

Supporting information

A bifunctional heterostructure promoting the kinetics and stability of sulfur cathode in advanced aluminum-sulfur batteries

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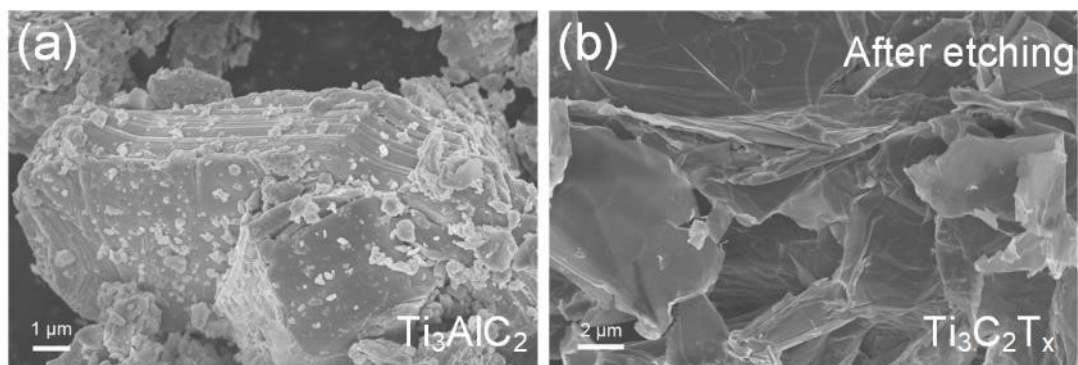


Figure S1. SEM images of (a) Ti_3AlC_2 MAX and (b) multi-layered $\text{Ti}_3\text{C}_2\text{T}_x$.

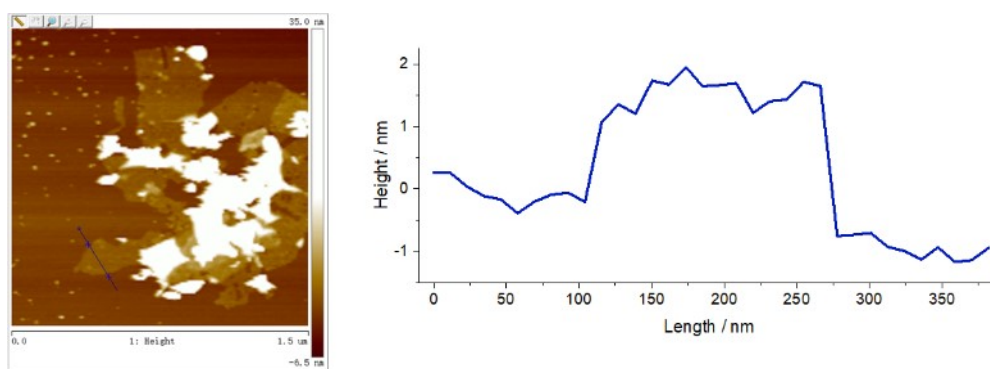


Figure S2. AFM image and the height profile of a $\text{Ti}_3\text{C}_2\text{T}_x$ flake.

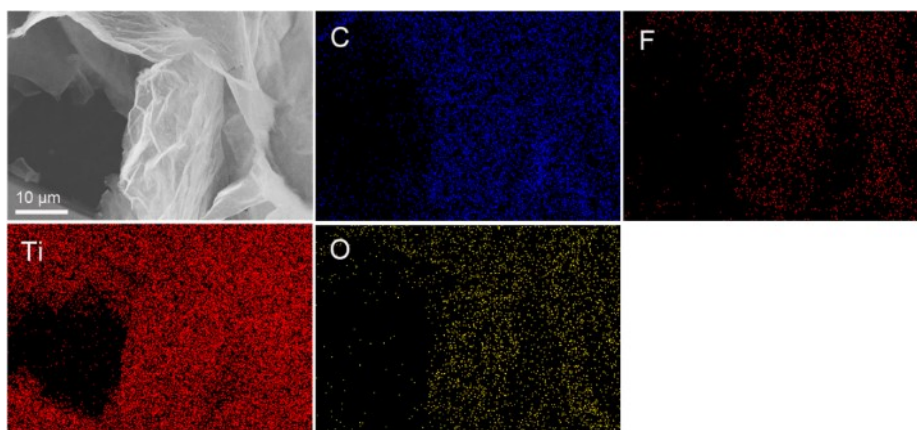


Figure S3. SEM and EDS images of the delaminated $\text{Ti}_3\text{C}_2\text{T}_x$.

