Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Three-dimensional $NiCo_2O_4/NiCo_2S_4$ Hybrid Nanostructures on Ni-foam as High-performance Supercapacitor Electrode

Shipra Raj,[1] Suneel Kumar Srivastava,[2] Pradip Kar[1] and Poulomi Roy[1]*

[1]Department of Chemistry, Birla Institute of Technology Mesra, Ranchi 835215, Jharkhand, India

[2]Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, West Bengal, India

**Email: poulomiroy@yahoo.com*

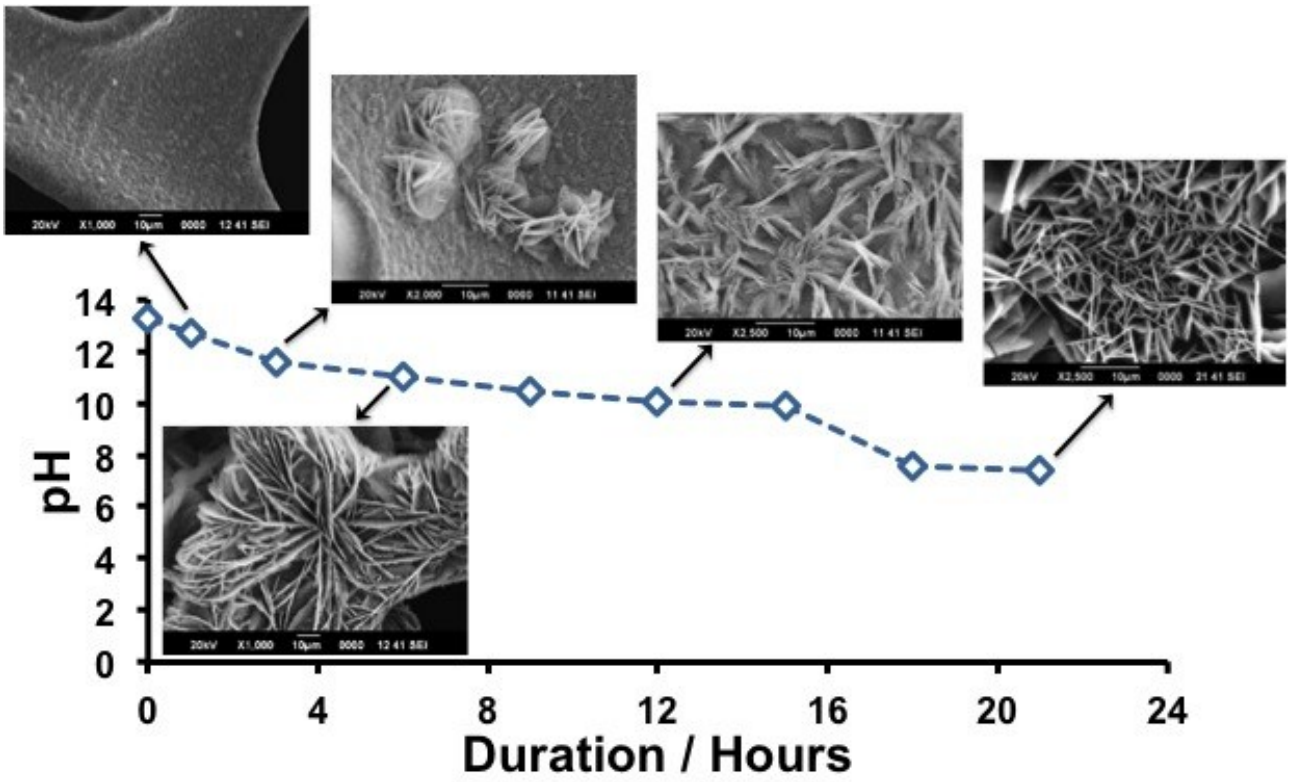

Figure S1: Growth process of NiCo-hydroxide precursor deposition on Ni-foam at different reaction durations and different pH.

