Nickel Hydroxide/Sulfide Hybrids: Halide Ion Controlled Synthesis, Structural Characteristics, and Electrochemical Performance

Qibin Wu,[a,c] Weining Li,[a] Xuefeng Zou,*[b] Bin Xiang*[a]

[a]Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.

[b]Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Education University, Guiyang 550018, China.

[c]State Key Laboratory of Advanced Chemical Power Sources, Guizhou Meiling Power Sources Co. Ltd., Zunyi, Guizhou 563003, China.

*Corresponding Author.

E-mail: njzouxf@gznc.edu.cn (X. Zou), xiangbin@cqu.edu.cn (B. Xiang)

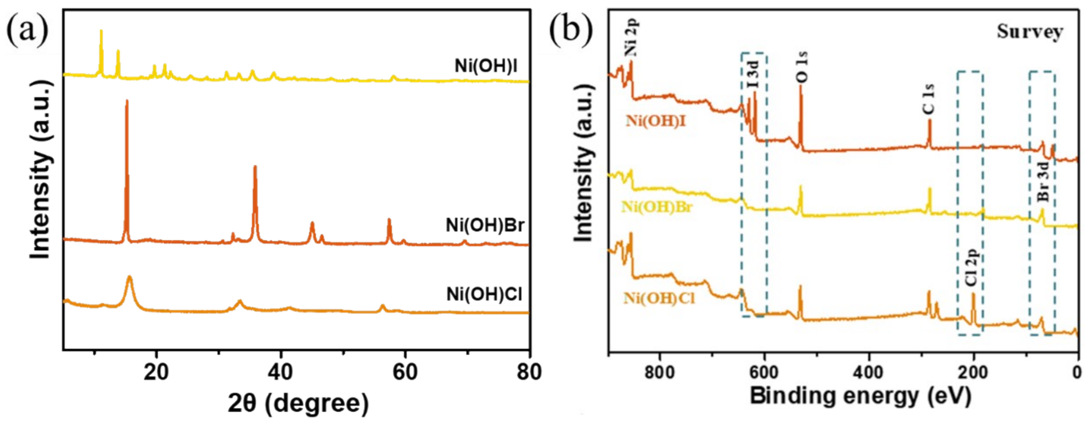

Figure S1. (a) XRD patterns of Ni(OH)Cl, Ni(OH)Br and Ni(OH)I. (b) XPS spectra of Ni(OH)Cl, Ni(OH)Br and Ni(OH)I.

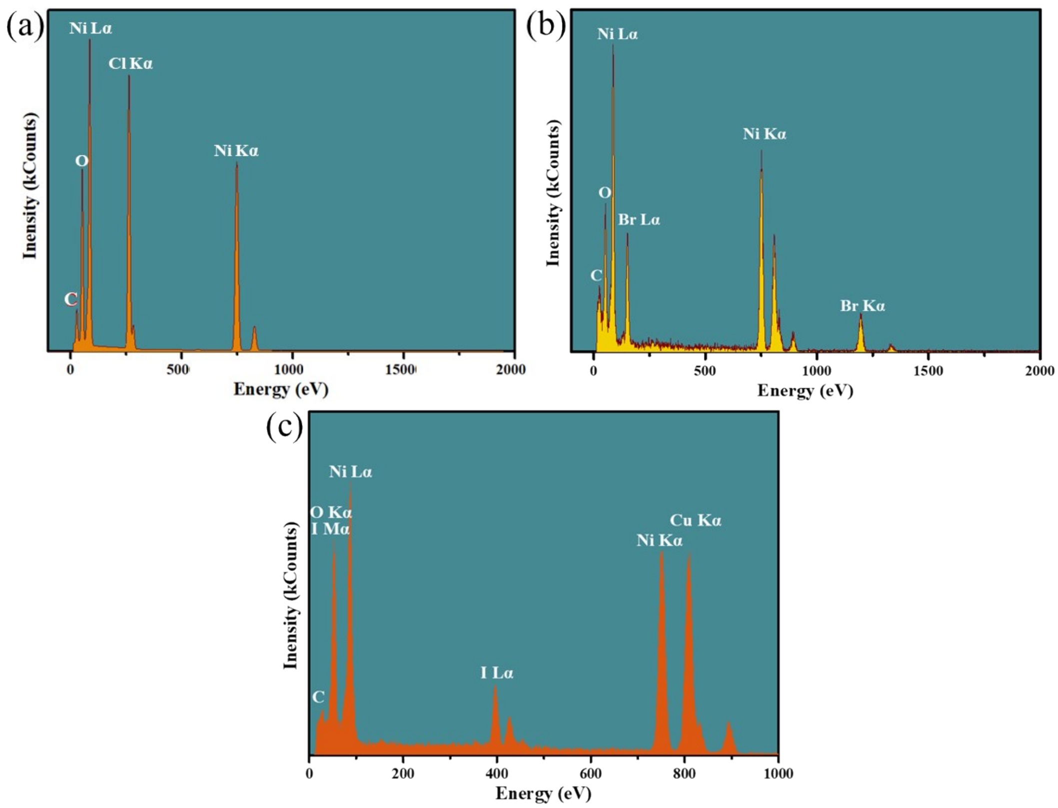

Figure S2. EDS spectra of (a) Ni(OH)Cl, (b) Ni(OH)Br, and (c) Ni(OH)I.

