

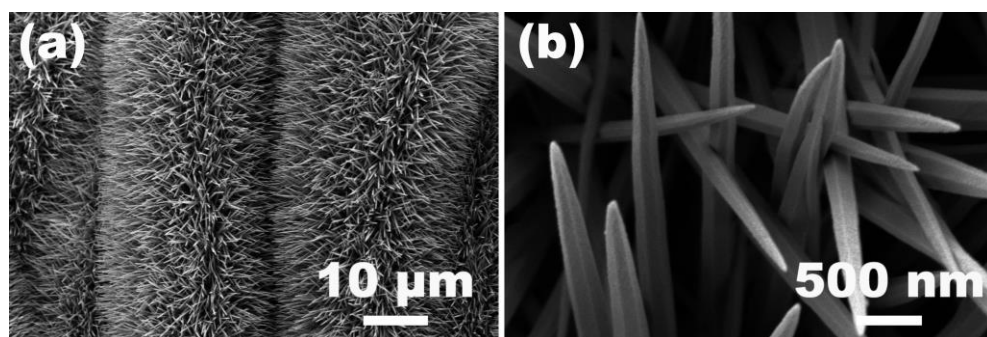
Supporting Information

# Fabrication of Hierarchical MOF-Derived $\text{NiCo}_2\text{S}_4$ @Mo-Doped Co-LDH Arrays for High-Energy-Density Asymmetric Supercapacitors

