Supplementary Information

MoS_2/CdS Nanosheets-on-Nanorod Heterostructure for Highly Efficient Photocatalytic H_2 Generation under Visible Light Irradiation

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This file includes Figure S1-S10 and Table S1.

Figure S1

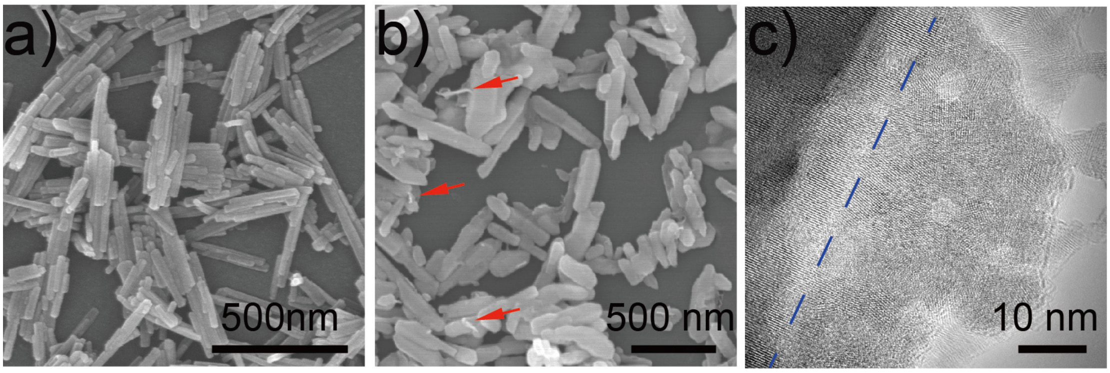

Figure S1. SEM images of (a) CdS nanorods and (b) MoS_2/CdS nanohybrid (10 wt %); (c) HRTEM image of the interface between MoS_2 nanosheet and CdS nanorod.