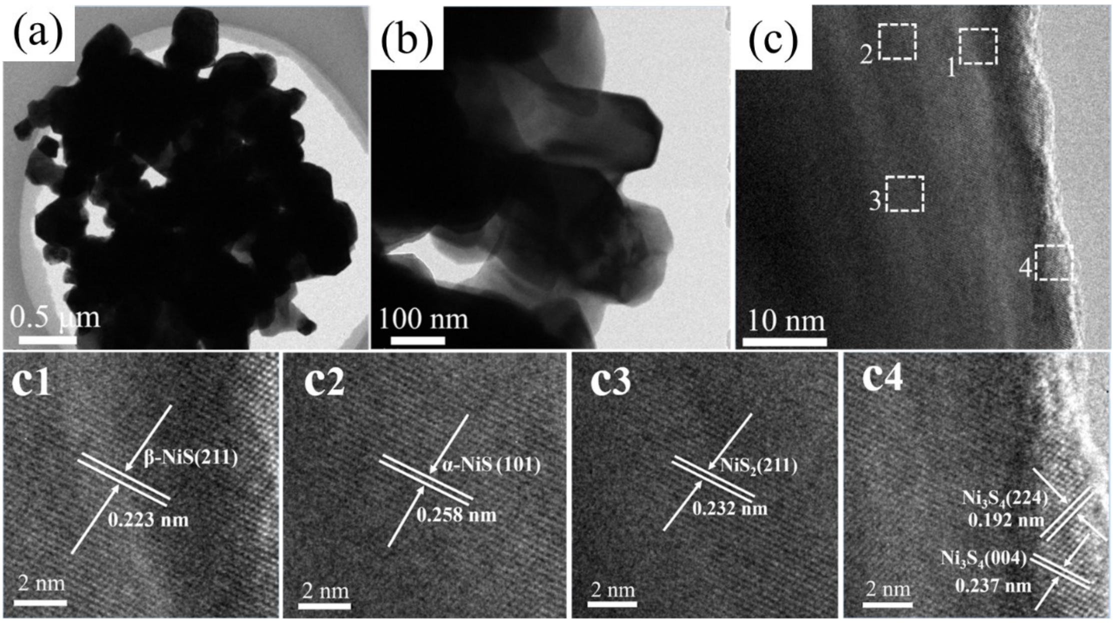

Figure S3. TEM images of S1.

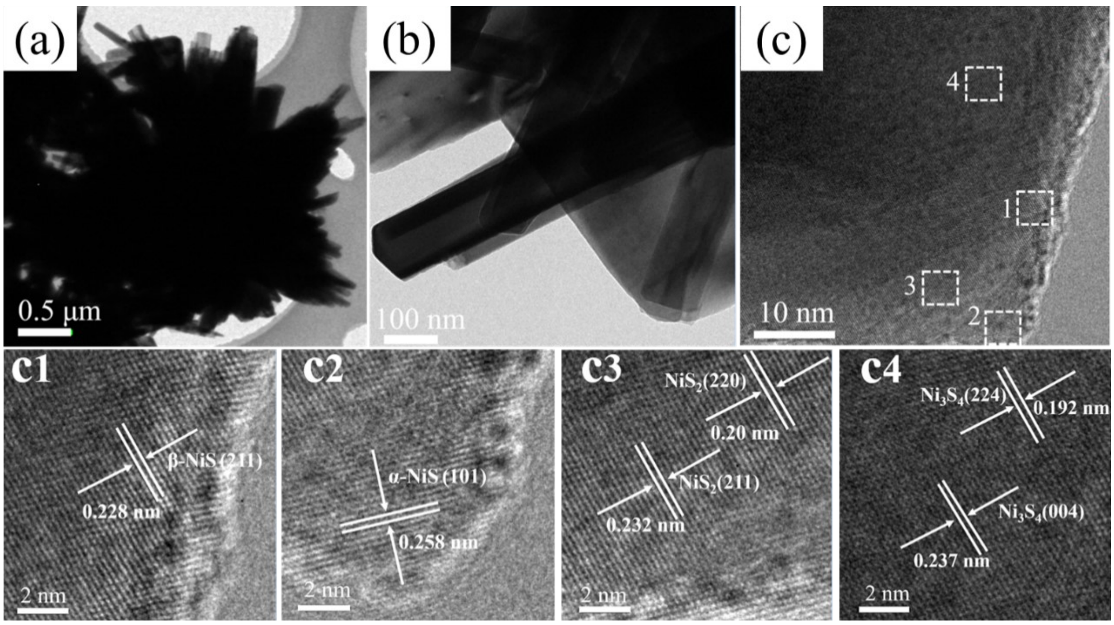

Figure S4. TEM images of S2.

