Electronic Supplementary Information (ESI)

Designing graphene-wrapped nanoporous $CuCo_2O_4$ hollow spheres electrodes for high-performance asymmetric supercapacitors

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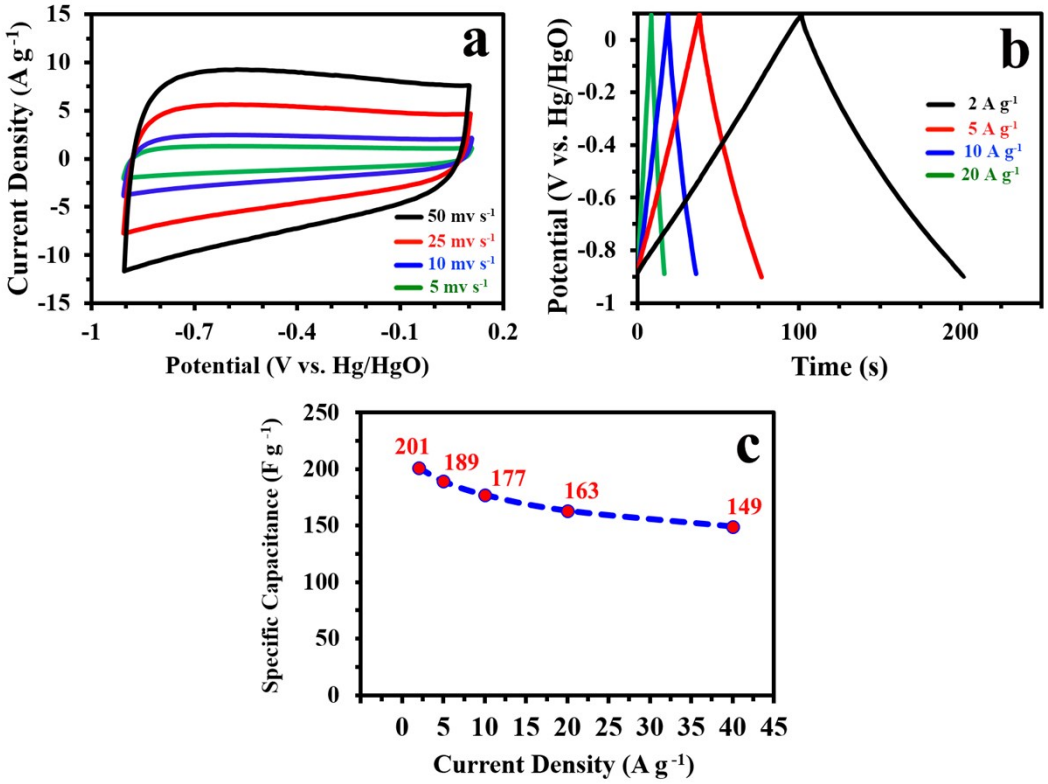

Fig. S1 (a) CV curves, (b) CD curves and (c) rate capability of the rGO negative electrode at different scan rates and current densities, respectively.

Table S1. Comparison of the electrochemical performance of GW-$CuCo_2O_4$ hollow spheres electrode in three- and two-electrode systems with other previously reported electrodes.

