

Supplementary Information

Boosting Visible-light-driven Hydrogen Evolution of Covalent Organic Frameworks through Compositing with MoS₂: A Promising Candidate of Noble-Metal-Free Photocatalysts

Meng-Yao Gao,^a Chang-Cheng Li,^a Hong-Liang Tang,^a Xiao-Jun Sun,^{*a} Hong Dong,^a and Feng-Ming Zhang^{*a}

^a. Key Laboratory of Green Chemical Engineering and Technology of College of Heilongjiang Province, College of Chemical and Environmental Engineering Harbin University of Science and Technology No. 4, Linyuan Road, Harbin 150040 (China).

The Turnover frequency (TOF) was calculated according to following equation:

$$TON = \frac{\text{Moles of evolved hydrogen}}{\text{Moles of MoS}_2 \text{ on photocatalyst}}$$

$$TOF = \frac{TON}{\text{reaction time (h)}}$$

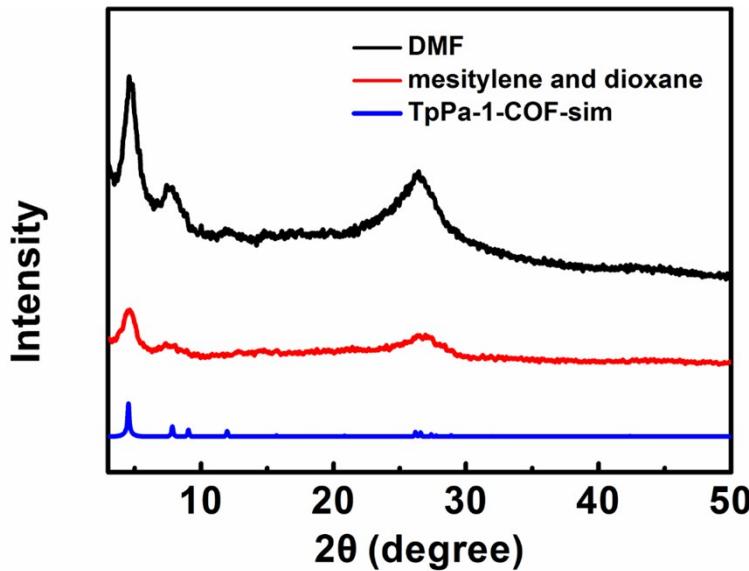


Figure S1. The XRD patterns of TpPa-1-COF in different reaction solvent.

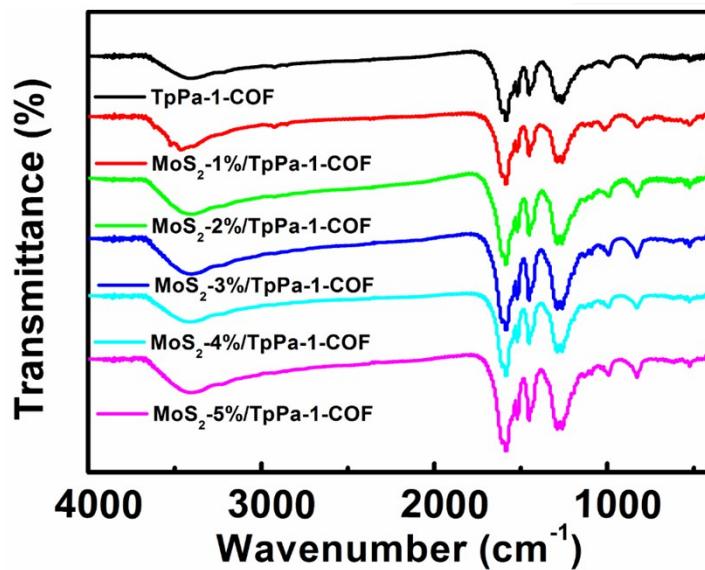


Figure S2. The FT-IR Spectra of samples with different loading amount of MoS₂ from 0 wt% to 5 wt%.