Figure S2

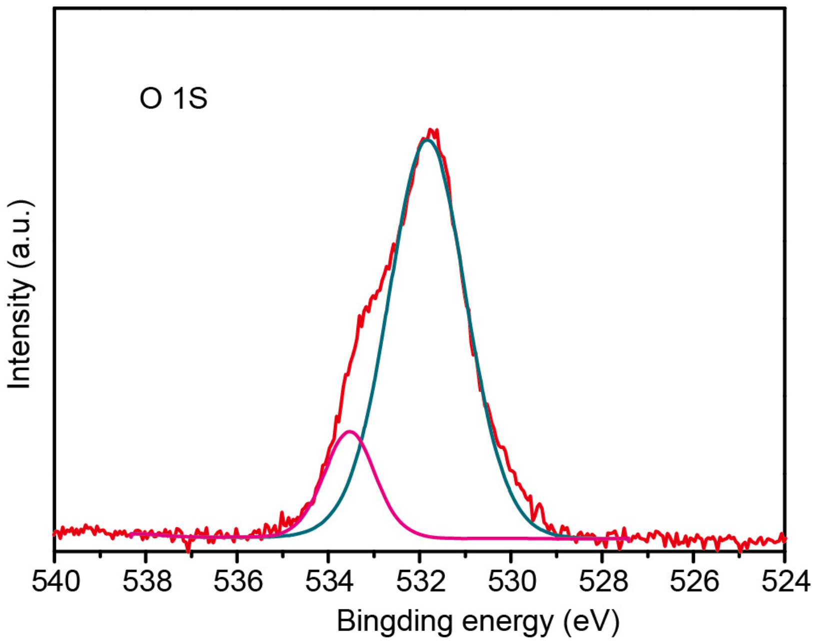

Figure S2. High-resolution XPS spectrum of O 1s

Figure S3

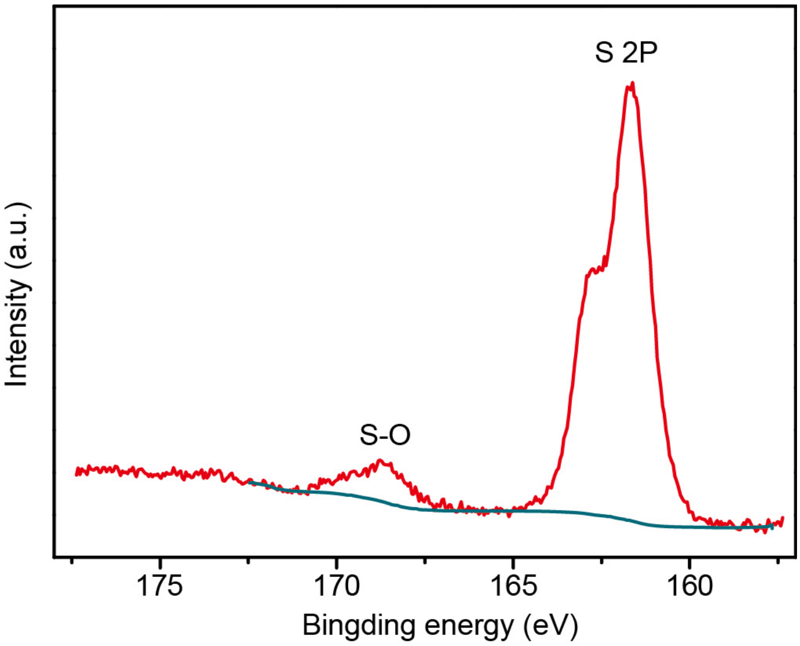

Figure S3. High-resolution XPS spectrum of S 2p

Figure S4

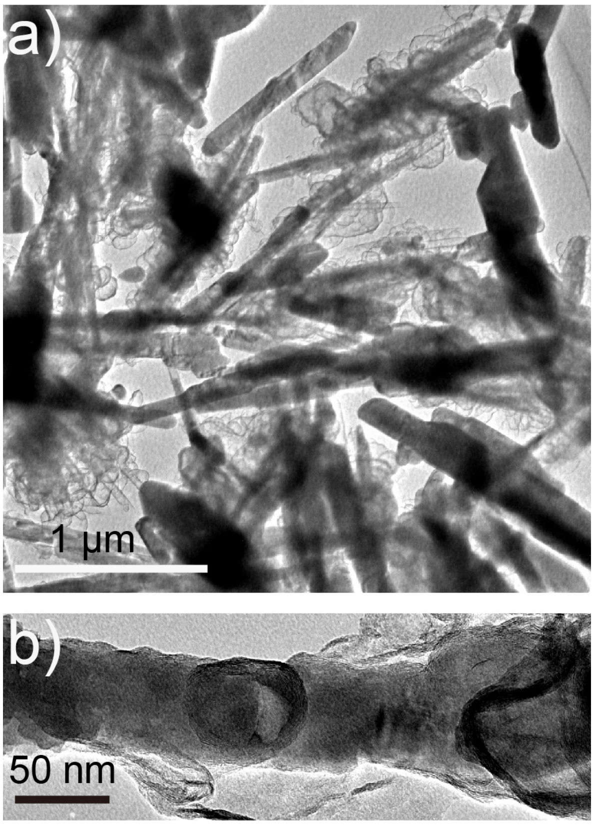

Figure S4. (a,b) TEM images of MoS_2/CdS (40 wt %) with large nanosheets coated on the surfaces of CdS nanorods.

Figure S5

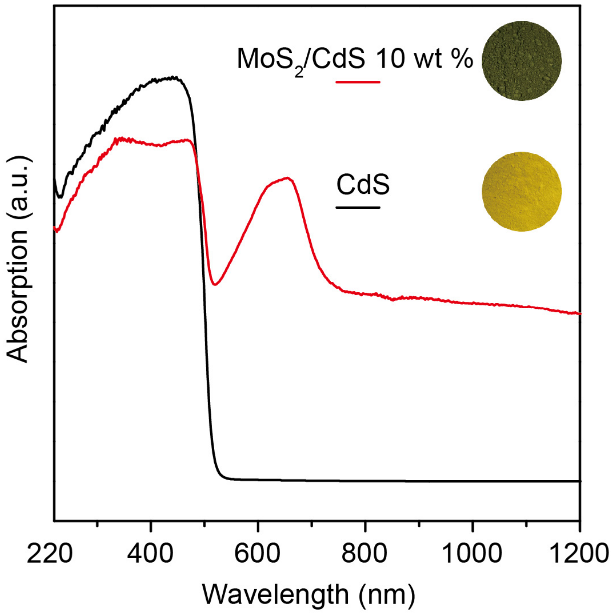

Figure S5. The UV-Vis-NIR curves of CdS and MoS_2/CdS nanohybrid (10 wt %)