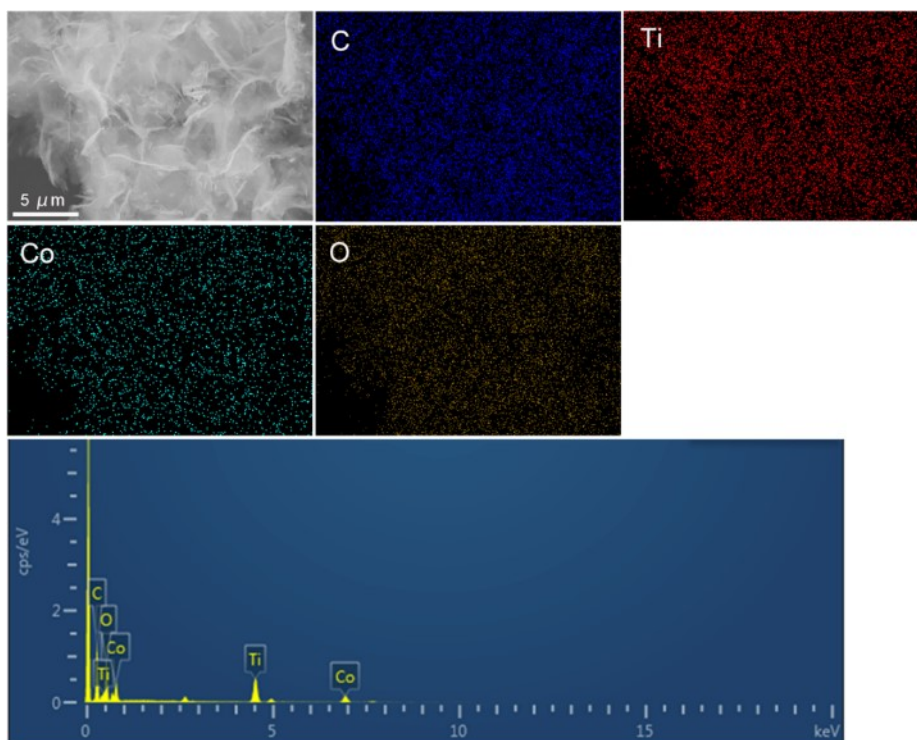


Figure S4. SEM and EDS images of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-Co}$ composite.

