

Supporting Information

A “Superaerophobic” Se-Doped CoS₂ Porous Nanowires Array for Cost-Saving Hydrogen Evolution

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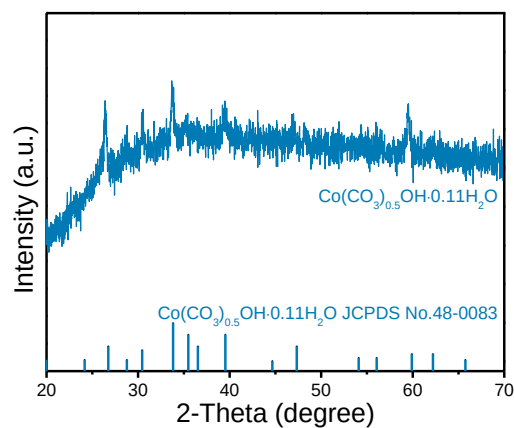


Figure S1. XRD spectrum of $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$ NW/CF.

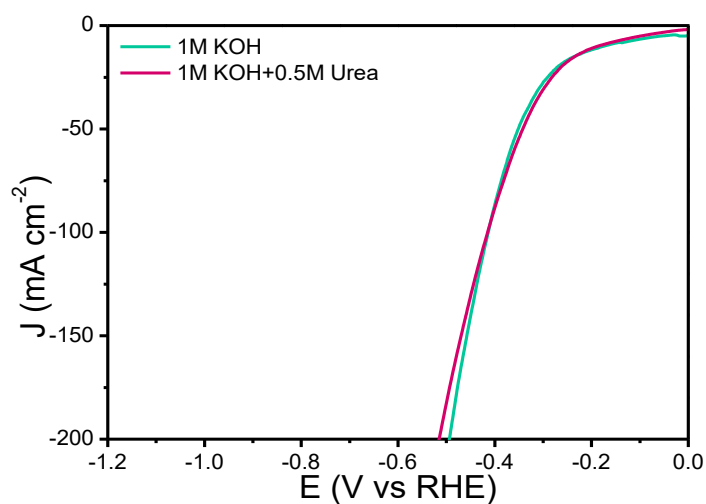


Figure S2. HER polarization curves of Se- CoS_2 NW/CF in 1.0 M KOH with and without 0.5 M urea.

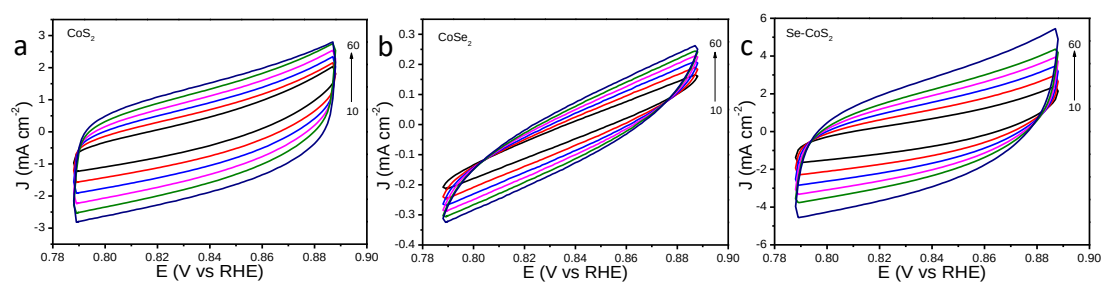


Figure S3. CV curves of (a) CoS_2 NW/CF, (b) CoSe_2 NW/CF, and (c) Se- CoS_2 NW/CF in 1.0 M KOH with 0.5 M urea.