Figure S6

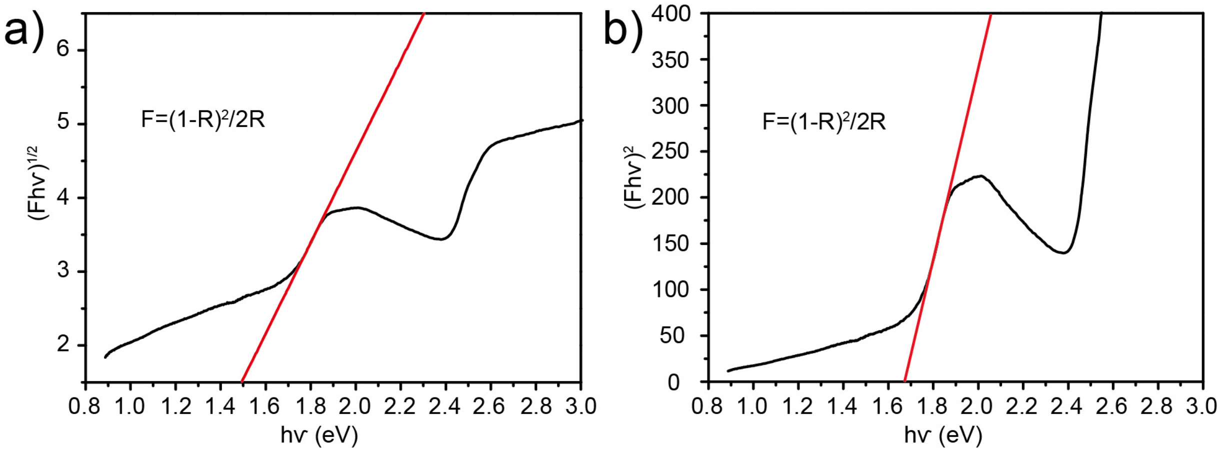

Figure S6. $(Fh\nu)^{1/2}$ (a) and $(Fh\nu)^2$ (b) as a function of photon energy (hν), where F is the Kubelka–Munk function of the diffuse reflectance R from the reflection spectrum of MoS_2/CdS (10 wt %) (Figure S7).

The bulk MoS_2 is indirect band gap semiconductor with band gap energy of ~1.3 eV while the single-layer MoS_2 is direct band gap semiconductor with band gap of 1.8 eV.[1-3] We measured the reflection spectra of MoS_2/CdS and calculated band gap of MoS_2 from the corresponding modified Kubelka–Munk function ($(Fh\nu)^n=A(h\nu-E_g)$, where n=1/2 for indirect band gap semiconductor; n = 2 for direct band gap semiconductor. As shown in the following Figures, the optical band energy of MoS_2 was calculated to be about 1.49 for indirect band gap model and 1.68 eV for direct band gap model. This result implies that MoS_2 grown on CdS is more like MoS_2 thin layers with a direct band gap,[2] which is consistent with the TEM observation (Figure 2f and g).