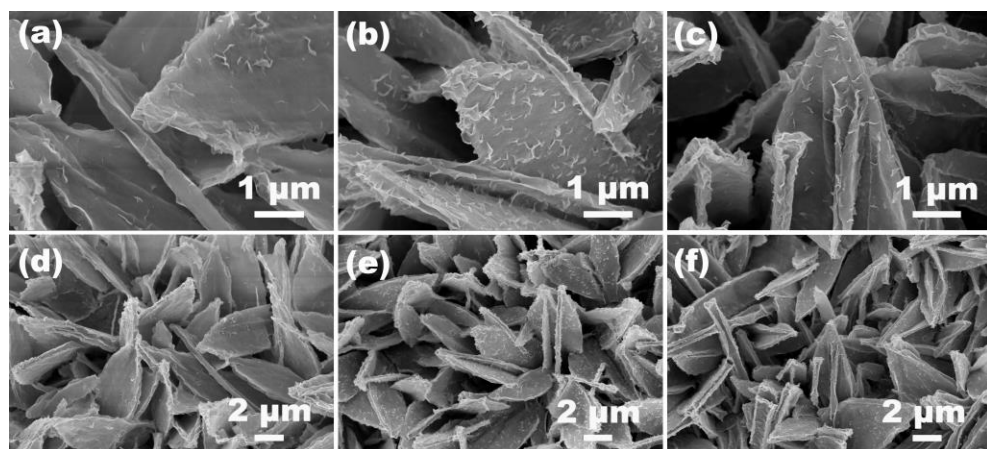
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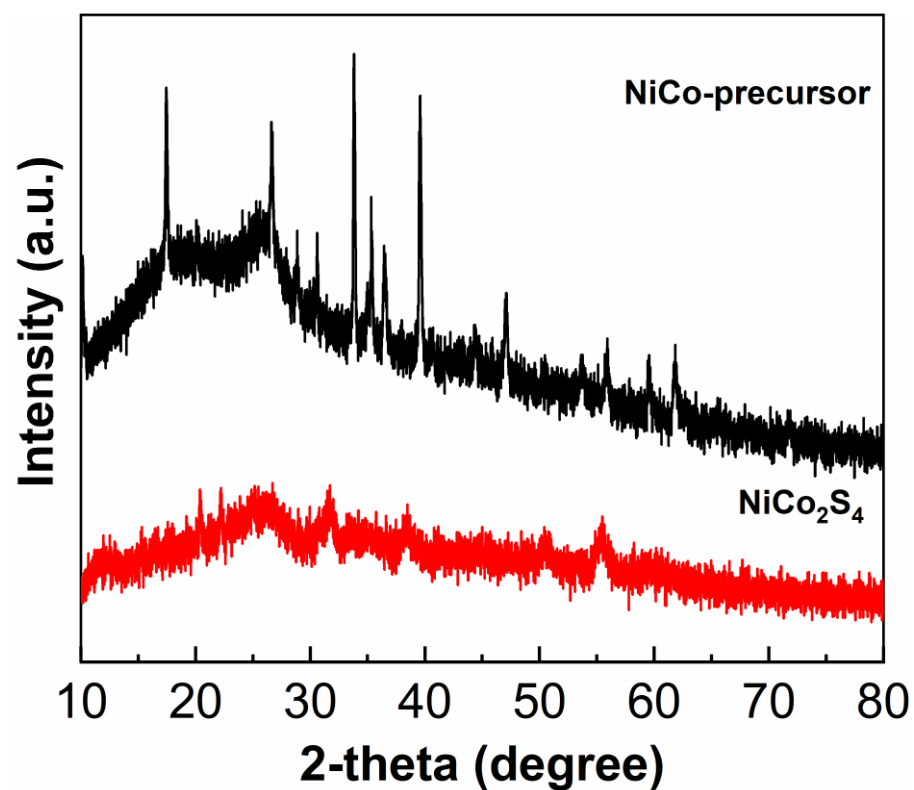
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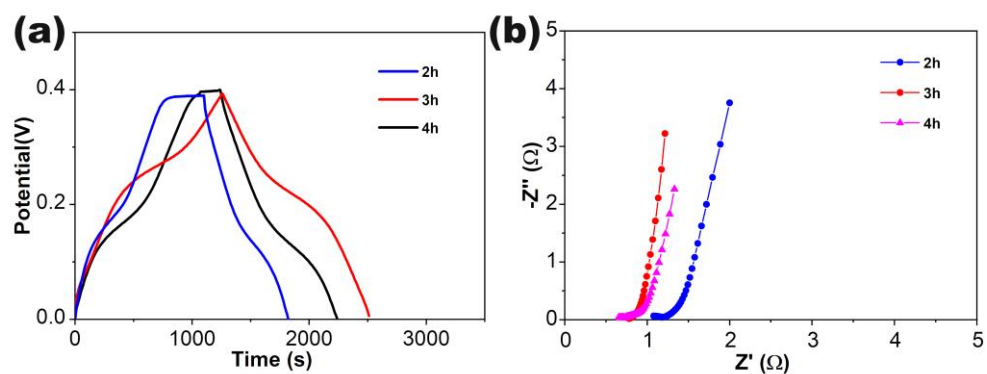
**Figure S1.** Low and high-resolution SEM images of the NiCo-precursor.



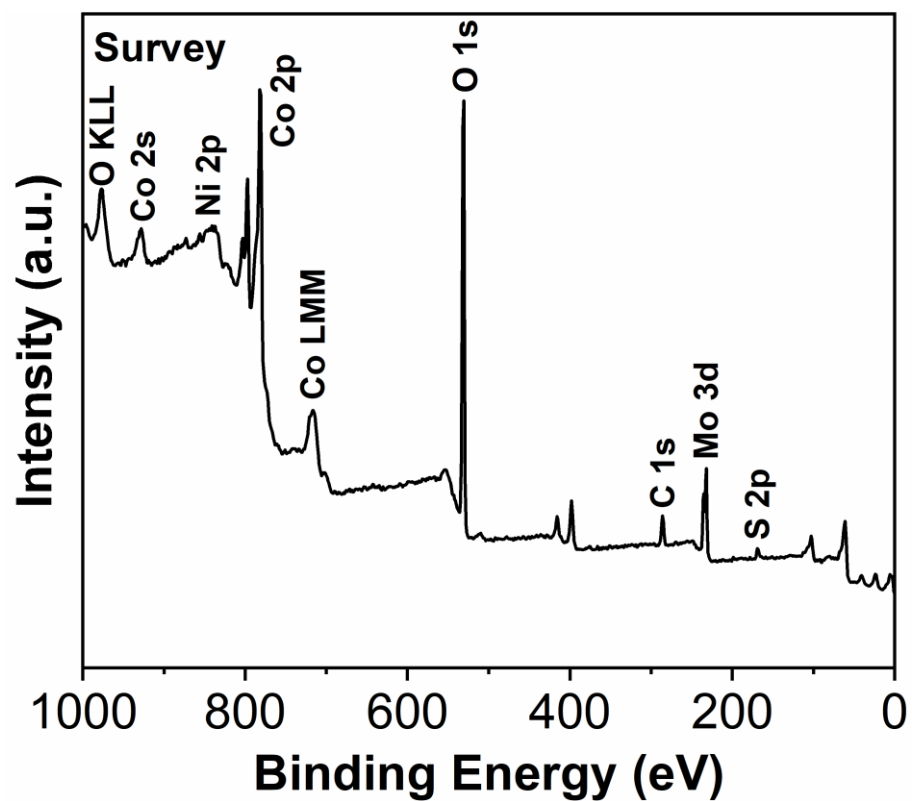
**Figure S2.** SEM of the  $\text{NiCo}_2\text{S}_4$ @Mo-doped Co-LDH at different synthesis time.



