

Interfacial Engineering of CuSe₂/FeSe₂ Heterojunction for Water Splitting: A Pathway to High-Performance Hydrogen and Oxygen Evolution Reactions

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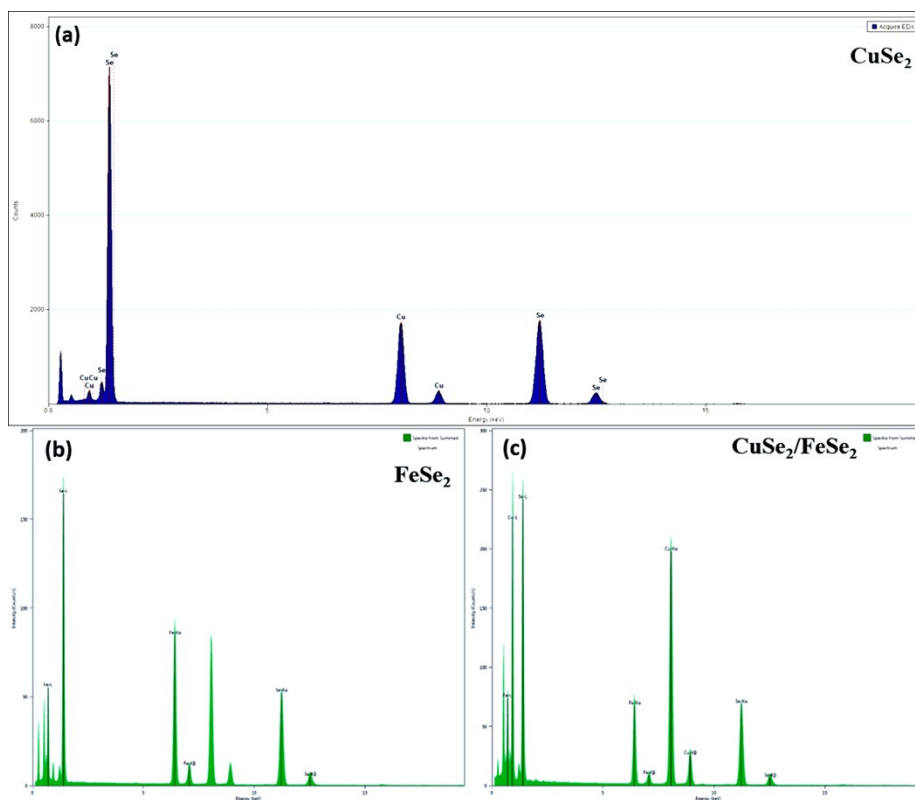


Figure S1. EDS analysis showing the elemental mapping of Cu, Fe and Se in (a) CuSe_2 (b) FeSe_2 (c) $\text{CuSe}_2/\text{FeSe}_2$.

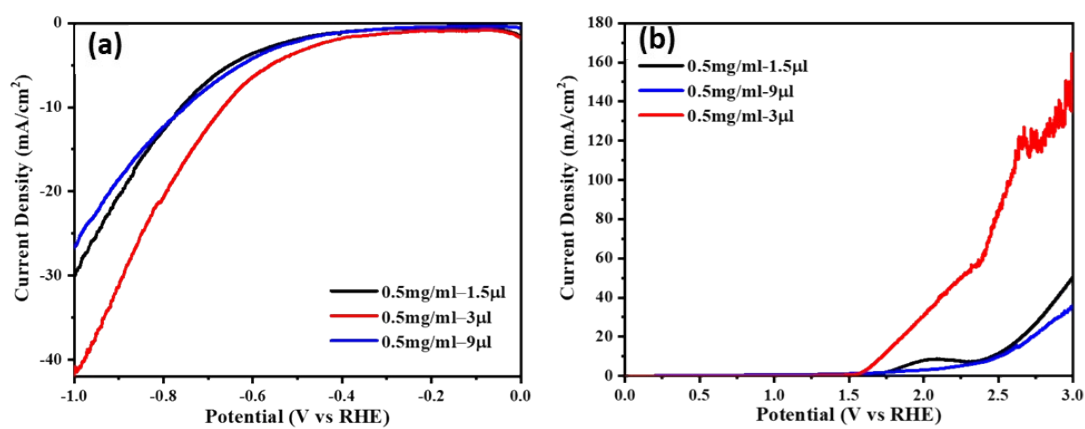


Figure S2. Polarization curves (a) HER and (b) OER for mass loading optimization of $\text{CuSe}_2/\text{FeSe}_2$ onto GCE.