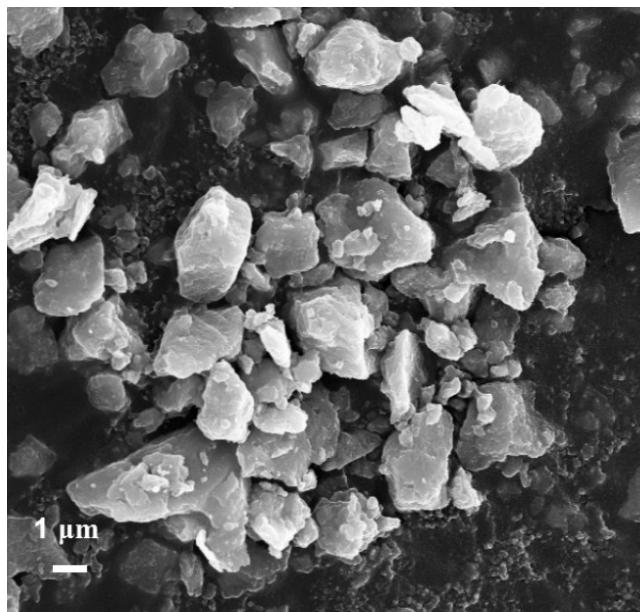


Figure S3. SEM image of bulk MoS₂.

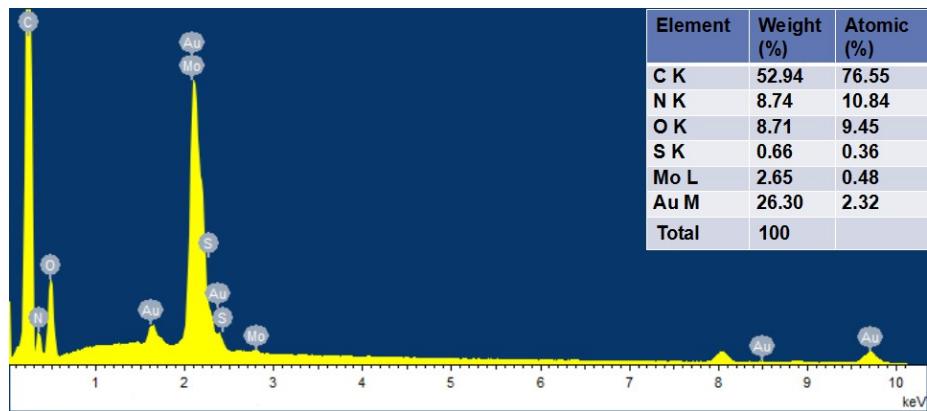


Figure S4. EDS spectra of MoS₂-3%/TpP-1-COF.

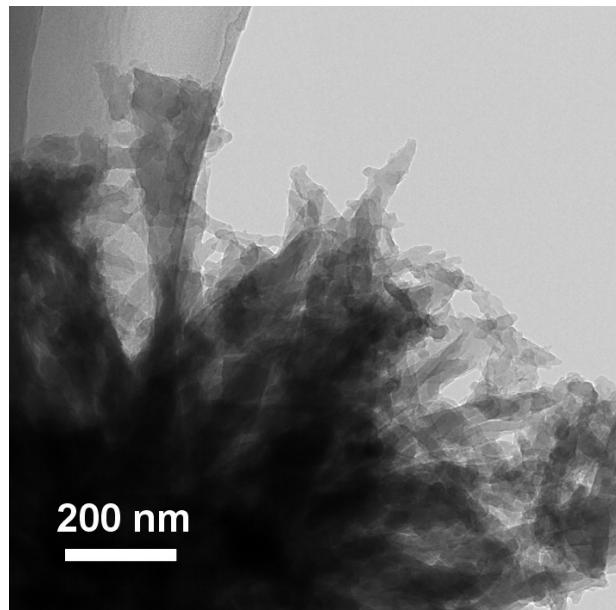


Figure S5. TEM image of TpPa-1-COF.

