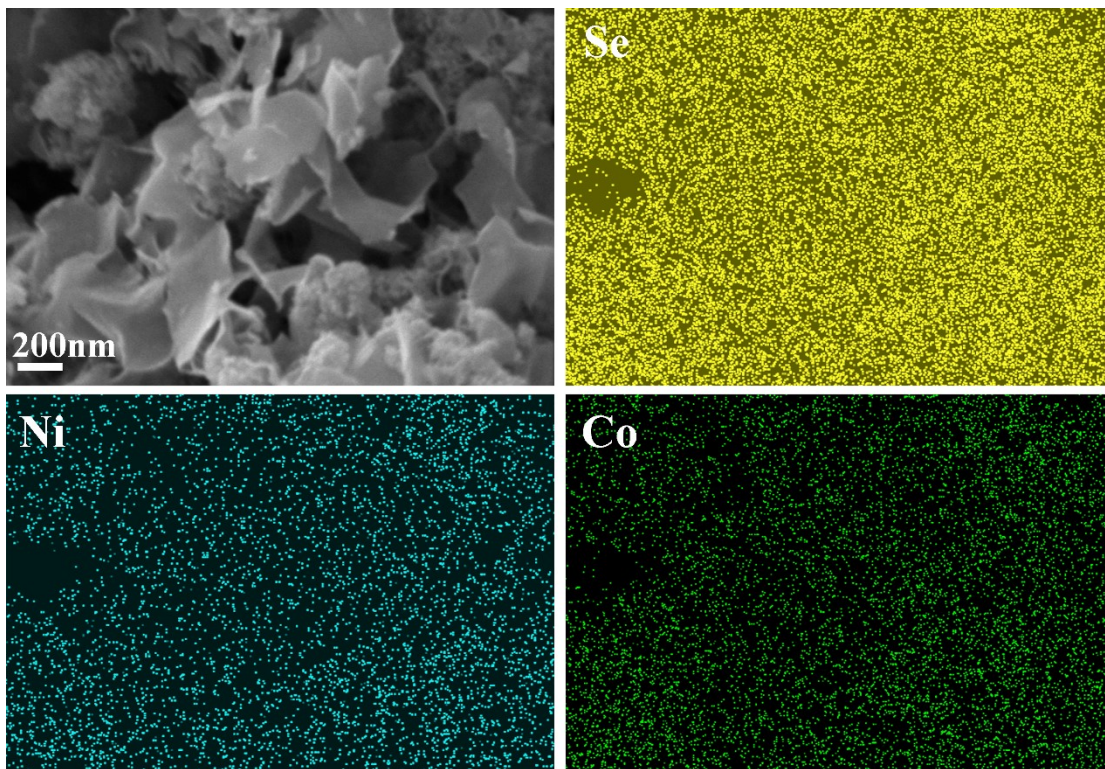
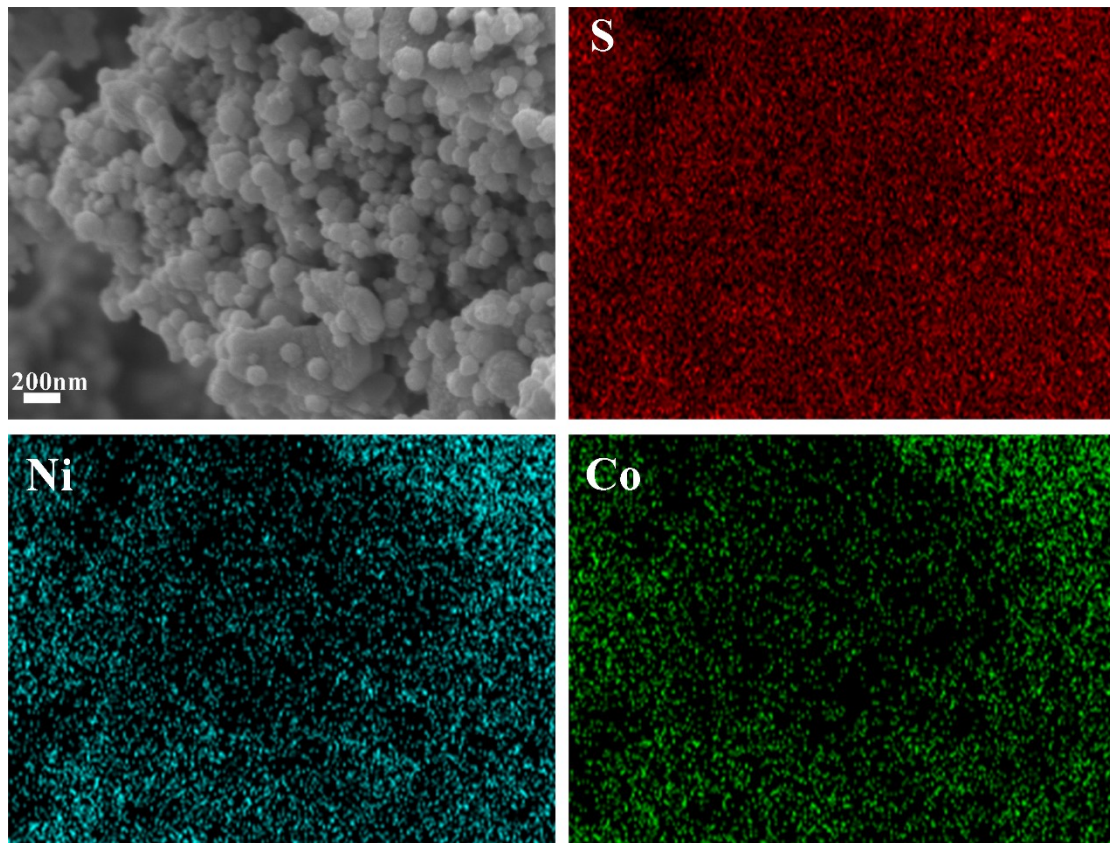