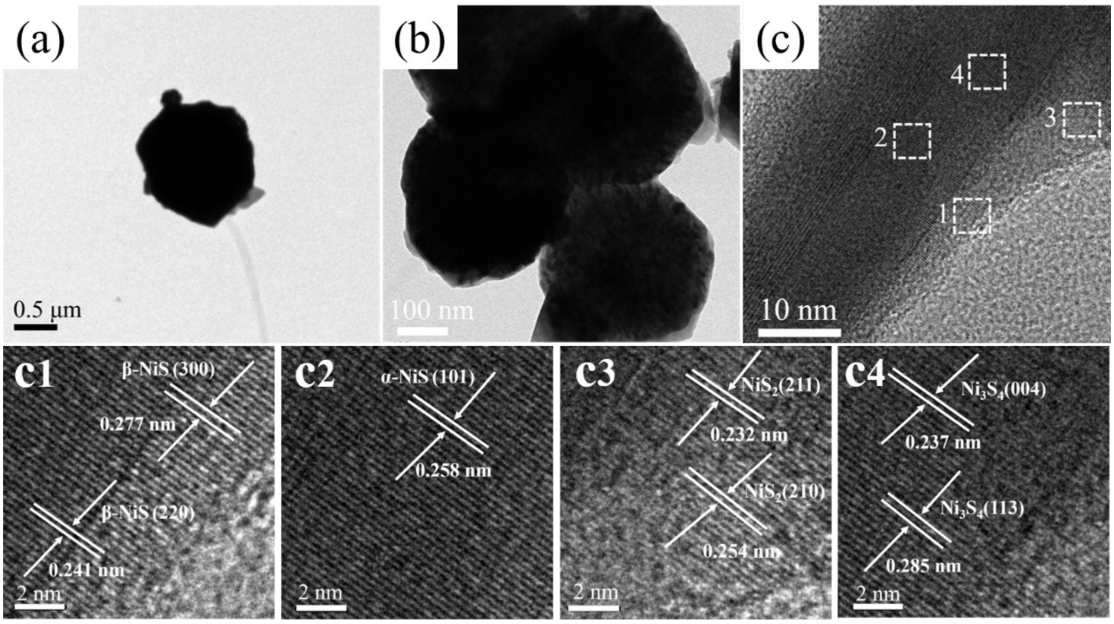

Figure S5. TEM images of S3.

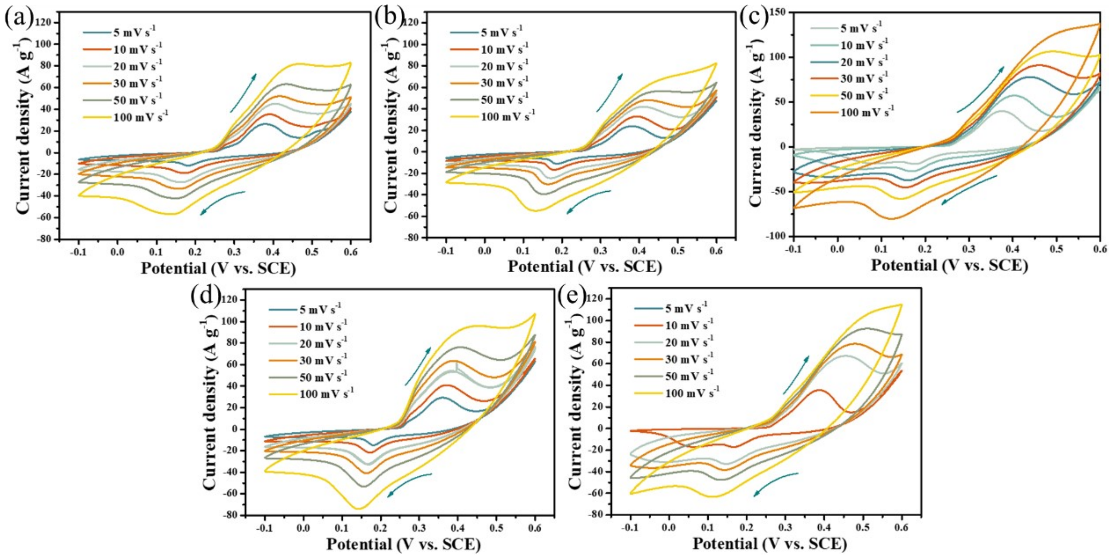

Figure S6. (a-e) CV curves of NS-1h, NS-3h, NS-6h, NS-12h, and NS-20h at different scan rates, successively.

