

Electronic Supporting Information

Rational design of 2D TiO₂-MoO₃ Step-scheme heterostructure for boosted photocatalytic overall water splitting

Gubran Alnaggar ^a, Khaled Alkanad ^b, Sujay Shekar G. Chandrashekar ^b, Mohammed Abdullah Bajiri ^c, Qasem A. Drmosh ^d, Lokanath N. Krishnappagowda ^b, Sannaiah Ananda ^{a,*}

^a Department of studies in Chemistry, University of Mysore, Manasagangothiri, Mysuru, 570006, India

^b Department of studies in Physics, University of Mysore, Manasagangothiri, Mysuru, 570006, India.

^c Department of Studies and Research in Industrial Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta-577 451, India

^d Interdisciplinary Research Center for Hydrogen and Energy Storage (IRC-HES), King Fahd University of Petroleum & Minerals (KFUPM), Dhahran 31261, Saudi Arabia.

* Corresponding author,

Email address: snananda@yahoo.com (S.Ananda)

CONTENTS

Fig.S1. Diagram representing the electrochemical synthesis process of TO-MO-30 heterostructure

Table.S1. The reported details of TiO₂/MoO₃

Fig.S2. SEM images of TO-MO-40 (a) and TO-MO-5 (b) heterostructure photocatalysts

Fig.S3. Selected area electron diffraction SAED image of TO-MO-30

Fig.S4. BJH Pore size distribution of pristine (a) MoO₃, (b) TiO₂ photocatalyst, and (c) TO-MO-5, (d) TO-MO-30, and (e) TO-MO-40 heterostructure photocatalysts

Fig.S5. EDX spectra of (a) TO-MO-5, (b) TO-MO-30, and (c) TO-MO-40 heterostructure photocatalyst

Fig.S6. SEM image of TO-MO-30 heterostructure photocatalyst after five cycles

Table S2. Photocatalytic water splitting comparison with existing MoO₃ based materials

Table S1.The reported details of TiO₂/MoO₃

Synthesis methods	Morphology	Application	Mechanism	Ref.
Electrochemical method	Sheets-like	Water splitting	Step-scheme	This work
Laser ablation	Spherical	Degradation (Methylene Blue)		1
impregnation method	NA	Degradation (Methylene Blue)		2
Ti-Mo alloy anodization	Nanotube layers	Water splitting	NA	3
incipient wetness method	Film	Gas 2-propanol		4
In-situ growth method	Nanobelts	Degradation Rhodamine B	heterojunction	5
sol-gel method	NA	Degradation Rhodamine B		6
hydrothermal treatment	sphere-like	Degradation benzyl alcohol	heterojunction	7
Langmuir blotting technique	Film	Degradation Stearic acid		8
Hydrothermal methods	Nanofiber	Degradation Rhodamine B		9
a modified sol-gel method	Mesoporous nanocrystals	Degradation Methylene Blue		10
sol-gel method	Rod decorated by sphere like	Degradation Molasses	Z-scheme	11
Hydrothermal method	Nanowire array	Lithium battery	NA	12
Hydrothermal and calcination	Nanofiber	Degradation Rhodamine B	Heterojunction	13
Sol-gel method	NA	Degradation Rhodamine B	Heterojunction	14
Impregnation method	NA	H ₂ production	Z-scheme	15
Hydrothermal	2D/1D	CO ₂ reduction	Plasmonic effect	16