## **Supplementary materials**

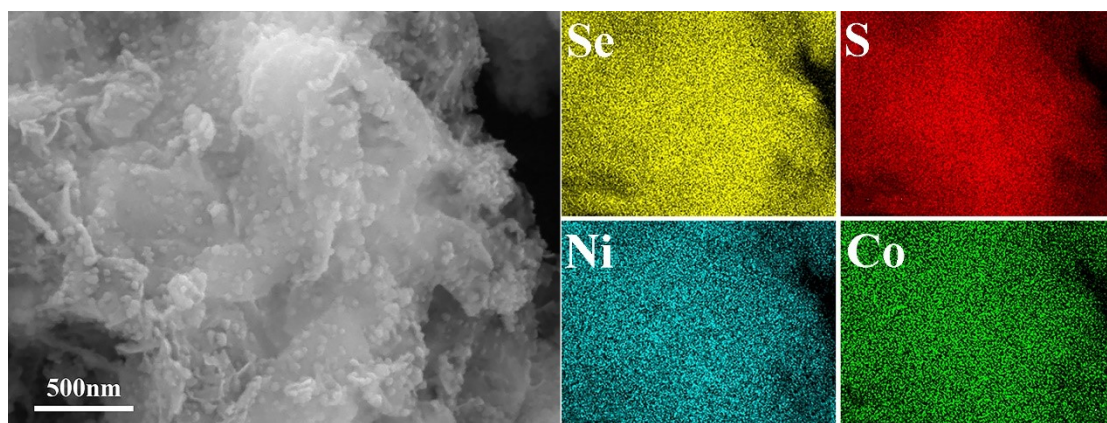
### **Constructing NiCo<sub>2</sub>Se<sub>4</sub>/NiCoS<sub>4</sub> heterostructures for high-performance aluminum batteries cathode**