Figure S7

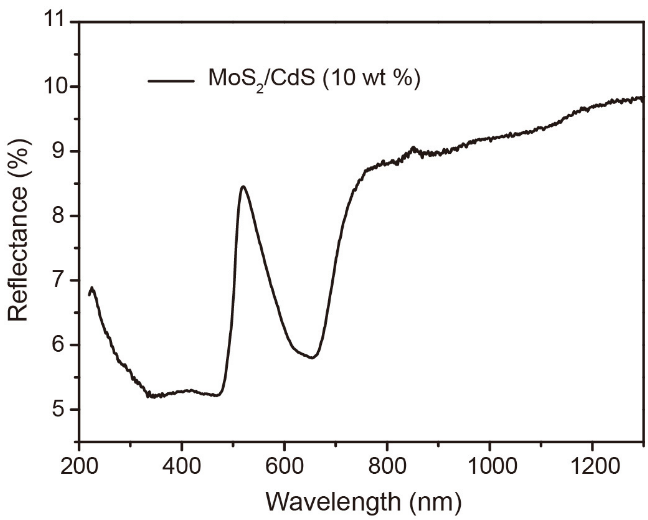

Figure S7. UV-Vis-NIR diffuse reflectance spectrum of MoS_2/CdS

Figure S8

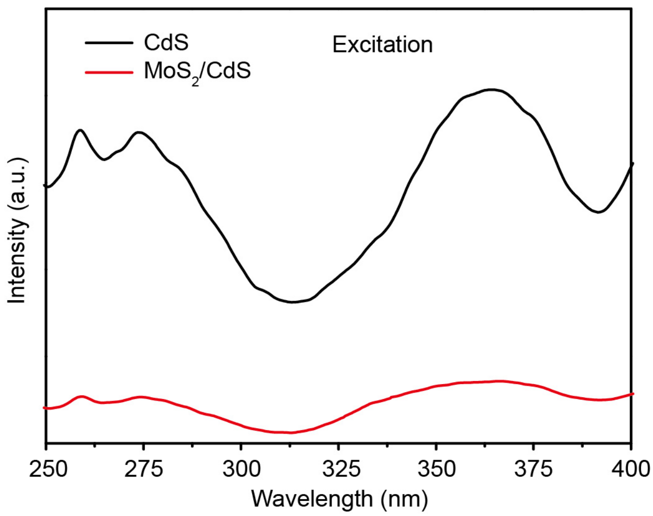

Figure S8. The fluorescence excitation spectra of CdS nanorods and MoS_2/CdS nanosheets-on-nanorods (10 wt %)

