Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary information for

Orbital Hybridization-Induced Direct Z-Scheme in $CuCoO_2/MoX_2$ Heterostructures for Overcoming Kinetic Imbalance in Overall Water Splitting

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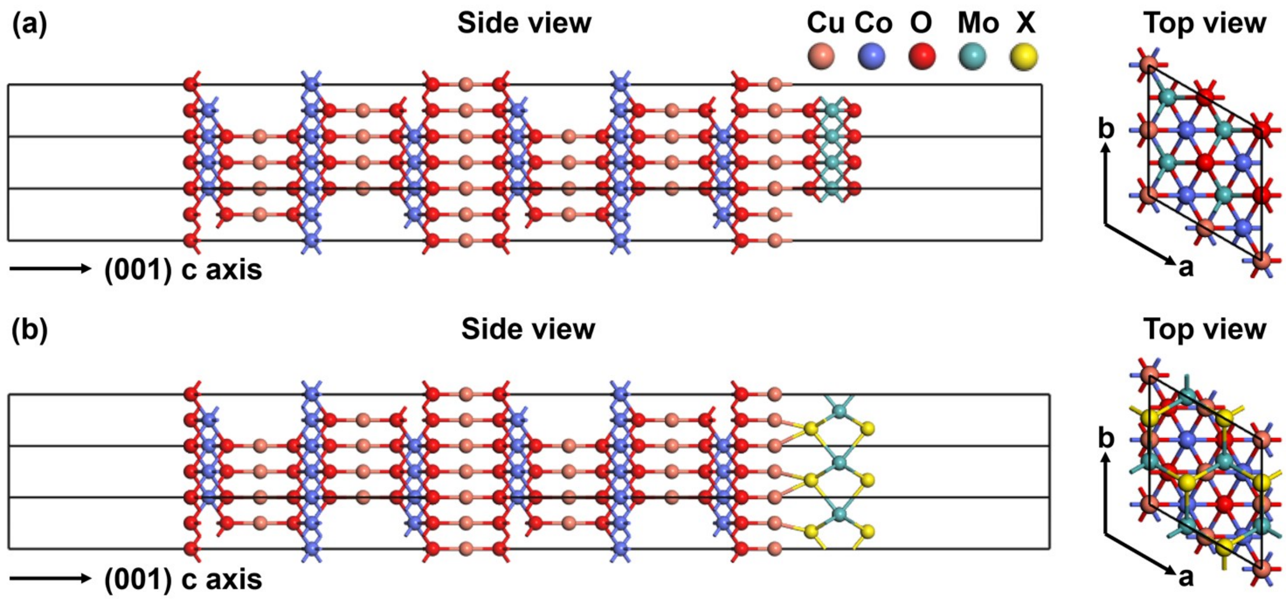

Figure S1. Initial structural models: (a) Side and top views of $CuCoO_2/MoO_2$; (b) Side and top views of $CuCoO_2/MoS_2$, $CuCoO_2/MoSe_2$, and $CuCoO_2/MoTe_2$.

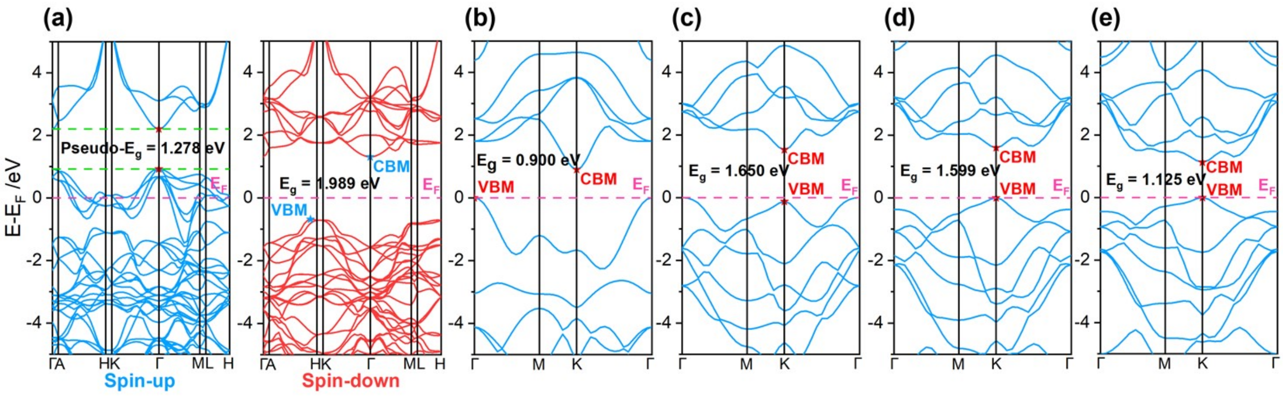

Figure S2. Electronic band structures of (a) bulk $CuCoO_2$ and monolayer (b) MoO_2, (c) MoS_2, (d) $MoSe_2$, and (e) $MoTe_2$.