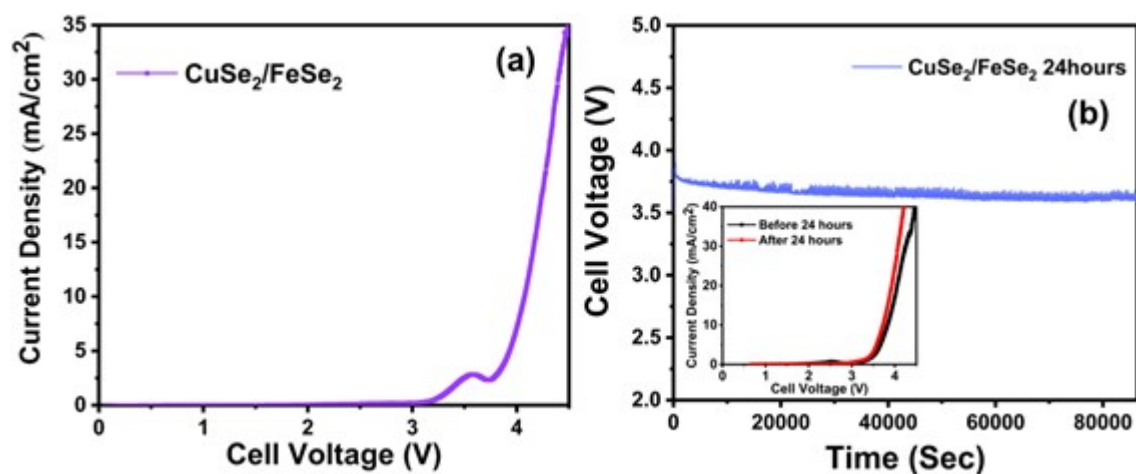


Figure S3. (a) Polarization curve, (b) Chronopotentiometric stability study at 10mA/cm², (Inset: LSV curve before and after 24 hours stability study) for CuSe₂/FeSe₂ in HER || OER overall water splitting configuration in 1M KOH.

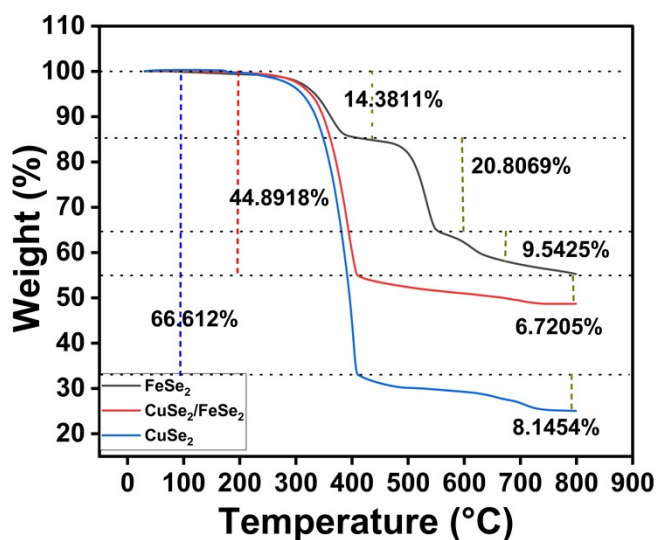


Figure S4. TGA curve showcasing varied percentages of weight loss at temperature range (30-800°C) for CuSe₂, FeSe₂, and CuSe₂/FeSe₂