Morphology/Composition	Capacitance @current density	Cell (Config)	Cycles	Retention	ED (Wh/kg)	Electrolyte	ΔV (V)	Reference (year)
$CuCo_2O_4$ nanostructures	338 F/g at 1 A/g	3E	-	-	-	KOH	0.5	S1 (2014)
$CuCo_2O_4$ nanowires	0.44 F/cm^2 at 1 mA/cm^2	3E	1500	90% at 1 mA/cm^2	-	KOH	0.45	S2(2015)
	0.47 F/cm^2 at 10 mV/s	2E (vs. AC)	3000	82% at 2 mA/cm^2	-	KOH	1.5	
$CuCo_2O_4$/CuO	57 F/g at 1 mA/cm^2	2E (vs. AC)	5000	79% at 5 mA/cm^2	18	KOH	1.5	S3 (2016)
$CuCo_2O_4$ NSs on graphite	1331 F/g at 1 A/g	3E	5000	80% at 10 A/g	-	KOH	0.6	S4 (2016)
$CuCo_2O_4$ nanobelts	809 F/g at 10 mV/s	3E	1800	127% at 26 mA/cm^2	-	KOH	0.45	S5 (2015)
$CuCo_2O_4$ nanowires	982 F/g at 1.5 A/g	3E	3000	101% at 50 mV/s	-	KOH	0.45	S6 (2017)
	118.5 F/g at 1 A/g	2E (Symm)	2000	82% at 4 A/g	16.9	KOH	1	
Ordered $CuCo_2O_4$	1210 F/g at 1 A/g	3E	-	-	-	KOH	0.5	S7 (2015)
	137 F/g at 1 A/g	2E (vs. AC)	5000	86% at 6 A/g	42.8	KOH	1.5	
$CuCo_2O_4$ @MnO_2 nanoflakes	416 F/g at 1 A/g	3E	4200	92% at 8 A/g	-	Na_2SO_4	1	S8 (2015)
	78 F/g at 1 A/g	2E (vs. AG)	-	-	43.3	Na_2SO_4	2	
$CuCo_2O_4$@$CuCo_2O_4$ nanowire	889 F/g at 2 mA/cm^2	3E	2000	102% at 50 mA/cm^2	-	KOH	0.45	S9 (2017)
	57.6 F/g at 2 mA/cm^2	2E (vs. AC)	2000	101% at 30 mA/cm^2	18	KOH	1.5	
$CuCo_2O_4$ @MnO_2 on carbon fibers	327 F/g at 1.25 A/g	3E	5000	90% at 6.25 A/g	-	KOH	0.5	S10 (2014)
	0.71 F/cm^2 at 1 mA/cm^2	2E (Symm)	-	-	-	PVA/KOH	1	
Double-Sell $CuCo_2O_4$	1472 F/g (2.94 F/cm^2) at 4 mA/cm^2	3E	5000	93.8 % at 10 mA/cm^2	-	KOH	0.5	S11 (2017)
	119 F/g (1.19 F/cm^2) at 20 mA/cm^2	2E (vs. AC)	6000	92.5 % at 50 mA/cm^2	37.3	KOH	1.5	
$CuCo_2O_4$ nanowire @$NiCo_2O_4$ nanosheet	2.6 F/cm^2 at 10 mA/cm^2	3E	4500	80% at 10 mA/cm^2	-	KOH	0.42	S12 (2015)