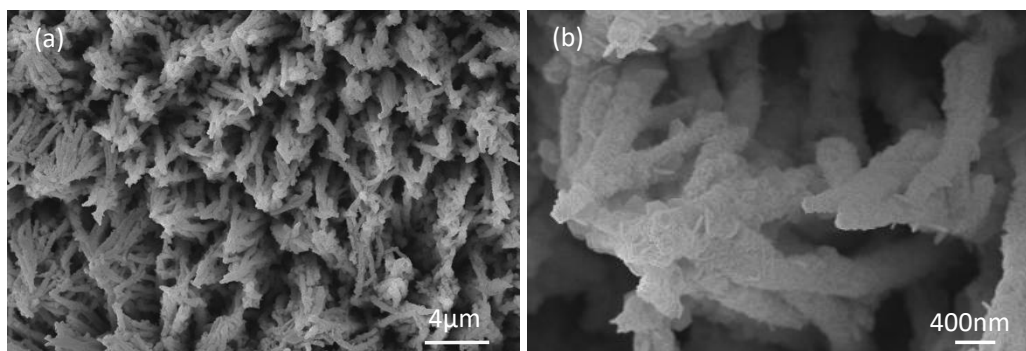


Figure S4. (a) Low- and (b) high-magnification SEM images of Se-CoS₂ NW/CF after I-t test.

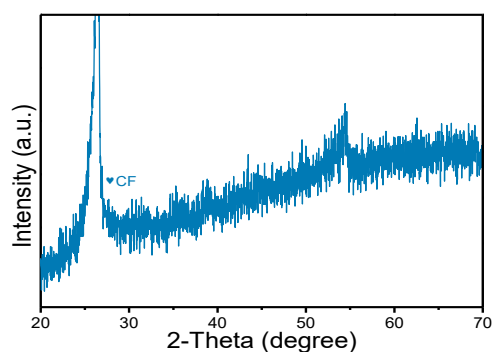


Figure S5. XRD spectrum of Se-CoS₂ NW/CF after I-t test.

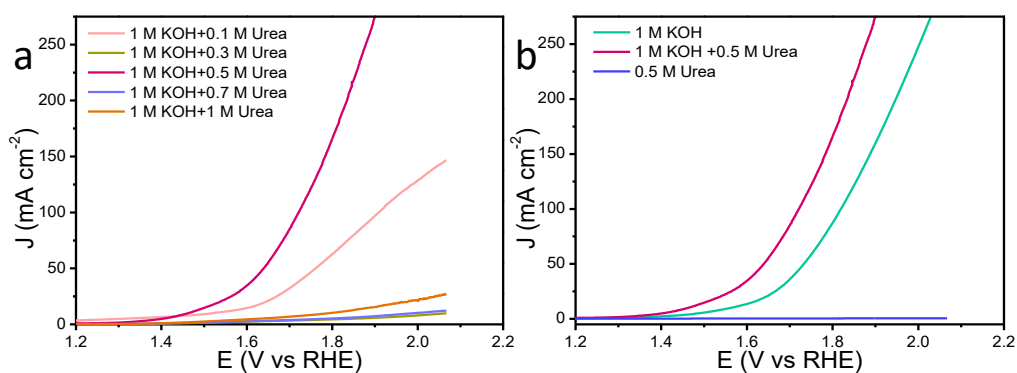


Figure S6. (a) UOR polarization curves of Se-CoS₂ NW/CF catalyst in 1 M KOH with various urea concentrations. (b) UOR polarization curves of Se-CoS₂ NW/CF in 1.0 M KOH with 0.5 M urea, 1.0 M KOH, and 0.5 M urea.