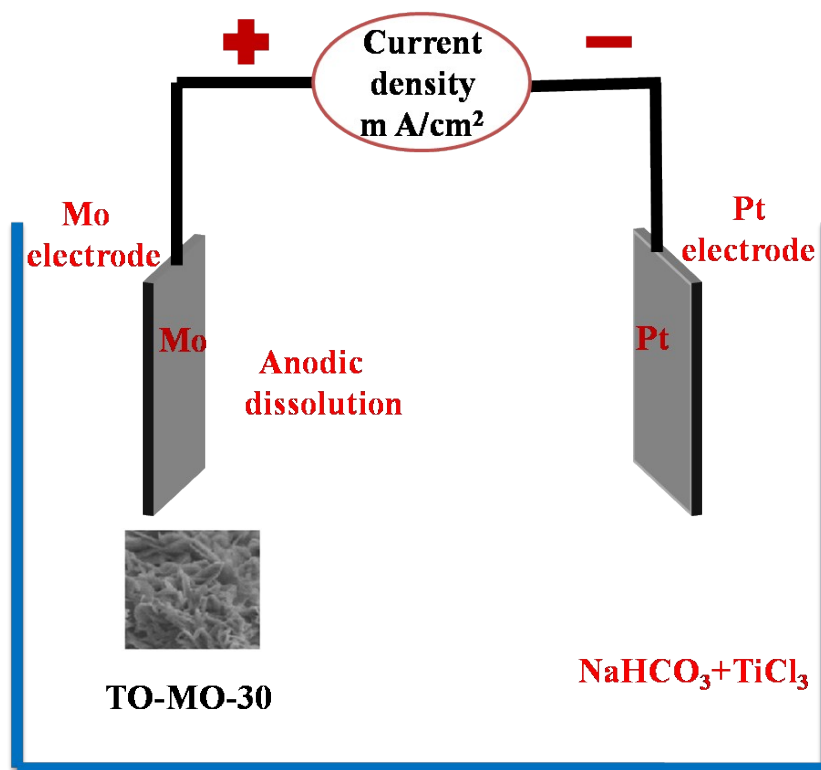


Fig.S1. Diagram representing the electrochemical synthesis process of TO-MO-30 heterostructure

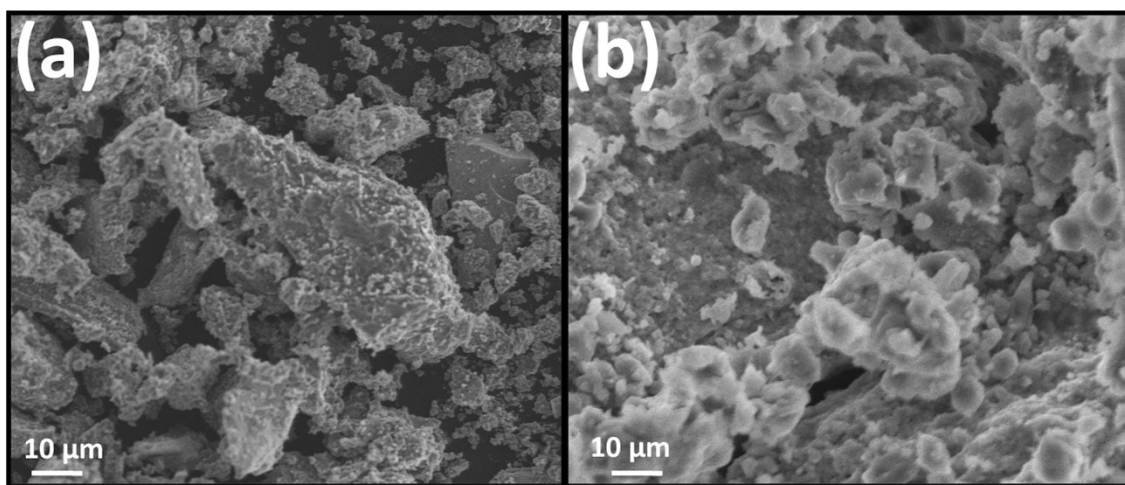


Fig.S2. SEM images of TO-MO-5 (a) and TO-MO-40 (b) heterostructure photocatalysts

