

Supplementary Material

Schottky junctions with Bi@Bi₂MoO₆ core-shell photocatalysts toward high-efficiency solar N₂-to-ammonia conversion in aqueous phase

Meijiao Wang,^a Guosong Wei,^a Renjie Li,^a Meng Yu,^a Guangbo Liu,^{b,*} Yanhua Peng^{a,*}

^aCollege of Chemistry and Chemical Engineering, Qingdao University, Qingdao 266071, Shandong, P. R. China.

^bKey Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, Shandong, China

*Corresponding Authors

Email: liugb@qibebt.ac.cn, yhpeng@qdu.edu.cn

Table S1. Comparison of photocatalytic N₂ reduction activity on Bi-based photocatalysts.

Catalyst	Light Source	NH ₃ /NH ₄ ⁺ Yield (μmol·g ⁻¹ ·h ⁻¹)	Ref.
Bi@Bi ₂ MoO ₆	300 W Xe lamp	86.0	This work
Bi ₂ MoO ₆ -Br-Ov	300 W Xe lamp (λ≥420 nm)	32.0	[1]
BiOBr-Fe-OVs	300 W Xe lamp (λ > 400 nm)	46.1	[2]
In-Bi ₂ MoO ₆	300 W Xe lamp (30.72 mW·cm ⁻²)	53.4	[3]
g-C ₃ N ₄ /Bi ₂ MoO ₆	500 W Xe lamp (λ > 420)	43.6	[4]
Bi/BiOBr	300 W Xe lamp	78.6	[5]
W-Bi ₂ MoO ₆	Two 45 W white LED bulbs	2240	[6]
S-Bi ₂ MoO ₆	300 W Xe lamp (λ≥420 nm)	122.1	[7]
Fe/Bi ₂ O _{2.33}	300 W Xe lamp	118.7	[8]
BiOBr/Bi ₄ O ₅ Br ₂	300 W Xe lamp (λ≥420 nm)	66.9	[9]
In ₂ O ₃ /Bi ₂ MoO ₆	300 W Xe lamp (30.72 mW·cm ⁻²)	150.9	[10]
Bi ₂ MoO ₆ /Bi-MOF	300 W Xe lamp (λ≥420 nm)	125.8	[11]
BiVO ₄ / Sv-ZnIn ₂ S ₄	300 W Xe lamp (λ > 400 nm)	80.6	[12]
Bi ₁₂ O ₁₇ Cl ₂ -OVs	500 W Xe lamp	23.43	[13]

CeO ₂ -AD/Au	300 W Xe lamp	215.1	[14]
AgPt-TiO ₂	300 W Xe lamp	38.4	[15]
Ag/AgBr-δ-Bi ₂ O ₃	400 W Xe lamp	364.2	[16]
Au/TiO ₂ -Vo	300 W Xe lamp (λ≥420 nm)	78.6	[17]
Au/end-CeO ₂	Semiconductor diode laser (808 nm)	114.3	[18]

Reference

- [1] Wang, G.; Huo, T.; Deng, Q.; Yu, F.; Xia, Y.; Li, H.; Hou, W. Surface-layer bromine doping enhanced generation of surface oxygen vacancies in bismuth molybdate for efficient photocatalytic nitrogen fixation. *Applied Catalysis B: Environmental* **2022**, *310*, 121319, doi:10.1016/j.apcatb.2022.121319.
- [2] Chen, X.; Zhang, X.; Li, Y.-H.; Qi, M.-Y.; Li, J.-Y.; Tang, Z.-R.; Zhou, Z.; Xu, Y.-J. Transition metal doping BiOBr nanosheets with oxygen vacancy and exposed {102} facets for visible light nitrogen fixation. *Applied Catalysis B: Environmental* **2021**, *281*, 119516, doi:10.1016/j.apcatb.2020.119516.
- [3] Ma, T.; Yang, C.; Guo, L.; Soomro, R.A.; Wang, D.; Xu, B.; Fu, F. Refining electronic properties of Bi₂MoO₆ by In-doping for boosting overall nitrogen fixation via relay catalysis. *Applied Catalysis B: Environmental* **2023**, *330*, 122643, doi:10.1016/j.apcatb.2023.122643.
- [4] Vesali-Kermani, E.; Habibi-Yangjeh, A.; Diarmand-Khalilabad, H.; Ghosh, S. Nitrogen photofixation ability of g-C₃N₄ nanosheets/Bi₂MoO₆ heterojunction photocatalyst under visible-light illumination. *Journal of Colloid and Interface Science* **2020**, *563*, 81-91, doi:10.1016/j.jcis.2019.12.057.
- [5] Huang, Y.; Zhu, Y.; Chen, S.; Xie, X.; Wu, Z.; Zhang, N. Schottky Junctions with Bi Cocatalyst for Taming Aqueous Phase N₂ Reduction toward Enhanced Solar Ammonia Production. *Advanced Science* **2021**, *8*, doi:10.1002/advs.202003626.
- [6] Sharma, M.; Kumar, A.; Gill, D.; Jaiswal, S.; Patra, A.; Bhattacharya, S.; Krishnan, V. Boosting Photocatalytic Nitrogen Fixation via Nanoarchitectonics Using Oxygen Vacancy Regulation in W-Doped Bi₂MoO₆ Nanosheets. *ACS Applied Materials & Interfaces* **2023**, *15*, 55765-55778, doi:10.1021/acsami.3c12563.
- [7] Liu, Z.; Luo, M.; Cao, Y.; Meng, L.; Yang, Y.; Li, X. Tuning the electronic properties of Bi₂MoO₆ by S-doping to boost efficient photocatalytic nitrogen fixation reactions. *Journal of Catalysis* **2024**, *430*, doi:10.1016/j.jcat.2024.115347.
- [8] Zhu, C.; Zhang, L.; Cui, L.; Zhang, Z.; Li, R.; Wang, Y.; Wang, Y.; Fan, C.; Yu, Z.; Liu, J. Fe-Bi dual sites regulation of Bi₂O_{2.33} nanosheets to promote photocatalytic nitrogen fixation activity. *Journal of Colloid and Interface Science* **2024**, *661*, 46-58, doi:10.1016/j.jcis.2024.01.082.
- [9] Wang, H.; Chen, Z.; Shang, Y.; Lv, C.; Zhang, X.; Li, F.; Huang, Q.; Liu, X.; Liu, W.; Zhao, L.; et al. Boosting Carrier Separation on a BiOBr/Bi₄O₅Br₂ Direct Z-Scheme Heterojunction for Superior Photocatalytic Nitrogen Fixation. *Acs Catalysis* **2024**, doi:10.1021/acscatal.3c06169.
- [10] Huang, X.; Du, R.; Zhang, Y.; Ren, J.; Yang, Q.; Wang, K.; Ni, Y.; Yao, Y.; Ali Soomro, R.; Guo, L.; et al. Modulating charge oriented accumulation via interfacial chemical-bond on In₂O₃/Bi₂MoO₆

