

Hollow Mesoporous Hetero-NiCo₂S₄/Co₉S₈ Submicro-Spindles: Unusual Formation and Appealing Pseudocapacitance towards Hybrid Supercapacitors

Linrui Hou ^a, Yaoyao Shi ^a, Siqi Zhu ^a, Muhammad Rehan ^a, Gang Pang ^{a, b}, Xiaogang Zhang ^b,
Changzhou Yuan ^{a,*}

- a. School of Materials Science & Engineering, Anhui University of Technology, Ma'anshan,
243002, P. R. China *Email: ayuancz@163.com
- b. College of Material Science & Engineering, Nanjing University of Aeronautics &
Astronautics, Nanjing, 210016, P. R. China

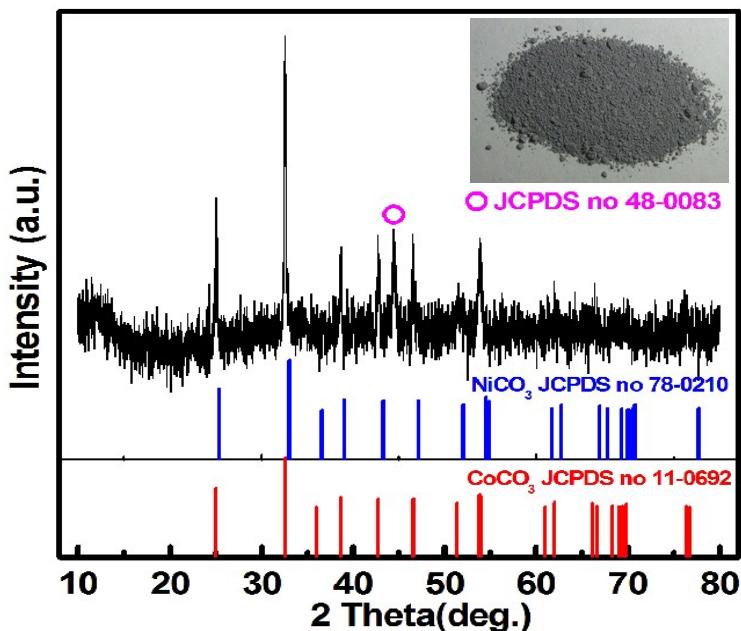


Fig. S1. Typical WAXRD pattern (b) of the as-obtained NCCO precursor. The red and blue vertical lines for the standard JCPDS profiles of NiCO₃ (JCPDS no. 78-0210) and CoCO₃ (JCPDS no. 11-0692). And the hollow magenta circle for the Co(CO₃)_{0.5}(OH)·0.11H₂O (JCPDS no. 48-0083), the inset for the optical image of the as-obtained NCCO powder