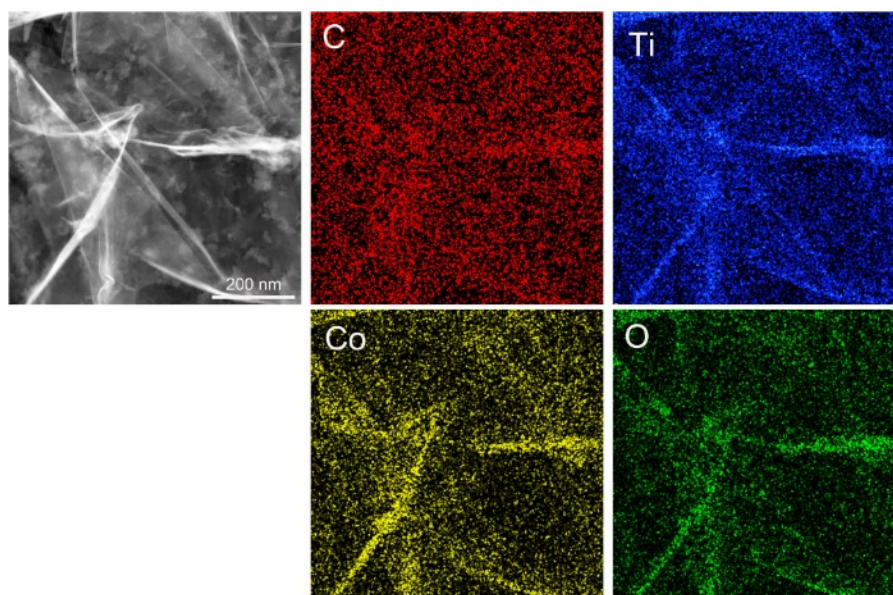


Figure S5. STEM image of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-Co}$ composite and corresponding EDX elemental mapping images of C, Ti, Co and O.

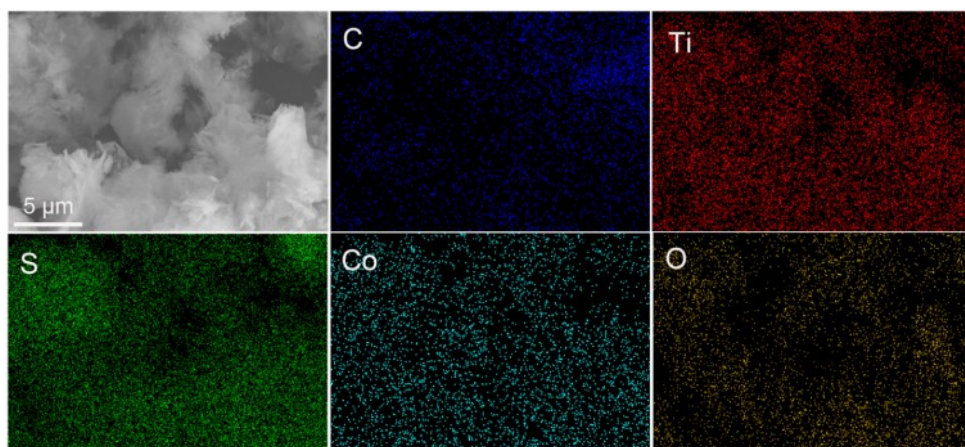


Figure S6. The SEM and EDS images of $\text{Ti}_3\text{C}_2\text{T}_x\text{-CoS}_x@\text{S}$ composite.

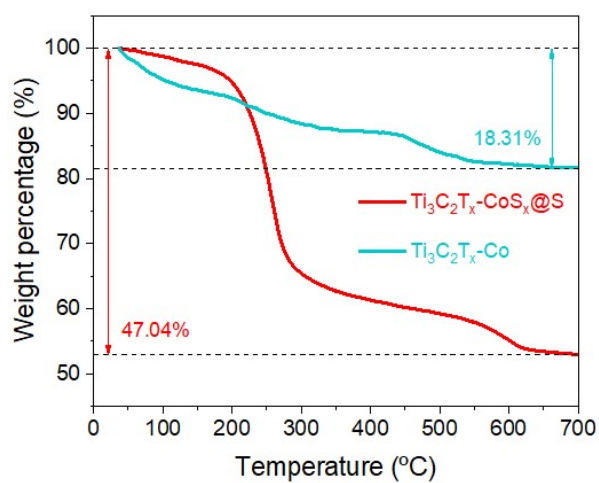


Figure S7. TGA profiles of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-Co}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-CoS}_x@\text{S}$ composite in N_2 atmosphere.