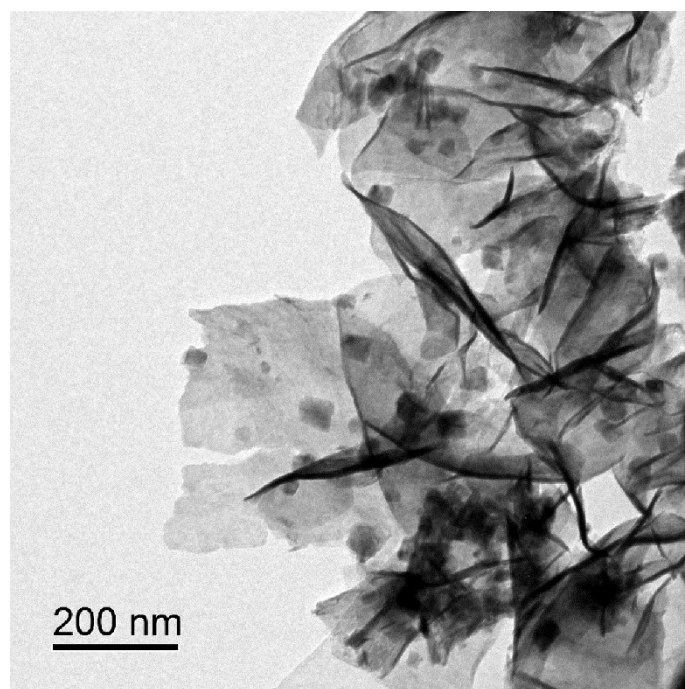
**Figure. S1** SEM image and corresponding elemental mapping of pure  $\text{NiCo}_2\text{Se}_4$ .



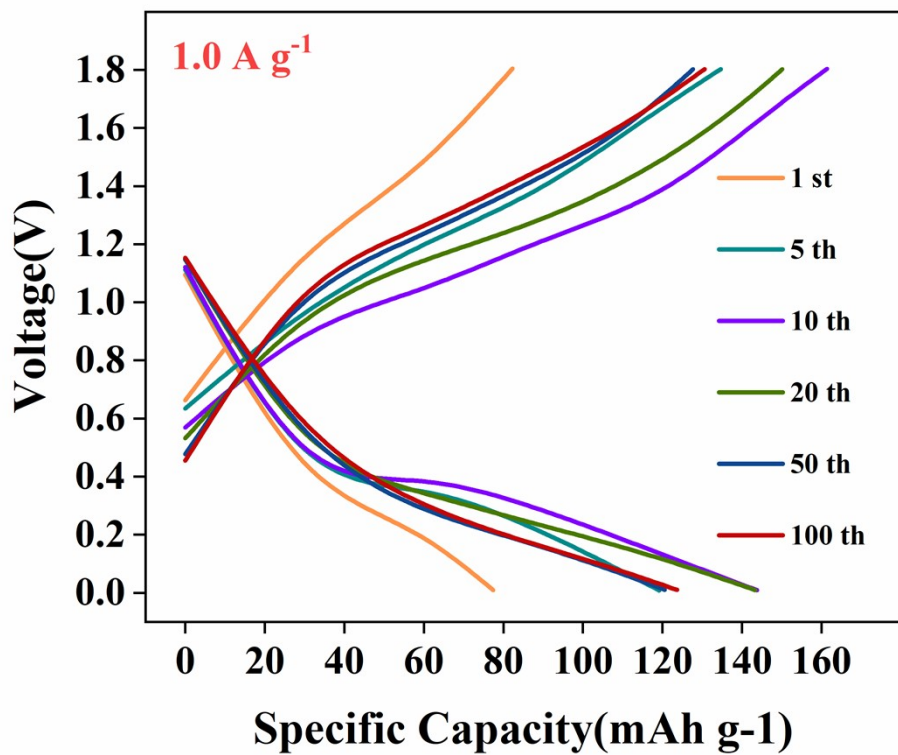
**Figure. S2** SEM image and corresponding elemental mapping of heterostructured NiCoS<sub>4</sub>.