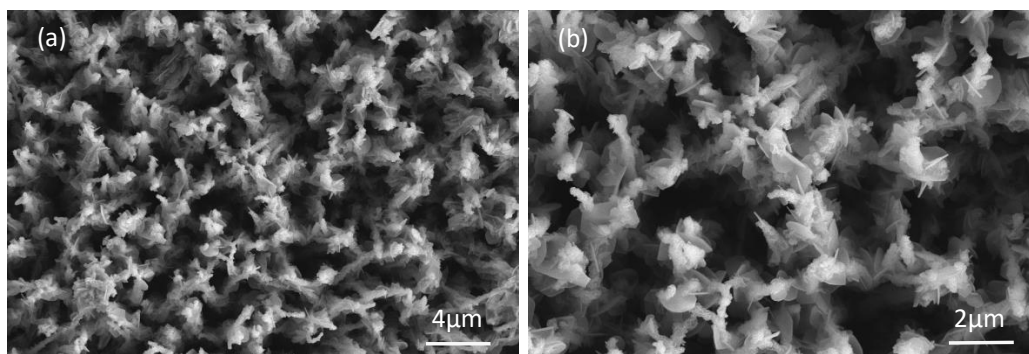


Figure S7. (a) Low- and (b) high-magnification SEM images of Se-CoS₂ NW/CF after UOR test.

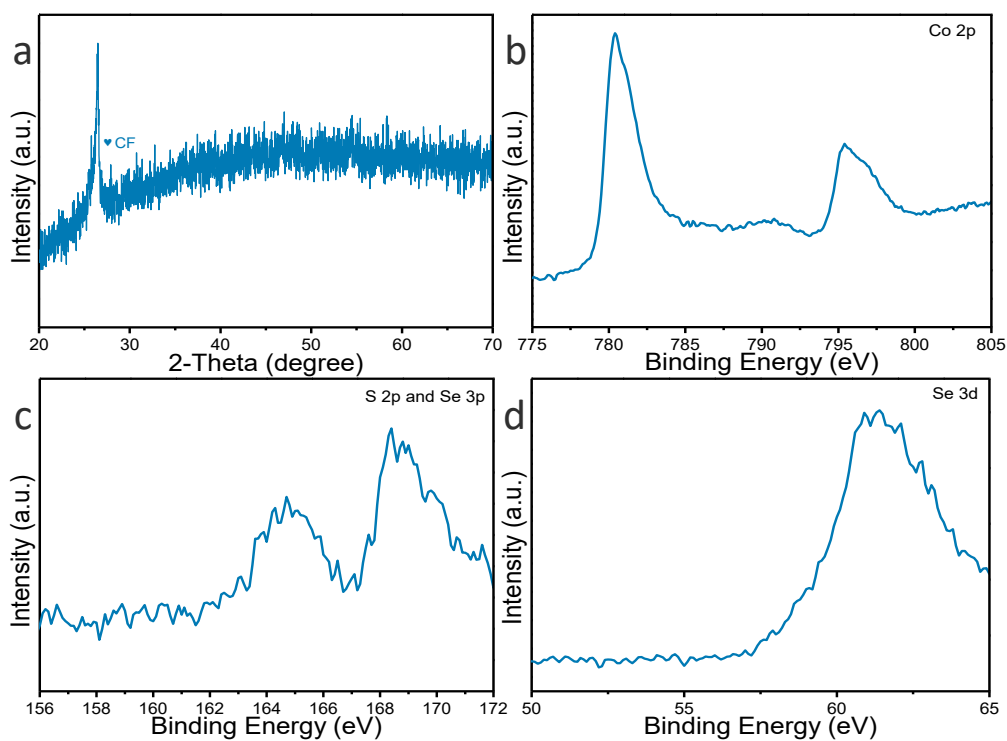


Figure S8. (a) XRD spectrum of Se-CoS₂ NW/CF after UOR test. XPS spectra of (b) Co 2p, (c) S 2p and Se 3p, and (d) Se 3d of Se-CoS₂ NW/CF after UOR test.



Figure S9. High-speed photographs of air bubbles escaping on the surface of Se-CoS₂ NW/FC after UOR test.