Figure S9

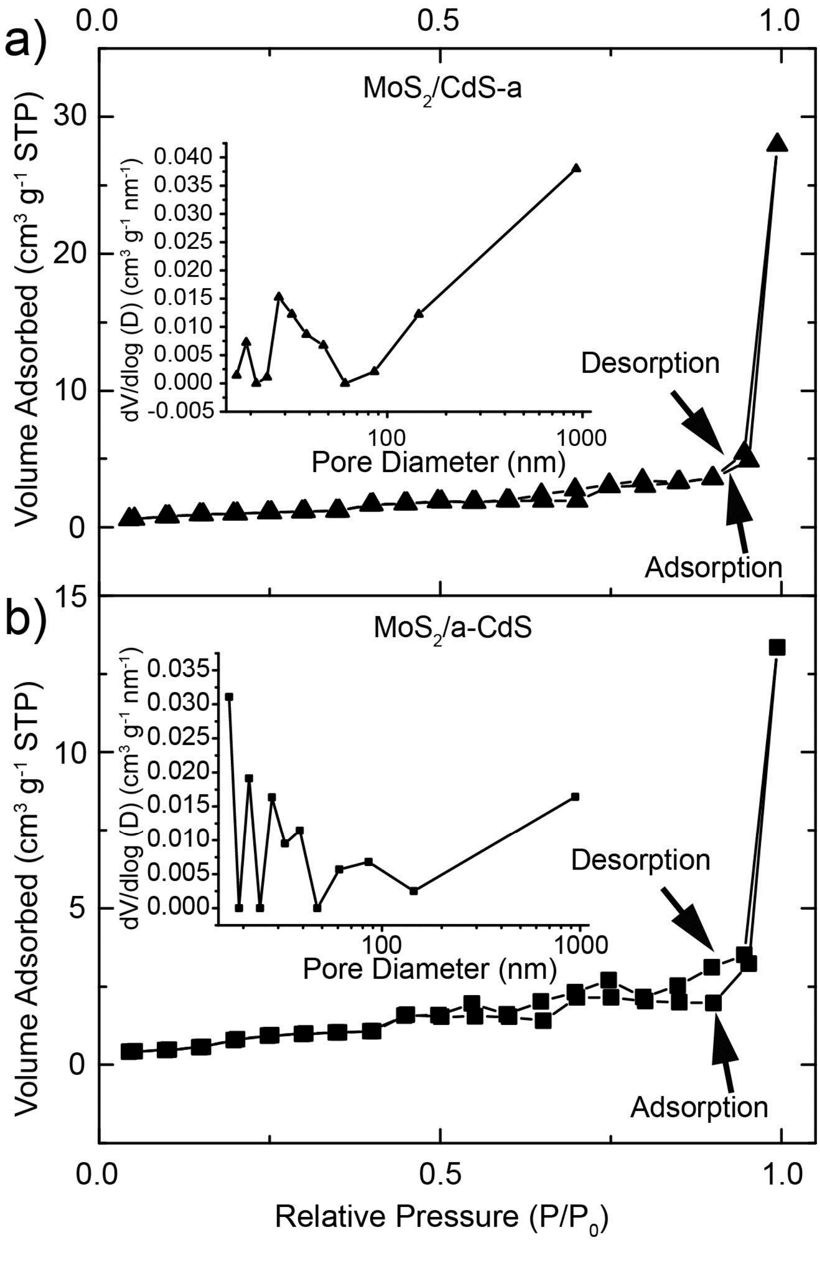

Figure S9. (a, b) N_2 adsorption/desorption isotherms, and the corresponding pore size distribution (insets) of MoS_2/CdS-a and MoS_2/a-CdS.