$CuCo_2O_4$/CuO nanowire	642 F/g at 1 A/g	3E	5000	95% at 8 A/g	-	KOH	0.6	S13 (2016)
	93 F/g at 0.25 A/g	2E (vs.Fe_2O_3)	5000	83% at	33	KOH	1.6	
$CuCo_2O_4$/$MnCo_2O_4$ on graphite paper	1434 F/g at 0.5 A/g	3E	5000	81.4% at 10 A/g	-	KOH	0.5	S14 (2016)
	118.4 F/g at 0.5 A/g	2E	10000	88.4 % at 5 A/g	42.1	KOH	1.6	
$CuCo_2O_4$@$Co(OH)_2$ core/shell	424 F/g at 0.5 A/g	3E	10000	86% at 3 A/g	-	KOH	0.4	S15 (2017)
	70 F/g at 0.5 A/g	2E (vs. AG)	-	-	19.2	KOH	1.4	
$CuCo_2O_4$ nanograsses	796 F/g at 2 A/g	3E	5000	94.7% at 2 A/g	-	KOH	0.6	S16 (2015)
Mesoporous $CuCo_2S_4$	752 F/g at 2 A/g	3E	5000	90% at 3 A/g	-	KOH	0.5	S17 (2016)
Flower-like $CuCo_2S_4$	909 F/g at 5 mA/cm^2	3E	2000	91.1% at 30 mA/cm^2	-	KOH	0.4	S18 (2017)
	93.5 F/g at 1 mA/cm^2	2E (vs. AC)	2000	126% at 25 mA/cm^2	29.2	KOH	1.5	
$CuCo_2S_4$/CNT/graphene	504 F/g at 10 A/g	3E	2000	92.3% at 20 A/g	-	KOH	0.4	S19 (2016)
$FeCo_2O_4$ tube arrays	0.67 F/cm^2 at 2 mA/cm^2	2E (sym)	2000	94% at 4 mA/cm^2	30.9	KOH	1	S20 (2016)
Co_3O_4@Co_3S_4 nanoarrays	1284 F/g at 2 mV/s	3E	5000	93.1% at 4 A/g	-	KOH	0.5	S21 (2016)
	1.28 F/cm3	2E (vs. AC)	6000	90.2% at 20 mA/cm^2	-	PVA-KOH	1.6	
$NiCo_2S_4$@$NiCo_2S_4$ nanosheets	4.38 F/cm^2 at 5 mA/cm^2	3E	5000	82% at 30 mA/cm^2	-	KOH	0.55	S22 (2015)
	75 F/g at 5 mA/cm^2	2E (vs.RGO)	5000	81% at 20 mA/cm^2	24.9	KOH	1.55	
$NiCo_2S_4$@Ni-Mn LDH/GS	1.74 F/cm^2 at 1 mA/cm^2	3E	1000	88.3% at 5 mA/cm^2	-	KOH	0.5	S23 (2015)
	0.5 F/cm^2 at 5 mA/cm^2	2E (vs. VN)	5000	84.5% at 20 mA/cm^2	-	KOH	1.5	
$NiCo_2S_4$@MnO_2 core/shell	2.6 F/cm^2 at 3 mA/cm^2	3E	5000	104% at 50 mV/s	-	KOH	0.55	S24 (2015)
$NiCo_2S_4$@MnO_2 heterostructures	1338 F/g at 2 A/g	3E	2000	82% at 10 A/g	-	KOH	0.45	S25 (2015)
$NiCo_2S_4$@$Ni_3V_2O_8$	512 C/g at 1 A/g	3E	-	-	-	KOH	0.4	S26 (2016)
	150 C/g at 0.5 A/g	2E (vs. AC)	5000	94% at 5 A/g	42.7	KOH	1.6	