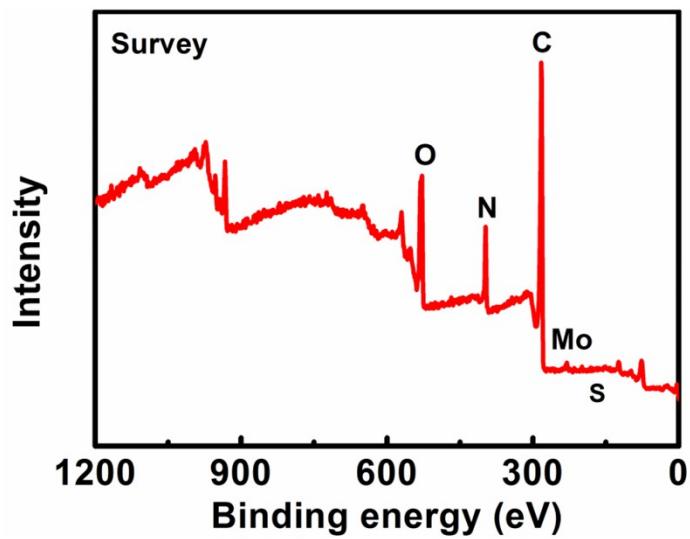


Figure S6. XPS survey spectrum of MoS₂-3%/TpPa-1-COF.

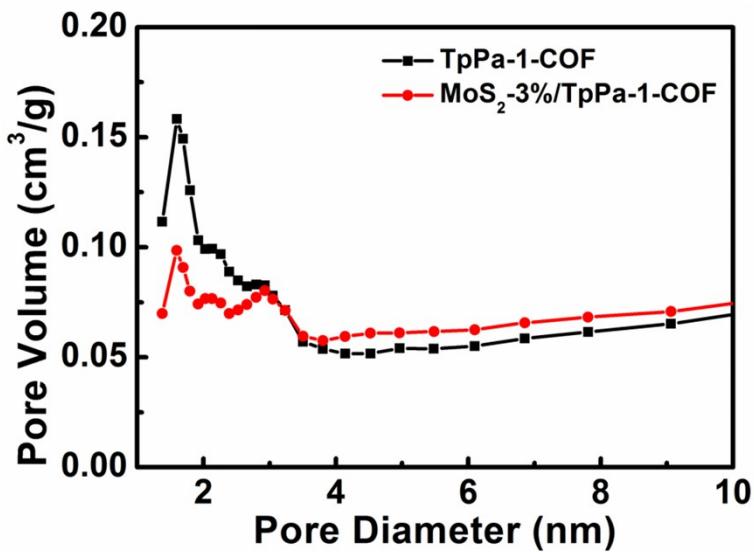


Figure S7. The pore size distribution curves for TpPa-1-COF and MoS₂-3%/TpPa-1-COF.

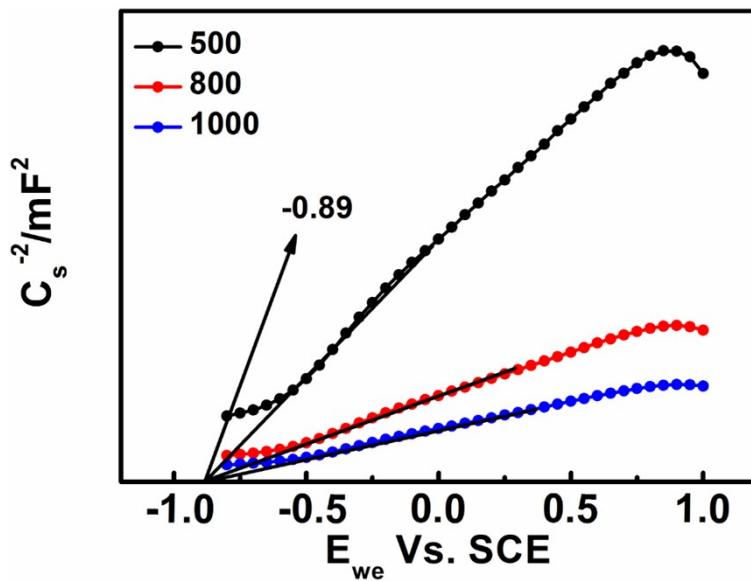


Figure S8. Mott-Schottky plots of TpPa-1-COF at three different frequencies.