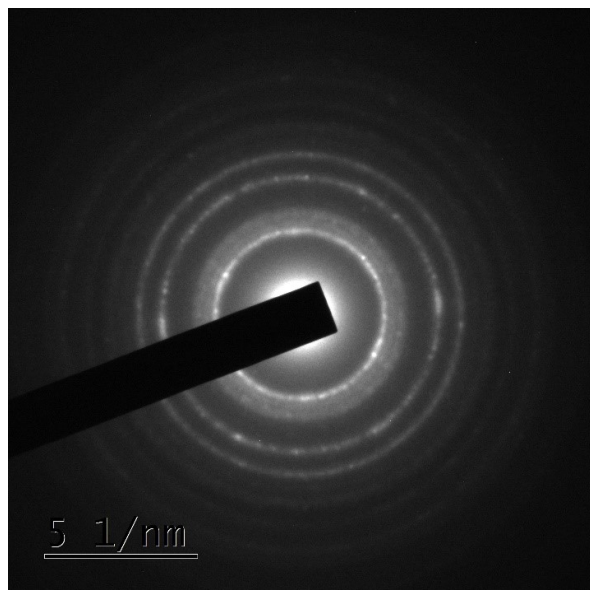


Fig.S3. Selected area electron diffraction SAED image of TO-MO-30

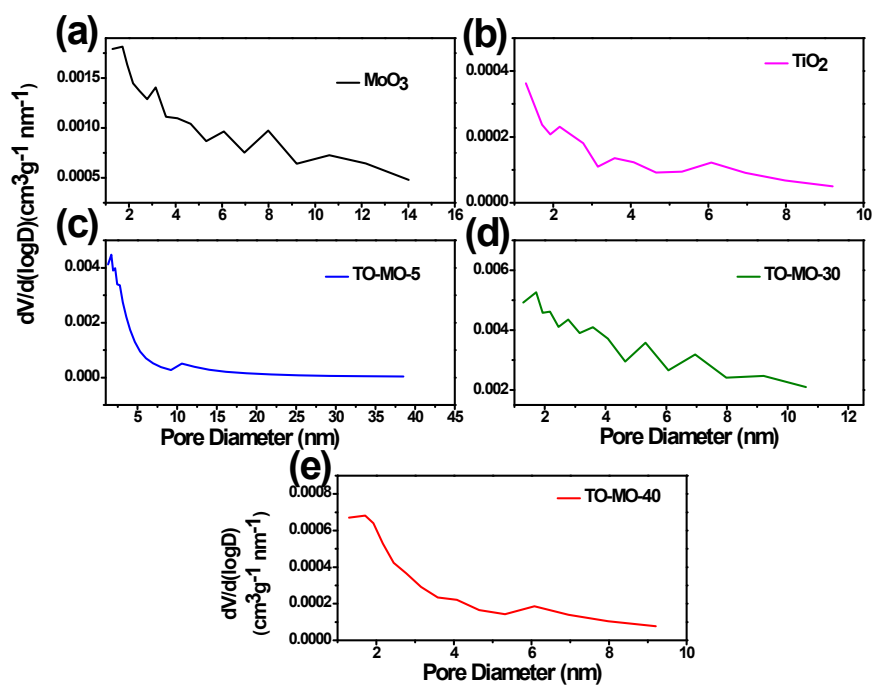


Fig.S4 BJH Pore size distribution of pristine (a) MoO₃, (b) TiO₂ photocatalyst, and (c) TO-MO-5, (d) TO-MO-30, and (e) TO-MO-40 heterostructure photocatalysts