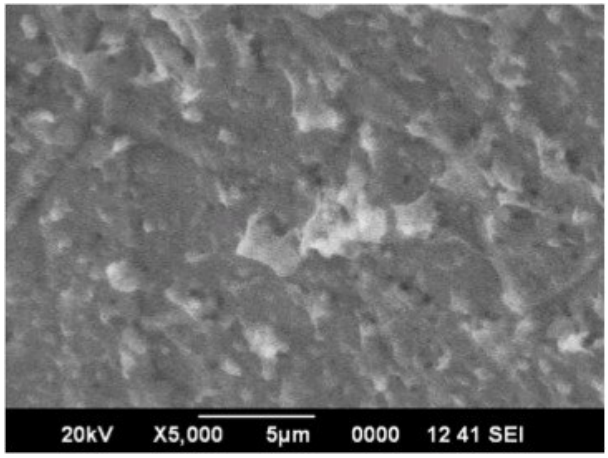

Figure S2: Deposition of NiCo-hydroxide precursor on Ni-foam at pH 11 adding few drops of ammonia.

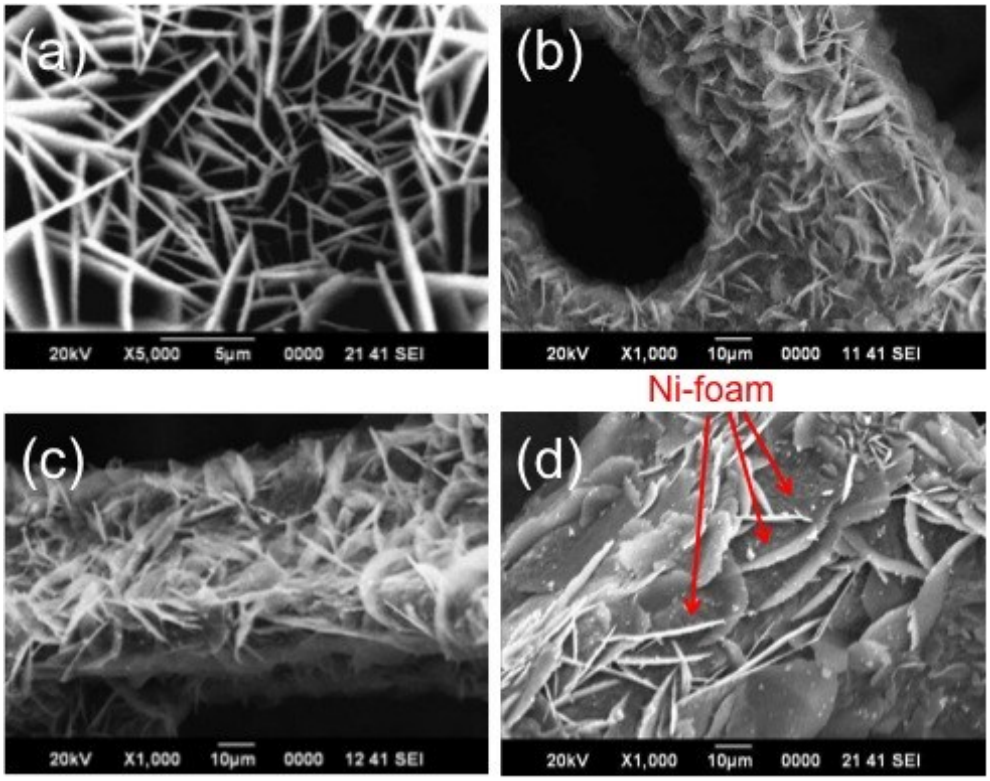

Figure S3: NiCo-hydroxide precursor deposition on Ni-foam at different ammonia : water ratios: (a) 50 : 0; (b) 40 : 10; (c) 30 : 20 and (d) 20 : 30.

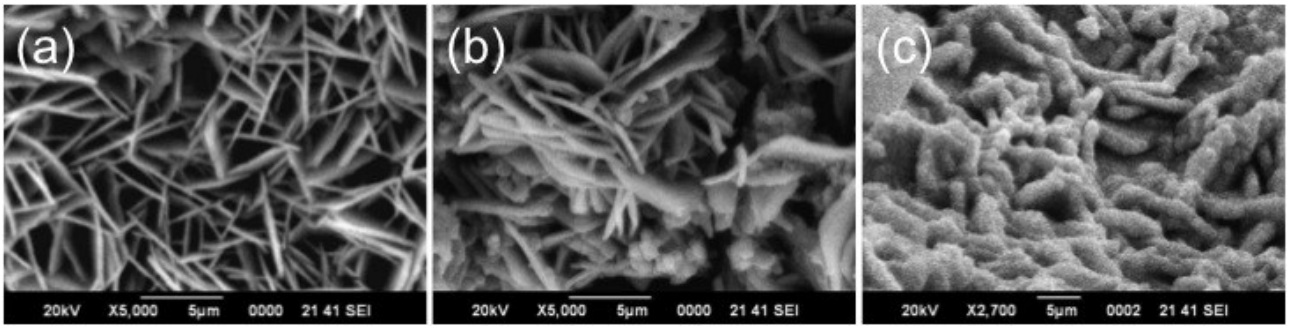

Figure S4: Variation of NiCo-hydroxide nanosheet thickness upon number of deposition: (a) Single deposition, (b) 3-times deposition and (c) 10-times deposition.