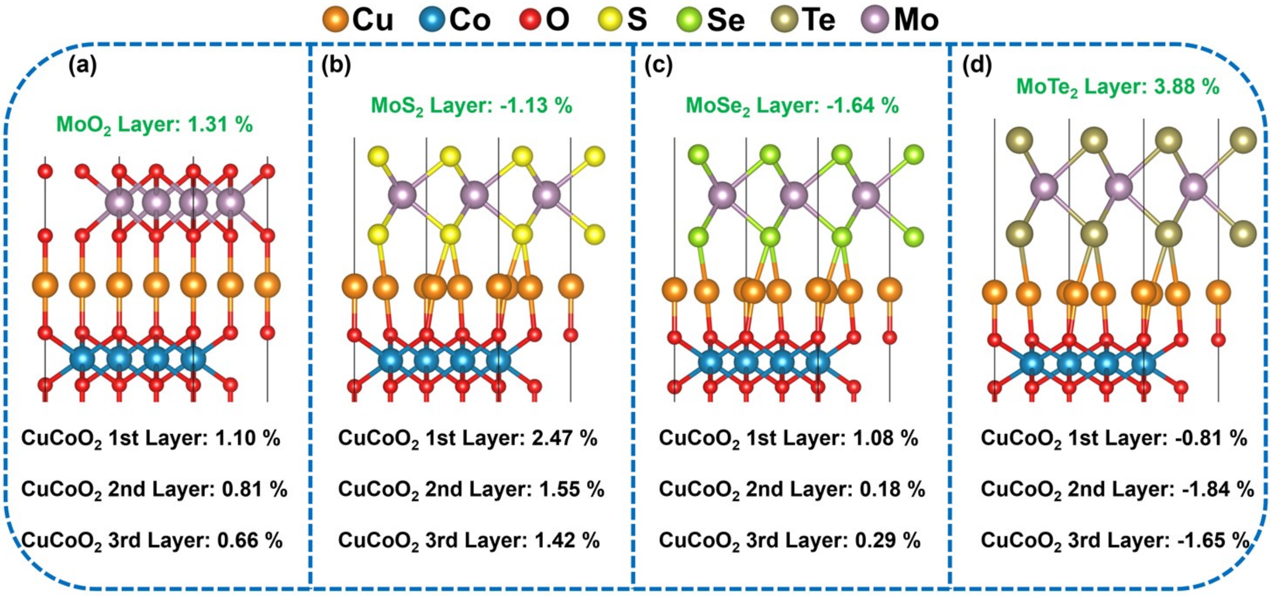

Figure S3. Atomic configurations and layer expansion rates at the interface of (a) $CuCoO_2/MoO_2$, (b) $CuCoO_2/MoS_2$, (c) $CuCoO_2/MoSe_2$, and (d) $CuCoO_2/MoTe_2$ heterostructures.

