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Photothermal–Excitonic Trade-Off in TiO_2/BiCuSeO Heterojunctions for Optimal Solar-Driven Hydrogen Production

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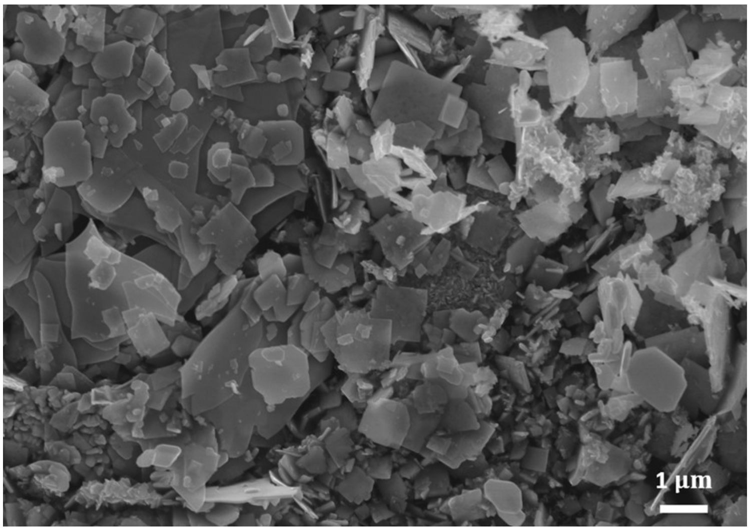

Figure S1. SEM image of BiCuSeO nanosheets.

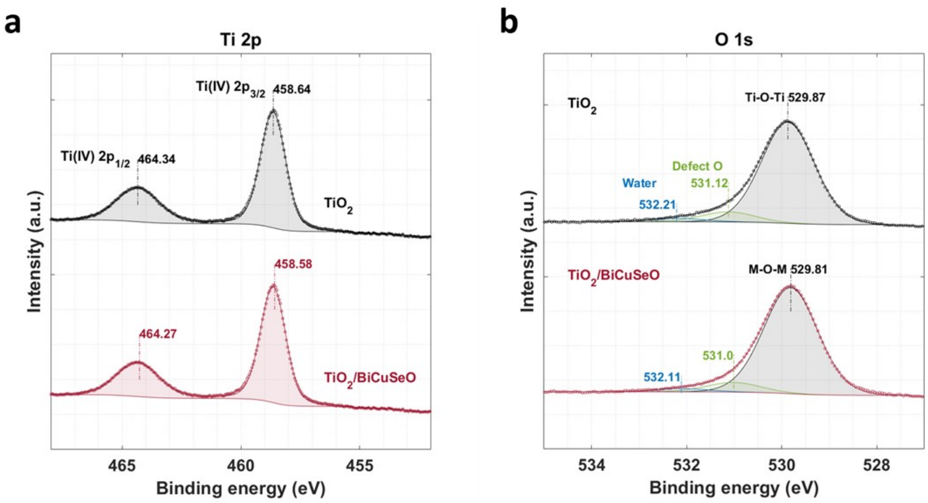

Figure S2. XPS spectra for TiO_2 and TiO_2/BiCuSeO in **a)** Ti 2p and **b)** O 1s regions.

Table S1. Summary of PGEC-integrated photothermal catalytic HER performance.