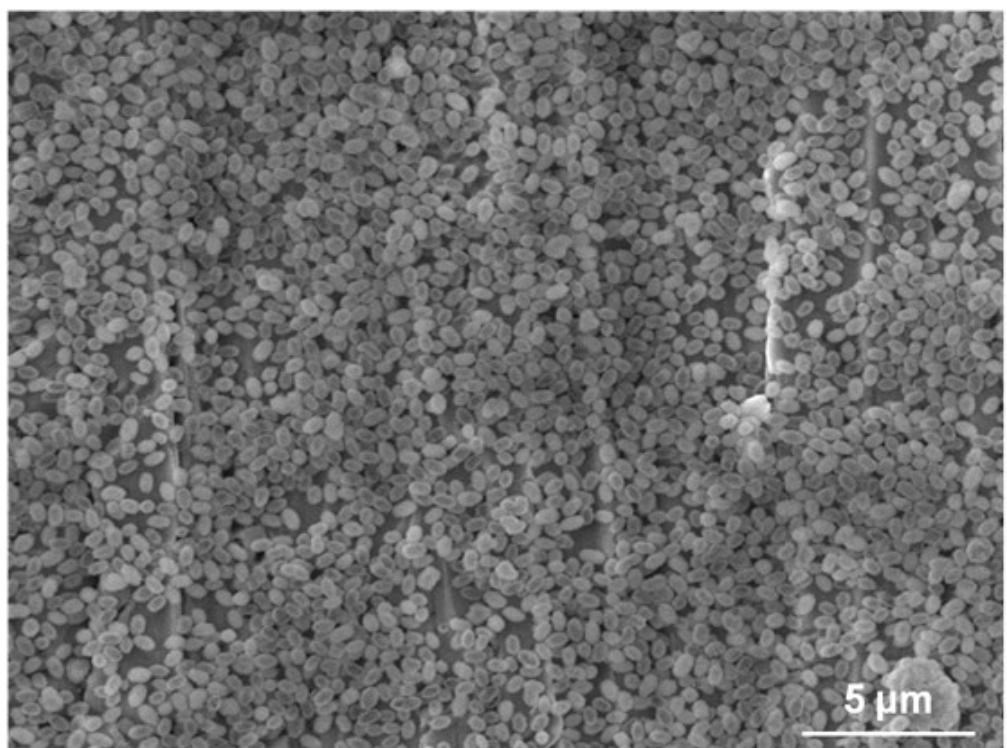


Fig. S2. Typical FESEM of the NCCO intermediate

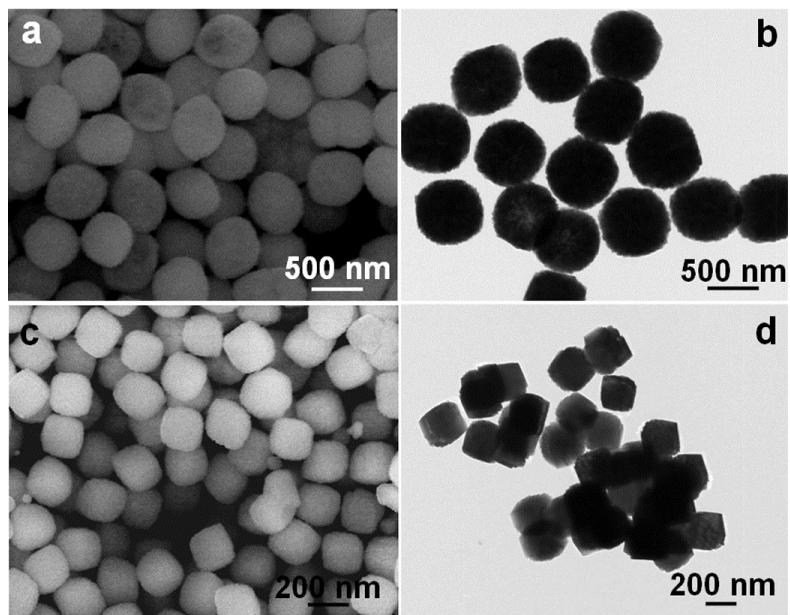


Fig. S3. Typical FESEM (a, c) and TEM (b, d) images of the intermediate NCCO-20 (a, b) and NCCO-30 (c, d)