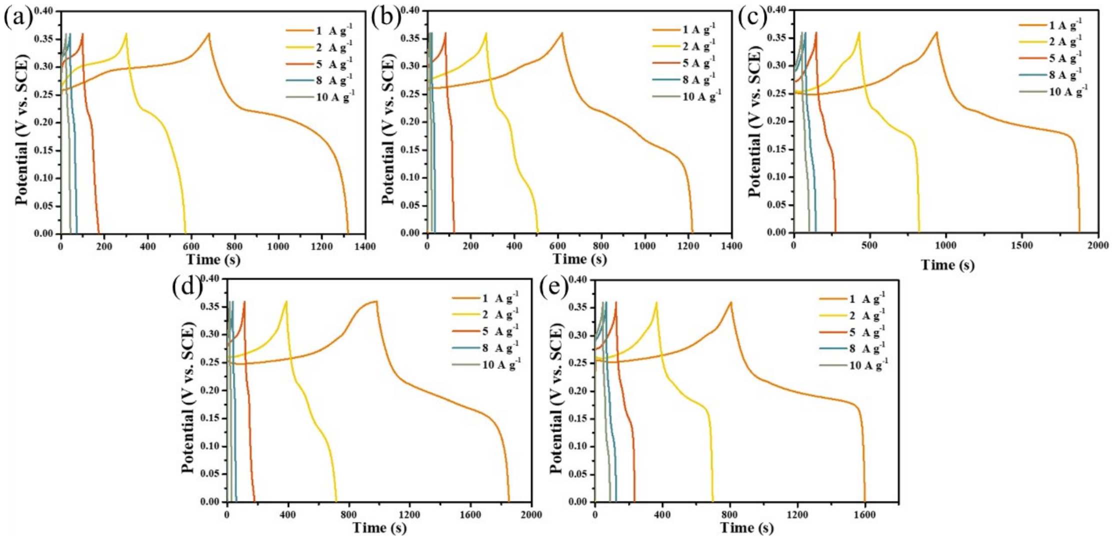

Figure S7. (a-e) GCD curves of NS-1h, NS-3h, NS-6h, NS-12h, and NS-20h at different scan rates.