Compounds	Light source	Reagent	Performance	Ref.
Bi_2Te_3 NRs/TiO_2	365 nm LED	25 vol% ethanol aq.	1494 μmol h^{-1} g^{-1}	[1]
Bi_2Se_3 NSs/CdS	>420 nm 300 W Xe lamp	~1 M Na_2S + 0.25 M Na_2SO_3 aq.	424 μmol h^{-1} g^{-1}	[2]
Bi_2Te_3 NSs	100 W Hg lamp	15 vol% TEOA aq. + 14 μmol Eosin Y	920 μmol h^{-1} g^{-1}	[3]
Bi_2Se_3 NSs/Bi_2SeO_2	UV cut-off 300 W Xe lamp		136 μmol h^{-1} g^{-1}	[4]
0.37 wt% Pt|7.7 wt% SnSe/g-C_3N_4	> 420 nm, Xe	20 vol% MeOH aq.	1064 μmol h^{-1} g^{-1}	[5]
20 mol% $Cu_2Se/CdS_{0.95}Se_{0.05}$	> 400 nm, 300 W, Xe	5 vol% LA aq.	570.7 μmol h^{-1} g^{-1}	[6]
Au/Cu_2Se yolk/shell NCs		0.25 M Na_2S + 0.35 M Na_2SO_3 aq.	66.3 μmol h^{-1} g^{-1}	[7]
Cu_2Se/amorphous C/graphene NBs/g-C_3N_4	> 420 nm, 300 W, Xe	15% TEOA aq.	127.3 μmol h^{-1} g^{-1}	[8]
Cu_2O/Cu_2Se multilayer NWs	> 420 nm, 300 W, Xe	10 vol% MeOH aq.	28.75 μmol h^{-1} g^{-1}	[9]
TiO_2/BiCuSeO (This work)	300 W Xe lamp	10 vol% methanol aq.	1946 μmol h^{-1} g^{-1}	

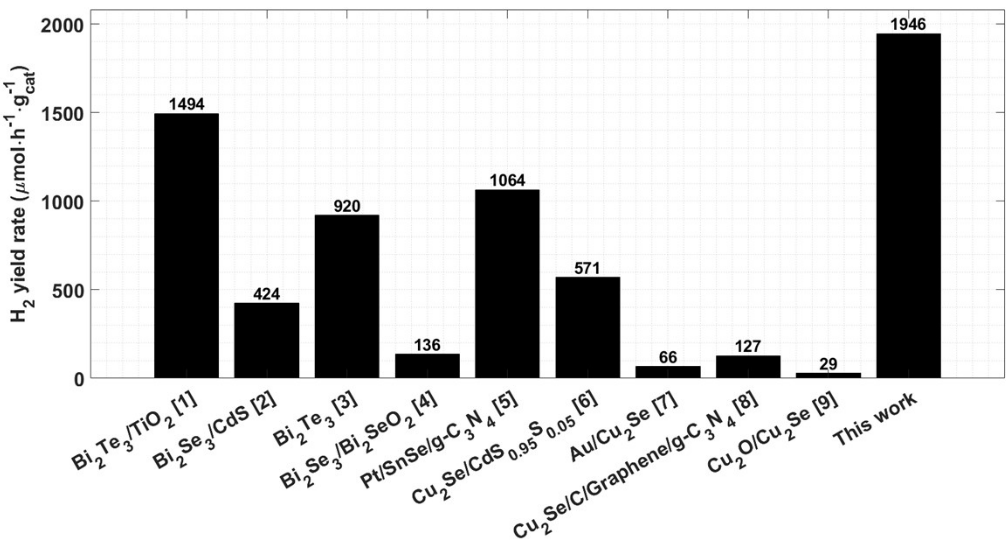

Figure S3. PGEC-integrated photothermal catalytic HER performance reported in the literature and this work.