$NiCo_2O_4$ nanowires on carbon textile	1283 F/g at 1 A/g	3E	5000	Negligible at 8 A/g	-	KOH	0.4	S27 (2014)
Nickel cobalt oxide nanowires	1479 F/g at 1 A/g	3E	-	-	-	KOH	0.5	S28 (2014)
	105 F/g at 3.6 mA/cm^2	2E(vs. AC)	3000	83 % at 20 mV/s	37.4	KOH	1.6	
Yolk-Shelled $NiGa_2S_4$	2225 F/g at 2 A/g	3E	6000	71% at 20 A/g	-	KOH	0.4	S29 (2017)
	123 F/g at 1.5 A/g	2E (Fe_2O_3)	5000	85% at 12 A/g	43.6	KOH	1.6	
Co_3O_4@PPy@MnO_2 nanowires	629 F/g at 1.2 mA/cm^2	3E	-	-	-	KOH	0.8	S30 (2014)
	96.5 F/g at 0.1 A/g	2E (vs. AC)	10000	100% at 3 A/g	34.3	KOH	1.6	
$ZnCo_2O_4$ nanowire	1625 F/g at 5 A/g	3E	5000	94% at 20 A/g	-	KOH	0.5	S31 (2014)
	0.34 F/cm^2 at 1 mA/cm^2	2E (Symm)	-	-	12.5	KOH	0.8	
$ZnCo_2O_4$ nanoflakes	1220 F/g at 2 A/g	3E	5000	94.2% at 2 A/g	-	KOH	0.6	S32 (2015)
CeO_2@MnO_2 core-shell	255 F/g at 0.25 A/g	3E	3000	90.1% at 2 A/g	-	Na_2SO_4	0.8	S33 (2015)
	49.5 F/g at 0.25 A/g	2E (vs. AGO)	-	-	25.7	Na_2SO_4	2	
$ZnCo_2O_4$@MnO_2 core-shell	2.4 F/cm^2 at 6 mA/cm^2	3E	5000	90% at 24 mA/cm^2	-	KOH	0.5	S34 (2015)
	0.4 F/cm^2 at 2.5 mA/cm^2	2E (Fe_2O_3)	5000	91% at 5 mA/cm^2	37.8	KOH	1.3	
$NiCo_2S_4$ Nanotube on carbon fiber paper	2.86 F/cm^2 at 4 mA/cm^2	3E	2000	96% at 10 mA/cm^2	-	KOH	0.5	S35 (2014)
Zn-Ni-Co ternary oxide	4.2 F/cm^2 at 1.7 mA/cm^2	3E	6000	80.9% at 10 A/g	-	KOH	0.5	S36 (2015)
	114 F/g at 1 A/g	2E (vs. AC)	6000	71.2% at 3 A/g	35.6	KOH	1.5	
$NiCo_2O_4$@$NiMoO_4$ nanowires	1067 F/g at 10 mA/cm^2	3E	5000	84% at 10 mA/cm^2	-	KOH	0.5	S37 (2015)
	-	2E (vs. AC)	5000	87% at 10 mA/cm^2	-	KOH	1.4	
Nickel copper oxide nanowires	2.24 F/cm^2 at 10 mA	3E	1000	90% at 10 A/g	-	KOH	0.5	S38 (2014)
	126 F/g at 2 mA/cm^2	2E (vs. AC)	5000	87% at 20 mA/cm^2	30	KOH	1.3	
Nanoporous CuO	1.5 F/cm^2 at 3.5 mA/cm^2	3E	3000	93% at 7 mA/cm^2	-	KOH	0.5	S39 (2015)
	72.4 F/g at 1 A/g	2E (vs. AC)	3000	96% at 15 mA/cm^2	19.7	KOH	1.4	
Double-shell $NiCo_2S_4$	1263 F/g at 2 A/g	3E	10000	94% at 10 A/g	-	KOH	0.5	S40 (2015)
Mesoporous $NiCo_2S_4$	1440 F/g at 3 A/g	3E	-	-	-	KOH	0.5	S41 (2015)
	90 F/g at 1 A/g	2E (vs. AC)	5000	91.7% at 3 A/g	28.3	KOH	1.5	
Mesoporous Hetero-	749 F/g at 4 A/g	3E	5000	72% at 15 A/g	-	KOH	0.8	S42 (2015)

$NiCo_2S_4/Co_9S_8$	107 F/g at 0.2 A/g	2E (vs. AC)	5000	65% at 5 A/g	33.5	KOH	1.5	
Al@Ni@MnO_x nanospike	942 F/g at 50 mV/s	3E	-	-	-	Na_2SO_4	0.8	S43 (2015)
	59 F/g at 10 mV/s	2E (vs. CCG)	1100	96.3% at 2 A/g	23.02	PVA/Na_2SO_4	1.8	
$NiCo_2S_4$ nano-petals	2036 F/g at 1 A/g	3E	5000	94.3% at 5 A/g	-	KOH	0.4	S44 (2015)
	100 F/g at 1 A/g	2E (vs. AC)	2000	84.2% at 10 A/g	35.6	KOH	1.6	
Carbon fiber paper@ $NiCo_2O_4$ nanowires	680 F/g at 0.5 A/g	3E	-	-	-	NaOH	0.45	S45 (2015)
	97.5 F/g at 1 A/g	2E (vs. GF)	10000	92.2% at 2 A/g	34.5	NaOH	1.6	
$GW\text{-}CuCo_2O_4$	**1813 F/g (3.63 F/cm²) at 4 mA/cm²**	**3E**	**5000**	**96.8% at 10 mA/cm²**	**-**	**KOH**	**0.5**	**This work**
	144.6 F/g (1.59 F/cm²) at 22 mA/cm²	**2E (vs. rGO)**	**6000**	**95.2% at 55 mA/cm²**	**45.2**	**KOH**	**1.5**	