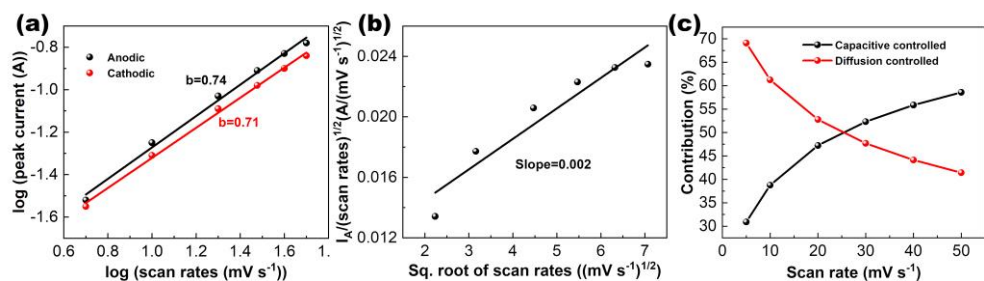
**Figure S3.** XRD patterns of the NiCo-precursor and NiCo<sub>2</sub>S<sub>4</sub>.



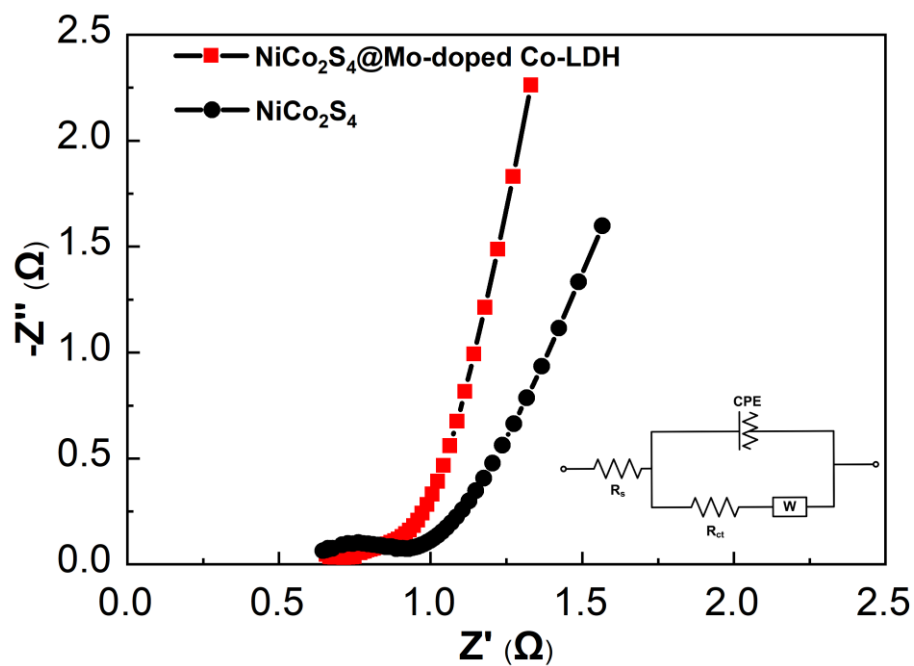
**Figure S4.** Comparison of GCD (a) and EIS (b) results of the NiCo<sub>2</sub>S<sub>4</sub>@Mo-doped Co-LDH at different synthesis time.