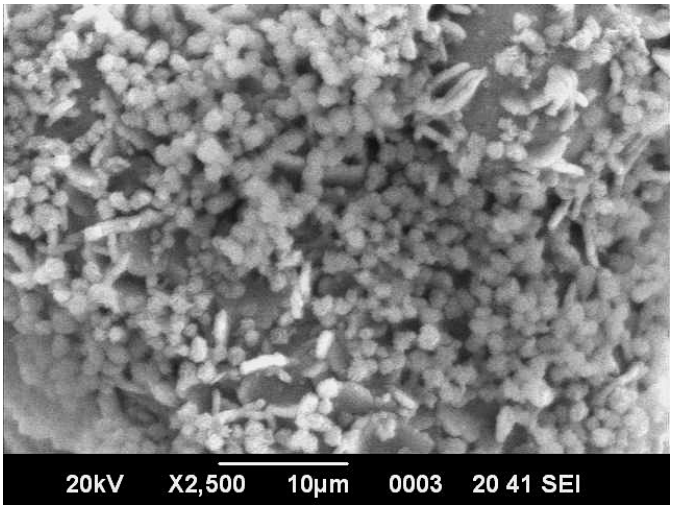

Figure S5: $NiCo_2S_4$ nanoflake balls deposited on $NiCo_2O_4$ nanosheets.

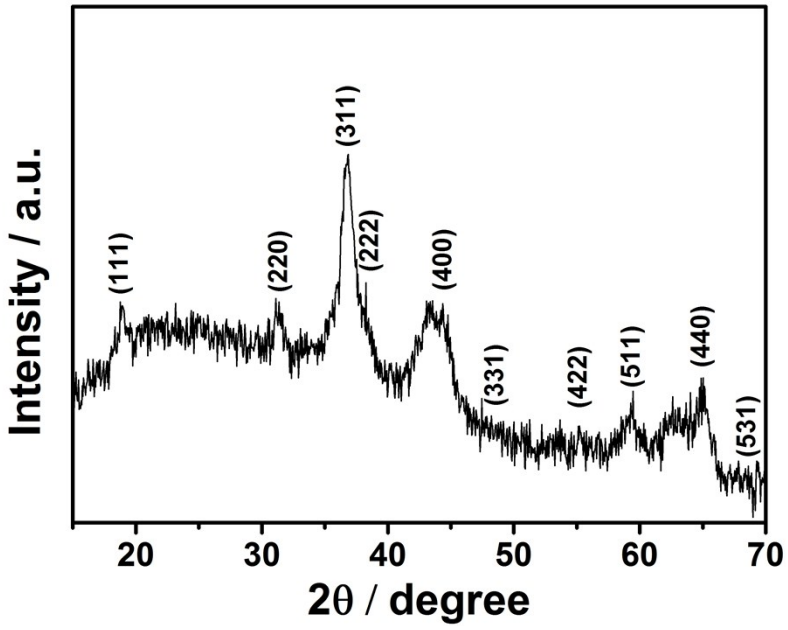

Figure S6: XRD pattern of $NiCo_2O_4$ nanosheets (JCPDS No. 20-0781) without Ni foam.