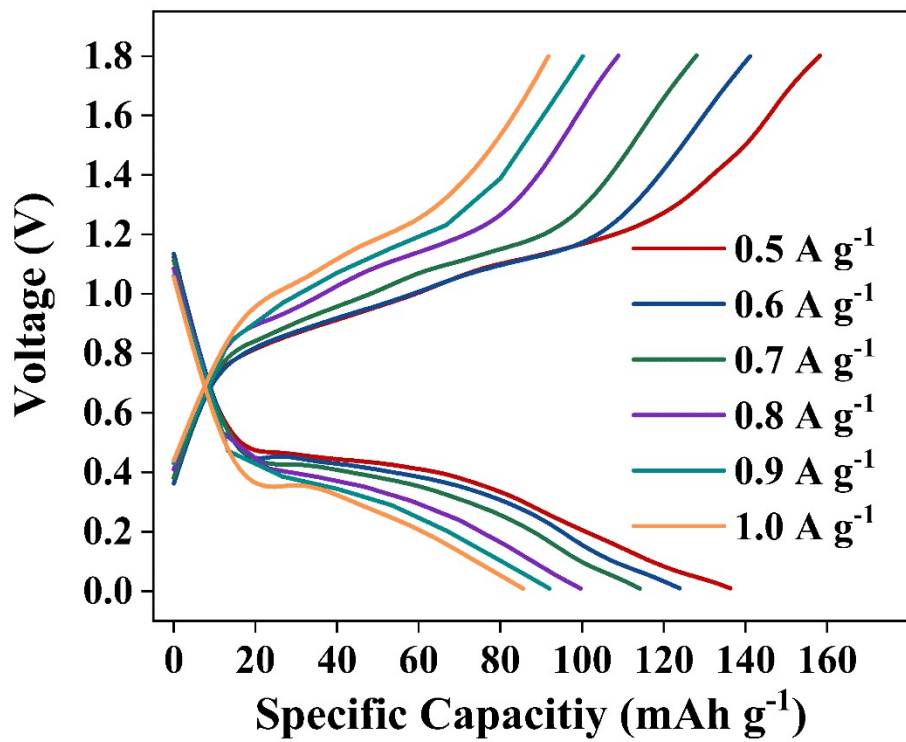
**Figure. S3** SEM image and corresponding elemental mapping of heterostructured  $\text{NiCo}_2\text{Se}_4/\text{NiCoS}_4$ .



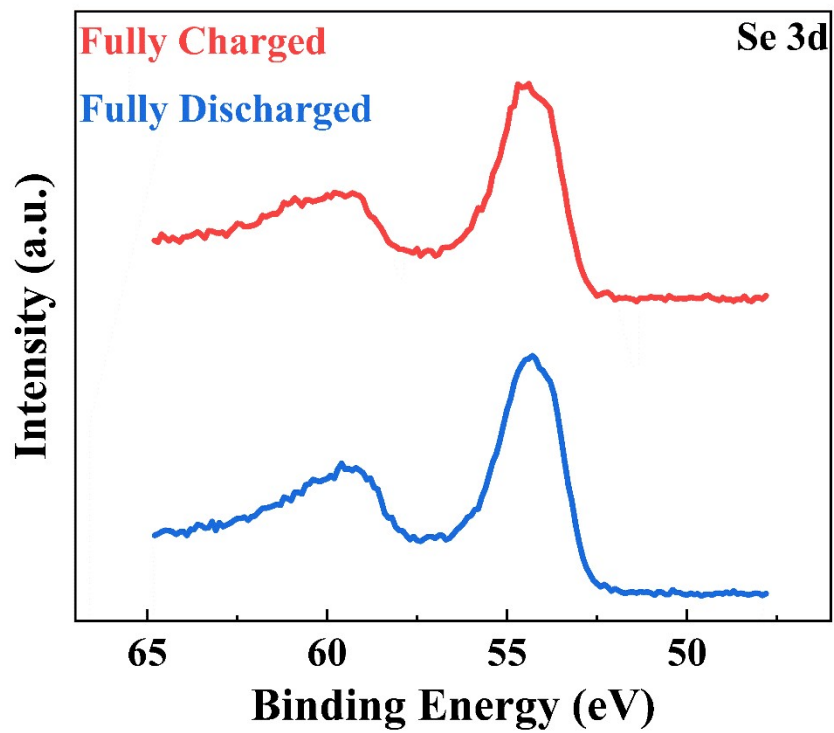
**Figure. S4** TEM image of heterostructured NiCo<sub>2</sub>Se<sub>4</sub>/ NiCoS<sub>4</sub>.