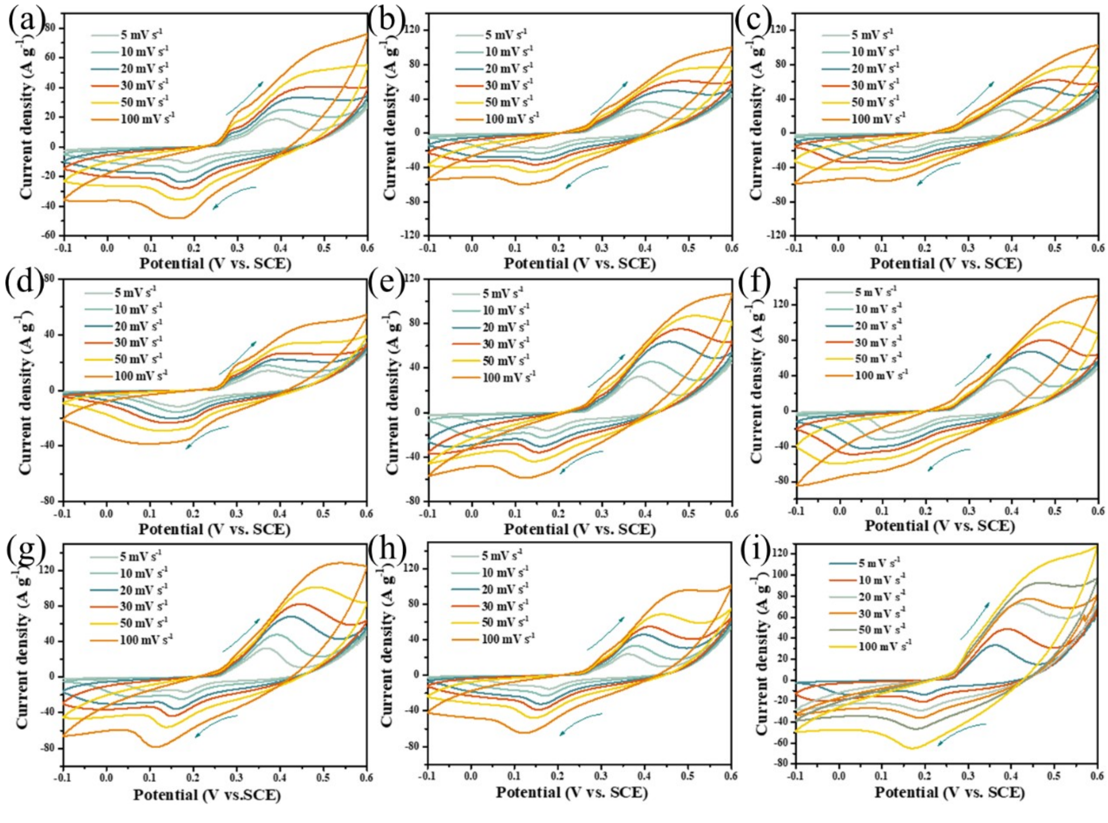

Figure S8. CV curves of N-1 to N-9.

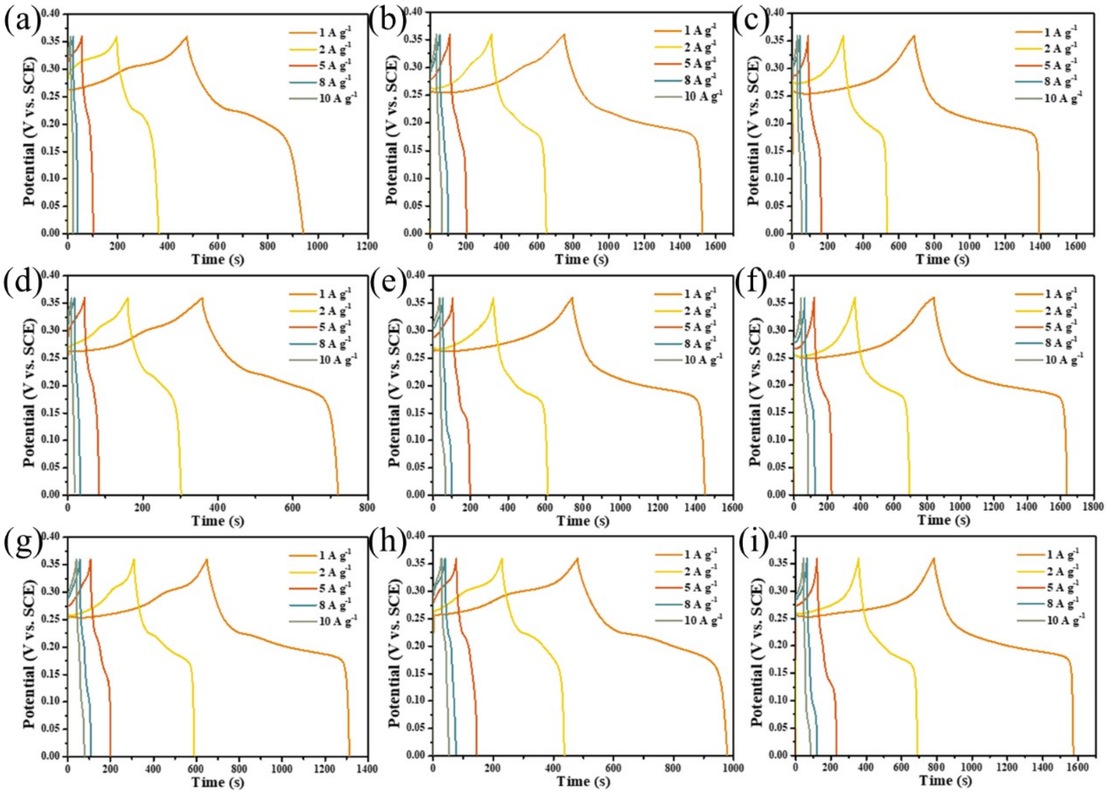

Figure S9. GCD curves of N-1 to N-9.