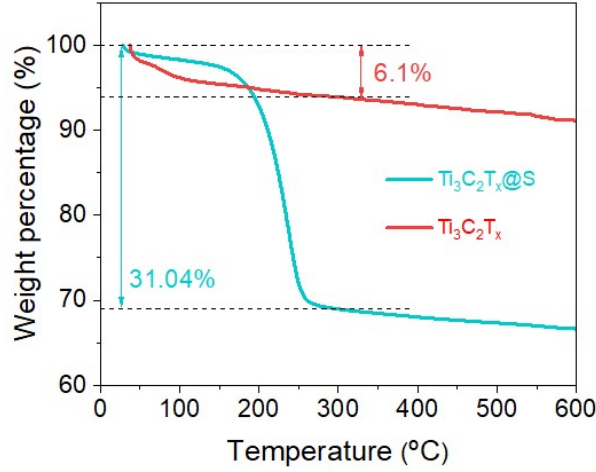


Figure S8. TGA profiles of the $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x@\text{S}$ composite in N_2 atmosphere.

According to our previous research,¹ the $\text{Ti}_3\text{C}_2\text{T}_x$ host material lost $\sim 6.1\%$ in the same temperature range, presumably due to the release of entrapped structural water. Therefore, the mass fraction of sulfur in the $\text{Ti}_3\text{C}_2\text{T}_x@\text{S}$ composite is estimated to be $\sim 24.9 \text{ wt}\%$.

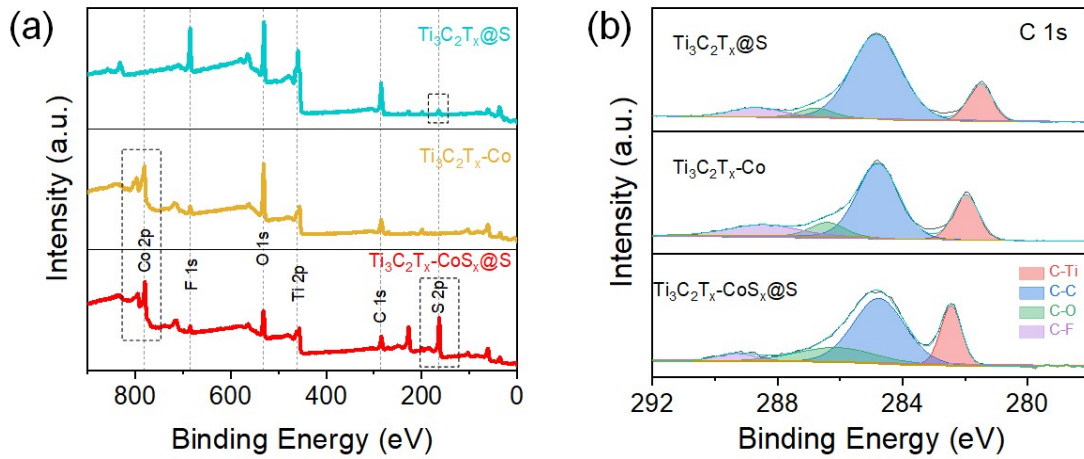


Figure S9. (a) XPS full-spectra of $\text{Ti}_3\text{C}_2\text{T}_x@\text{S}$, $\text{Ti}_3\text{C}_2\text{T}_x\text{-Co}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-CoS}_x@\text{S}$. (b)

High-resolution XPS spectra of C 1s in $\text{Ti}_3\text{C}_2\text{T}_x@\text{S}$, $\text{Ti}_3\text{C}_2\text{T}_x\text{-Co}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-CoS}_x@\text{S}$.

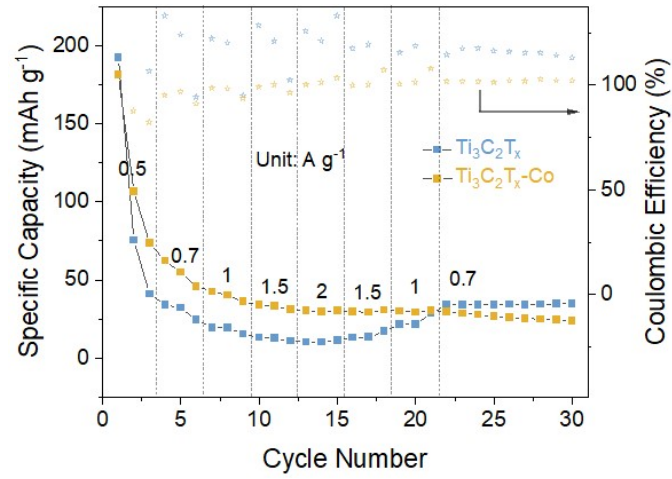


Figure S10. Rate performances of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-Co}$ cathodes from 0.5 to 2 A g^{-1} .