heterostructures for photocatalytic nitrogen fixation. *Journal of colloid and interface science* **2024**, 664, 33-44, doi:10.1016/j.jcis.2024.03.018.

[11] Dong, Q.; Li, X.; Sun, J.; Zhu, Y.; Liang, X.; Ren, H.; Labidi, A.; Wang, D.; Li, F.; Wang, C. Regulating concentration of surface oxygen vacancies in Bi₂MoO₆/Bi-MOF for boosting photocatalytic ammonia synthesis. *Journal of Catalysis* **2024**, 433, doi:10.1016/j.jcat.2024.115489.

[12] Zhang, G.; Yuan, X.; Xie, B.; Meng, Y.; Ni, Z.; Xia, S. S vacancies act as a bridge to promote electron injection from Z-scheme heterojunction to nitrogen molecule for photocatalytic ammonia synthesis. *Chemical Engineering Journal* **2022**, 433, doi:10.1016/j.cej.2021.133670.

[13] Kok, S.H.W.; Lee, J.; Chong, W.K.; Ng, B.-J.; Kong, X.Y.; Ong, W.J.; Chai, S.-P.; Tan, L.-L. Bismuth-rich Bi₁₂O₁₇Cl₂ nanorods engineered with oxygen vacancy defects for enhanced photocatalytic nitrogen fixation. *Journal of Alloys and Compounds* **2023**, 952, doi:10.1016/j.jallcom.2023.170015.

[14] Li, H.; Zhang, J.; Deng, X.; Wang, Y.; Meng, G.; Liu, R.; Huang, J.; Tu, M.; Xu, C.; Peng, Y.; et al. Structure and Defect Engineering Synergistically Boost High Solar-to-Chemical Conversion Efficiency of Cerium oxide/Au Hollow Nanomushrooms for Nitrogen Photofixation. *Angewandte Chemie-International Edition* **2024**, 63, doi:10.1002/anie.202316384.

[15] Bian, X.; Zhao, Y.; Zhang, S.; Li, D.; Shi, R.; Zhou, C.; Wu, L.-Z.; Zhang, T. Enhancing the Supply of Activated Hydrogen to Promote Photocatalytic Nitrogen Fixation. *Acs Materials Letters* **2021**, 3, 1521-1527, doi:10.1021/acsmaterialslett.1c00504.

[16] Gao, X.; Shang, Y.; Liu, L.; Gao, K. Ag plasmon resonance promoted 2D AgBr-δ-Bi₂O₃ nanosheets with enhanced photocatalytic ability. *Journal of Alloys and Compounds* **2019**, 803, 565-575, doi:10.1016/j.jallcom.2019.06.311.

[17] Yang, J.; Guo, Y.; Jiang, R.; Qin, F.; Zhang, H.; Lu, W.; Wang, J.; Yu, J.C. High-Efficiency "Working-in-Tandem" Nitrogen Photofixation Achieved by Assembling Plasmonic Gold Nanocrystals on Ultrathin Titania Nanosheets. *Journal of the American Chemical Society* **2018**, 140, 8497-8508, doi:10.1021/jacs.8b03537.

[18] Jia, H.; Du, A.; Zhang, H.; Yang, J.; Jiang, R.; Wang, J.; Zhang, C.-y. Site-Selective Growth of Crystalline Ceria with Oxygen Vacancies on Gold Nanocrystals for Near-Infrared Nitrogen Photofixation. *Journal of the American Chemical Society* **2019**, 141, 5083-5086, doi:10.1021/jacs.8b13062.