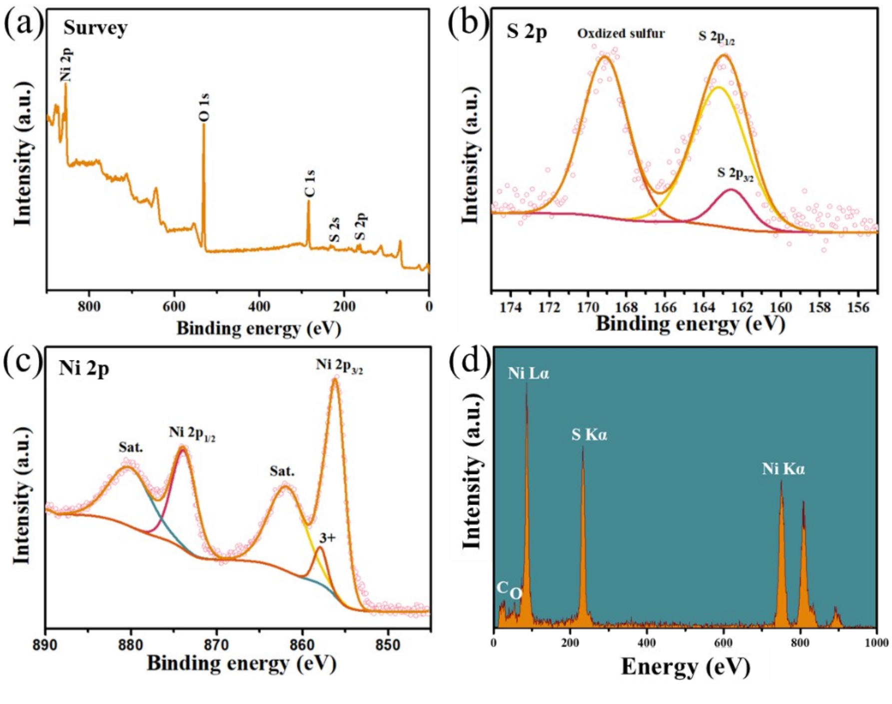

Figure S10. (a) Survey XPS spectrum of NCS. (b) S2p XPS spectrum of NCS. (c) Ni2p XPS spectrum of NCS. (d) EDS spectrum of NCS.

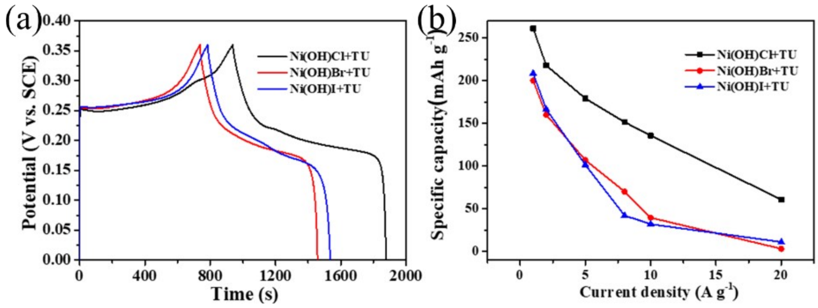

Figure S11. (a) GCD curves of NCS, NBS, and NIS. (b) Specific capacities of NCS, NBS, and NIS at diverse current densities.

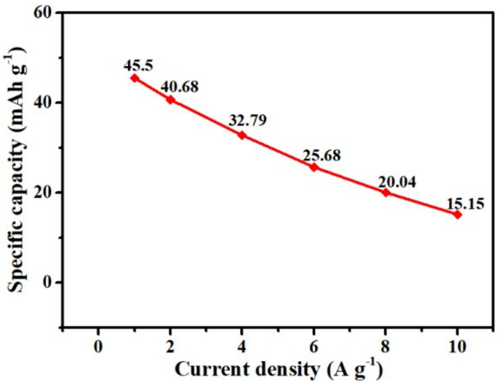

Figure S12. Specific capacities of the fabricated supercapacitor at different current densities.

Table S1. L9(3^4) orthogonal experimental data.

Col. / No.	A t (h)	B T (°C)	C -	D n(Ni(OH)Cl)/n(TU)	C_m $mAh\cdot g^{-1}$
1	1(6)	1(120)	1	1(0.15)	129.5
2	1	2(160)	2	2(0.3)	214
3	1	3(200)	3	3(1)	196.3
4	2(12)	1	2	3	100.7
5	2	2	3	1	196.1
6	2	3	1	2	222.4
7	3(20)	1	3	2	184.5
8	3	2	1	3	138.3
9	3	3	2	1	220.7
K_{1j}	539.8	414.7	-	546.3	-
K_{2j}	519.2	548.4	-	620.9	-
K_{3j}	543.5	639.4	-	435.3	-
k_{1j}	179.9	138.2	-	182.1	-
k_{2j}	173.1	182.8	-	207.0	-
k_{3j}	181.2	213.1	-	145.1	-
R	8.1	74.9	-	61.9	-
Factor Order	T > n(Ni(OH)Cl)/n(TU) > t				
Optimal Scheme	$B_3C_2A_3$				

Table S2. Quantitative analysis of S1, S2, and S3 by XRD data.

Sample	Phase	Weight Percentage (%)
S1	β-NiS	66.1
	Ni_3S_4	23.5
	α-NiS	8.2
	NiS_2	2.2
S2	β-NiS	75.6
	Ni_3S_4	15.6
	α-NiS	5.7
	NiS_2	3.1
S3	β-NiS	67.7
	Ni_3S_4	16.6
	α-NiS	7.4
	NiS_2	8.3

Table S3. A comparison of the specific capacity of nickel-based materials reported previously.