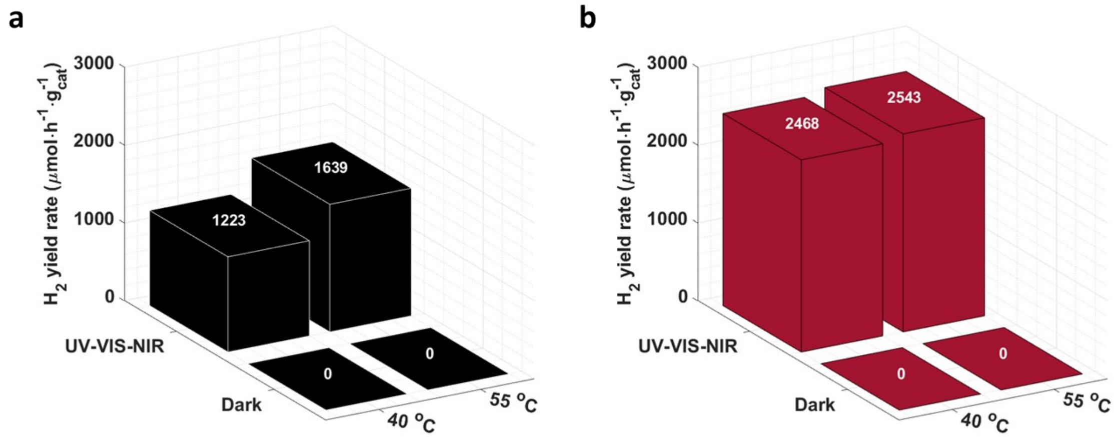

Figure S4. Photocatalytic HER profiles for **a)** TiO_2 and **b)** TiO_2/BiCuSeO under variable-temperature (40 °C and 55 °C) conditions.

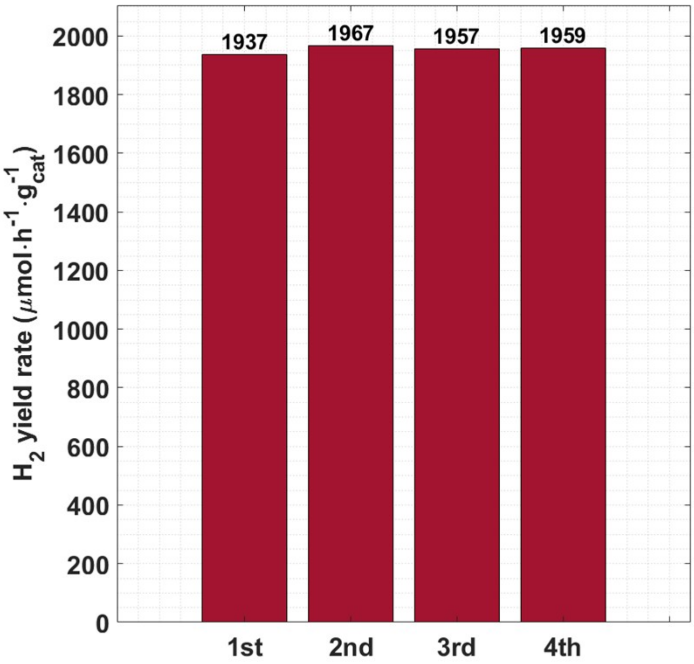

Figure S5. Cycling HER experiments for TiO_2/BiCuSeO.

Table S2. Open-circuit potentials for each (photo)electrochemical analysis.

SAMPLES	OCP (V)
TiO_2	0.267
TiO_2/BiCuSeO (0.5 wt%)	0.231
TiO_2/BiCuSeO (2 wt%)	0.227
TiO_2/BiCuSeO (8 wt%)	0.225