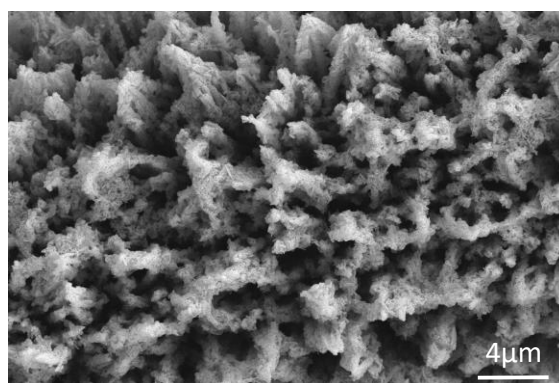


Figure S10. SEM image of Se-CoS₂ NW/CF after I-t test.

Table S1. Comparison of the HER performance of Se-CoS₂ NW/CF with other reported catalysts.

Catalyst	$\eta_j = 10 \text{ mA cm}^{-2} \text{ (mV)}$	electrolyte solution	Reference
Se-CoS ₂ NW/CF	188	1 M KOH with 0.5 M Urea	This work
CNTs@CoS _x Se _{2(1-x)}	225	1 M KOH	[1]
Co ₃ S ₄ /MoS ₂ /Ni ₂ P	214	1 M KOH	[2]
CoS ₂ @Co ₃ O ₄	320	1 M KOH	[3]
CoS ₂ @N-GN	204	1 M KOH	[4]
CoS ₂ HNSs	193	1 M KOH	[5]
Zn-Co-S NN/CFP	234	1 M KOH	[6]
NiCo ₂ S ₄ NW/NF	210	1 M KOH	[7]
CoS ₂ NTA/CC	193	1 M KOH	[8]
CNTs@Co-S	190	1 M KOH	[9]

Table S2. Comparison of the UOR performance of Se-CoS₂ NW/CF catalyst with other reported UOR catalysts.

Catalyst	$\eta_j = 10 \text{ mA cm}^{-2} \text{ (mV)}$	electrolyte solution	Reference
Se-CoS ₂ NW/CF	1.46	1 M KOH with 0.5 M Urea	This work
Pt/C	1.48	1 M KOH with 0.5 M Urea	[10]
ZIF-67-S	1.49	1 M KOH with 0.5 M Urea	[11]
Ni-MOF-8	1.483	1 M KOH with 0.5 M Urea	[12]
Co(OH) ₂ &Co+3O(OH)/Ti	1.536	1 M KOH with 0.3 M urea	[13]
IrO ₂	1.54	1 M KOH with 0.5 M Urea	[14]

Table S3. Comparison of the activity of urea electrocatalysis with other reported ones.

Catalyst	$\eta_j = 10 \text{ mA cm}^{-2} \text{ (mV)}$	electrolyte solution	Reference
Se-CoS ₂ NW/CF	1.44	1 M KOH with 0.5 M Urea	This work
CoS _x /Co-MOF	1.48	1 M KOH with 0.5 M urea	[11]
HC-NiMoS/Ti	1.59	1 M KOH with 0.5 M urea	[15]
Ni-Co ₉ S ₈	1.52	1 M KOH with 0.33 M urea	[16]
NiCo ₂ S ₄ NS/CC	1.45	1 M KOH with 0.33 M urea	[17]
Ni-MOF-0.5	1.52	1 M KOH with 0.5 M urea	[12]
Ni _{0.9} Fe _{0.1} O _x	1.455	1 M KOH with 0.33 M urea	[18]
MOF-Ni@MOF-Fe-S	1.539	1 M KOH with 0.5 M urea	[19]
NiFeCo LDH/NF	1.49	1 M KOH with 0.33 M urea	[20]
MnO ₂ /MnCo ₂ O ₄ /Ni	1.55	1 M KOH with 0.5 M urea	[21]
FQD/CoNi-LDH/NF	1.45	1 M KOH with 0.5 M urea	[22]

