Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

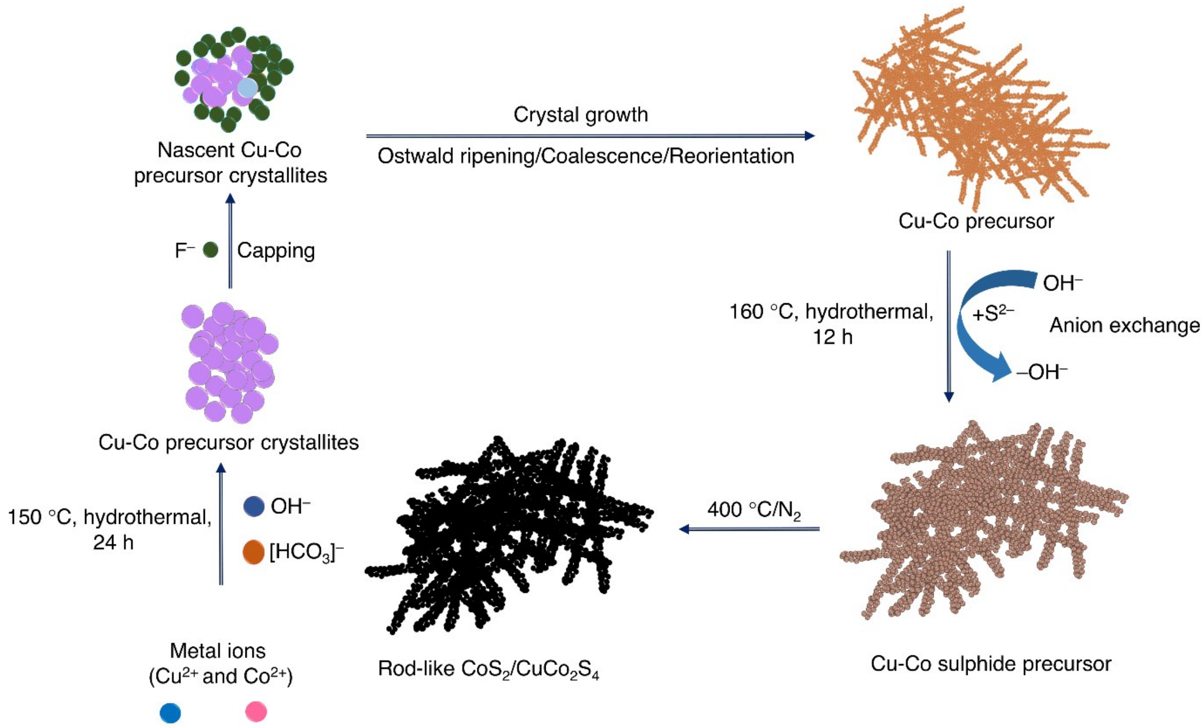
Supplementary Information

The rational design of hierarchical $CoS_2/CuCo_2S_4$ for three-dimensional all-solid-state hybrid supercapacitors with high energy density, rate efficiency, and operational stability

Yogesh Kumar Sonia,[a] Mahesh Kumar Paliwal,[a] and Sumanta Kumar Meher*[a]

[a]Department of Chemistry, Malaviya National Institute of Technology Jaipur, Rajasthan 302017, India

Email*: skmeher.chy@mnit.ac.in



Scheme S1 Plausible mechanism for the formation of $CoS_2/CuCo_2S_4$ rod-like microstructure.

Table S1. List of major peaks (binding energy) as shown in the survey XPS profile of $CoS_2/CuCo_2S_4$ and their corresponding attributions

Binding energy (eV)	Attribution
952.30	Cu $2p_{1/2}$
932.40	Cu $2p_{3/2}$
838.42	shake-up satellite
796.78	shake-up satellite
778.3	Co 2p
712.27	shake-up satellite
530.9	O 1s
284.15	C 1s
224.46	S 2s
160.76	S 2p
121.89	Cu 3s
102.5	Co 3s
74.99	Cu 3p
58.18	Co 3p

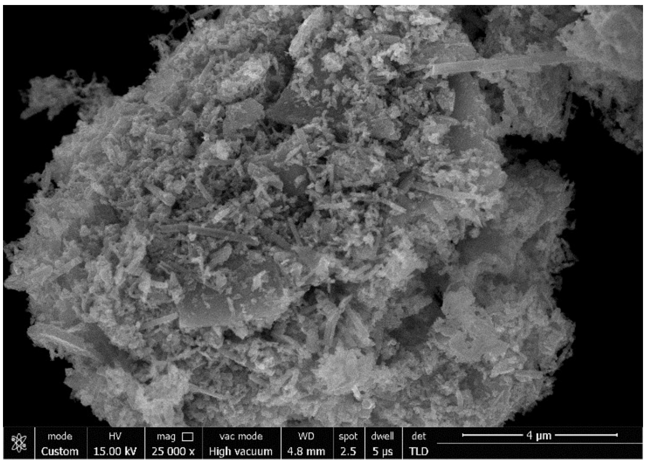


Fig. S1 FESEM image of $CoS_2/CuCo_2S_4$, which has been used for EDX elemental mapping.