Sample	Capacity ($mAh\cdot g^{-1}$)	Current density ($A\cdot g^{-1}$)	Electrolyte	Ref.
5-NiS@CoS	168.1	1	2 M KOH	1
NiS-C	168.3	0.5	3 M KOH	2
$NiCo_2S_4/Co_9S_8$ hollow nanospheres	126.0	1	1 M KOH	3
NiS nanostructures	120.5	1	2 M KOH	4
NiS hierarchical hollow cubes	133.6	1	2 M KOH	5
RHAC/$NiCo_2S_4$	233.3	1	2 M KOH	6
Ni_3S_4@rGO	203.3	2	2 M KOH	7
NiS/NiO	118.1	2	2 M KOH	8
NiS/NTA-2	191.3	1	2 M KOH	9
NiS@C QDs-CNTs-rGO	241.0	1	1 M KOH	10
Ni_3S_4–NiS/rGO	219.2	1	2 M KOH	11
H-NiS_{1-X}/C-50	216.0	1	6 M KOH	12
R-NiS/rGO	206.6	1	2 M KOH	13
C@MoS_2/Ni_3S_4	132.1	2	2 M KOH	14
Ni1-Co2-S/$Co(OH)_2$	195.1	1	3 M KOH	15
Cu-doped Ni_3S_2	105.9	1	3 M KOH	16
Ni_3S_4–MoS_2	136.8	1	3 M KOH	17
pyrite NiS_2 nanoparticles	163.9	2	6 M KOH	18
β-NiS@Ni	191.1	2	1 M KOH	19
NCS	261.2	1	2 M KOH	This work

Table S4. A comparison of some supercapacitors reported previously.

ECs	Energy density ($Wh \cdot kg^{-1}$)	Power density ($W \cdot kg^{-1}$)	Ref.
5-NiS@CoS//AC	24.1	752.15	1
NiS-C//AC	35.07	420.0	2
$NiCo_2S_4/Co_9S_8$ hollow nanospheres//AC	36.7	800.0	3
NiS nanostructures//AC	16.5	250.0	4
NiS hierarchical hollow cubes//AC	34.9	387.5	5
RHAC/$NiCo_2S_4$//RHAC	41.6	150.0	6
Ni_3S_4@rGO//AC	37.3	398	7
NiS/NTA-2//AC	30.8	4187.2	9
NiS@C QDs-CNTs-rGO//Graphene	21.0	811	10
H-NiS_{1-X}/C-50//AC	36.88	750	12
Ni1-Co2-S/$Co(OH)_2$//AC	48.8	800	15
Cu-doped Ni_3S_2//AC	33.7	850.1	16
Ni_3S_4–MoS_2//AC	58.43	385.95	17
pyrite NiS_2 nanoparticles//AC	54.2	940.0	18
β-NiS@Ni//AC	40.0	720.0	19
NCS//rGO	36.4	800.0	This work

References

1. Miao, Y.; Zhang, X.; Zhan, J.; Sui, Y.; Qi, J.; Wei, F.; Meng, Q.; He, Y.; Ren, Y.; Zhan, Z.; Sun, Z., Hierarchical NiS@CoS with controllable core-shell structure by two-step strategy for supercapacitor electrodes. *Advanced Materials Interfaces* **2020,** *7* (3), 1901618.
2. Harish, S.; Naveen, A. N.; Abinaya, R.; Archana, J.; Ramesh, R.; Navaneethan, M.; Shimomura, M.; Hayakawa, Y., Enhanced performance on capacity retention of hierarchical NiS hexagonal nanoplate for highly stable asymmetric supercapacitor. *Electrochimica Acta* **2018,** *283*, 1053-1062.
3. Shen, Y.; Zhang, K.; Chen, B.; Yang, F.; Xu, K.; Lu, X., Enhancing the electrochemical performance of nickel cobalt sulfides hollow nanospheres by structural modulation for asymmetric supercapacitors. *Journal of Colloid and Interface Science* **2019,** *557*, 135-143.
4. Nandhini, S.; Muralidharan, G., Facile microwave-hydrothermal synthesis of NiS nanostructures for supercapacitor applications. *Applied Surface Science* **2018,** *449*, 485-491.
5. Ma, X.; Zhang, L.; Xu, G.; Zhang, C.; Song, H.; He, Y.; Zhang, C.; Jia, D., Facile synthesis of NiS hierarchical hollow cubes via Ni formate frameworks for high performance supercapacitors. *Chemical Engineering Journal* **2017,** *320*, 22-28.
6. Wang, H.; Wu, D.; Zhou, J., Gasified rice husk based RHAC/$NiCo_2S_4$ composite for high performance asymmetric supercapacitor. *Journal of Alloys and Compounds* **2019,** *811*, 152073.
7. Hu, Q.; Zou, X.; Huang, Y.; Wei, Y.; YaWang; Chen, F.; Xiang, B.; Wu, Q.; Li, W., Graphene oxide-drove transformation of NiS/Ni_3S_4 microbars towards Ni_3S_4 polyhedrons for supercapacitor. *Journal of Colloid and Interface Science* **2020,** *559*, 115-123.
8. Wang, Y.; Pan, A.; Zhang, Y.; Shi, J.; Lin, J.; Liang, S.; Cao, G., Heterogeneous NiS/NiO multi-shelled hollow microspheres with enhanced electrochemical performances for hybrid-type asymmetric supercapacitors. *Journal of Materials*