References

S1. A. Pendashteh, M. S. Rahmanifar, R. B. Kaner and M. F. Mousavi, *Chem. Commun.*, 2014, **50**, 1972.
S2. Q. Wang, D. Chen and D. Zhang, *RSC Adv.*, 2015, **5**, 96448.
S3. A. Shanmugavani and R. K. Selvan, *Electrochim. Acta*, 2016, **188**, 852.
S4. S. Liu, K. S. Hui and K. N. Hui, *ACS Appl. Mater. Interfaces*, 2016, **8**, 3258.
S5. S. Vijayakumar, S.-H. Lee and K.-S. Ryu, *Electrochim. Acta*, 2015, **182**, 979.
S6. L. Liao, H. Zhang, W. Li, X. Huang, Z. Xiao, K. Xu, J. Yang, R. Zou and J. Hu, *J. Alloys Compd.*, 2016, DOI: 10.1016/j.jallcom.2016.12.004.
S7. A. Pendashteh, S. E. Moosavifard, M. S. Rahmanifar, Y. Wang, M. F. El-Kady, R. B. Kaner and M. F. Mousavi, *Chem. Mater.*, 2015, **27**, 3919.
S8. M. Kuang, X. Y. Liu, F. Dong and Y. X. Zhang, *J. Mater. Chem. A*, 2015, **3**, 21528.
S9. Y. Zhang, J. Xu, Y. Zheng, Y. Zhang, X. Hu and T. Xu, *RSC Adv.*, 2017, **7**, 3983.
S10. Q. Wang , J. Xu, X. Wang, B. Liu, X. Hou, G. Yu, P. Wang, D. Chen and G. Shen, *ChemElectroChem*, 2014, **1**, 559.
S11. S. Kamari Kaverlavani, S. E. Moosavifard and A. Bakouei, *Chem. Commun.*, 2017, **53**, 1052.
S12. K. Zhang, W. Zeng, G. Zhang, S. Hou, F. Wang, T. Wang and H. Duan, *RSC Adv.*, 2015, **5**, 69636.
S13. Y. Wang, C. Shen, L. Niu, R. Li, H. Guo, Y. Shi, C. Li, X. Liu and Y. Gong, *J. Mater. Chem. A*, 2016, **4**, 9977.
S14. S. Liu, K. San Hui, K. N. Hui, J. M. Yun and K. H. Kim, *J. Mater. Chem. A*, 2016, **4**, 8061.
S15. Y. Zhang, H. Liu, M. Huang, J. M. Zhang, W. Zhang, F. Dong and Y. X. Zhang, *ChemElectroChem*, 2017, **4**, 721.
S16. J. Cheng, H. Yan, Y. Lu, K. Qiu, X. Hou, J. Xu, L. Han, X. Liu, J.-K. Kim and Y. Luo, *J. Mater. Chem. A*, 2015, **3**, 9769.
S17. Y. Zhu, X. Ji, H. Chen, L. Xi, W. Gong and Y. Liu, *RSC Adv.*, 2016, **6**, 84236.
S18. Y. Zhang, J. Xu, Y. Zhang, Y. Zheng, X. Hu and Z. Liu, *J. Mater. Sci.*, 2017, DOI: 10.1007/s10853-017-1119-1.
S19. J. Shen, J. Tang, P. Dong, Z. Zhang, J. Ji, R. Baines and M. Ye, *RSC Adv.*, 2016, **6**, 13456.
S20. B. Zhu, S. Tang, S. Vongehr, H. Xie, J. Zhu and X. Meng, *Chem. Commun.*, 2016, **52**, 2624.
S21. B. Liu, D. Kong, J. Zhang, Y. Wang, T. Chen, C. Cheng and H. Y. Yang, *J. Mater. Chem. A*, 2016, **4**, 3287.
S22. H. Chen, S. Chen, H. Shao, C. Li, M. Fan, D. Chen, G. Tian and K. Shu, *Chemistry, an Asian journal*, 2015, DOI: 10.1002/asia.201500972, n/a.
S23. H. Wan, J. Liu, Y. Ruan, L. Lv, L. Peng, X. Ji, L. Miao and J. Jiang, *ACS. Appl. Mater. Interfaces*, 2015, **7**, 15840.
S24. K. Xu, Q. Ren, Q. Liu, W. Li, R. Zou and J. Hu, *RSC Adv.*, 2015, **5**, 44642.
S25. J. Yang, M. Ma, C. Sun, Y. Zhang, W. Huang and X. Dong, *J. Mater. Chem. A*, 2015, **3**, 1258.
S26. L. Niu, Y. Wang, F. Ruan, C. Shen, S. Shan, M. Xu, Z. Sun, C. Li, X. Liu and Y. Gong, *J. Mater. Chem. A*, 2016, **4**, 5669.
S27. L. Shen, Q. Che, H. Li and X. Zhang, *Adv. Funct. Mater.*, 2014, **24**, 2630.
S28. X. Wang, C. Yan, A. Sumboja and P. S. Lee, *Nano Energy*, 2014, **3**, 119.
S29. S. Liu, K. H. Kim, J. M. Yun, A. Kundu, K. V. Sankar, U. M. Patil, C. Ray and S. Chan Jun, *J. Mater. Chem. A*, 2017, **5**, 6292.
S30. L. Han, P. Tang and L. Zhang, *Nano Energy*, 2014, **7**, 42.
S31. S. Wang, J. Pu, Y. Tong, Y. Cheng, Y. Gao and Z. Wang, *J. Mater. Chem. A*, 2014, **2**, 5434.
S32. J. Cheng, Y. Lu, K. Qiu, H. Yan, X. Hou, J. Xu, L. Han, X. Liu, J.-K. Kim and Y. Luo, *Phys. Chem. Chem. Phys.*, 2015, **17**, 17016.