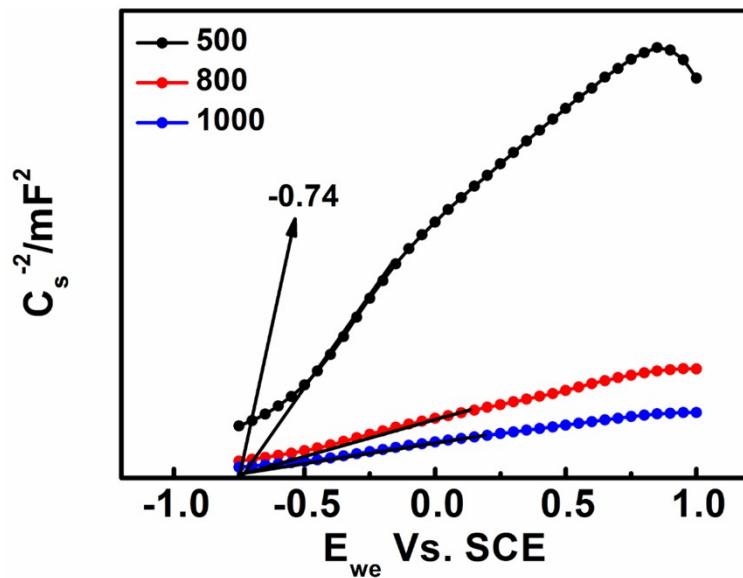


Figure S9. Mott-Schottky plots of $\text{MoS}_2\text{-3\%}/\text{TpPa-1-COF}$ at three different frequencies.

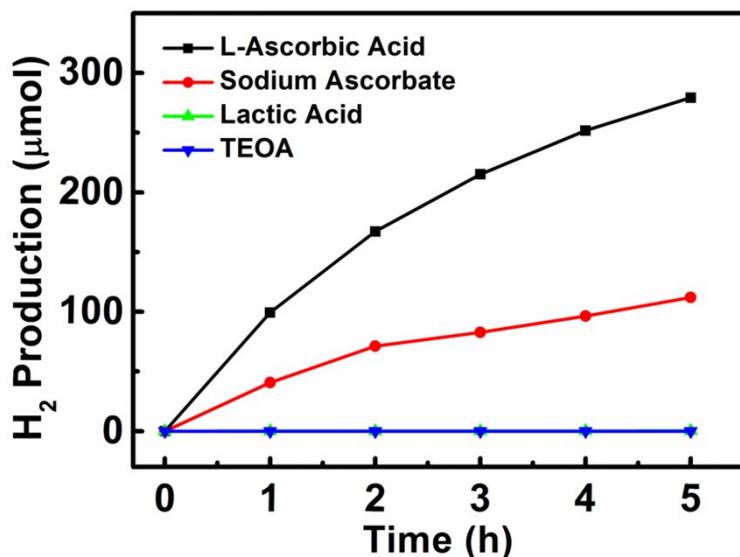


Figure S10. Comparison of the photocatalytic hydrogen evolution of $\text{MoS}_2\text{-3\%}/\text{TpPa-1-COF}$ under different sacrificial systems.

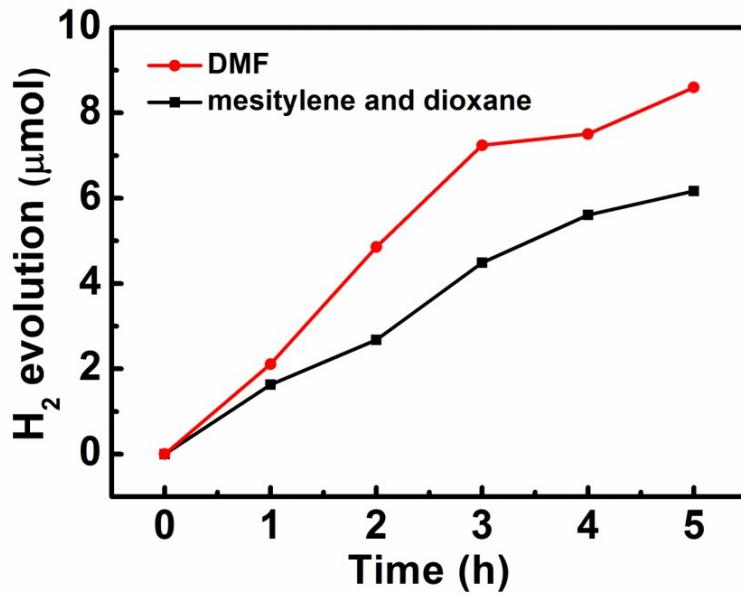


Figure S11. Comparison of the photocatalytic hydrogen evolution of TpPa-1-COF in different reaction solvent.