Chemistry A **2018,** *6* (19), 9153-9160.

9. Wu, D.; Xie, X.; Ma, Y.; Zhang, J.; Hou, C.; Sun, X.; Yang, X.; Zhang, Y.; Kimura, H.; Du, W., Morphology controlled hierarchical NiS/carbon hexahedrons derived from nitrilotriacetic acid-assembly strategy for high-performance hybrid supercapacitors. *Chemical Engineering Journal* **2021**, 133673.

10. Zhang, R.; Lu, C.; Shi, Z.; Liu, T.; Zhai, T.; Zhou, W., Hexagonal phase NiS octahedrons co-modified by 0D-, 1D-, and 2D carbon materials for high-performance supercapacitor. *Electrochimica Acta* **2019,** *311*, 83-91.

11. Azizi Darsara, S.; Seifi, M.; Askari, M. B.; Osquian, M., Hierarchical 3D starfish-like Ni_3S_4–NiS on reduced graphene oxide for high-performance supercapacitors. *Ceramics International* **2021,** *47* (15), 20992-20998.

12. Huang, C.; Gao, A.; Yi, F.; Wang, Y.; Shu, D.; Liang, Y.; Zhu, Z.; Ling, J.; Hao, J., Metal organic framework derived hollow NiS@C with S-vacancies to boost high-performance supercapacitors. *Chemical Engineering Journal* **2021,** *419*, 129643.

13. Qu, C.; Zhang, L.; Meng, W.; Liang, Z.; Zhu, B.; Dang, D.; Dai, S.; Zhao, B.; Tabassum, H.; Gao, S.; Zhang, H.; Guo, W.; Zhao, R.; Huang, X.; Liu, M.; Zou, R., MOF-derived α-NiS nanorods on graphene as an electrode for high-energy-density supercapacitors. *Journal of Materials Chemistry A* **2018,** *6* (9), 4003-4012.

14. Qin, S.; Yao, T.; Guo, X.; Chen, Q.; Liu, D.; Liu, Q.; Li, Y.; Li, J.; He, D., MoS_2/Ni_3S_4 composite nanosheets on interconnected carbon shells as an excellent supercapacitor electrode architecture for long term cycling at high current densities. *Applied Surface Science* **2018,** *440*, 741-747.

15. Xu, T.; Li, G.; Zhao, L., Ni-Co-S/$Co(OH)_2$ nanocomposite for high energy density all-solid-state asymmetric supercapacitors. *Chemical Engineering Journal* **2018,** *336*, 602-611.

16. Li, G.; Cui, X.; Song, B.; Ouyang, H.; Wang, K.; Sun, Y.; Wang, Y., One-pot synthesis of Cu-doped Ni_3S_2 nano-sheet/rod nanoarray for high performance supercapacitors. *Chemical Engineering Journal* **2020,** *388*, 124319.

17. Luo, W.; Zhang, G.; Cui, Y.; Sun, Y.; Qin, Q.; Zhang, J.; Zheng, W., One-step extended strategy for the ionic liquid-assisted synthesis of Ni_3S_4–MoS_2 heterojunction

electrodes for supercapacitors. *Journal of Materials Chemistry A* **2017,** *5* (22), 11278-11285.

18. Zhang, J.; Zhang, D.; Yang, B.; Shi, H.; Wang, K.; Han, L.; Wang, S.; Wang, Y., Targeted synthesis of NiS and NiS_2 nanoparticles for high−performance hybrid supercapacitor via a facile green solid−phase synthesis route. *Journal of Energy Storage* **2020,** *32*, 101852.

19. Bhagwan, J.; Khaja Hussain, S.; Krishna, B. N. V.; Yu, J. S., β-NiS 3D micro-flower-based electrode for aqueous asymmetric supercapacitors. *Sustainable Energy & Fuels* **2020,** *4* (11), 5550-5559.