Reference

1. Zhang, Y. Y.; Qiu, Y. F.; Ji, X. Y.; Ma, T. G.; Ma, Z.; Hu, P. A. Direct growth of CNTs@CoS_xSe₂(1-x) on carbon cloth for overall water splitting. *ChemSusChem* **2019**, *12*, 3792.
2. Lin, H. F.; Li, H. Y.; Li, Y. Y.; Liu, J. L.; Wang, X.; Wang, L. Hierarchical CoS/MoS₂ and Co₃S₄/MoS₂/Ni₂P nanotubes for efficient electrocatalytic hydrogen evolution in alkaline media. *J. Mater. Chem. A* **2017**, *5*, 25410–25419.
3. Aftab, U.; Tahira, A.; Samo, A. H.; Abro, M. I.; Baloch, M. M.; Kumar, M.; Sirajuddin; Ibupoto, Z. H. Mixed CoS₂@Co₃O₄ composite material: An efficient nonprecious electrocatalyst for hydrogen evolution reaction. *Int. J. Hydrog. Energy* **2020**, *45*, 13805–13813.
4. Zhang, W.; Han, X. P.; Ma, X. Y.; Zhong, C.; Ma, T. Y.; Deng, Y. D.; Hu, W. B. Pyrite-type CoS₂ nanoparticles supported on nitrogen-doped graphene for enhanced water splitting. *Front. Chem.* **2018**, *6*, 569.
5. Ma, X. Y.; Zhang, W.; Deng, Y. D.; Zhong, C.; Hu, W. B.; Han, X. P. Phase and composition controlled synthesis of cobalt sulfide hollow nanospheres for electrocatalytic water splitting. *Nanoscale* **2018**, *10*, 4816–4824.
6. Wu, X. Y.; Han, X. P.; Ma, X. Y.; Zhang, W.; Deng, Y. D.; Zhong, C.; Hu, W. B. Morphology-controllable synthesis of Zn-Co-mixed sulfide nanostructures on carbon fiber paper toward efficient rechargeable zinc-air batteries and water electrolysis. *ACS Appl. Mater. Interfaces* **2017**, *9*, 12574–12583.
7. Sivanantham, A.; Ganesan, P.; Shanmugam, S. Hierarchical NiCo₂S₄ nanowire arrays supported on Ni foam: an efficient and durable bifunctional electrocatalyst for oxygen and hydrogen evolution reactions. *Adv. Funct. Mater.* **2016**, *26*, 4661–4672.
8. Guan, C.; Liu, X. M.; Elshahawy, A. M.; Zhang, H.; Wu, H. J.; Pennycook, S. J.; Wang, J. Metal-organic framework derived hollow CoS₂ nanotube arrays: an efficient bifunctional electrocatalyst for overall water splitting. *Nanoscale Horiz.* **2017**, *2*, 342–348.
9. Wang, J.; Zhong, H. X.; Wang, Z. L.; Meng, F. L.; Zhang, X. B. Integrated three-dimensional carbon paper/carbon tubes/cobalt-sulfide sheets as an efficient electrode for overall water splitting. *ACS Nano* **2016**, *10*, 2342–2348.
10. Chen, S.; Duan, J. J.; Vasileff, A.; Qiao, S. Z. Size fractionation of two-dimensional sub-nanometer thin manganese dioxide crystals towards superior urea electrocatalytic conversion. *Angew. Chem. Int. Ed.* **2016**, *55*, 3804–3808.
11. Xu, H. Z.; Ye, K.; Zhu, K.; Yin, J. L.; Yan, J.; Wang, G. L.; Cao, D. X. Template-directed assembly of urchin-like CoS_x/Co-MOF as an efficient bifunctional electrocatalyst for overall water and urea electrolysis. *Inorg. Chem. Front.* **2020**, *7*, 2602.
12. Zheng, S. S.; Zheng, Y.; Xue, H. G.; Pang, H.; Ultrathin nickel terephthalate nanosheet three-dimensional aggregates with disordered layers for highly efficient overall urea electrolysis. *Chem. Eng. J.* **2020**, *395*, 125166–125174.