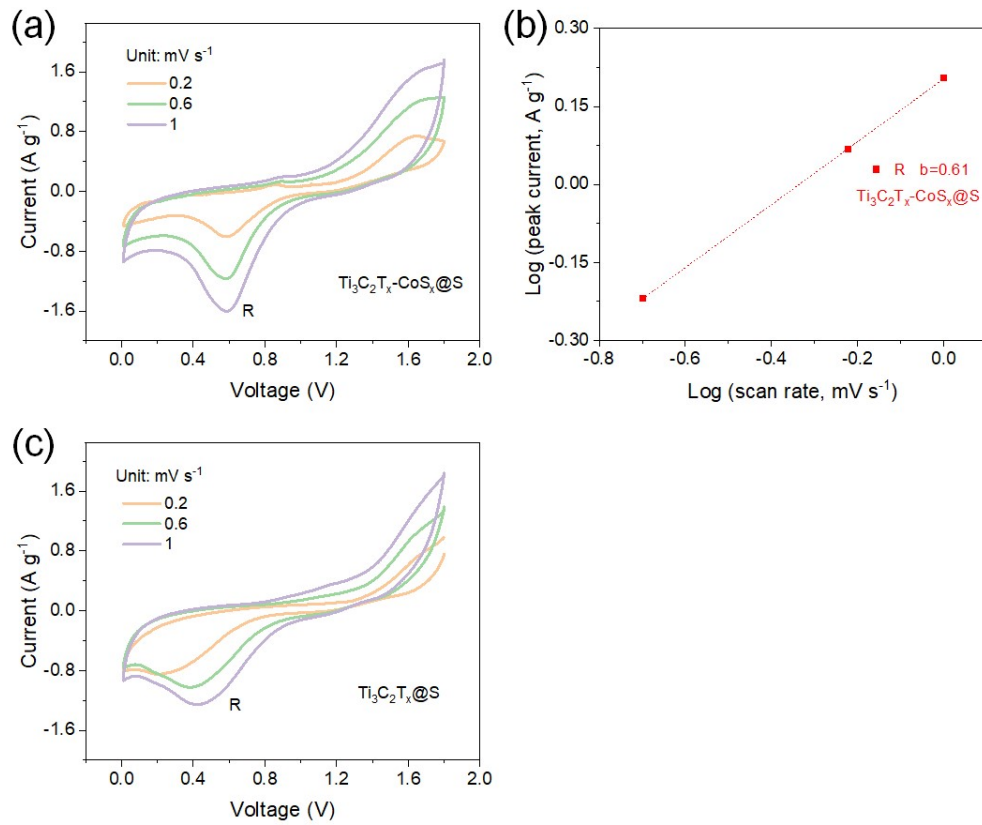


Figure S11. (a) CV curves of $\text{Ti}_3\text{C}_2\text{T}_x\text{-CoS}_x\text{@S}$ cathode at sweep rates of 0.2~1 mV s^{-1} . (b) Logarithmic curve of peak current versus sweep rate from (a). (c) CV curves of $\text{Ti}_3\text{C}_2\text{T}_x\text{@S}$ cathode at sweep rates of 0.2~1 mV s^{-1} .