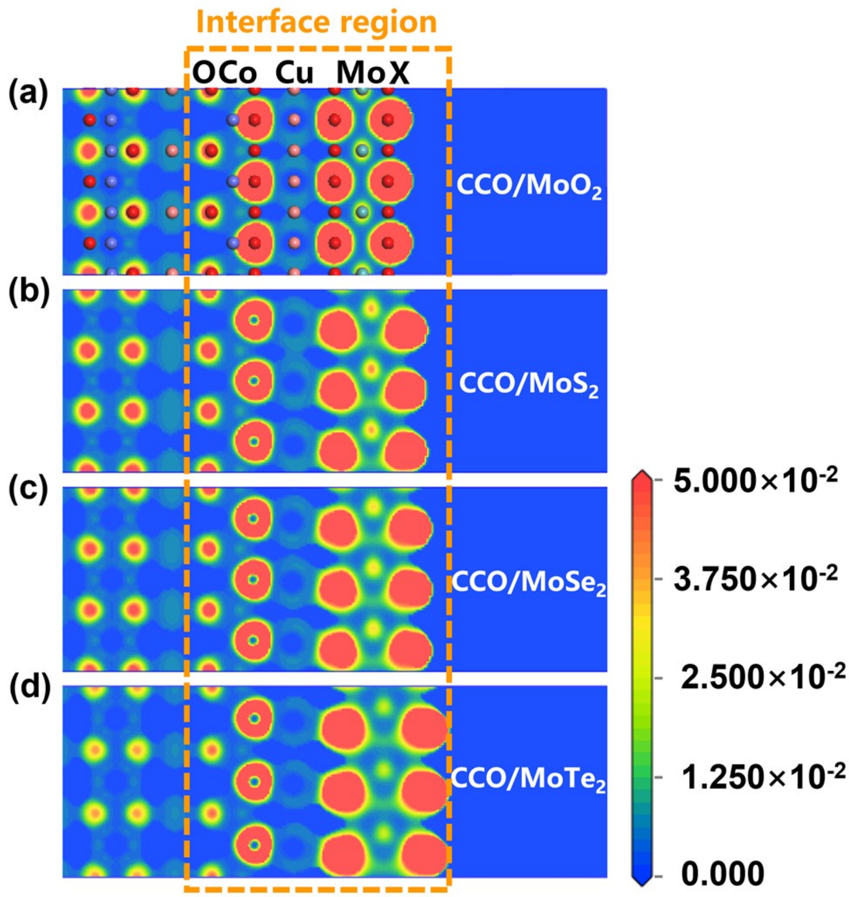

Figure S4. Electron localization function (ELF) cross-sections at the interface of (a) $CuCoO_2/MoO_2$, (b) $CuCoO_2/MoS_2$, (c) $CuCoO_2/MoSe_2$, and (d) $CuCoO_2/MoTe_2$ heterostructures.

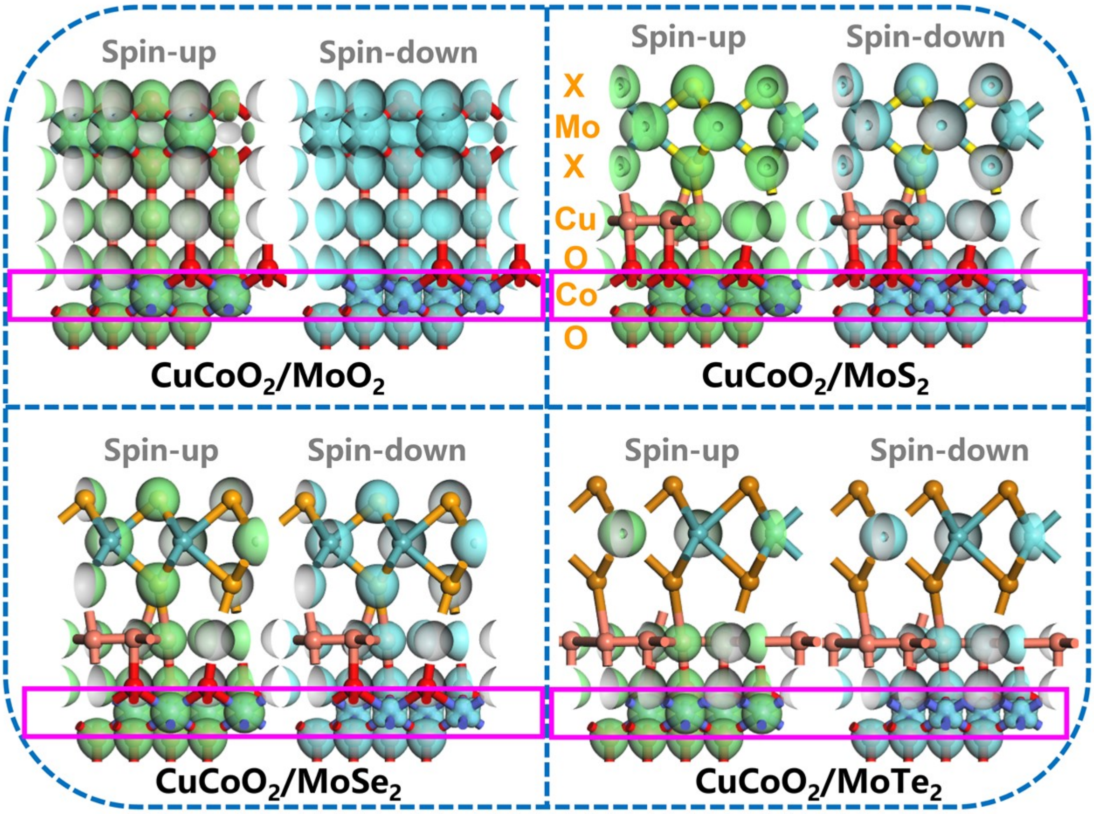

Figure S5. Three-dimensional spin charge density isosurfaces at the interface of $CuCoO_2/MoX_2$ heterostructures.

Table S1. Crystal structure parameters of bulk $CuCoO_2$ and MoX_2 monolayer.

Model	a, b (Å)		c (Å)		Bond length cal. (Å)	
	cal.	exp.	cal.	exp.	Cu–O/Mo–X	M–O
$CuCoO_2$	2.896	2.855	16.956	16.916 [1]	1.839	1.942
MoO_2	2.817	/	/		2.035	/
MoS_2	3.201	3.20 [2]	/		2.413	/
$MoSe_2$	3.286	3.30 [3]	/		2.532	/
$MoTe_2$	3.559	3.52 [4]	/		2.735	/

Table S2. Band edge positions (vs. SHE) and bandgaps of bulk $CuCoO_2$ and MoX_2 monolayers.

