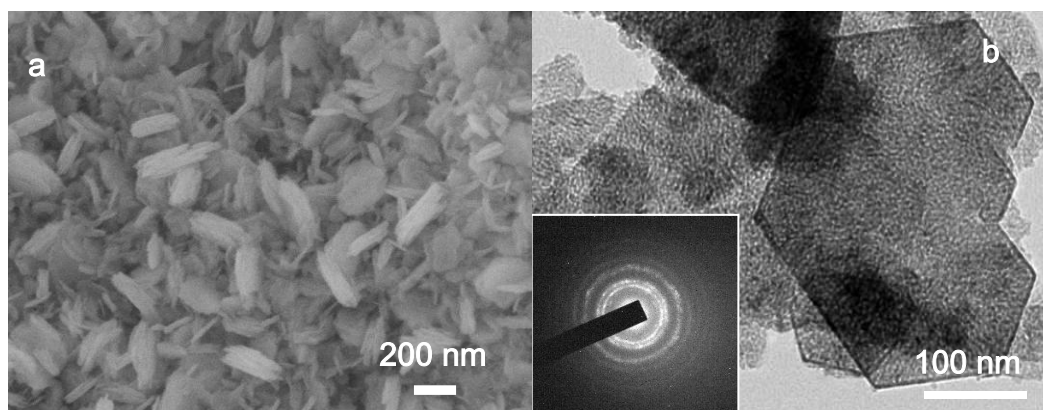


Fig. S7 (a) SEM, (b) TEM images and SAED pattern (the inset in b) of the NiO nanosheets

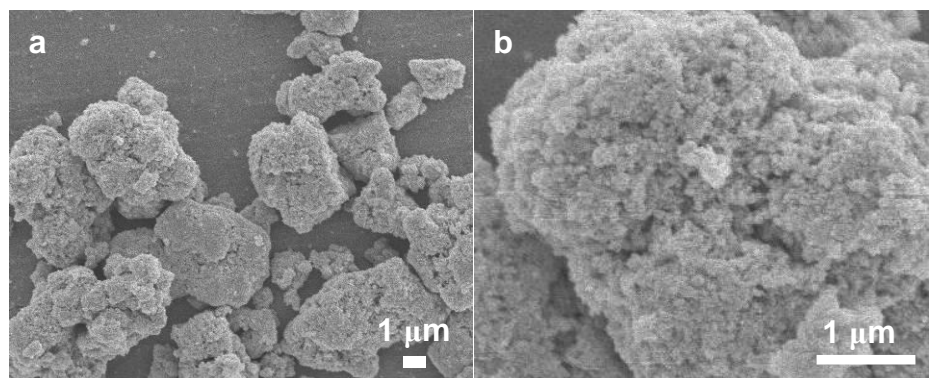


Fig. S8 FESEM images of the NiCo_2O_4 obtained from the bottom of the three-neck bottle

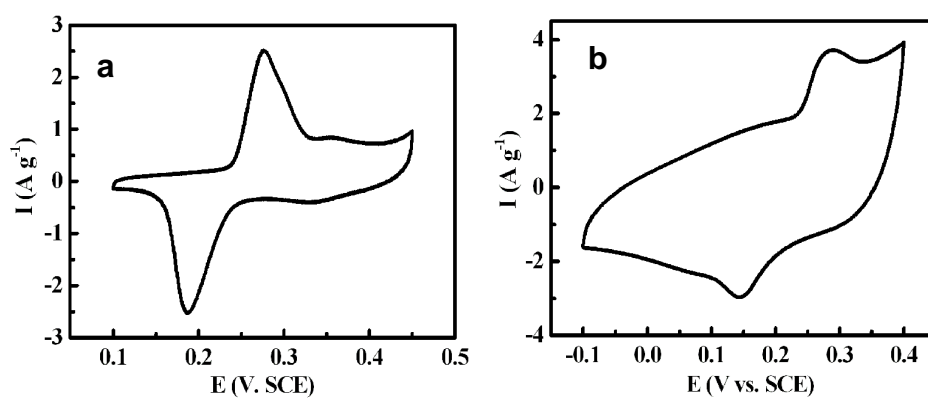


Fig. S9 CV curves (10 mV s⁻¹) of the Co₃O₄ NWs (a) and NiO nanosheets (b), respectively.

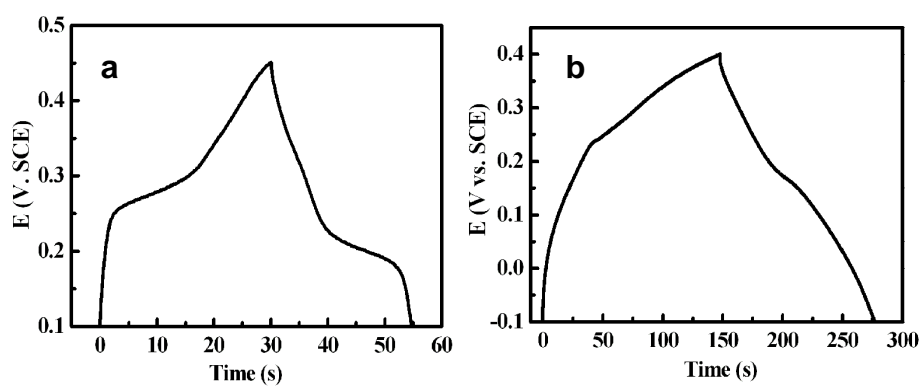


Fig. S10 CP plots (1 A g^{-1}) of the Co_3O_4 NWs (a) and NiO nanosheets (b), respectively.