**Figure. S5** The charge-discharge curves of heterostructured  $\text{NiCo}_2\text{Se}_4/\text{NiCoS}_4$  for different cycles.



**Figure. S6** The charge-discharge curves corresponding to Figure 2c of the heterostructured NiCo<sub>2</sub>Se<sub>4</sub>/NiCoS<sub>4</sub> cathode from 0.5 A g<sup>-1</sup> to 1 A g<sup>-1</sup>.



**Figure. S7** The XPS spectra of Se 3d at fully charged and discharged states, respectively.



**Table. S1** The element content of Se and S in NiCo<sub>2</sub>Se<sub>4</sub>/NiCoS<sub>4</sub> by ICP-OES.

Sample Quantity $m_0$ (g)	Constant Volume $V_0$ (mL)	Element	Element Concentration of Solution $C_0$ (mg/L)	Dilution Multiple $f$	Element Concentration in Digestion Solution $C_1$ (mg/L)	Element Content $C_x$ (mg/kg)	Element Content $W$ (%)
0.0523	25	S	2.889	100	288.900	138097.51	13.810
0.0523	25	Se	5.019	100	501.900	239913.96	23.991

The element content ( $W$ ) of Se and S was calculated by the following equation:

$$W(\%) = \frac{C_x(\text{mg/kg})}{10^6} * 100\%$$

$$C_x(\text{mg/kg}) = \frac{C_0(\text{mg/L}) * f * V_0(\text{mL}) * 10^{-3}}{m_0(\text{g}) * 10^{-3}} = \frac{C_1(\text{mg/L}) * V_0(\text{mL}) * 10^{-3}}{m_0(\text{g}) * 10^{-3}}$$

$$C_1(\text{mg/L}) = C_0(\text{mg/L}) * f$$

**Table. S2** Comparison of energy storage performance between NiCo<sub>2</sub>Se<sub>4</sub>/NiCoS<sub>4</sub> and other AIB cathode materials previously reported.