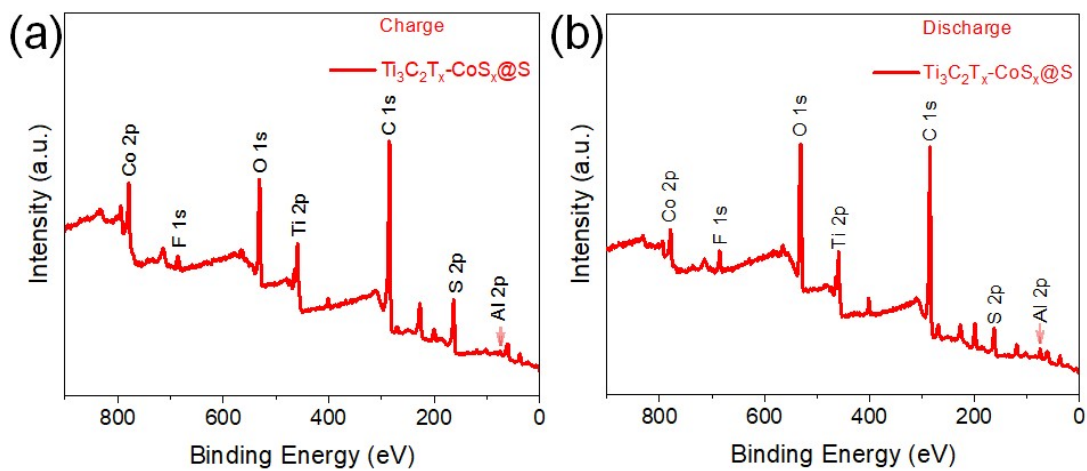


Figure S12. XPS full-spectra of $\text{Ti}_3\text{C}_2\text{T}_x\text{-CoS}_x@\text{S}$ cathodes at charged-1.8 V (a) and discharged-0.01 V (b) states.

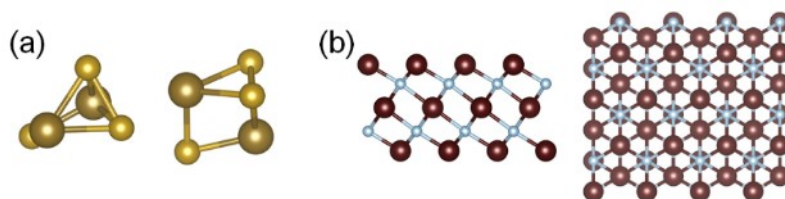


Figure S13. (a) The molecular structures of Al_2S_3 . (b) Side (left) and top (right) views of the optimized structure of $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer.

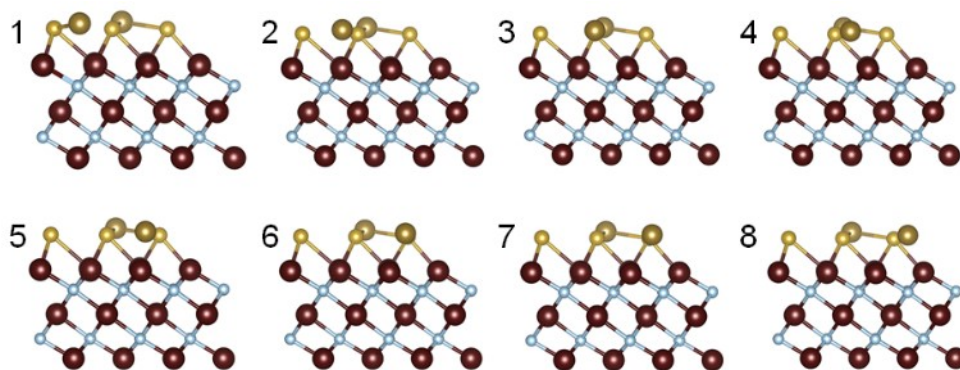


Figure S14. Side views of the stable adsorption and dissociation configurations of Al_2S_3

on $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer.