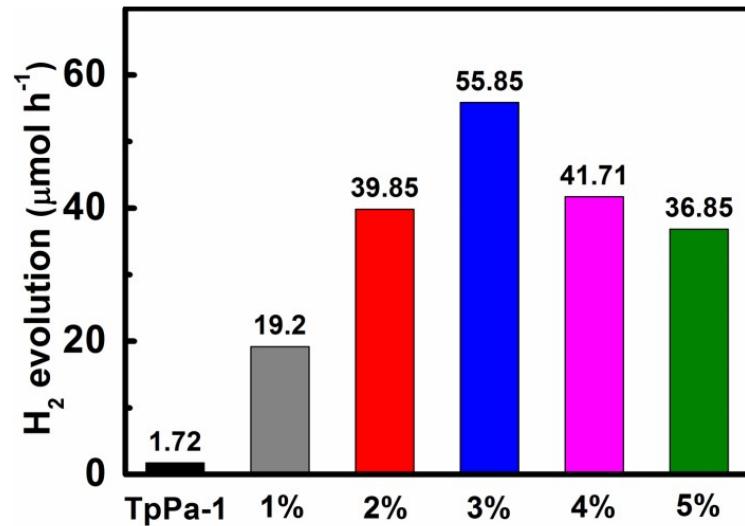


Figure S12. Average photocatalytic H₂ evolution rate of TpPa-1-COF and MoS₂/TpPa-1-COF photocatalysts with varying MoS₂ loading.

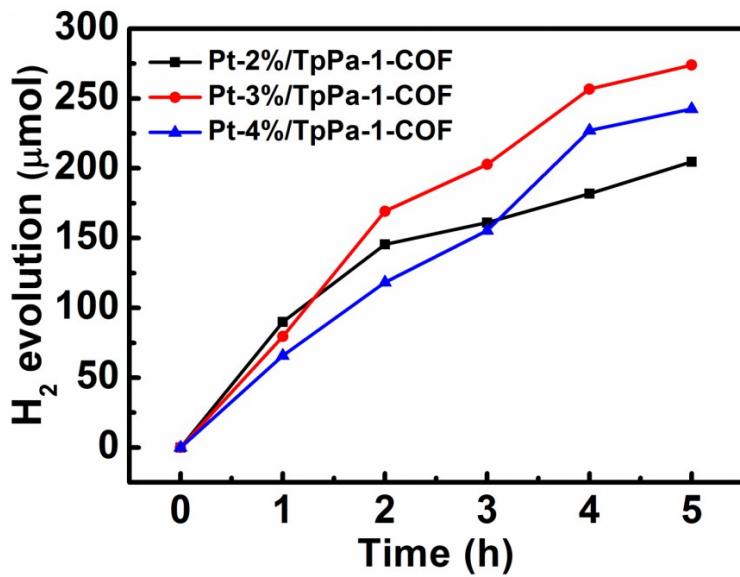


Figure S13. Photocatalytic H_2 evolution rates for *TpPa*-1-COF with varying amounts (2 wt%, 3 wt%, and 4 wt%) of Pt as cocatalyst.