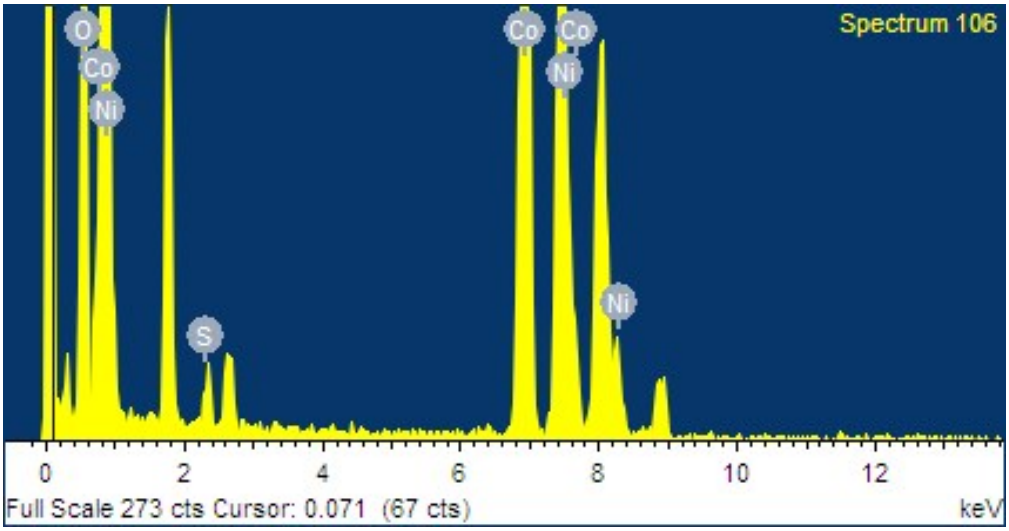

Figure S7: Energy dispersive x-ray analysis of $NiCo_2O_4/NiCo_2S_4$ nanohybrids.

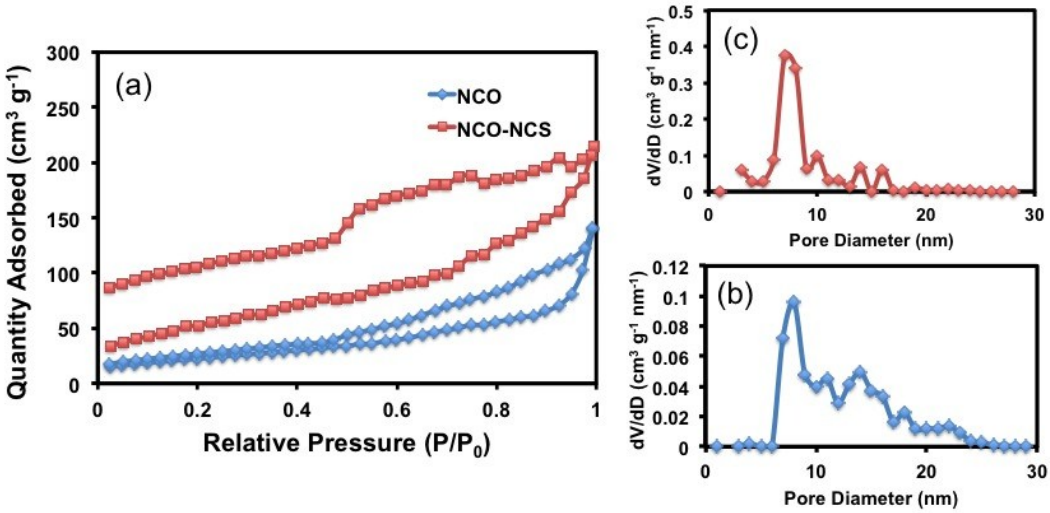

Figure S8: (a) N_2 adsorption–desorption isotherm of NCO and NCO-NCS and (b-c) BJH pore size distribution of NCO (b) and NCO-NCS (c).

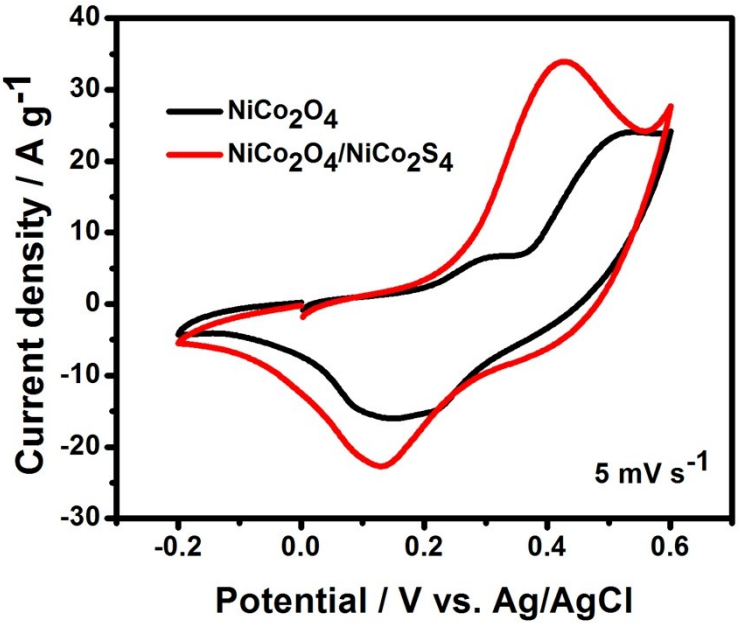

Figure S9: CV diagram of $NiCo_2O_4$ nanosheets and $NiCo_2O_4/NiCo_2S_4$ hybrid nanostructures at a scan rate 5 mV s^{-1}