Cathode materials	Electrolyte	Cycling performance	Ref.
		capacity, current density, cycle number	
NiCo <sub>2</sub> Se <sub>4</sub> /NiCoS <sub>4</sub>	AlCl <sub>3</sub> : [EMIm]Cl =1.1:1	112mAh g <sup>-1</sup> /1000mA g <sup>-1</sup> /195cycle	This work
Ni <sub>2</sub> P/rGO	AlCl <sub>3</sub> : [EMIm]Cl =1.3:1	73mAh g <sup>-1</sup> /100mA g <sup>-1</sup> /500th	1
graphite nanoflakes	AlCl <sub>3</sub> : [EMIm]Cl =1.3:1	73mAh g <sup>-1</sup> /200mA g <sup>-1</sup> /1000th	2
Cu <sub>2-x</sub> Se	AlCl <sub>3</sub> : [EMIm]Cl =1.3:1	100mAh g <sup>-1</sup> /200mA g <sup>-1</sup> /100th	3
CoSe	AlCl <sub>3</sub> : [EMIm]Cl= 1.3:1	62.4mAh g <sup>-1</sup> /5000mA g <sup>-1</sup> /100th	4
Zn/Co-Se@C	AlCl <sub>3</sub> : [EMIm]Cl= 1.3:1	79mAh g <sup>-1</sup> /1000mA g <sup>-1</sup> /400th	5
Co <sub>3</sub> S <sub>4</sub>	AlCl <sub>3</sub> : [EMIm]Cl= 1.3:1	90mAh g <sup>-1</sup> /50mA g <sup>-1</sup> /150th	6
SnSe	AlCl <sub>3</sub> : [EMIm]Cl =1.3:1	107mAh g <sup>-1</sup> /300mA g <sup>-1</sup> /100th	7
MoS <sub>2</sub>	AlCl <sub>3</sub> : [EMIm]Cl =1.3:1	66.7mAh g <sup>-1</sup> /40mA g <sup>-1</sup> /100th	8
Ni <sub>3</sub> S <sub>2</sub> @graphene	AlCl <sub>3</sub> : [EMIm]Cl =1.3:1	60 mAh g <sup>-1</sup> /100 mA g <sup>-1</sup> /100th	9

## References:

1. J. Tu, M. Wang, X. Xiao, H. Lei and S. Jiao, Nickel Phosphide Nanosheets Supported on Reduced Graphene Oxide for Enhanced Aluminum-Ion Batteries, *ACS Sustainable Chemistry & Engineering*, 2019, **7**, 6004-6012.
2. J. Tu, J. Wang, S. Li, W. L. Song, M. Wang, H. Zhu and S. Jiao, High-efficiency transformation of amorphous carbon into graphite nanoflakes for stable aluminum-ion battery cathodes, *Nanoscale*, 2019, **11**, 12537-12546.
3. J. Jiang, H. Li, T. Fu, B. J. Hwang, X. Li and J. Zhao, One-Dimensional Cu<sub>2</sub>-xSe Nanorods as the Cathode Material for High-Performance Aluminum-Ion Battery, *ACS Appl Mater Interfaces*, 2018, **10**, 17942-17949.
4. W. Xing, D. Du, T. Cai, X. Li, J. Zhou, Y. Chai, Q. Xue and Z. Yan, Carbon-encapsulated CoSe nanoparticles derived from metal-organic frameworks as advanced cathode material for Al-ion battery, *Journal of Power Sources*, 2018, **401**, 6-12.
5. Z. Li, W. Lv, G. Wu and W. Zhang, Rhombic dodecahedron hetero-structure Zn/Co–Se@C as cathode material for aluminum batteries with excellent electrochemical performance, *Journal of Power Sources*, 2021, **511**.
6. H. Li, H. Yang, Z. Sun, Y. Shi, H.-M. Cheng and F. Li, A highly reversible Co<sub>3</sub>S<sub>4</sub> microsphere cathode material for aluminum-ion batteries, *Nano Energy*, 2019, **56**, 100-108.
7. Y. Zhang, B. Zhang, J. Li, J. Liu, X. Huo and F. Kang, SnSe nano-particles as advanced positive electrode materials for rechargeable aluminum-ion batteries, *Chemical Engineering Journal*, 2021, **403**.
8. Z. Li, B. Niu, J. Liu, J. Li and F. Kang, Rechargeable Aluminum-Ion Battery Based on MoS<sub>2</sub> Microsphere Cathode, *ACS Appl Mater Interfaces*, 2018, **10**, 9451-9459.
9. S. Wang, Z. Yu, J. Tu, J. Wang, D. Tian, Y. Liu and S. Jiao, A Novel Aluminum-Ion Battery: Al/AlCl<sub>3</sub>-[EMIm]Cl/Ni<sub>3</sub>S<sub>2</sub>@Graphene, *Advanced Energy Materials*, 2016, **6**.