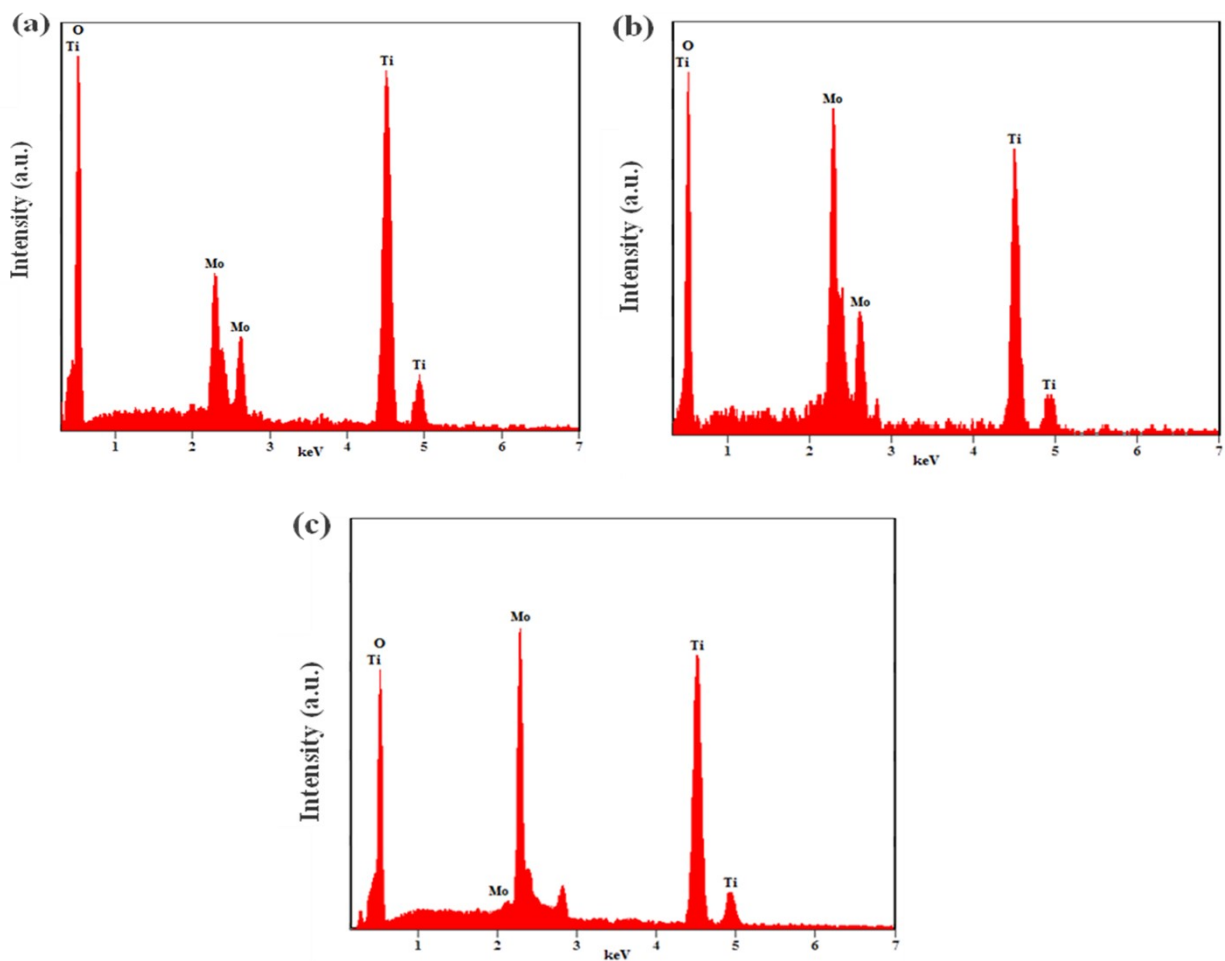


Fig.S5. EDX spectra of (a) TO-MO-5, (b) TO-MO-30, and (c) TO-MO-40 heterostructure photocatalyst

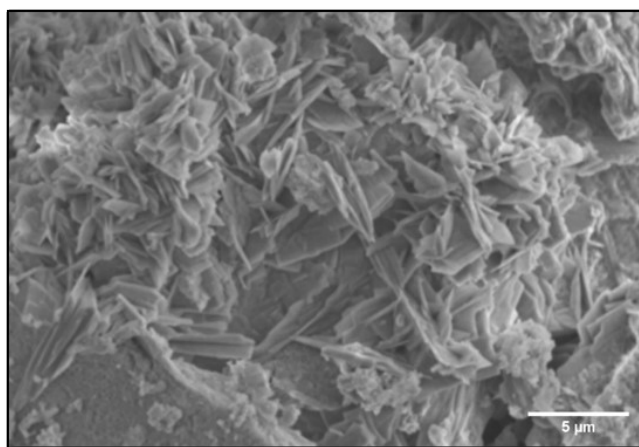


Fig.S6. SEM image of TO-MO-30 heterostructure photocatalyst after five cycles

Table S2. Photocatalytic water splitting comparison with existing MoO₃ based materials

	Catalyst	Evolved H ₂	Evolved O ₂	AQE (H ₂)	Light source	Reff.
1	MoO ₃ /Polyamide	~1000 μmol/h/g	----	2.3% at 420 nm	Solar light	17
2	Pt/MoO ₃ /TiO ₂	169 μmol/h/g	-----	-----	UV light	18
3	2D/2D MoO ₃ -x/g-C ₃ N ₄	85 μmol/h/g	-----	7.8 % at λ > 420 nm	Visible light	19
4	MoO ₃ /g-C ₃ N ₄	512.5 μmol/ h/ g	-----	-----	Visible light	20
5	amine-CdS/MoO ₃	1029.8 μmol/h/g	-----	-----	Visible light	21
6	Cu ₂ S-MoO ₃	21.568 μmol/h/g	-----	-----	400W Xenon lamp (UV-Vis)	22
7	MoO ₃ /ZnO	2.5 ml (Volume)	-----	-----	Visible light	23
8	CdS QD/ MoO ₃ -OV/g-C ₃ N ₄	294.32 μmol/h/g and 1408.57 μmol/h/g	-----	16.35% at 420 nm	Visible light and Solar light	24
9	MoO ₃ /g-C ₃ N ₄	20.52 μmol/h/g	-----	-----	Visible light	25
10	HxMoO ₃ @ZnIn ₂ S ₄ (HZ)	110 μmol/h/g	-----	32.95 % at 420 nm	Visible light	26
11	TiO ₂ -MoO ₃	151 μmol/h/g	76 μmol/h/g	1.38% at 420 nm	Simulated solar light	This work