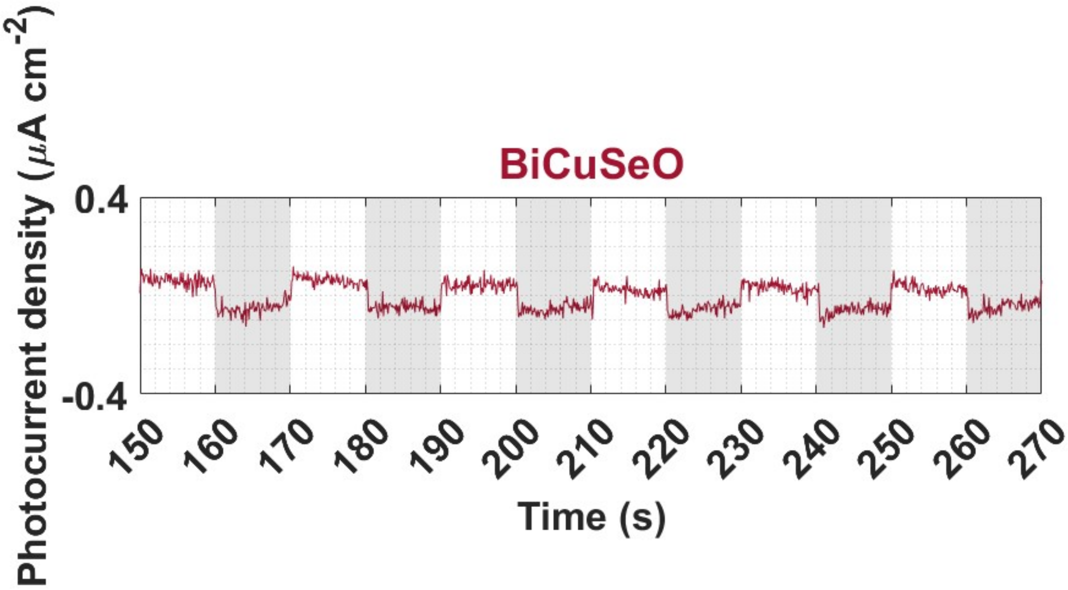

Figure S6. Transient photocurrent response for pure BiCuSeO.

References

1. Dong, L., X. Wang, P. Wang, and H. Yu, *A one-step solvothermal synthesis of the topological insulator Bi_2Te_3 nanorod-modified TiO_2 photocatalyst for enhanced H_2-evolution activity.* Journal of Materials Chemistry C, 2022. **10**(16): p. 6402-6410.
2. Li, N., H. Fan, J. Su, Y. Gao, and L. Ge, *Ultrathin Bi_2Se_3/CdS composite for efficient photocatalytic hydrogen evolution via high interfacial charge separation and photothermal effect.* New Journal of Chemistry, 2022. **46**(44): p. 21409-21417.
3. Rajamathi, C.R., U. Gupta, K. Pal, N. Kumar, H. Yang, Y. Sun, C. Shekhar, B. Yan, S. Parkin, U.V. Waghmare, C. Felser, and C.N.R. Rao, *Photochemical Water Splitting by Bismuth Chalcogenide Topological Insulators.* ChemPhysChem, 2017. **18**(17): p. 2322-2327.
4. Wang, X., X. Yang, L. Miao, J. Gao, L. Wu, N. Wang, and X. Li, *Decoration of Bi_2Se_3 nanosheets with a thin Bi_2SeO_2 layer for visible-light-driven overall water splitting.* International Journal of Hydrogen Energy, 2018. **43**(24): p. 10950-10958.
5. Chen, P., X. Dai, P. Xing, X. Zhao, Q. Zhang, S. Ge, J. Si, L. Zhao, and Y. He, *Microwave heating assisted synthesis of novel SnSe/g-C_3N_4 composites for effective photocatalytic H_2 production.* Journal of Industrial and Engineering Chemistry, 2019. **80**: p. 74-82.
6. Du, S., G. Li, X. Lin, S. Zhang, H. Xu, and P. Fang, *Highly efficient H_2 generation over Cu_2Se decorated $CdS_{0.95}Se_{0.05}$ nanowires by photocatalytic water reduction.* Chemical Engineering Journal, 2021. **409**: p. 128157.
7. Lai, T.-H., C.-W. Tsao, M.-J. Fang, J.-Y. Wu, Y.-P. Chang, Y.-H. Chiu, P.-Y. Hsieh, M.-Y. Kuo, K.-D. Chang, and Y.-J. Hsu, *Au@Cu_2O Core–Shell and Au@Cu_2Se Yolk–Shell Nanocrystals as Promising Photocatalysts in Photoelectrochemical Water Splitting and Photocatalytic Hydrogen Production.* ACS Applied Materials & Interfaces, 2022. **14**(36): p. 40771-40783.
8. Liu, B., L. Ning, C. Zhang, H. Zheng, S.F. Liu, and H. Yang, *Enhanced Visible-Light Photocatalytic H_2 Evolution in Cu_2O/Cu_2Se Multilayer Heterostructure Nanowires Having {111} Facets and Physical Mechanism.* Inorganic Chemistry, 2018. **57**(13): p. 8019-8027.
9. Liu, X., Y. Li, and P. Li, *Construction of multi-dimensional Cu_2Se@amorphous carbon@graphene nanobelt/g-C_3N_4 Z-scheme heterojunctions for photocatalytic hydrogen production.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2024. **686**: p. 133411.