S33. S. J. Zhu, J. Q. Jia, T. Wang, D. Zhao, J. Yang, F. Dong, Z. G. Shang and Y. X. Zhang, *Chem. Commun.*, 2015, **51**, 14840.
S34. W. Ma, H. Nan, Z. Gu, B. Geng and X. Zhang, *J. Mater. Chem. A*, 2015, **3**, 5442.
S35. J. Xiao, L. Wan, S. Yang, F. Xiao and S. Wang, *Nano Lett.*, 2014, **14**, 831.
S36. C. Wu, J. Cai, Q. Zhang, X. Zhou, Y. Zhu, P. K. Shen and K. Zhang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 26512.
S37. Z. Gu, H. Nan, B. Geng and X. Zhang, *J. Mater. Chem. A*, 2015, **3**, 12069.
S38. L. Zhang, C. Tang and H. Gong, *Nanoscale*, 2014, **6**, 12981.
S39. S. E. Moosavifard, M. F. El-Kady, M. S. Rahmanifar, R. B. Kaner and M. F. Mousavi, *ACS Appl. Mater. Interfaces*, 2015, **7**, 4851.
S40. C. Xia and H. N. Alshareef, *Chem. Mater.*, 2015, **27**, 4661.
S41. Y. Zhu, Z. Wu, M. Jing, X. Yang, W. Song and X. Ji, *J. Power Sources*, 2015, **273**, 584.
S42. L. Hou, Y. Shi, S. Zhu, M. Rehan, G. Pang, X. Zhang and C. Yuan, *J. Mater. Chem. A*, 2017, **5**, 133.
S43. J. Yang, G. Li, Z. Pan, M. Liu, Y. Hou, Y. Xu, H. Deng, L. Sheng, X. Zhao, Y. Qiu and Y. Zhang, *ACS. Appl. Mater. Interfaces*, 2015, **7**, 22172.
S44. Y. Wen, S. Peng, Z. Wang, J. Hao, T. Qin, S. Lu, J. Zhang, D. He, X. Fan and G. Cao, *J. Mater. Chem. A*, 2017, **5**, 7144.
S45. Q. Tang, M. Chen, L. Wang and G. Wang, *J. Power Sources*, 2015, **273**, 654.