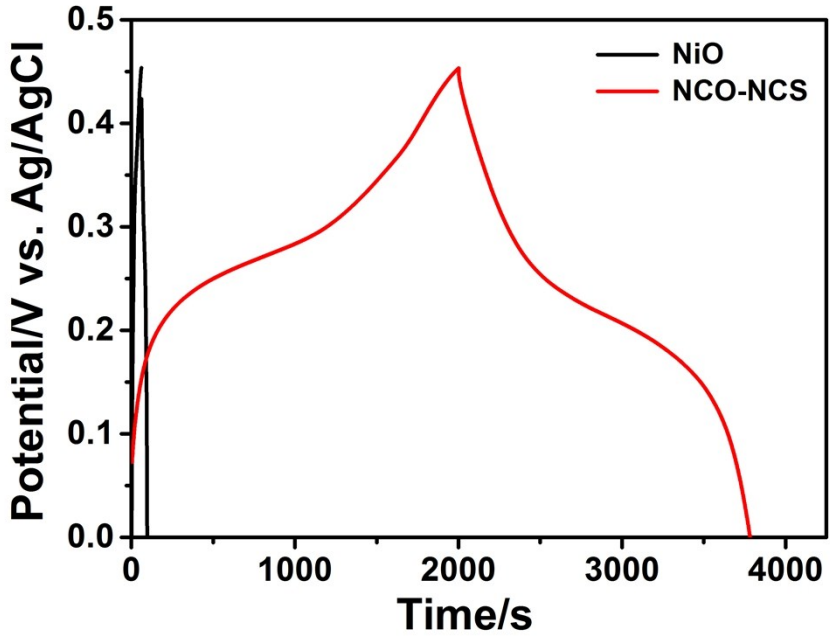

Figure S10: Charge-discharge profile of NiO (formed on Ni foam by annealing) and $NiCo_2O_4/NiCo_2S_4$ hybrid electrode at current density 1.33 mA cm^{-2} showing negligible contribution of NiO (Areal capacitance C_a = 0.106 F cm^{-2}) in the performance of hybrid nanostructure (Areal capacitance C_a = 5.24 F cm^{-2}).

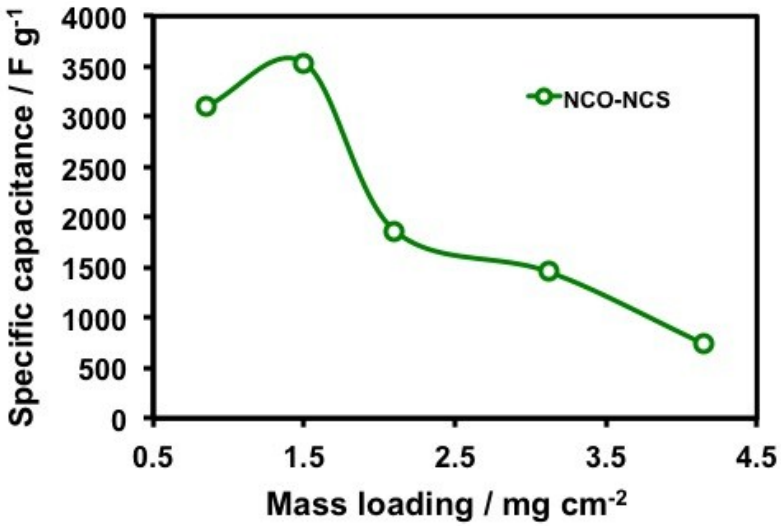

Figure S11: Specific capacitance (@ 1 A g^{-1}) as a function of mass loading for $NiCo_2O_4/NiCo_2S_4$ hybrid nanostructures on Ni foam.