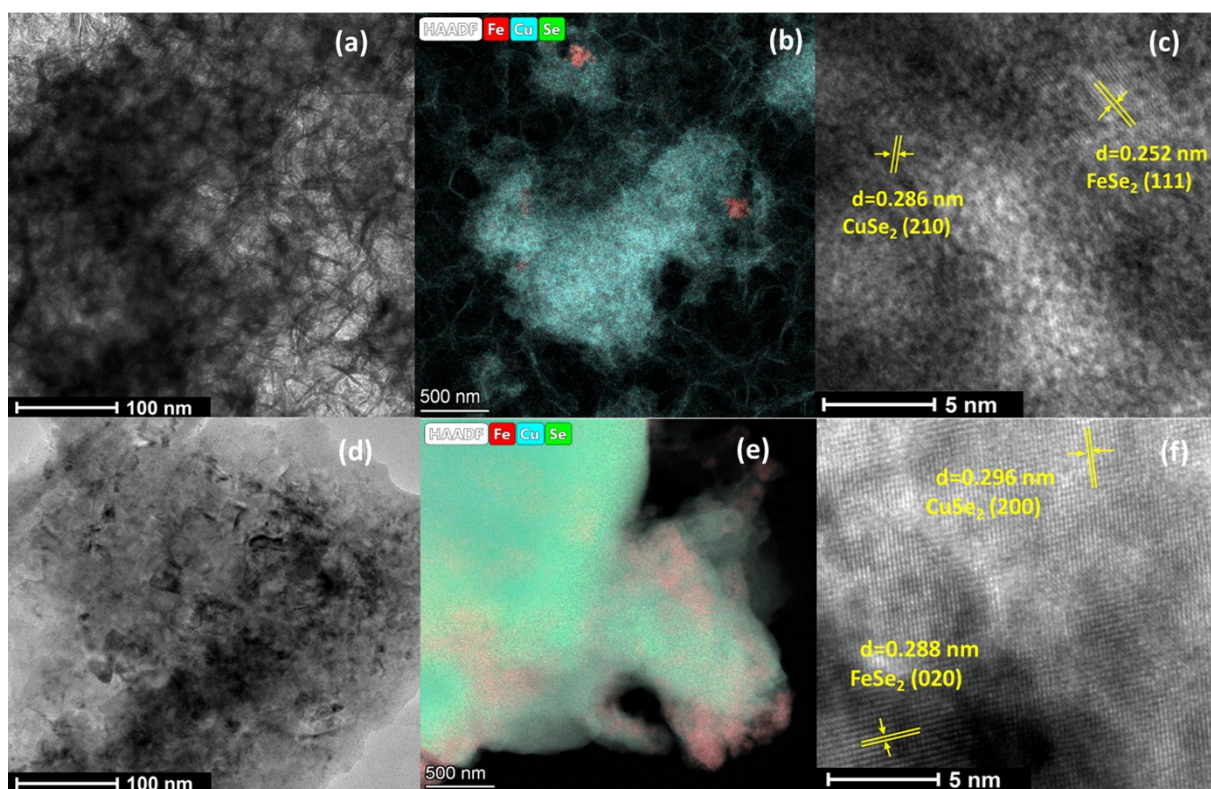


Figure S5. HAADF-STEM analysis with elemental mapping of the $\text{CuSe}_2/\text{FeSe}_2$ composite following 24-hour stability testing under (a-c) HER and (d-f) OER conditions.

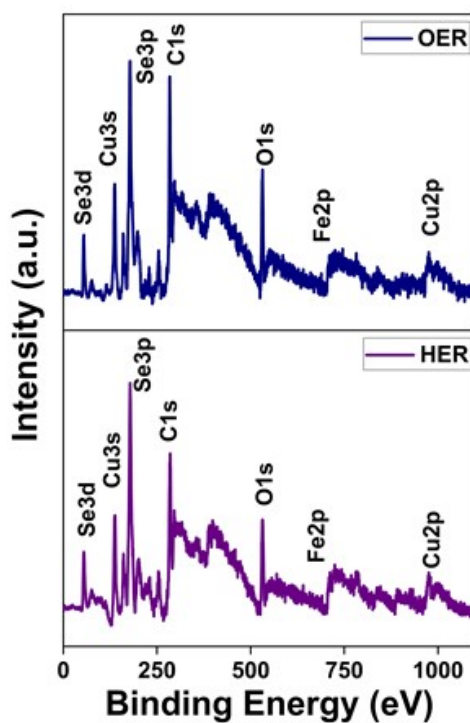


Figure S6. XPS comparison of the catalyst surface after 24 hours of HER and OER stability studies