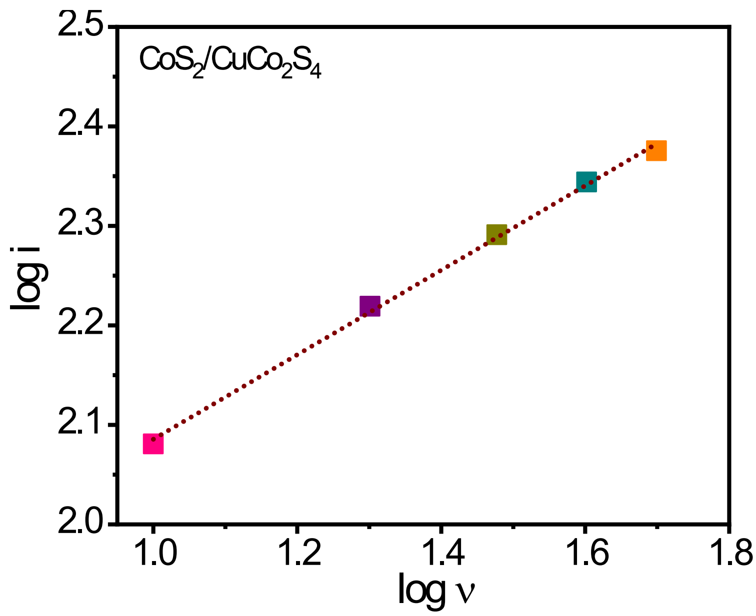


Fig. S2 Linear-fitted *log ν* vs. *log i* plot of $CoS_2/CuCo_2S_4$

Table S2. Comparison of the specific capacitance and charge transfer resistance values of $CoS_2/CuCo_2S_4$ with reported $CuCo_2S_4$-based materials.

Sl. No.	Sample Name	C_S@Current Density (3-Electrode Setup)	C_S@Scan Rate (3-Electrode Setup)	R_{ct} (Ω) from EIS (3-Electrode Setup)	Reference
1	$CuCo_2S_4$ dandelion-like	424 F g^{-1} @1 A g^{-1}	-	-	[s1]
2	$CuCo_2S_4$@CNT	1690 F g^{-1}@1 A g^{-1}	-	-	[s2]
3	$CuCo_2S_4$-rGO	525 F g^{-1}@1 A g^{-1}; 425 F g^{-1}@5 A g^{-1}; 370 F g^{-1}@10 A g^{-1}; 326 F g^{-1}@15 A g^{-1}; 303 F g^{-1}@20 A g^{-1}	665 F g^{-1} @ 7.5 mV s^{-1}	-	[s3]
4	CNTs@NC@$CuCo_2S_4$	1604 F g^{-1}@1 A g^{-1}; 1044 F g^{-1}@2 A g^{-1}; 1000 F g^{-1}@5 A g^{-1}; 955 F g^{-1}@10 A g^{-1}; 896 F g^{-1}@20 A g^{-1}	-	135.6	[s4]
5	$CuCo_2S_4$-HNN (hollow nano-needle arrays)	2163 F g^{-1}@6 A g^{-1}	-	-	[s5]
6	$CuCo_2S_4$/CNT/Graphene	504 F g^{-1}@10 A g^{-1}	-	-	[s6]