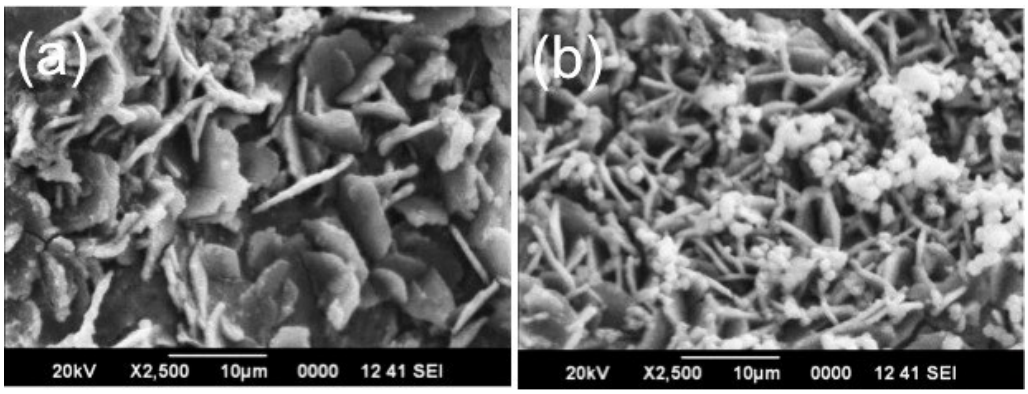

Figure S12: SEM images of (a) NCO and (b) NCO-NCS after stability tests of several thousand cycles.

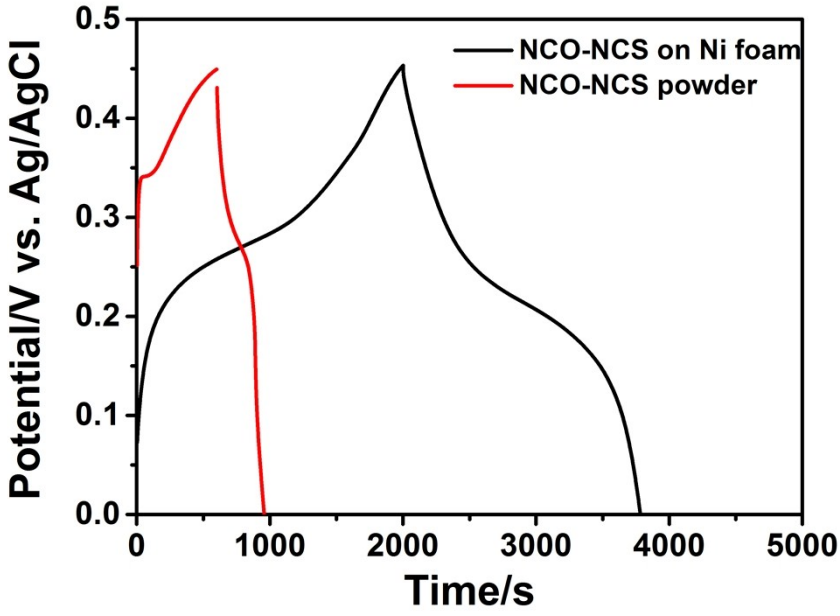

Figure S13: Charge-discharge profile comparison of physically mixed $NiCo_2O_4$ and $NiCo_2S_4$ in 3:1 ratio (791 F g^{-1} @ 1 A g^{-1}) and directly grown $NiCo_2O_4$/$NiCo_2S_4$ hybrid nanostructure on Ni foam (3542 F g^{-1} @ 0.9 A g^{-1}). Physically mixed $NiCo_2O_4$ and $NiCo_2S_4$ powder based electrode was fabricated by mixing 80% of sample with 10% PVDF and 10% C-black in NMP.