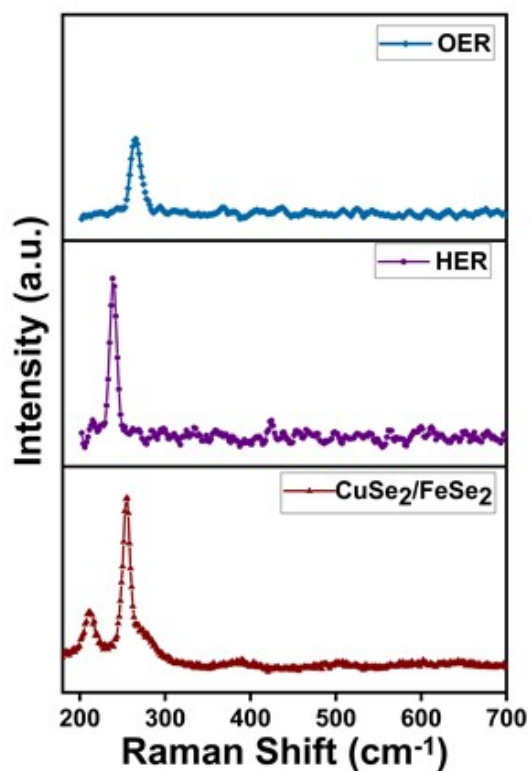


Figure S7. Raman shifts comparison of the catalyst surface after 24 hours of HER and OER stability studies

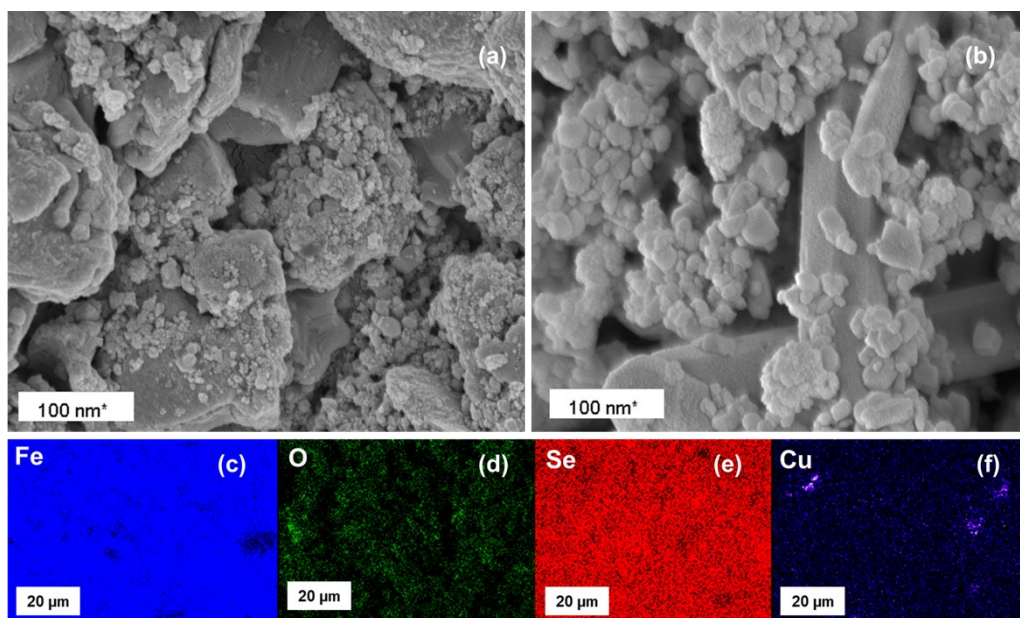


Figure S8. SEM images and elemental mapping of the catalyst surface after 24 hrs of electrochemical stability studies. **(a)** SEM micrograph chronopotentiometric OER testing **(b)** SEM image after HER operation **(c-f)** EDS elemental maps for Fe, O, Se, and Cu indicating uniform elemental distribution