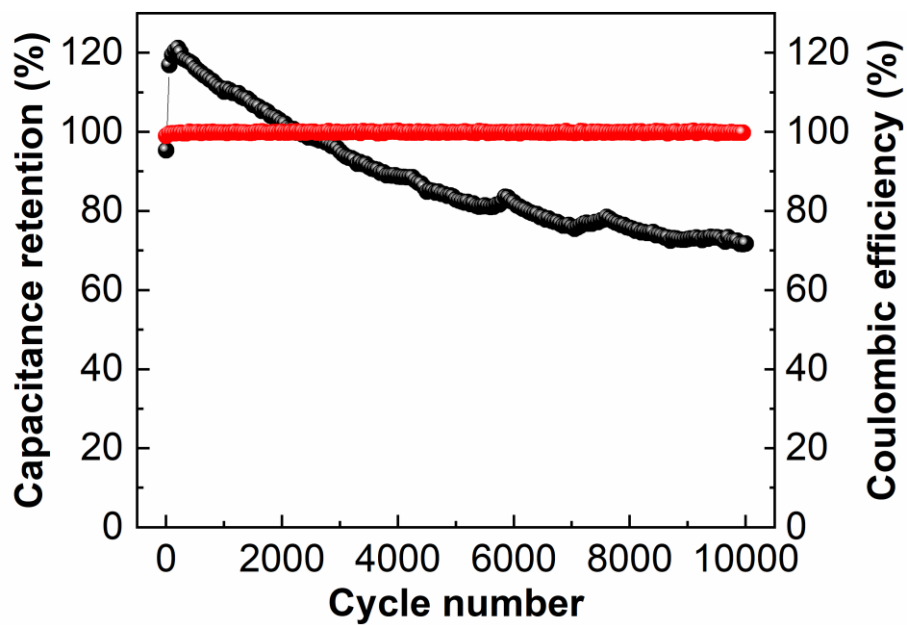
**Figure S5.** Survey XPS spectra of the  $\text{NiCo}_2\text{S}_4$ @Mo-doped Co-LDH.



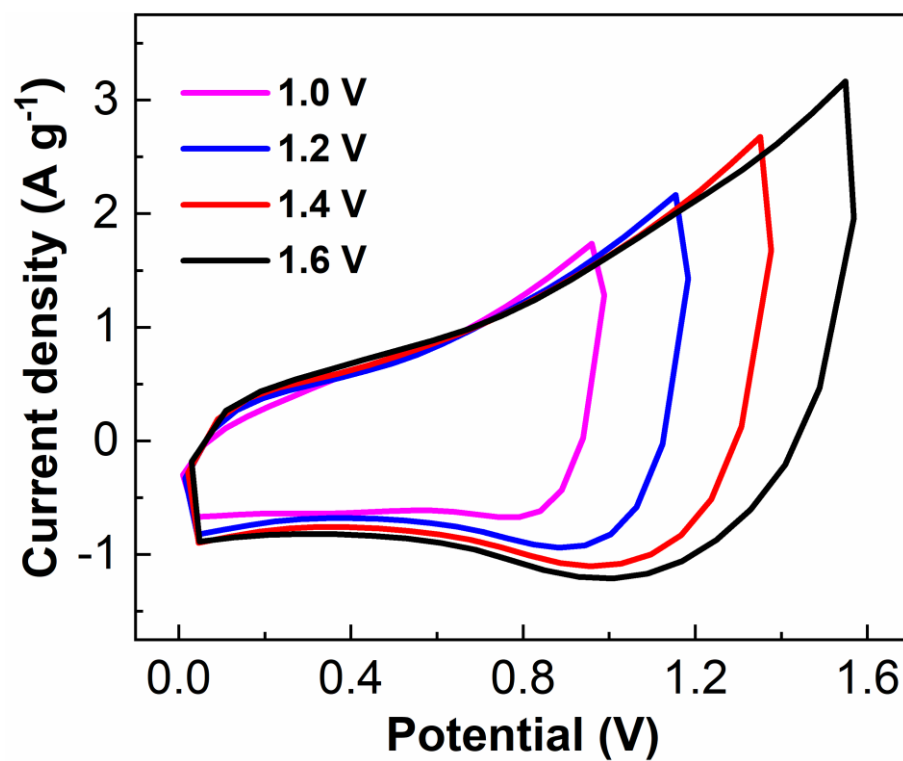
**Figure S6.** (a) Linear variation of log peak current and log scan rates. (b) Linear relation of  $i/v$  vs  $v$ . (c) Diffusion contribution and capacitive contribution at various scan rates.