13. Jiang, Y.; Gao, S. S.; Liu, J. L.; Xu, G. C.; Qiang, J.; Chen, F. S.; Song, X. M. Ti-Mesh supported porous CoS₂ nanosheet self-interconnected networks with high oxidation states for efficient hydrogen production via urea electrolysis. *Nanoscale* **2020**, *12*, 11573–11581.
14. Zhao, Z. J.; Zhao, J.; Wang, H. B.; Li, X. L.; Yang, L. Q.; Zhao, Z. W.; Liu, X. Y.; Liu, Y. Z.; Liu, P.; Cai, Z. Y. Porous flower-like nickel nitride as highly efficient bifunctional electrocatalysts for less energy-intensive hydrogen evolution and urea oxidation. *Int. J. Hydrog. Energy* **2020**, *45*, 14199–14207.
15. Wang, X. X.; Wang, J. M.; Sun, X. P.; Wei, S.; Cui, L.; Yang, W. R.; Liu, J. Q.; Hierarchical coral-like NiMoS nanohybrids as highly efficient bifunctional electrocatalysts for overall urea electrolysis. *Nano Res.* **2017**, *11*, 988–996.
16. Hao, P.; Zhu, W. Q.; Li, L. Y.; Tian, J.; Xie, J. F.; Lei, F. C.; Cui, G. W.; Zhang, Y. Q.; Tang, B. Nickel incorporated Co₉S₈ nanosheet arrays on carbon cloth boosting overall urea electrolysis. *Electrochim. Acta* **2020**, *338*, 135883.
17. Zhu, W. X.; Ren, M. R.; Hu, N.; Zhang, W. T.; Luo, Z. T.; Wang, R.; Wang, J.; Huang, L. J.; Suo, Y. R.; Wang, J. L. Traditional NiCo₂S₄ phase with porous nanosheets array topology on carbon cloth: a flexible, versatile and fabulous electrocatalyst for overall water and urea electrolysis. *ACS Sustain. Chem. Eng.* **2018**, *6*, 5011–5020.
18. Wu, F. C.; Ou, G.; Yang, J.; Li, H. N.; Gao, Y. X.; Chen, F. M.; Wang, Y.; Shi, Y. M. Bifunctional nickel oxide-based nanosheets for highly efficient overall urea splitting. *ChemComm* **2019**, *55*, 6555.
19. Xu, H. Z.; Ye, K.; Zhu, K.; Yin, J. L.; Yan, J.; Wang, G. L.; Cao, D. X. Efficient bifunctional catalysts synthesized from three-dimensional Ni/Fe bimetallic organic frameworks for overall urea electrolysis. *Dalton Trans.* **2020**, *49*, 5646–5652.
20. Babar, P.; Lokhande, A.; Karade, V.; Pawar, B.; Gang, M. G.; Pawar, S.; Kim, J. H. Bifunctional 2D electrocatalysts of transition metal hydroxide nanosheet arrays for water splitting and urea electrolysis. *ACS Sustain. Chem. Eng.* **2019**, *7*, 10035–10043.
21. Xiao, C. L.; Li, S. N.; Zhang, X. Y.; MacFarlane, D. R. MnO₂/MnCo₂O₄/Ni heterostructure with quadruple hierarchy: a bifunctional electrode architecture for overall urea oxidation. *J. Mater. Chem. A* **2017**, *5*, 7825–7832.
22. Feng, Y. Q.; Wang, X.; Huang, J. F.; Dong, P. P.; Ji, J.; Li, J.; Cao, L. Y.; Feng, L. L.; Jin, P.; Wang, C. R. Decorating CoNi layered double hydroxides nanosheet arrays with fullerene quantum dot anchored on Ni foam for efficient electrocatalytic water splitting and urea electrolysis. *Chem. Eng. J.* **2020**, *390*, 124525.