Supplementary Information

Hierarchical MnCo₂O₄@NiMoO₄ as Free-Standing Core-Shell Nanowire Arrays with Synergistic Effect for Enhanced Supercapacitor Performance

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Figure S1. (a) typical SEM image of MnCo₂O₄ NWAs in a low magnification, (b) SEM image of MnCo₂O₄@NiMoO₄ core-shell NWAs in low magnification, (c) and (d) typical SEM images of pure NiMoO₄ grown directly over the NF with high and low magnification.



Figure S2. Typical (a) and (b) SEM images of MnCo₂O₄ nanowires growth procedure with different reaction time duration (1 hour and 2 hours), respectively. (c) and (d) typical SEM images of MnCo₂O₄@NiMoO₄ core-shell structure with different hydrothermal reaction duration (3 hours and 12 hours), respectively.



Figure S3. Typical (a),(b) and (d) TEM images of a single MnCo₂O₄ nanowire, (c) HRTEM image of single MnCo₂O₄ nanowire.



Figure S4. (a) Demonstrating MnCo₂O₄ hierarchical structure of a single nanowire, (b-d) corresponding EDS mapping.



Figure S5. XPS spectra of as-synthesized MnCo₂O₄@NiMoO₄NWAs.



Figure S6. (a) XPS spectra of as-synthesized MnCo₂O₄ NWAs, (b-d) XPS survey scan of Mn 2p, Co 2p and O 1s regions, respectively.



Figure S7. CV curves comparison of $MnCo_2O_4$ (a)NiMoO₄ and nickel foam current collector at scan rate of 1 mV s⁻¹.



Figure S8. (a) CV curves of MnCo₂O₄@NiMoO₄ obtained at different scanning rates, (b) EIS measurements of MnCo₂O₄, NiMoO₄ and MnCo₂O₄@NiMoO₄ electrodes.



Figure S9. Coulombic efficiency profiles of (a) MnCo₂O₄, (b) NiMoO₄ and (c) MnCo₂O₄@NiMoO₄ during 2500 successive cycles at 5 A g⁻¹.



Figure S10. (a) CV curves of MnCo₂O₄ at different scanning rates, (b) CV curves of NiMoO₄ at different scanning rates, (c) and (d) GCD of MnCo₂O₄ and NiMoO₄, respectively at different current densities.



Figure S11. (a) Typical SEM images of MnCo₂O₄ after cycling (b) MnCo₂O₄@NiMoO₄ SEM images after cycling.



Figure S12. (a) CV curve of AC at a scanning rate of 10 mV s⁻¹. (b) Galvanostatic chargedischarge of AC at a current density of 1 A g⁻¹.



Figure S13. Ragone plot of MnCo₂O₄@NiMoO₄//AC device.

Table S1. Comparison of the maximum C_s of some reported manganese or cobalt oxide/hydroxide based composites as pseudocapacitor electrode material and the present work.

Electrodes based on material	Electrolyte	Specific capacitance	Reference
MnCo ₂ O ₄ Nanowire arrays	1 М КОН	349.8 F g ⁻¹ @ 1 Ag ⁻¹	1
MnCo ₂ O ₄ Nanosheet films	-	400 F g ⁻¹ @ 1 Ag ⁻¹	2
Urchin like MnCo ₂ O _{4.5}	-	129.2 F g ⁻¹ @ 0.1 Ag ⁻¹	3
MnCo ₂ O ₄ nanosheets	6 M KOH	420 F g ⁻¹ @ 1 Ag ⁻¹	4
MnCo ₂ O ₄ @Ni(OH) ₂ hierarchical structure	2 M KOH	2154 F g ⁻¹ @ 5 Ag ⁻¹	5
MnCo ₂ O ₄ @MnO ₂ hierarchical structure	3 М КОН	858 F g ⁻¹ @ 1 Ag ⁻¹	6
MnO ₂ @NiMoO ₄ core-shell hierarchical structure	2 M KOH	582.2 F g ⁻¹ @ 1 Ag ⁻¹	7
Nanosheet-based CoMoO ₄ - NiMoO ₄ nanotubes	3 М КОН	751 F g ⁻¹ @ 1 Ag ⁻¹	8
NiCo ₂ O ₄ -rGO composite	2 M KOH	1222 F g ⁻¹ @ 0.5 Ag ⁻¹	9
MnCo ₂ O ₄ @NiMoO ₄ core- shell heterostructure	1 М КОН	1244 F g ⁻¹ @ 1 Ag ⁻¹	This work

References

- L. Li, Y. Q. Zhang, X. Y. Liu, S. J. Shi, X. Y. Zhao, H. Zhang, X. Ge, G. F. Cai, C. D. Gu, X. L. Wang and J. P. Tu, *Electrochimica Acta*, 2014, **116**, 467–474.
- 2 T. Nguyen, M. Boudard, L. Rapenne, O. Chaix-Pluchery, M. J. Carmezim and M. F. Montemor, *RSC Adv.*, 2015, **5**, 27844–27852.
- 3 W. Li, K. Xu, G. Song, X. Zhou, R. Zou, J. Yang, Z. Chen and J. Hu, *CrystEngComm*, 2014, **16**, 2335–2339.
- 4 L. Li, F. He, S. Gai, S. Zhang, P. Gao, M. Zhang, Y. Chen and P. Yang, *CrystEngComm*, 2014, **16**, 9873–9881.
- 5 Y. Zhao, L. Hu, S. Zhao and L. Wu, Adv. Funct. Mater., 2016, 26, 4085–4093.
- 6 X. Zheng, Y. Ye, Q. Yang, B. Geng and X. Zhang, *Dalton transactions* (*Cambridge, England : 2003*), 2016, **45**, 572–578.
- 7 X. Wang, H. Xia, J. Gao, B. Shi, Y. Fang and M. Shao, *J. Mater. Chem. A*, 2016, **4**, 18181–18187.
- 8 Q. Yang and S.-Y. Lin, RSC Adv., 2016, 6, 10520–10526.
- 9 X. Wang, W. S. Liu, X. Lu and P. S. Lee, J. Mater. Chem., 2012, 22, 23114.