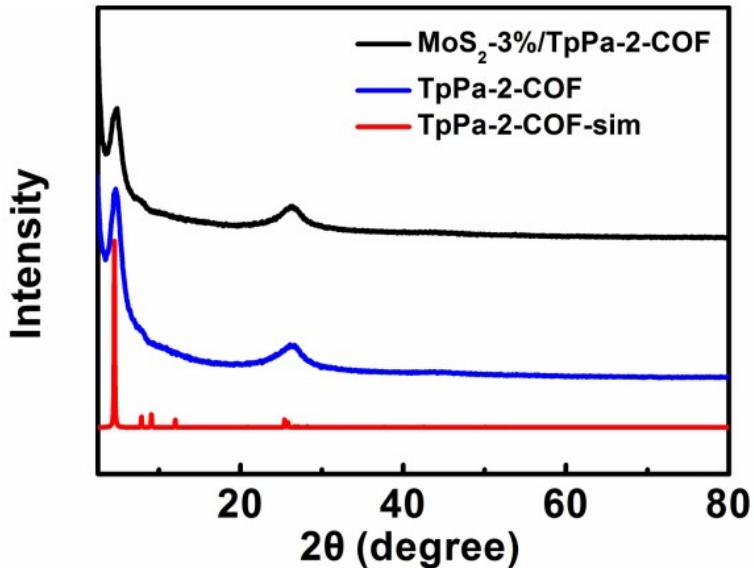


Figure S14. The XRD patterns of TpPa-2-COF and MoS_2 -3% /TpPa-2-COF.

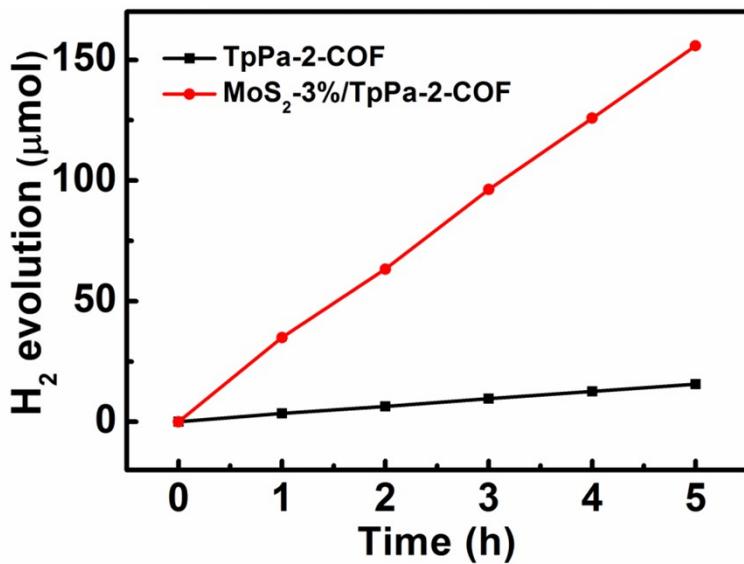


Figure S15. Photocatalytic H_2 evolution rates for TpPa-2-COF and MoS₂-3%/TpPa-2-COF.

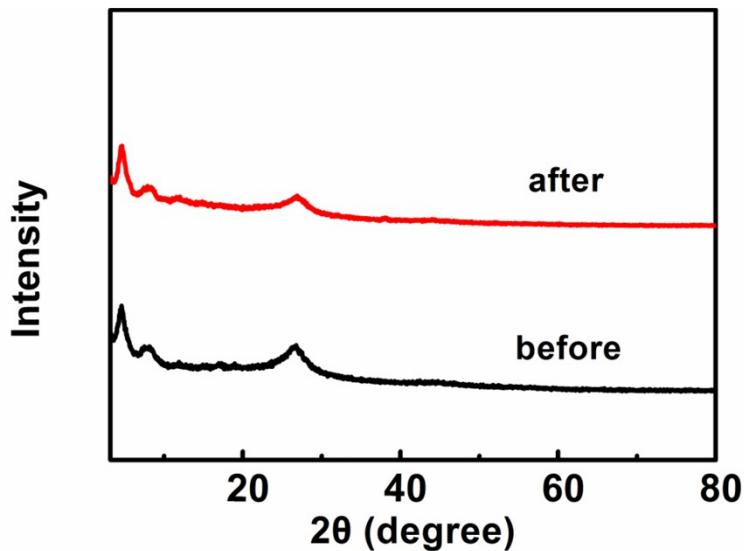


Figure S16. The XRD patterns of MoS₂-3%/TpPa-1-COF composite before and after photocatalytic reaction.