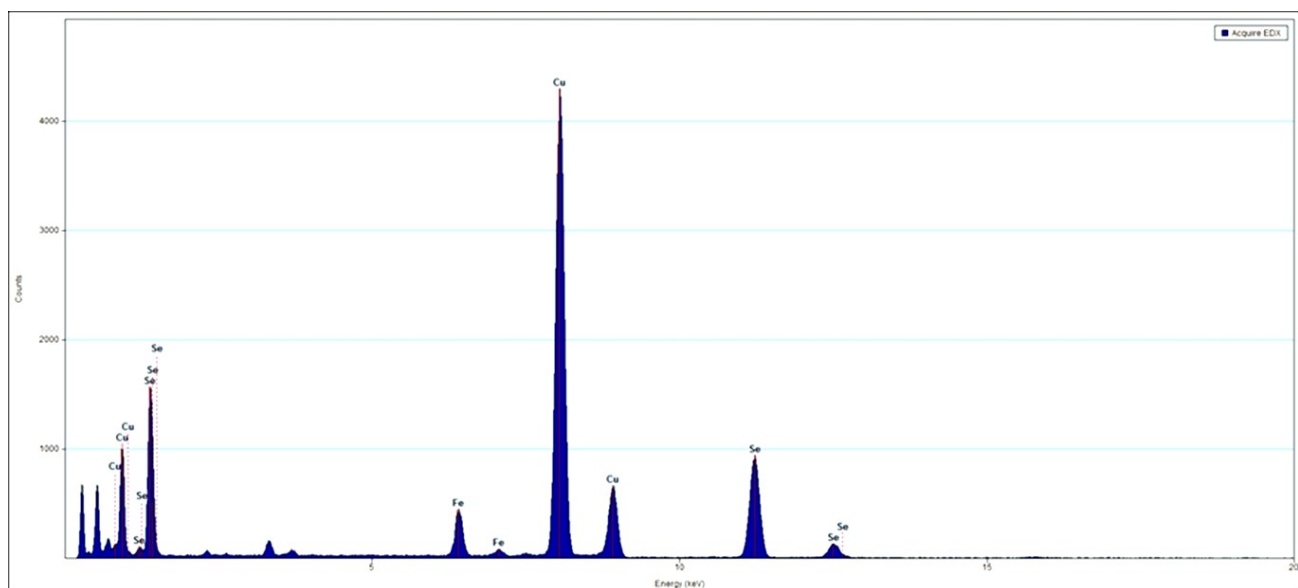


Figure S9. Elemental mapping images of the $\text{CuSe}_2/\text{FeSe}_2$ heterojunction after 24 hours of continuous operation.