7	$CuCo_2S_4$ nanowire	875 F g^{-1}@1 A g^{-1}	-	1.96	[s7]
8	$CuCo_2S_4$ nanorod array	1536 F g^{-1}@1 A g^{-1}; 1295 F g^{-1}@5 A g^{-1}; 1157 F g^{-1}@10 A g^{-1}; 1026 F g^{-1}@20 A g^{-1}	-	-	[s8]
9	$CuCo_2S_4$/GA (graphene aerogel)	668 F g^{-1}@1 A g^{-1}; 620 F g^{-1}@2 A g^{-1}; 588 F g^{-1}@5 A g^{-1}; 535 F g^{-1}@10 A g^{-1}; 480 F g^{-1}@20 A g^{-1}	-	-	[s9]
10	$CuCo_2S_4$ micro-sphere	516 F g^{-1}@10 A g^{-1}	665 F g^{-1}@10 mV s^{-1}; 482 F g^{-1}@50 mV s^{-1}	0.26	[s10]
11	$CuCo_2S_4$ nanoparticle	772 F g^{-1}@2 A g^{-1}	-	-	[s11]
12	$CuCo_2S_4$ ball-in-ball	442 F g^{-1}@0.5 A g^{-1}	-	-	[s12]
13	$CuCo_2S_4$ agglomerate nanoparticle	580 F g^{-1}@1 A g^{-1}; 529 F g^{-1}@2 A g^{-1}; 482 F g^{-1}@3 A g^{-1}; 437 F g^{-1}@4 A g^{-1}; 406 F g^{-1}@5 A g^{-1}; 354 F g^{-1}@7 A g^{-1}	-	5.65	[s13]
14	$CuCo_2S_4$ microsphere	1566 F g^{-1}@2 A g^{-1}	-	0.27	[s14]
15	$CuCo_2S_4$/NG (N-doped graphene)	1005 F g^{-1}@1 A g^{-1}; 978 F g^{-1}@3 A g^{-1}; 949 F g^{-1}@5 A g^{-1}; 901 F g^{-1}@10 A g^{-1}; 831 F g^{-1}@20 A g^{-1}	-	-	[s15]
16	C@$CuCo_2S_4$	854 F g^{-1}@1 A g^{-1}; 774 F g^{-1}@3 A g^{-1}; 681 F g^{-1}@5 A g^{-1}; 597 F g^{-1}@7 A g^{-1}; 485 F g^{-1}@10 A g^{-1}	-	-	[s16]
17	$CuCo_2S_4$ nanoparticles	449 F g^{-1}@1 A g^{-1}; 443 F g^{-1}@1.5 A g^{-1}; 433 F g^{-1}@3 A g^{-1}; 401 F g^{-1}@5 A g^{-1}	-	0.56	[s17]
18	GQD (graphene quantum dots)/$CuCo_2S_4$	1725 F g^{-1}@0.1 A g^{-1}	-		[s18]

19	N-doped C-coated $CuCo_2S_4$	1228 F g^{-1}@1 A g^{-1}; 1070 F g^{-1}@2 A g^{-1}; 1003 F g^{-1}@3 A g^{-1}; 933 F g^{-1}@5 A g^{-1}; 864 F g^{-1}@10 A g^{-1}; 784 F g^{-1}@20 A g^{-1}	2002 F g^{-1}@5 mV s^{-1}; 1831 F g^{-1}@10 mV s^{-1}; 1535 F g^{-1}@ 20 mV s^{-1}; 1168 F g^{-1}@50 mV s^{-1}; 921 F g^{-1}@ 100 mV s^{-1}	0.39	[s19]
20	$CoS_2/CuCo_2S_4$	2438 F g^{-1}@2 A g^{-1}; 1995 F g^{-1}@3 A g^{-1}; 1730 F g^{-1}@4 A g^{-1}; 1590 F g^{-1}@5 A g^{-1}; 1492 F g^{-1}@6 A g^{-1}	4653 F g^{-1}@10 mV s^{-1}; 3618 F g^{-1}@20 mV s^{-1}; 3007 F g^{-1}@ 30 mV s^{-1}; 2552 F g^{-1}@40 mV s^{-1}; 2169 F g^{-1}@ 50 mV s^{-1}	0.23	This work

Table S3. Comparison of the energy density, power density and multiple-cycle capacitance retention of $CoS_2/CuCo_2S_4$||N-rGO ASSHSC device with reported $CuCo_2S_4$-based hybrid supercapacitor devices.

Sl. No.	Hybrid Supercapacitor Device	Energy Density (E_D; W h Kg^{-1})	Power Density (P_D; W Kg^{-1})	Capacitance Retention (%/No. of cycle)	Reference
1	$CuCo_2S_4$/CC||AC	17.12	194.4	78.4 / 3,000	[s20]
2	$CuCo_2S_4$||GA	22	1080	70.4 / 5,000	[s9]
3	$CuCo_2S_4$/CNT||AC	23.2	402.7	85.7 / 10,000	[s21]
4	$CuCo_2S_4$/N,S-RGO||N,S-RGO	10.8	400	88.9 / 5,000	[s22]
5	$CuCo_2S_4$@$NiCo_2S_4$||AC	23.4	400	71 / 3,000	[s23]
6	$CuCo_2S_4$||AC	15.0	422.5	94.7 / 5,000	[s17]
7	$CuCo_2S_4$||AC-ASC	16	240	99.5 / 6,000	[s13]
8	$CuCo_2S_4$||AC	22	405	62 / 20,000	[s1]
9	$CoS_2/CuCo_2S_4$||N-rGO	32.4	4000	92.8 /10,000	This work

References

[s1] J. P. Chen, S. Q. Gao, P. P. Zhang, B. Q. Wang, X. C. Wang and F. Liu, *J. Alloys Compd.* **2020**, *825*, 153984.