Figure S10

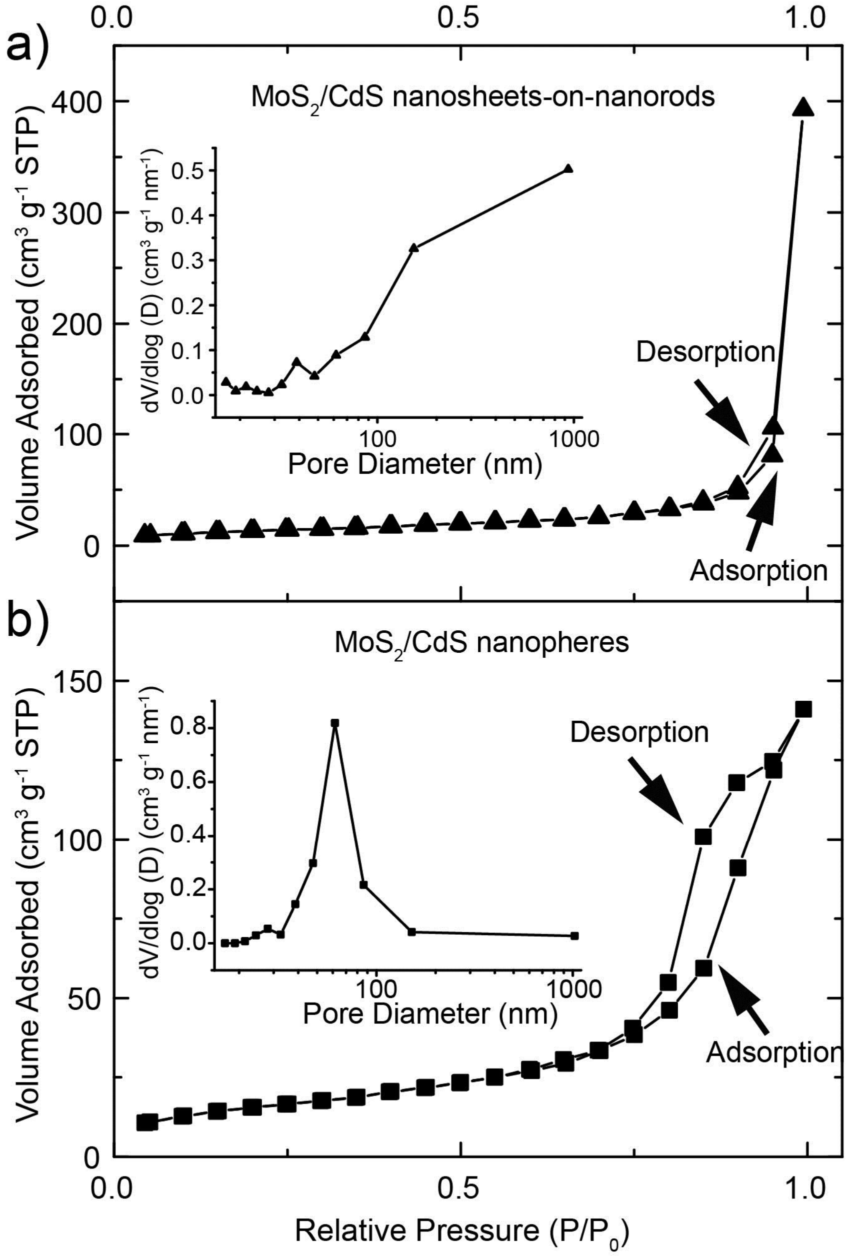

Figure S10. (a, b) N_2 adsorption/desorption isotherms, and the corresponding pore size distribution (insets) of MoS_2/CdS nanosheets-on-nanorods and MoS_2/CdS nanospheres.

Table S1. Performance comparison of CdS-based photocatalysts with MoS_2 and noble metal as a cocatalyst recently reported.

Samples	Mass (g)	Light source	Incident light	Sacrificial agents	H_2 (mmol/g/h)	AQE (%)	Ref.
MoS_2/CdS	0.08	300W Xe	≥420 nm	Na_2S-Na_2SO_3	4.77	------	4
MoS_2-Cr/CdS	0.01	300W Xe	≥420 nm	Na_2S-Na_2SO_3	3.80	------	5
MoS_2/CdS	0.1	300W Xe	≥420 nm	lactic acid	5.4	------	6
MoS_2/CdS	0.01	300W Xe	≥420 nm	lactic acid	1.47	------	7
MoS_2/CdS	0.1	300W Xe	≥420 nm	lactic acid	5.33	------	8
MoS_2/CdS	0.2	300W Xe	≥420 nm	lactic acid Na_2S-Na_2SO_3	12.95 10.05	38.4 30.2	2
MoS_2/CdS	0.1	300W Xe	≥400 nm	lactic acid	4.06	------	9
MoS_2/CdS /Gr	0.02	300W Xe	≥420 nm	lactic acid	6.27	------	10
MoS_2/CdS/Gr	0.2	300W Xe	≥420 nm	lactic acid	9.0	28.1	11
MoS_2-UiO-66/CdS	0.02	300W Xe	≥420 nm	lactic acid	32.5	23.6	12
TiO_2/MoS_2/Gr	0.08	350W Xe	UV-365nm	ethanol	2.07	9.7	13
MoS_2/TiO_2	0.016	300W Xe		Na_2S-Na_2SO_3	1.6	------	14
MoS_2/g-CN	0.02	300W Xe	≥420 nm	lactic acid	0.97	2.1	15
MoS_2/TiO_2	0.001	UV-LED		lactic acid	0.55	9.7	16
MoS_2/Gr	0.01	300W Xe	AM 1.5	ethanol	24.8×10^{-3}	------	17
MoS_2/Gr	0.02	300W Xe	≥420 nm	triethanolamine	4.19	24	18
MoS_2/$Zn_xCd_{1-x}S$	0.02	300W Xe	≥420 nm	Na_2S-Na_2SO_3	0.42	------	19
MoS_2/TiO_2	0.2	300W Xe	UV(250-380)	methanol	0.75	------	20
Pt/CdS	------	LED	455 nm	sulfite	0.003	9.6%	21
Ru/CdS-N	0.05	300W Xe	≥400 nm	lactic acid	12.89	------	22
Pt/CdS	0.05	300W Xe	≥420 nm	$(NH_4)_2SO_3$	33	31%	23

CdS/Pt/Gr	0.05	300W Xe	≥400 nm	Na_2S-Na_2SO_3	3.984	------	24
CdS/Pt/Gr	0.05	Hg Lamp	365 nm	methanol	5.029	------	25
MoS_2/CdS Nanosheets-on-nanorods	0.2	300W Xe	≥420 nm	lactic acid	49.80	41.37	This work