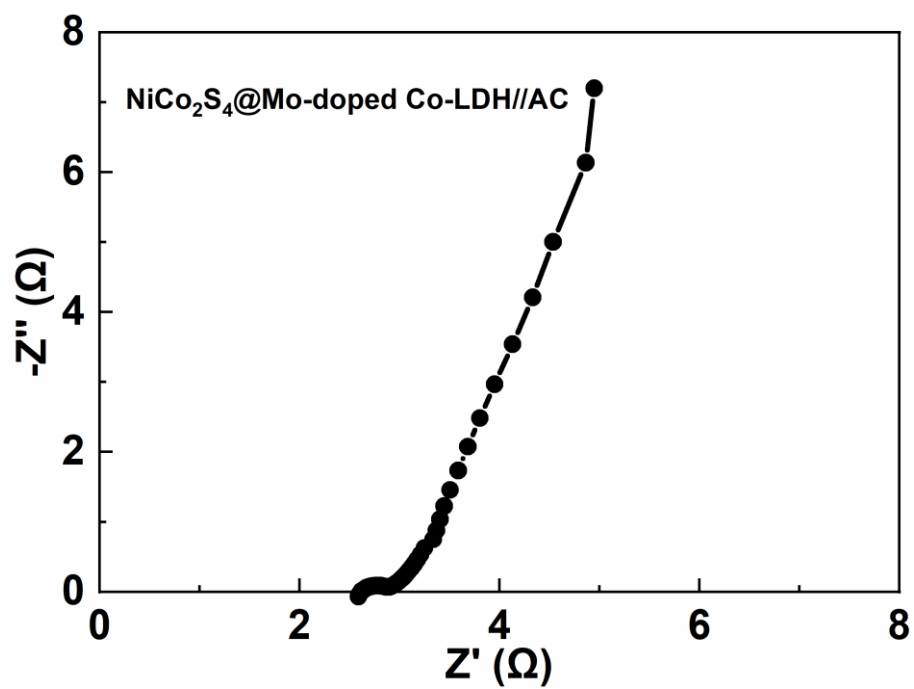
**Figure S7.** EIS results of the  $\text{NiCo}_2\text{S}_4$  and  $\text{NiCo}_2\text{S}_4$ @Mo-doped Co-LDH. Inset: the corresponding equivalent circuit.