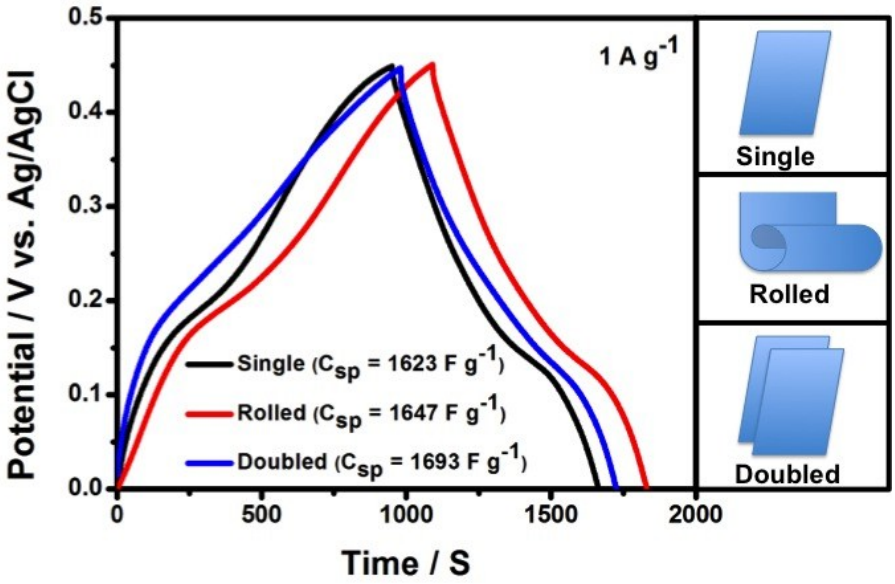

Figure S14: Flexibility test of $NiCo_2O_4$/$NiCo_2S_4$ hybrid electrode: Galvanostatic charge-discharge profile of 'single', 'rolled' and 'doubled' experiment at current density 1 A g^{-1}.

Table S1: Comparison of specific capacitance and capacity retention values of reported $NiCo_2O_4$ and $NiCo_2S_4$-based electrodes with the present work.

Electrode Material	Method	Specific capacitance ($F\ g^{-1}$)	Current density ($A\ g^{-1}$)	Capacity retention	Ref.
$NiCo_2O_4$ nanosheets	Microwave	467	10	95% after 5000 cycles @10 A g^{-1}	1
$NiCo_2O_4$ nanotubes	Electrospinning technique	1647 1300	1 10	93.6% after 3000 cycles @10 A g^{-1}	2
Urchin-like $NiCo_2O_4$ nanostructures	Hydrothermal	1650 1348	1 15	90.8% after 2000 cycles @8 A g^{-1}	3
$NiCo_2O_4$ microstructure	Hydrothermal	700	10	78.7% after 5000 cycles @10 A g^{-1}	4
$NiCo_2O_4$ hollow sphere	Solvothermal	1141 862	1 10	94.7% after 4000 cycles @5 A g^{-1}	5
$NiCo_2S_4$ hollow spheres	Hydrothermal	1263	2	94% after 20000 cycles @10 A g^{-1}	6
$NiCo_2S_4$ hexagonal plates	Hydrothermal	1085 852	0.5 10	95.6% after 2000 cycles @10 A g^{-1}	7
$NiCo_2S_4$ ball-in-ball hollow spheres	Solvothermal	1036 760	1 10	87% after 2000 cycles @5 A g^{-1}	8
$NiCo_2O_4$ nanoneedle on Ni foam	Hydrothermal	2193 1490	1 10	72% after 2000 cycles @5 A g^{-1}	9
$NiCo_2O_4$ multiple hierarchical structures on Ni foam	Hydrothermal	2623 2121	1 10	94% after 3000 cycles @10 A g^{-1}	10
$NiCo_2O_4$ nanowires on C-Frame	Hydrothermal	1696 1231	1 8	88% after 2000 cycles @5 A g^{-1}	11
$NiCo_2O_4$ nanosheet on Ni foam	Co-electrodeposition	2010 1596	2 12	94% after 2300 cycles @2 A g^{-1}	12
Flower-like $NiCo_2O_4$ on graphene foam	Electrodeposition	1402 1220	1 10	76.6% after 5000 cycles @5 A g^{-1}	13
$NiCo_2S_4$ nanoflakes on Ni foam	Solution method	2732 2200	1 10	85.2% after 3000 cycles @30 A g^{-1}	14
$NiCo_2S_4$ nanoflakes on C-cloth	Electrodeposition	1418	5	82.2% after 20000 cycles @5 A g^{-1}	15
$NiCo_2O_4$@$NiCo_2O_4$ nanocactus	Hydrothermal/ Electrodeposition	1264 810	2 10	93.4% after 5000 cycles @1 A g^{-1}	16
$NiCo_2O_4$-Ppy on C-textile	Hydrothermal/ polymerization	2244 1358	1 30	89.5% after 5000 cycles @3 A g^{-1}	17
$NiCo_2O_4$@Ppy core–shell nanowires on C-microfiber	Hydrothermal/ Electrodeposition	2055 742	1 50	90% after 5000 cycles @4 A g^{-1}	18
$NiCo_2O_4$@Ni_3S_2 core/shell nanothorn	Hydrothermal/ Electrodeposition	1716 1104	1 20	83.7% after 2000 cycles @4 A g^{-1}	19
$NiCo_2O_4$@$NiCo_2O_4$ core–shell nanoarray	Hydrothermal	1917 1645	1 10	More than initial value after 2000 cycles @5 A g^{-1}	20
$NiCo_2S_4$@MnO_2 nanoheterostructure	Hydrothermal	1338 800	2 10	82% after 2000 cycles @20 A g^{-1}	21
$NiCo_2O_4$ nanosheets on Ni foam	Solution method	3184 1363	1.2 12	69% after 2000 cycles @6 A g^{-1}	This work
$NiCo_2O_4$/$NiCo_2S_4$ nanohybrids on Ni-foam		3542 2767	0.9 9	84% after 2000 cycles @10 A g^{-1}	