References

1. Radisavljevic B.; Radenovic A.; Brivio J.; Giacometti V.; Kis A., Single-layer MoS_2 transistors. *Nat. Nano.* **2011,** *6*, 147-150.
2. Chang, K.; Li, M.; Wang, T.; Ouyang, S.; Li, P.; Liu, L.; Ye, J., Drastic Layer-Number-Dependent Activity Enhancement in Photocatalytic H_2 Evolution over nMoS_2/CdS (n ≥ 1) Under Visible Light. *Adv. Energy Mater.* **2015,** *5*, 1402279.
3. Conley, H. J.; Wang, B.; Ziegler, J. I.; Haglund, R. F.; Pantelides, S. T.; Bolotin, K. I., Bandgap Engineering of Strained Monolayer and Bilayer MoS_2. *Nano Lett.* **2013,** *13*, 3626-3630.
4. Xiong, J.; Liu, Y.; Wang, D.; Liang, S.; Wu, W.; Wu, L., An Efficient Cocatalyst of Defect-Decorated MoS_2 Ultrathin Nanoplates for the Promotion of Photocatalytic Hydrogen Evolution over CdS Nanocrystal. *J. Mater. Chem. A* **2015,** *3*, 12631-12635.
5. Yang, L.; Zhong, D.; Zhang, J.; Yan, Z.; Ge, S.; Du, P.; Jiang, J.; Sun, D.; Wu, X.; Fan, Z.; Dayeh, S. A.; Xiang, B., Optical Properties of Metal-Molybdenum Disulfide Hybrid Nanosheets and Their Application for Enhanced Photocatalytic Hydrogen Evolution. *ACS Nano* **2014,** *8*, 6979–6985.
6. Zong, X.; Yan, H.; Wu, G.; Ma, G.; Wen, F.; Wang, L.; Li, C., Enhancement of Photocatalytic H_2 Evolution on CdS by Loading MoS_2 as Cocatalyst under Visible Light Irradiation. *J. Am. Chem. Soc.* **2008,** *130*, 7176-7177.
7. Chen, J.; Wu, X.; Yin, L.; Li, B.; Hong, X.; Fan, Z.; Chen, B.; Xue, C.; Zhang, H., One-pot Synthesis of CdS Nanocrystals Hybridized with Single-Layer Transition-Metal Dichalcogenide Nanosheets for Efficient Photocatalytic Hydrogen Evolution. *Angew. Chem.* **2015,** *127*, 1226-1230.
8. Zong, X.; Han, J.; Ma, G.; Yan, H.; Wu, G.; Li, C., Photocatalytic H_2 Evolution on CdS Loaded with WS_2 as Cocatalyst under Visible Light Irradiation. *J. Phys. Chem. C* **2011,** *115*, 12202-12208.
9. Xu, J.; Cao, X., Characterization and Mechanism of MoS_2/CdS Composite Photocatalyst Used for Hydrogen Production from Water Splitting under Visible Light. *Chem. Eng. J.* **2015,** *260*, 642-648.
10. Jia, T.; Kolpin, A.; Ma, C.; Chan, R. C.; Kwok, W. M.; Tsang, S. C., A Graphene Dispersed CdS-MoS_2 Nanocrystal Ensemble for Cooperative Photocatalytic Hydrogen Production from Water. *Chem. Commun.* **2014,** *50*, 1185-1188.
11. Chang, K.; Mei, Z.; Wang, T.; Kang, Q.; Ouyang, S.; Ye, J., MoS_2/Graphene Cocatalyst for Efficient Photocatalytic H_2 Evolution under Visible Light Irradiation. *ACS Nano* **2014,** *8*, 7078–7087
12. Shen, L.; Luo, M.; Liu, Y.; Liang, R.; Jing, F.; Wu, L., Noble-Metal-Free MoS_2 Co-Catalyst Decorated UiO-66/CdS Hybrids for Efficient Photocatalytic H_2 Production. *Appl. Catal. B* **2015,** *166*, 445-453.