**Figure S8.** Cycling performance of the  $\text{NiCo}_2\text{S}_4$  electrode at  $10 \text{ A g}^{-1}$ .



**Figure S9.** CV curves of the NiCo<sub>2</sub>S<sub>4</sub>@Mo-doped Co-LDH//AC ASC at various voltage window.



**Figure S10.** EIS curve of the NiCo<sub>2</sub>S<sub>4</sub>@Mo-doped Co-LDH//AC ASC device.

**Table S1.** Comparison of NiCo<sub>2</sub>S<sub>4</sub>@Mo-doped Co-LDH with other materials.

Materials	Current density	Specific capacitance	Energy density	Power density	Ref
NiCo <sub>2</sub> S <sub>4</sub> @CoMoO <sub>4</sub> //AC	1 A g <sup>-1</sup>	2118.8 F g <sup>-1</sup>	66.6 Wh kg <sup>-1</sup>	800 W kg <sup>-1</sup>	1
NiCo <sub>2</sub> S <sub>4</sub> /Co <sub>9</sub> S <sub>8</sub> HSs//AC	1 A g <sup>-1</sup>	2180 F g <sup>-1</sup>	96.5 Wh kg <sup>-1</sup>	800 W kg <sup>-1</sup>	2
NiCo <sub>2</sub> S <sub>4</sub> @Co <sub>9</sub> S <sub>8</sub> //AC	1 A g <sup>-1</sup>	2390.2 F g <sup>-1</sup>	47.7 Wh kg <sup>-1</sup>	1275 W kg <sup>-1</sup>	3
CoMoO <sub>4</sub> -Co(OH) <sub>2</sub> //AC	1 A g <sup>-1</sup>	2028 F g <sup>-1</sup>	61 Wh kg <sup>-1</sup>	800 W kg <sup>-1</sup>	4
ZnS/NiCo <sub>2</sub> S <sub>4</sub> /Co <sub>8</sub> S <sub>9</sub> nanotube	1 A g <sup>-1</sup>	1618.1 F g <sup>-1</sup>	66 Wh kg <sup>-1</sup>	750 W kg <sup>-1</sup>	5
RGO@NiCo <sub>2</sub> S <sub>4</sub> @NiMo-LDH	1 A g <sup>-1</sup>	1346 F g <sup>-1</sup>	59.38 Wh kg <sup>-1</sup>	808.19W kg <sup>-1</sup>	6
NiCo <sub>2</sub> S <sub>4</sub> @NiMoO <sub>4</sub>	5mA/cm <sup>2</sup>	2006 F g <sup>-1</sup>	12.6 Wh kg <sup>-1</sup>	1158W kg <sup>-1</sup>	7
CuCo <sub>2</sub> S <sub>4</sub> @ CoMoO <sub>4</sub> //AC	1mA/cm <sup>2</sup>	2058 F g <sup>-1</sup>	45.73 Wh kg <sup>-1</sup>	198.8 W kg <sup>-1</sup>	8
CoNi-LDH/NiCo <sub>2</sub> S <sub>4</sub> /RGO//AC	1A g <sup>-1</sup>	1846.66 F g <sup>-1</sup>	28.8 Wh kg <sup>-1</sup>	800 W kg <sup>-1</sup>	9
NiCo <sub>2</sub> S <sub>4</sub> @MoS <sub>2</sub> //AC	3mA/cm <sup>2</sup>	719.32 F g <sup>-1</sup>	48.63 Wh kg <sup>-1</sup>	250.1 W kg <sup>-1</sup>	10
ZnCo <sub>2</sub> O <sub>4</sub> @ CoMoO <sub>4</sub> //AC	10mA/cm <sup>2</sup>	1096.08 C g <sup>-1</sup>	29.24 Wh kg <sup>-1</sup>	884.57 W kg <sup>-1</sup>	11
NiCo <sub>2</sub> S <sub>4</sub> @Mo-doped Co-LDH//AC	1 A g <sup>-1</sup>	3052.88 Fg <sup>-1</sup>	95.56 Wh kg <sup>-1</sup>	797.93 W kg <sup>-1</sup>	This work

## References

[1] Zhao, Yunhe, Xinyi He, Rongrong Chen, Qi Liu, Jingyuan Liu, Dalei Song, Hongsen Zhang et al. "Hierarchical NiCo<sub>2</sub>S<sub>4</sub>@ CoMoO<sub>4</sub> core-shell heterostructures nanowire arrays as advanced electrodes for flexible all-solid-state asymmetric supercapacitors." Applied Surface Science 453 (2018): 73-82.