[s2] J.-M. Xu, X.-C. Wang and J.-P. Cheng, *ACS. Omega* **2020**, *5*, 1305−1311.

[s3] L.-L. Liu, K. P. Annamalai and Y.-S. Tao, *New Carbon Mater.* **2016**, *31*, 336−342.

[s4] R. Jin, Y. Cui, S. Gao, S. Zhang, L. Yang and G. Li, *Electrochim. Acta* **2018**, *273*, 43−52.

[s5] S. E. Moosavifard, S. Fani and M. Rahmanian, *Chem. Commun*. **2016**, *52*, 4517−4520.

[s6] J. Shen, J. Tang, P. Dong, Z. Zhang, J. Ji, R. Baines and M. Ye, *RSC Adv*. **2016**, *6*, 13456−13460.

[s7] S. Liu, Y. Yin, K. S. Hui, K. N. Hui, S. C. Lee and S.-C. Jun, *Adv. Sci.* **2018**, *5*, 1800733.

[s8] S. Cheng, T. Shi, C. Chen, Y. Zhong, Y. Huang, X. Tao, J. Li, G. Liao and Z. Tang, *Sci. Rep.* **2017**, *7*, 6681.

[s9] Z. Tian, X. Wang, B. Li, H. Li and Y. Wu, *Electrochim. Acta* **2019**, *298*, 321−329.

[s10] A. T. A. Ahmed, H. S. Chavan, Y. Jo, S. Cho, J. Kim, S. M. Pawar, J. L. Gunjakar, A. I. Inamdar, H. Kim and H. Im, *J. Alloys Compd.* **2017**, *724*, 744−751.

[s11] Y. Zhu, X. Ji, H. Chen, L. Xi, W. Gong and Y. Liu, *RSC Adv.* **2016**, *6*, 84236−84241.

[s12] Y. H. Lee, B. K. Kang, M. S. Kim, H. W. Choi, D. S. Choi, M. Kumar and D. H. Yoon, *Phys. Status Solidi A* **2018**, *215,* 1700936.

[s13] F. Wang, J. Zheng, G. Li, J. Ma, C. Yang and Q. Wang, *Mater. Chem. Phys.* **2018**, *215*, 121−126.

[s14] A. Mohammadi, S. E. Moosavifard, A. G. Tabrizi, M. M. Abdi and G. Karimi, *ACS Appl. Energy Mater.* **2019**, *2*, 627−635.

[s15] M. Guo, J. Balamurugan, T. D. Thanh, N. H. Kim and J. H. Lee, *J. Mater. Chem. A* **2016**, *4*, 17560−17571.

[s16] F. Wang, J. Zheng, J. Ma, K. Zhou and Q. Wang, *J. Nanopart. Res.* **2019**, *21*, 189.

[s17] Y. Xu, T. Zhou, X. Cao, W. Zhao, J. Chang, W. Zhu, W. Guo and W. Du, *Mater. Res. Bull.* **2017**, *91*, 68−76.

[s18] Y. Huang, L. Lin, T. Shi, S. Cheng, Y. Zhong, C. Chen and Z. Tang, *Appl. Surf. Sci.* **2019**, *463*, 498−503.

[s19] Z. Wang, Z. Zhu, Q. Zhang, M. Zhai, J. Gao, C. Chen and B. Yang, *Ceram. Int*. **2019**, *45*, 21286−21292.

[s20] T. Xie, Y. Gai, Y. Shang, C. Ma, L. Su, J. Liu and L. Gong, *Eur. J. Inorg. Chem*. **2018,** *43*, 4711−4719.

[s21] H. Li, Z. Li, Z. Wu, M. Sun, S. Han, C. Cai, W. Shen, X. Liu and Y. Fu, *J. Colloid Interface Sci*. **2019**, *549*, 105−113.

[s22] Z. Li, H. Lv, Z. Wang, A. Gu, X. He and L. Wang, *Mater. Res. Express* **2019**, *6*, 085523.

[s23] L. Ma, T. Chen, S. Li, P. Gui and G. Fang, *Nanotechnology* **2019**, *30*, 255603.