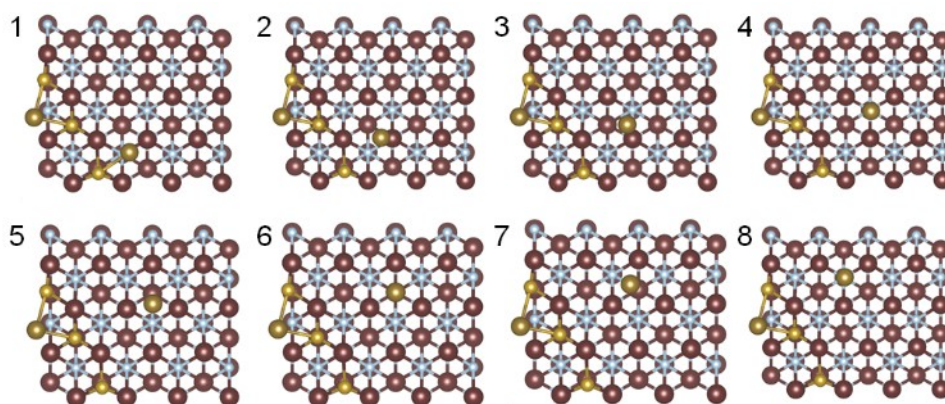


Figure S15. Top views of the stable adsorption and dissociation configurations of Al_2S_3 on $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer.

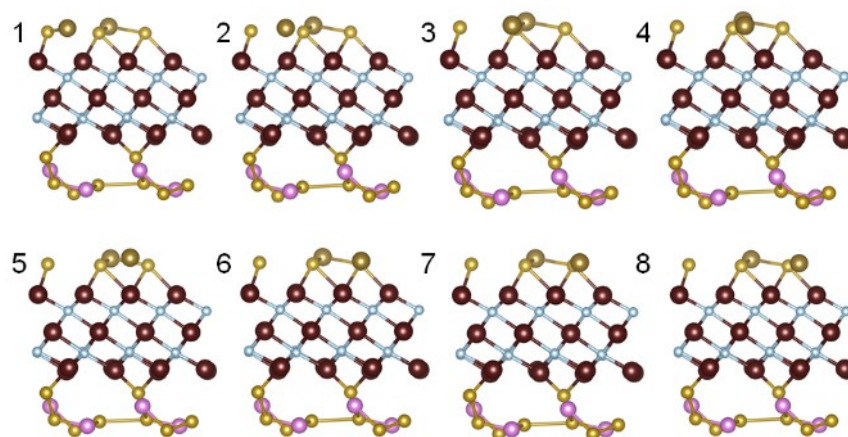


Figure S16. Side views of the stable adsorption and dissociation configurations of Al_2S_3 on $\text{Ti}_3\text{C}_2\text{T}_x\text{-CoS}_2$ heterostructure surface.

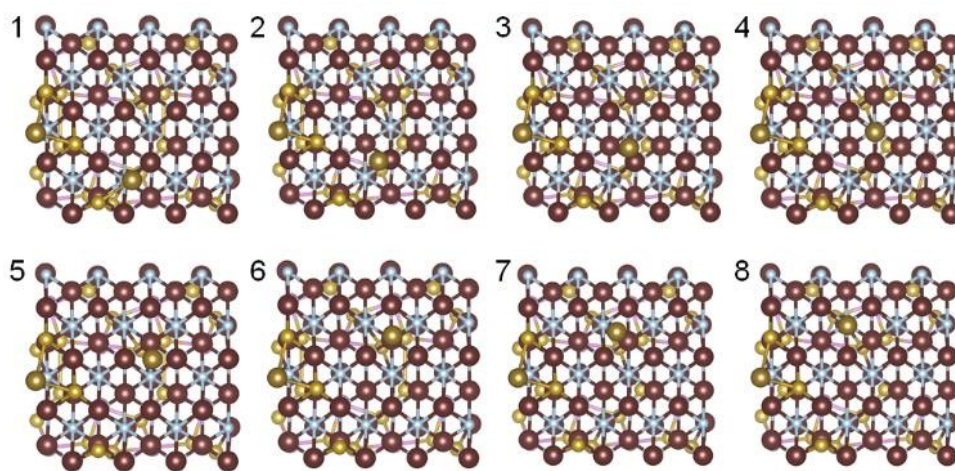


Figure S17. Top views of the stable adsorption and dissociation configurations of Al_2S_3 on $\text{Ti}_3\text{C}_2\text{T}_x\text{-CoS}_2$ heterostructure surface.