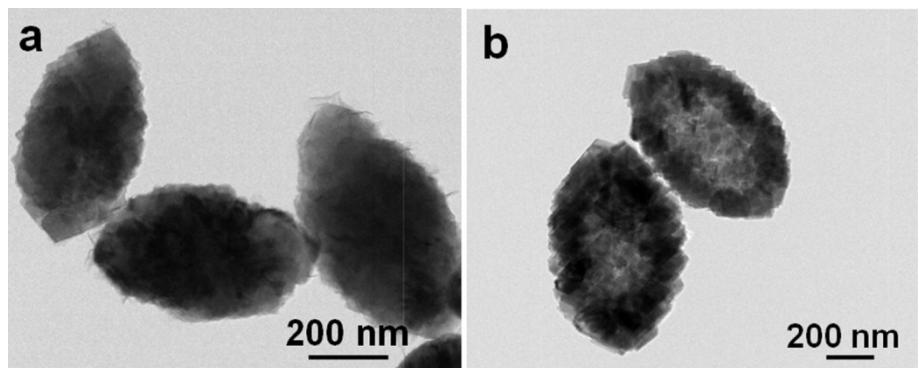


Fig. S4. TEM image of the (a) NCCO-10 and (b) NCCO-25h samples

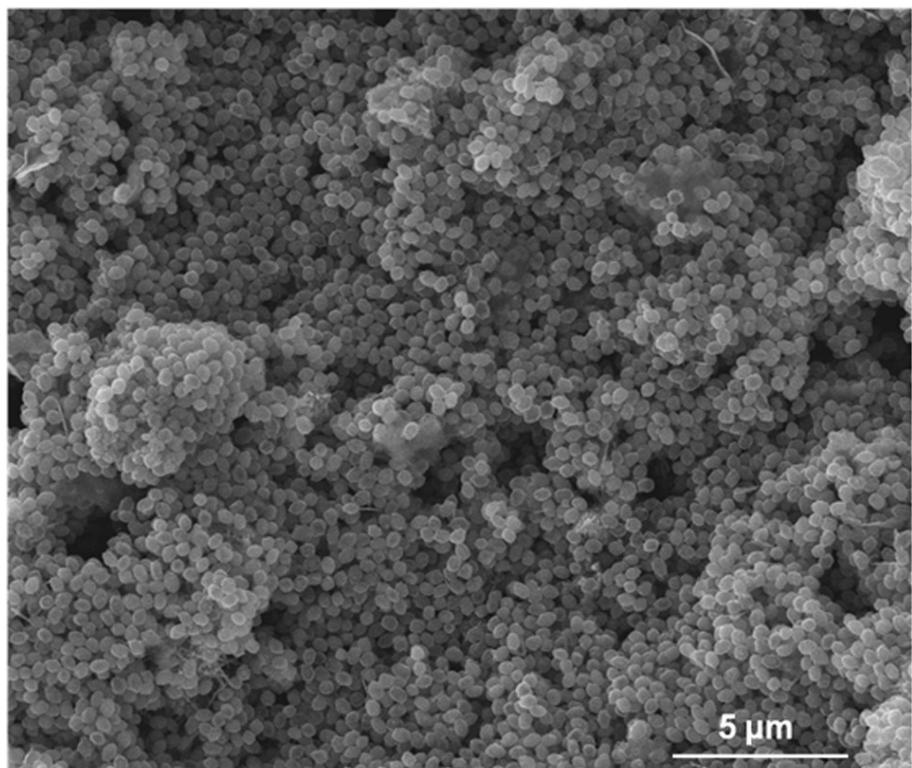


Fig. S5. Typical FESEM image for the resultant NCCS sample

Table S1 Electrochemical comparisons between the hollow hetero-NCCS submicro-spindles with other NiCo₂S₄-based electrodes and Co₉S₈ electrodes in three-electrode systems

NiCo ₂ S ₄ -based electrodes	SCs (F g ⁻¹) / current density (A g ⁻¹)	Loadings (mg cm ⁻²) of electroactive materials	Ref.
hollow hetero-NCCS submicro-spindles	749 / 4.0 660 / 10.0	5.0	This work
Mesoporous NiCo ₂ S ₄ nanosheets	744 / 1.0	1.0	[1]
NiCo ₂ S ₄ nanoplates	437 / 4.0	2.4	[2]
NiCo ₂ S ₄ nano-aggregates	592 / 0.5	2.5 ~ 3.5	[3]
NiCo ₂ S ₄ nanotubes	738 / 4.0	4.2	[4]
NiCo ₂ S ₄ nanosheets	653 / 10.0	0.8	[5]
NiCo ₂ S ₄ /Ni _x Co _{9-x} S ₈	540 / 9.0	4.0	[6]
Ni _{0.24} Co _{2.58} S ₄ microflowers	379 / 0.5	unknown	[7]
NiCo ₂ S ₄ nanotubes	665 / ~0.93	4.3	[8]
NiCo ₂ S ₄ @30% graphene	~620 / 1.0	5.0	[9]
NiCo ₂ S ₄ nanosheets	~550 / 5.0	4.0 ~ 6.0	[10]
NiCo ₂ S ₄ nanoboxes	~481 / 10.0	5.0	[11]
Co ₉ S ₈ nanoparticles	~350 / 5.0 mV s ⁻¹	2.0	[12]
Flower-like Co ₉ S ₈	~397 / 2.0	10.0	[13]
Co ₉ S ₈ nanotubes	~261.3 / 2.0	Unknown	[14]
Co ₉ S ₈ nanorod arrays	~450 / 5.0	0.6	[15]
Co ₉ S ₈ nanorod arrays	~783.3 / 5.0 mV s ⁻¹	3.0	[16]