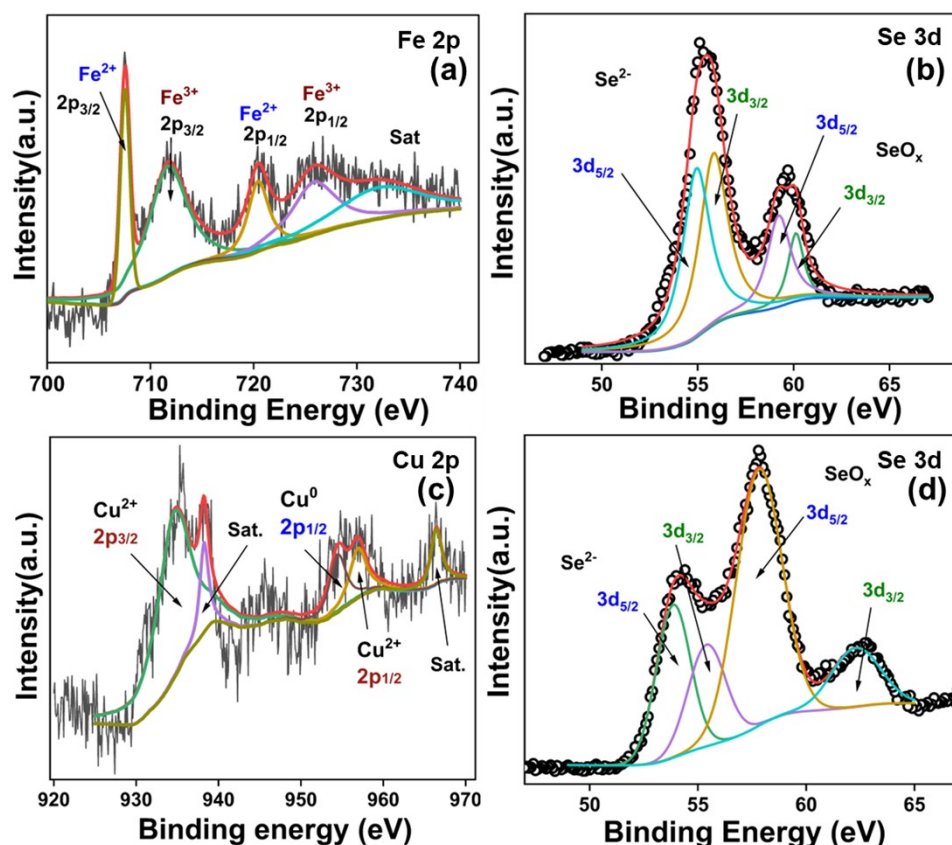


Figure S10. XPS spectra of (a) Fe 2p in FeSe₂, (b) Se 3d in FeSe₂, (c) Cu 2p in CuSe₂, and (d) Se 3d in CuSe₂.

Table S1. Comparative study of different heterojunction electrocatalysts for overall water splitting on the basis of overpotential 10mA/cm².

S. N	Material System	Overpotential (mV)	Reaction Type	Advantages	Ref.
1	PbO ₂ /Co ₃ O ₄	526.5	OER	High charge separation efficiency and stability.	[1]
2	Se-CuO/CF	440	OER	Decreased charge recombination, efficient charge transport	[2]
3	FeV ₃ O ₈ /MoS ₂	160	HER	Effective electron transfer, increased lattice active sites	[3]
4	W ₂ N/WC	320	OER	High surface area and stability under oxidative conditions	[4]
5	CdSe/gC ₃ N ₄	218	OER	Effective electron transfer, Increase in the adsorption sites	[5]
6	WO _x /WC	233	HER	High catalytic efficiency and stability, even in acidic media	[6]

7	CuSe₂/FeSe₂	666 (for HER) and 490 (for OER)	HER & OER	High catalytic efficiency and electron delocalization	Our Work
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References

1. Y. Dan, L. Wu, Y. Cao, Y. Liu, W. Zhong, C. Liu, Q. Gu, X. Li and L. Chen, *J. Environ. Chem. Eng*, 2024, **12**, 112978.
2. L. Tabassum, H. Tasnim, S. Shubhashish, I. Perera, T. Bhosale, M. Li, S. March, M. K. Islam and S. L. Suib, *Appl. Mater. Today*, 2022, **27**, 101485.
3. Z. Huang, X. Tang, J. Zhao, H. Lin, M. Nie and Q. Li, *J. Mater. Chem. C*, 2022, **10**, 3489-3499.
4. J. Diao, Y. Qiu, S. Liu, W. Wang, K. Chen, H. Li, W. Yuan, Y. Qu and X. Guo, *Adv. Mater*, 2020, **32**, 1905679.
5. A. Mehtab and T. Ahmad, *ACS Catal*, 2024, **14**, 691-702.
6. Y. Cui, X. Tan, K. Xiao, S. Zhao, N. M. Bedford, Y. Liu, Z. Wang, K.-H. Wu, J. Pan and W. H. Saputera, *ACS Energy Lett*, 2020, **5**, 3560-3568.