- [2] Han, Xinru, Qun Chen, Hong Zhang, Yonghong Ni, and Li Zhang. "Template synthesis of  $\text{NiCo}_2\text{S}_4/\text{Co}_9\text{S}_8$  hollow spheres for high-performance asymmetric supercapacitors." *Chemical Engineering Journal* 368 (2019): 513-524.
- [3] Jia, Hong, Jie Wang, Wenwen Fu, Junhua Hu, and Yu Liu. "In-situ MOFs-derived hollow  $\text{Co}_9\text{S}_8$  polyhedron welding on the top of  $\text{MnCo}_2\text{S}_4$  nanoneedles for high performance hybrid supercapacitors." *Chemical Engineering Journal* 391 (2020): 123541.
- [4] Zhao, Yunhe, Hongxing Dong, Xinyi He, Jing Yu, Rongrong Chen, Qi Liu, Jingyuan Liu, Hongsen Zhang, Jia Yu, and Jun Wang. "Carbon cloth modified with metal-organic framework derived  $\text{CC}@\text{CoMoO}_4\text{-Co(OH)}_2$  nanosheets array as a flexible energy-storage material." *ChemElectroChem* 6, no. 13 (2019): 3355-3366.
- [5] Sui, Yanwei, Yuanming Zhang, Haihua Hu, Qin Xu, Fei Yang, and Zhaosheng Li. "High energy density asymmetric supercapacitor based  $\text{ZnS/NiCo}_2\text{S}_4/\text{Co}_9\text{S}_8$  nanotube composites materials." *Advanced Materials Interfaces* 5, no. 12 (2018): 1800018.
- [6] Cheng, Cheng, Yongjin Zou, Fen Xu, Cuili Xiang, Qingli Sui, Jian Zhang, Lixian Sun, and Zhenming Chen. "Ultrathin graphene@  $\text{NiCo}_2\text{S}_4$ @ Ni-Mo layered double hydroxide with a 3D hierarchical flowers structure as a high performance positive electrode for hybrid supercapacitor." *Journal of Energy Storage* 52 (2022): 105049.
- [7] Zhang, Yan, Jie Xu, Yayun Zheng, Yingjiu Zhang, Xing Hu, and Tingting Xu. " $\text{NiCo}_2\text{S}_4$ @  $\text{NiMoO}_4$  core-shell heterostructure nanotube arrays grown on Ni foam as a binder-free electrode displayed high electrochemical performance with high capacity." *Nanoscale research letters* 12 (2017): 1-9.
- [8] Mao, Xiaoqi, Ying Wang, Cuili Xiang, Dan Zhan, Huanzhi Zhang, Erhu Yan, Fen Xu et al. "Core-shell structured  $\text{CuCo}_2\text{S}_4$ @  $\text{CoMoO}_4$  nanorods for advanced electrode materials." *Journal of Alloys and Compounds* 844 (2020): 156133.
- [9] Guo, Yaning, Chen Hao, Xiaokun Wang, Ying Yang, Xiaohong Wang, Jingbo Wu, and Yutang Shen. "Facile fabrication of CoNi-Layered Double Hydroxide/ $\text{NiCo}_2\text{S}_4$ /Reduced Graphene Oxide composites by in situ hydrothermal growth strategy for supercapacitor performance." *Ceramics International* 48, no. 12 (2022): 17644-17653.

[10] Tang, Yu, Xilong Liu, Yang Chen, Leiyun Han, Dianfeng Dai, Liangyu Liu, Chongtai Wang, Yingjie Hua, Xudong Zhao, and Xiaoyang Liu. "NiCo<sub>2</sub>S<sub>4</sub>@MoS<sub>2</sub> core/shell nanorod arrays for fabrication of high-performance asymmetric supercapacitors with high mass loading." *Journal of Energy Storage* 51 (2022): 104518.

[11] Yu, Deyang, Yifei Teng, Xilong Liu, and Xiaoyang Liu. "A high-performance electrode based on the ZnCo<sub>2</sub>O<sub>4</sub>@CoMoO<sub>4</sub> core-shell nanosheet arrays on nickel foam and their application in battery-supercapacitor hybrid device." *Electrochimica Acta* 347 (2020): 136278.