Model	VBM cal. (eV)	CBM cal. (eV)	Band gap ref. (eV)	VBM cal. ref. (eV)	CBM cal. ref. (eV)	VBM exp. (eV)	CBM exp. (eV)
$CuCoO_2$	3.12	−0.62	3.74 [1]	3.10	−0.60 [5]	2.36	−1.38 [1]
MoO_2	2.269	−0.151	2.42 [6]	/	/	/	/
MoS_2	1.424	−1.286	2.71 [7]	1.84	−0.52 [8]	1.37	−0.54 [9]
$MoSe_2$	0.802	−1.568	2.37 [7]	1.18	−0.86 [8]	0.35	−0.79 [10]
$MoTe_2$	0.306	−1.584	1.89 [7]	0.68	−0.86 [8]	1.86	−0.81 [11]

Table S3. Work function, ΔQ (from the Mulliken population), Electric field (by Δρ) direction, and DFT energy of $CuCoO_2/MoX_2$ heterostructures and their constituent slabs before contact.

Model	Work function Φ /eV	ΔQ of MoX_2 side /e	Electric field (by Δρ) direction	DFT energy /eV
$CuCoO_2$ (001) slab (2×2 supercell)	5.456	/	/	−87771.211
MoO_2 monolayer (2×2 supercell)	6.709	/	/	−11261.689
MoS_2 monolayer ($\sqrt{3} \times \sqrt{3}$ supercell)	5.864	/	/	−7633.325
$MoSe_2$ monolayer ($\sqrt{3} \times \sqrt{3}$ supercell)	5.242	/	/	−26355.692
$MoTe_2$ monolayer ($\sqrt{3} \times \sqrt{3}$ supercell)	4.746	/	/	−9239.311
$CuCoO_2/MoO_2$	5.928	0.24 (gain)	$CuCoO_2$ to MoO_2	−99034.641
$CuCoO_2/MoS_2$	5.841	−0.14 (loss)	MoS_2 to $CuCoO_2$	−95404.421
$CuCoO_2/MoSe_2$	5.553	−1.33 (loss)	$MoSe_2$ to $CuCoO_2$	−114129.004
$CuCoO_2/MoTe_2$	5.059	−1.41 (loss)	$MoTe_2$ to $CuCoO_2$	−97016.887

References

1. Y. M. Zhang, Z. Y. Zhao, Y. K. Zhao and C. X. Wang, *J. Mater. Sci.*, 2022, **57**, 18687-18710.
2. J. Shen, X. Xie, W. Li, C. Deng, Y. Ma, H. Chen, H. Fu, F.-S. Li, B. Yuan, C. Ji, R. He, J. Guan and W. Kong, *Sci. Adv.*, 2025, **11**, eadr9753.
3. J. Lu, G. Niu, X. Ren, D. Bao, H. Chen, H. Yang, X. Lin, S. Du and H.-J. Gao, *Nanoscale*, 2021, **13**, 19165-19171.
4. Y. Pan, R. Guzman, S. Li, W. Xu, Y. Li, N. Tang, H. Yin, J. He, A. Wu, J. Chen, W. Zhou, X. Xu and Y. Ye, *Nature Synthesis*, 2022, **1**, 701-708.
5. Y. M. Zhang, Z. Y. Zhao, W. Tang, J. Y. Feng, J. Zhang, Q. J. Liu, Z. S. Li and Z. G. Zou, *J. Mater. Chem. A*, 2023, **11**, 20151-20164.
6. C. Ataca, H. Şahin and S. Ciraci, *J. Phys. Chem. C.*, 2012, **116**, 8983-8999.
7. C. Zhang, C. Gong, Y. Nie, K.-A. Min, C. Liang, Y. J. Oh, H. Zhang, W. Wang, S. Hong, L. Colombo, R. M. Wallace and K. Cho, *2D Mater.*, 2017, **4**, 015026.
8. R. Yang, Y. Fan, Y. Zhang, L. Mei, R. Zhu, J. Qin, J. Hu, Z. Chen, Y. Hau Ng, D. Voiry, S. Li, Q. Lu, Q. Wang, J. C. Yu and Z. Zeng, *Angew. Chem. Int. Ed.*, 2023, **62**, e202218016.
9. Q. Mao, K. Wei, T. Li, J. Zhu, H. Han, K. Hu, C. Ma and S. Feng, *Environ. Res.*, 2025, **286**, 122966.
10. F. Wang, X. Xiao, Y. Yao and C. Ling, *J. Environ. Chem. Eng.*, 2025, **13**, 117802.
11. Z. Yuan, Y. Xiang, X. Jian, H. Zhang, M. Liu, R. Cao, Y. Hu and X. Gao, *Sep. Purif. Technol.*, 2025, **359**, 129836.