References

1. Khan AQ, Yuan S, Niu S, Zheng L, Li W, Zeng H. Synthesis of molybdenum oxide-titanium dioxide nanocomposites with ultrashort laser ablation in water. *Optics express*. 2017 Jun 12;25(12):A539-46.
2. Yang H, Li X, Wang A, Wang Y, Chen Y. Photocatalytic degradation of methylene blue by MoO₃ modified TiO₂ under visible light. *Chinese Journal of Catalysis*. 2014 Jan 1;35(1):140-7.
3. Yang M, Zhang L, Jin B, Huang L, Gan Y. Enhanced photoelectrochemical properties and water splitting activity of self-ordered MoO₃-TiO₂ nanotubes. *Applied Surface Science*. 2016 Feb 28;364:410-5.
4. Song KY, Park MK, Kwon YT, Lee HW, Chung WJ, Lee WI. Preparation of transparent particulate MoO₃/TiO₂ and WO₃/TiO₂ films and their photocatalytic properties. *Chemistry of materials*. 2001 Jul 16;13(7):2349-55.
5. Liu H, Lv T, Zhu C, Zhu Z. Direct bandgap narrowing of TiO₂/MoO₃ heterostructure composites for enhanced solar-driven photocatalytic activity. *Solar Energy Materials and Solar Cells*. 2016 Aug 1;153:1-8.
6. Bai S, Liu H, Sun J, Tian Y, Chen S, Song J, Luo R, Li D, Chen A, Liu CC. Improvement of TiO₂ photocatalytic properties under visible light by WO₃/TiO₂ and MoO₃/TiO₂ composites. *Applied Surface Science*. 2015 May 30;338:61-8.
7. Diniz J, Nunes CD, Monteiro OC. Novel approach to synthesise MoO₃-TiO₂ nanocomposites for the photo-assisted oxidation of benzyl alcohol to benzaldehyde. *Inorganic Chemistry Communications*. 2020 Sep 1;119:108099.