13. Xiang, Q.; Yu, J.; Jaroniec, M., Synergetic Effect of MoS_2 and Graphene as Cocatalysts for Enhanced Photocatalytic H_2 Production Activity of TiO_2 Nanoparticles. *J. Am. Chem. Soc.* **2012,** *134*, 6575-6578.
14. Zhou, W.; Yin, Z.; Du, Y.; Huang, X.; Zeng, Z.; Fan, Z.; Liu, H.; Wang, J.; Zhang, H., Synthesis of Few-Layer MoS_2 Nanosheet-Coated TiO_2 Nanobelt Heterostructures for Enhanced Photocatalytic Activities. *Small* **2013,** *9*, 140-147.
15. Hou, Y.; Laursen, A. B.; Zhang, J.; Zhang, G.; Zhu, Y.; Wang, X.; Dahl, S.; Chorkendorff, I., Layered Nanojunctions for Hydrogen-Evolution Catalysis. *Angew. Chem. Int. Ed.* **2013,** *52*, 3621-3625.
16. Zhang, P.; Tachikawa, T.; Fujitsuka, M.; Majima, T., Efficient Charge Separation on 3D Architectures of TiO_2 Mesocrystals Packed with A Chemically Exfoliated MoS_2 Shell in Synergetic Hydrogen Evolution. *Chem. Commun.* **2015,** *51*, 7187-7190.
17. Meng, F.; Li, J.; Cushing, S. K.; Zhi, M.; Wu, N., Solar Hydrogen Generation by Nanoscale p-n Junction of p-type Molybdenum Disulfide/n-type Nitrogen-Doped Reduced Graphene Oxide. *J. Am. Chem. Soc.* **2013,** *135*, 10286-10289.
18. Min, S.; Lu, G., Sites for High Efficient Photocatalytic Hydrogen Evolution on a Limited-Layered MoS_2 Cocatalyst Confined on Graphene Sheets—The Role of Graphene. *J. Phys. Chem. C* **2012,** *116*, 25415-25424.
19. Nguyen, M.; Tran, P. D.; Pramana, S. S.; Lee, R. L.; Batabyal, S. K.; Mathews, N.; Wong, L. H.; Graetzel, M., In Situ Photo-Assisted Deposition of MoS_2 Electrocatalyst onto Zinc Cadmium Sulphide Nanoparticle Surfaces to Construct an Efficient Photocatalyst for Hydrogen Generation. *Nanoscale* **2013,** *5*, 1479–1482.
20. Zhu, Y.; Ling, Q.; Liu, Y.; Wang, H.; Zhu, Y., Photocatalytic H_2 Evolution on MoS_2-TiO_2 Catalysts Synthesized via Mechanochemistry. *Phys.Chem.Chem.Phys.* **2015,** *17*, 933-940.
21. Wu, K.; Chen, Z.; Lv, H.; Zhu, H.; Hill, C. L.; Lian, T., Hole Removal Rate Limits Photodriven H_2 Generation Efficiency in CdS-Pt and CdSe/CdS-Pt Semiconductor Nanorod-Metal Tip Heterostructures. *J. Am. Chem. Soc.* **2014,** *136*, 7708-7016.
22. Zhang, L.; Fu, X.; Meng, S.; Jiang, X.; Wang, J.; Chen, S., Ultra-Low Content of Pt Modified CdS Nanorods: One-Pot Synthesis and High Photocatalytic Activity for H_2 Production under Visible Light. *J. Mater. Chem. A* **2015,** *3*, 23732–23742.
23. Luo, M.; Yao, W.; Huang, C.; Wu, Q.; Xu, Q., Shape Effects of Pt Nanoparticles on Hydrogen Production via Pt/CdS Photocatalysts under Visible Light. *J. Mater. Chem. A* **2015,** *3*, 13884-13891.
24. Cao, M.; Wang, P.; Ao, Y.; Wang, C.; Hou, J.; Qian, J., Investigation on Graphene and Pt Co-Modified CdS Nanowires with Enhanced Photocatalytic Hydrogen Evolution Activity under Visible Light Irradiation. *Dalton Trans.* **2015,** *44*, 16372-16382.
25. Gao, P.; Liu, J.; Lee, S.; Zhang, T.; Sun, D., High Quality Graphene Oxide–CdS–Pt Nanocomposites for Efficient Photocatalytic Hydrogen Evolution. *J. Mater. Chem.* **2012,** *22*, 2292-2298.