- [1] Z. B. Wu, X. L. Pu, X. B. Ji, Y. R. Zhu, M. J. Jing, Q. Y. Chen and F. P. Jiao, *Electrochim. Acta*, 2015, **174**, 238.
- [2] J. Pu, F. Cui, S. Chu, T. Wang, E. Sheng and Z. Wang, *ACS Sustainable Chem. Eng.*, 2014, **2**, 809.
- [3] L. Liu, *Nanoscale*, **2013**, *5*, 11615.
- [4] J. Pu, T. Wang, H. Wang, Y. Tong, C. Lu, W. Kong and Z. Wang, *ChemPlusChem*, 2014, **79**, 577.
- [5] W. Chen, C. Xia and H. N. Alshareef, *ACS Nano*, 2014, **9**, 9531.
- [6] Y. F. Zhang, C. C. Sun, H. Q. Su, W. Huang and X. C. Dong, *Nanoscale*, 2015, **7**, 3155.
- [7] L. M. Mi, Y. Gao, S. Z. Cui, H. W. Hou and W. H. Chen, *Inorg. Chem. Front.*, 2014, **1**, 745.
- [8] J. Xiao, L. Wan, S. Yang, F. Xiao and S. Wang, *Nano Lett.*, 2014, **14**, 831.
- [9] W. M. Du, Z. Y. Wang, Z. Q. Zhu, S. Hu, X. Y. Zhu, Y. F. Shi, H. Pang and X. F. Qian, *J. Mater. Chem. A*, 2014, **2**, 9613.
- [10] S. J. Peng, L. L. Li, C. C. Li, H. T. Tan, R. Cai, H. Yu, S. Mhaisalkar, M. Srinivasan, S. Ramakrishna and Q. Y. Yan, *Chem. Commun.*, 2013, **49**, 10178.
- [11] L. R. Hou, H. Hua, R. Q. Bao, Z. Y. Chen, C. Yang, S. Q. Zhu, G. Pang, L. N. Tong, C. Z. Yuan and X. G. Zhang, *ChemPlusChem*, 2016, **81**, 557.
- [12] R. Ramachandran, M. Saranya, C. Santhosh, V. Velmurugan, B. P. C. Raghupathy, S. K. Jeong and A. N. Grace, *RSC Adv.*, 2014, **4**, 21151.
- [13] L. Yin, L. Q. Wang, X. H. Liu, Y. S. Gai, L. H. Su, B. H. Qu and L. Y. Gong, *Eur. J. Inorg. Chem.*, 2015, **2015**, 2457.
- [14] J. W. Yu, H. Z. Wan, J. J. Jiang, Y. J. Ruan, L. Miao, L. Zhang, D. D. Xia and K. Xu, *J. Electrochem. Soc.*, 2014, **161**, A996.
- [15] J. Wen, S. Z. Li, B. R. Li, Z. C. Song, H. N. Wang, R. Xiong and G. J. Fang, *J. Power Sources*, 2015, **284**, 279.
- [16] J. Xu, Q. F. Wang, X. W. Wang, Q. Y. Xiang, B. Liang, D. Chen and G. Z. Shen, *ACS Nano*, 2013, **6**, 5453.

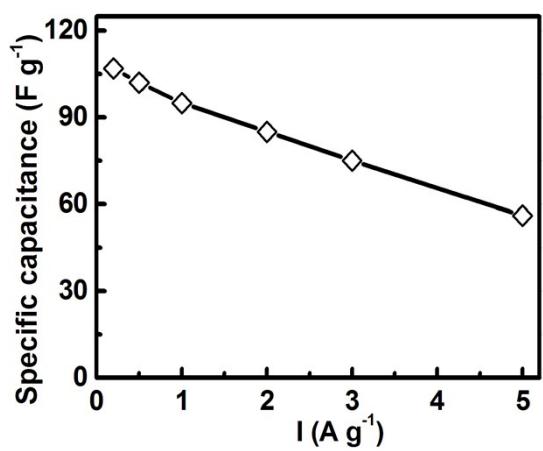


Fig. S6 SCs of the hybrid AC/hollow hetero-NCCS device as a function of current density

Table S2 Electrochemical comparisons between the AC//hollow hetero-NCCS submicro-spindles asymmetric device with other hybrid ESCs