8. Natori H, Kobayashi K, Takahashi M. Fabrication and photocatalytic activity of TiO₂/MoO₃ particulate films. *Journal of Oleo Science*. 2009;58(4):203-11.
9. Lu M, Shao C, Wang K, Lu N, Zhang X, Zhang P, Zhang M, Li X, Liu Y. p-MoO₃ nanostructures/n-TiO₂ nanofiber heterojunctions: controlled fabrication and enhanced photocatalytic properties. *ACS applied materials & interfaces*. 2014 Jun 25;6(12):9004-12.
10. Kong F, Huang L, Luo L, Chu S, Wang Y, Zou Z. Synthesis and characterization of visible light driven mesoporous nano-photocatalyst MoO₃/TiO₂. *Journal of nanoscience and nanotechnology*. 2012 Mar 1;12(3):1931-7.
11. Navgire M, Yelwande A, Tayde D, Arbad B, Lande M. Photodegradation of molasses by a MoO₃-TiO₂ nanocrystalline composite material. *Chinese Journal of Catalysis*. 2012 Feb 1;33(2-3):261-6.
12. Wang C, Wu L, Wang H, Zuo W, Li Y, Liu J. Fabrication and shell optimization of synergistic TiO₂-MoO₃ core-shell nanowire array anode for high energy and power density lithium-ion batteries. *Advanced Functional Materials*. 2015 Jun;25(23):3524-33.
13. Lu M, Shao C, Wang K, Lu N, Zhang X, Zhang P, Zhang M, Li X, Liu Y. p-MoO₃ nanostructures/n-TiO₂ nanofiber heterojunctions: controlled fabrication and enhanced photocatalytic properties. *ACS applied materials & interfaces*. 2014 Jun 25;6(12):9004-12.
14. Bai S, Liu H, Sun J, Tian Y, Chen S, Song J, Luo R, Li D, Chen A, Liu CC. Improvement of TiO₂ photocatalytic properties under visible light by WO₃/TiO₂ and MoO₃/TiO₂ composites. *Applied Surface Science*. 2015 May 30;338:61-8.
15. Ma BJ, Kim JS, Choi CH, Woo SI. Enhanced hydrogen generation from methanol aqueous solutions over Pt/MoO₃/TiO₂ under ultraviolet light. *International journal of hydrogen energy*. 2013 Mar 27;38(9):3582-7.
16. Ma BJ, Kim JS, Choi CH, Woo SI. Enhanced hydrogen generation from methanol aqueous solutions over Pt/MoO₃/TiO₂ under ultraviolet light. *International journal of hydrogen energy*. 2013 Mar 27;38(9):3582-7.
17. Ma C, Zhou J, Cui Z, Wang Y, Zou Z. In situ growth MoO₃ nanoflake on conjugated polymer: An advanced photocatalyst for hydrogen evolution from water solution under solar light. *Solar Energy Materials and Solar Cells*. 2016 Jun 1;150:102-11.
18. Ma BJ, Kim JS, Choi CH, Woo SI. Enhanced hydrogen generation from methanol aqueous solutions over Pt/MoO₃/TiO₂ under ultraviolet light. *International journal of hydrogen energy*. 2013 Mar 27;38(9):3582-7.
19. Guo Y, Chang B, Wen T, Zhang S, Zeng M, Hu N, Su Y, Yang Z, Yang B. A Z-scheme photocatalyst for enhanced photocatalytic H₂ evolution, constructed by growth of 2D plasmonic MoO₃-x nanoplates onto 2D g-C₃N₄ nanosheets. *Journal of colloid and interface science*. 2020 May 1;567:213-23.
20. Shi J, Zheng B, Mao L, Cheng C, Hu Y, Wang H, Li G, Jing D, Liang X. MoO₃/g-C₃N₄ Z-scheme (S-scheme) system derived from MoS₂/melamine dual precursors for enhanced photocatalytic H₂ evolution driven by visible light. *International Journal of Hydrogen Energy*. 2021 Jan 11;46(3):2927-35.
21. Wang S, Zhao X, Sharif HM, Chen Z, Chen Y, Zhou B, Xiao K, Yang B, Duan Q. Amine-CdS for exfoliating and distributing bulk MoO₃ for photocatalytic hydrogen evolution and Cr (VI) reduction. *Chemical Engineering Journal*. 2021 Feb 15;406:126849.
22. Patil SB, Kishore B, Manjunath K, Reddy V, Nagaraju G. One step hydrothermal synthesis of novel Cu₂S-MoO₃ nanocomposite for lithium ion battery and photocatalytic applications. *International Journal of Hydrogen Energy*. 2018 Feb 22;43(8):4003-14.

23. Bounache K, Boudjemaa A, Boumaza S, Haddad M, Tallas W, Belhadi A, Trari M. Visible Light Hydrogen Evolution over α -MoO₃ and α -MoO₃/ZnO Hetero-Junction. *Open Journal of Physical Chemistry*. 2021 Jun 28;11(3):144-56.
24. Devarayapalli KC, Lee K, Nam ND, Vattikuti SP, Shim J. Microwave synthesized nano-photosensitizer of CdS QD/MoO₃-OV/g-C₃N₄ heterojunction catalyst for hydrogen evolution under full-spectrum light. *Ceramics International*. 2020 Dec 15;46(18):28467-80.
25. Li K, Wu W, Jiang Y, Wang Z, Liu X, Li J, Xia D, Xu X, Fan J, Lin K. Highly enhanced H₂ evolution of MoO₃/g-C₃N₄ hybrid composites based on a direct Z-scheme photocatalytic system. *Inorganic Chemistry Frontiers*. 2021;8(5):1154-65.
26. Xing F, Cheng C, Zhang J, Liu Q, Chen C, Huang C. Tunable charge transfer efficiency in HxMoO₃@ ZnIn₂S₄ hierarchical direct Z-scheme heterojunction toward efficient visible-light-driven hydrogen evolution. *Applied Catalysis B: Environmental*. 2021 May 15;285:119818.