References

1. A. K. Mondal, D. W. Su, S. Q. Chen, K. Kretschmer, X. Q. Xie, H. J. Ahn and G. X. Wang, *ChemPhysChem.* 2015, **16**, 169-175.
2. L. Li, S. Peng, Y. Cheah, P. Teh, J. Wang, G. Wee, Y. Ko, C. Wong and M. Srinivasan, *Chem. Eur. J*, 2013, **19**, 5892-5898.
3. Q. Wang, B. Liu, X. Wang, S. Ran, L. Wang, D. Chen and G. Shen, *J Mater Chem*, 2012, **22**, 21647–21653.
4. N. Xiang, Y. Ni and X. Ma, *Chem. Asian. J.* 2015, **10**, 1972-1978.
5. L. Shen, L. Yu, X. Y. Yu, X. Zhang and X. W. Lou, *Angew. Chem. Int. Ed.* 2015, **54**, 1868-1872.
6. C. Xia and H. N. Alshareef, *Chem. Mater.* 2015, **27**, 4661-4668.
7. J. Yang, W. Guo, D. Li, Q. Qin, J. Zhang, C. Wei, H. Fan, L. Wu and W. Zheng, *Electrochim Acta* 2014, **144**, 16-21.
8. L. Shen, L. Yu, H. B. Wu, X.-Y. Yu, X. Zhang and X. W. D. Lou, *Nat. Commun.*, 2015, **6**, 6694.
9. J. Wu, R. Mi, S. Li, P. Guo, J. Mei, H. Liu, W.-M. Lau and L.-M. Liu, *RSC Adv.* 2015, **5**, 25304–25311.
10. Q. Zhou, J. Xing, Y. Gao, X. Lv, Y. He, Z. Guo and Y. Li, *ACS Appl. Mater. Interf.* 2014, **6**, 11394-11402.
11. W. Xiong, Y. Gao, X. Wu, X. Hu, D. Lan, Y. Chen, X. Pu, Y. Zeng, J. Su and Z. Zhu, *ACS Appl. Mater. Interf.* 2014, **6**, 19416-19423.
12. C. Yuan, J. Li, L. Hou, X. Zhang, L. Shen and X. W. D. Lou, *Adv Funct Mater* 2012, **22**, 4592-4597.
13. C. Zhang, T. Kuila, N. H. Kim, S. H. Lee and J. H. Lee, *Carbon*, 2015, **89**, 328-339.
14. J.-G. Wang, R. Zhou, D. Jin, K. Xie and B. Wei, *Energy Storage Mater.* 2016, **2**, 1-7.

15. W. Chen, C. Xia and H. N. Alshareef, *ACS Nano*, 2014, **8**, 9531-9541.

16. J. Cheng, Y. Lu, K. Qiu, H. Yan, J. Xu, L. Han, X. Liu, J. Luo, J. K. Kim and Y. Luo, *Sci. Rep.* 2015, **5**, 12099.

17. D. Kong, W. Ren, C. Cheng, Y. Wang, Z. Huang and H. Y. Yang, *ACS Appl. Mater. Interf.* 2015, **7**, 21334-21346.

18. W. Xiong, X. Hu, X. Wu, Y. Zeng, B. Wang, G. He and Z. Zhu, *J Mater Chem A* 2015, **3**, 17209–17216.

19. J. Wang, S. Wang, Z. Huang and Y. Yu, *J Mater Chem A* 2014, **2**, 17595-176701.

20. W. Zhou, D. Kong, X. Jia, C. Ding, C. Cheng and G. Wen, *J Mater Chem A* 2014, **2**, 6310–6315.

21. J. Yang, M. Ma, C. Sun, Y. Zhang, W. Huang and X. Dong, *J Mater Chem A* 2015, **3**, 1258-1264.