Table S1. Comparison of the electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x\text{-CoS}_x@\text{S}$ cathode in this work with other cathode materials reported for AIBs.

Cathodes	Initial capacity (mAh g ⁻¹)	Final capacity (mAh g ⁻¹)	Rate (mA g ⁻¹)	CE (%)	Ref.
ZnSe/SnSe₂	386	124 (150th)	100	98	2
Co₃Se₄/ZnSe@C	207	116 (500th)	200	95	3
CoSe₂@TiO₂/Ti₃C₂	100	102 (500th)	1600	80	4
Co₉S₈ NP@NPC@MXene	160	111 (1000th)	1000	98	5
MXene@BDTO	229	134 (500th)	500	98	6
TBAOH-FL-V₂CT_x	190	80 (100th)	200	95	7
Ti₃C₂@CTAB-Se	250	132 (400th)	200	95	8
Cu/MoO₂@C@S	967	254 (100th)	500	98	9
Ti₃C₂T_x-CoS_x@S	358	215 (1000th)	1000	100	This work
	308	190 (1500th)	1500		

References

1. X. Zheng, Z. Wang, J. Li and L. Wei, Binder-free S@Ti₃C₂T_x sandwich structure film as a high-capacity cathode for a stable aluminum-sulfur battery, *Sci. China Mater.*, 2022, **65**, 1463-1475.
2. J. Li, W. Luo, Z. Zhang, F. Li, Z. Chao and J. Fan, ZnSe/SnSe₂ hollow microcubes as cathode for high performance aluminum ion batteries, *J. Colloid Interface Sci.*, 2023, **639**, 124-132.
3. T. Liu, G. Lv, M. Liu, C. Zhao, L. Liao, H. Liu, J. Shi, J. Zhang and J. Guo, Synergistic Transition-Metal Selenide Heterostructure as a High-Performance Cathode for Rechargeable Aluminum Batteries, *ACS Appl. Mater. Interfaces*, 2023, **15**, 11906-11913.
4. Z. Yuan, Q. Lin, Y. Li, W. Han and L. Wang, Effects of Multiple Ion Reactions Based on a CoSe₂/MXene Cathode in Aluminum-Ion Batteries, *Adv. Mater.*, 2023, **35**, 2211527.
5. L. Yao, S. Ju and X. Yu, Rational surface engineering of MXene@N-doped hollow carbon dual-confined cobalt sulfides/selenides for advanced aluminum batteries, *J. Mater. Chem. A*, 2021, **9**, 16878-16888.
6. G. Wu, C. Lv, W. Lv, X. Li, W. Zhang and Z. Li, Anthraquinone derivatives supported by Ti₃C₂(MXene) as cathode materials for aluminum-organic batteries, *J. Energy Chem.*, 2022, **74**, 174-183.
7. A. VahidMohammadi, A. Hadjikhani, S. Shahbazmohamadi and M. Beidaghi, Two-Dimensional Vanadium Carbide (MXene) as a High-Capacity Cathode

- Material for Rechargeable Aluminum Batteries, *ACS Nano*, 2017, **11**, 11135-11144.
8. Z. Li, X. Wang, W. Zhang and S. Yang, Two-dimensional $\text{Ti}_3\text{C}_2\text{@CTAB-Se}$ (MXene) composite cathode material for high-performance rechargeable aluminum batteries, *Chem. Eng. J.*, 2020, **398**, 125679.
 9. Q. Zhou, X. Jiang, X. Zhang, D. Wang, G. Yang, H. Zhou, Y. Wu, F. Guo, M. Chen, G. Diao and L. Ni, Polyoxomolybdate-Based Metal-Organic Framework-Derived Cu-Embedded Molybdenum Dioxide Hybrid Nanoparticles as Highly Efficient Electrocatalysts for Al-S Batteries, *ChemSusChem*, 2024, **n/a**, e202400424.