Asymmetric ESCs	Specific energy densities and power densities	Ref.
AC//hollow hetero-NCCS submicro-spindles	17.5 Wh kg ⁻¹ at 3.75 kW kg ⁻¹ 33.5 Wh kg ⁻¹ at 150 W kg ⁻¹	This work
AC//NaMnO ₂	13.2 Wh kg ⁻¹ at 1.0 kW kg ⁻¹	[1]
AC//MnO ₂ nanorods	17.0 Wh kg ⁻¹ at 2.0 kW kg ⁻¹	[2]
AC//LiTi ₂ (PO ₄) ₃	15.0 Wh kg ⁻¹ at 1.0 kW kg ⁻¹	[3]
AC//K _{0.27} MnO ₂ ·0.6H ₂ O	17.6 Wh kg ⁻¹ at 2.0 kW kg ⁻¹	[4]
AC//Ni(OH) ₂	10.5 Wh kg ⁻¹ at 690 W kg ⁻¹	[5]
Fe ₂ O ₃ //MnO ₂	7.0 Wh kg ⁻¹ at 820 W kg ⁻¹	[6]
AC//Co ₃ O ₄ -rGO	13.4 Wh kg ⁻¹ at 2.1 kW kg ⁻¹	[7]
AC//NiCo ₂ O ₄	14.7 Wh kg ⁻¹ at 175 W kg ⁻¹	[8]
graphene/NF//Cu _{1.79} Co _{0.21} CH/NF	21.5 Wh kg ⁻¹ at 200 W kg ⁻¹	[9]
AC//Ni ₃ S ₂ @CNTs	19.8 Wh kg ⁻¹ at 798 W kg ⁻¹	[10]
AC//Co ₃ O ₄ @MnO ₂	17.7 Wh kg ⁻¹ at 600 W kg ⁻¹	[11]
Carbon//NiO	15.0 Wh kg ⁻¹ at 447 W kg ⁻¹	[12]
AC//NiCo ₂ O ₄ -graphene	19.5 Wh kg ⁻¹ at 100 W kg ⁻¹	[13]
AC//CoMoO ₄ -NiMoO ₄ ·xH ₂ O	24.95 Wh kg ⁻¹ at 164.5 W kg ⁻¹	[14]
AC//amorphous NiWO ₄	25.3 Wh kg ⁻¹ at 200 W kg ⁻¹	[15]
AC//NiMoO ₄ -CoMoO ₄ ·xH ₂ O	28.0 Wh kg ⁻¹ at 100 W kg ⁻¹	[16]

- [1] Q. T. Qu, Y. Shi, S. Tian, Y. H. Chen, Y. P. Wu and R. Holze, *J. Power Sources*, 2009, **194**, 1222.
- [2] Q. Qu, P. Zhang, B. Wang, Y. Chen, S. Tian, Y. Wu and R. Holze, *J. Phys. Chem. C*, 2009, **113**, 14020.
- [3] J. Y. Luo and Y. Y. Xia, *J. Power Sources*, 2009, **186**, 224.
- [4] Q. T. Qu, L. Li, S. Tian, W. L. Guo, Y. P. Wu and R. Holze, *J. Power Sources*, 2010, **195**, 2789.
- [5] J. Huang, P. Xu, D. Cao, X. Zhou, S. Yang, Y. Li and G. Wang, *J. Power Sources*, 2014, **246**, 371.
- [6] T. Brousse and D. Bélanger, *Electrochim. Solid-State Lett.*, 2003, **6**, A244.
- [7] C. Z. Yuan, L. H. Zhang, L. R. Hou, G. Pang and W. C. Oh, *RSC Adv.*, 2014, **4**, 14408.
- [8] R. Ding, L. Qi, M. Jia and H. Wang, *Electrochim. Acta*, 2013, **107**, 494.
- [9] S. D. Liu, K. S. Hui, K. N. Hui, V. V. Jadhav, Q. X. Xia, J. M. Yun, Y. R. Cho, R. S. Mane and K. H. Kim, *Electrochim. Acta*, 2016, **188**, 898.
- [10] C. S. Dai, P. Y. Chien, J. Y. Lin, S. W. Chou, W. K. Wu, P. H. Li, K. Y. Wu and T. W. Lin, *ACS Appl. Mater. Interfaces*, 2013, **5**, 12168.
- [11] Z. B. Lei, J. T. Zhang and X. S. Zhao, *J. Mater. Chem.*, 2012, **22**, 153.
- [12] X. Lu, M. Yu, T. Zhai, G. Wang, S. Xie, T. Liu, C. Liang, Y. X. Tong and Y. Li, *Nano Lett.*, 2013, **12**, 2628.
- [13] H. Wang, C.M.B. Holt, Z. Li, X. Tan, B.S. Amirkhiz, Z. Xu, B.C. Olsen, T. Stephenson and D. Mitlin, *Nano Res.*, 2012, **5**, 605.
- [14] M. C. Liu, L. B. Kong, C. Lu, X. J. Ma, X. M. Li, Y. C. Luo and L. Kang, *J. Mater. Chem. A*, 2013, **1**, 1380.
- [15] L. Y. Niu, Z. Li, Y. Xu, J. Sun, W. Hong, X. Liu, J. Wang and S. Yang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8044.
- [16] B. Senthilkumar, D. Meyrick, Y. S. Lee and R. K. Selvan, *RSC Adv.*, 2013, **3**, 16542.