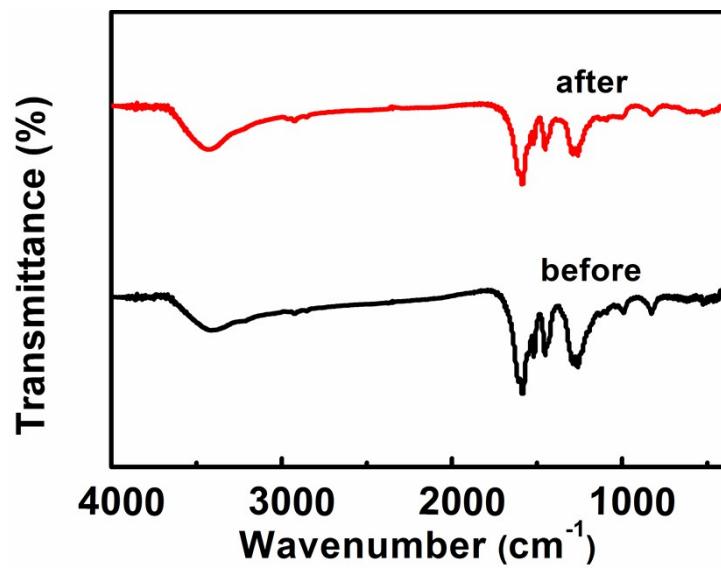


Figure S17. The IR spectrum of MoS₂-3%/TpPa-1-COF composite before and after photocatalytic reaction.

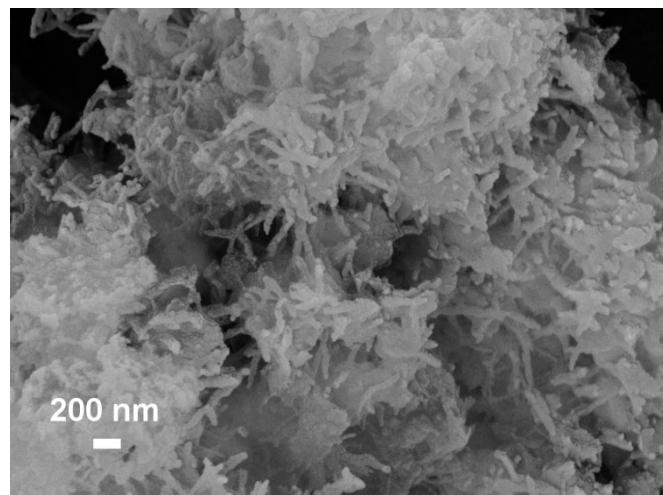


Figure S18. The SEM image of MoS₂-3%/TpPa-1-COF composite after photocatalysis.

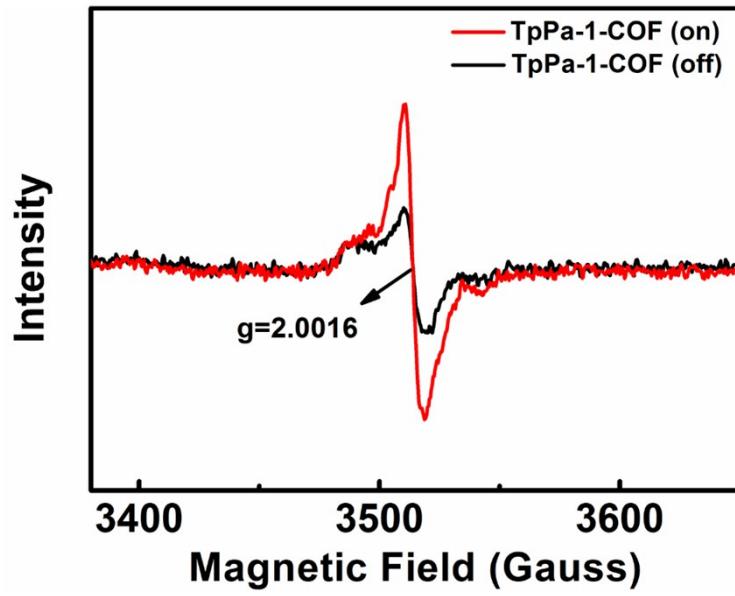


Figure S19. EPR spectra of TpPa-1-COF with light on and off.

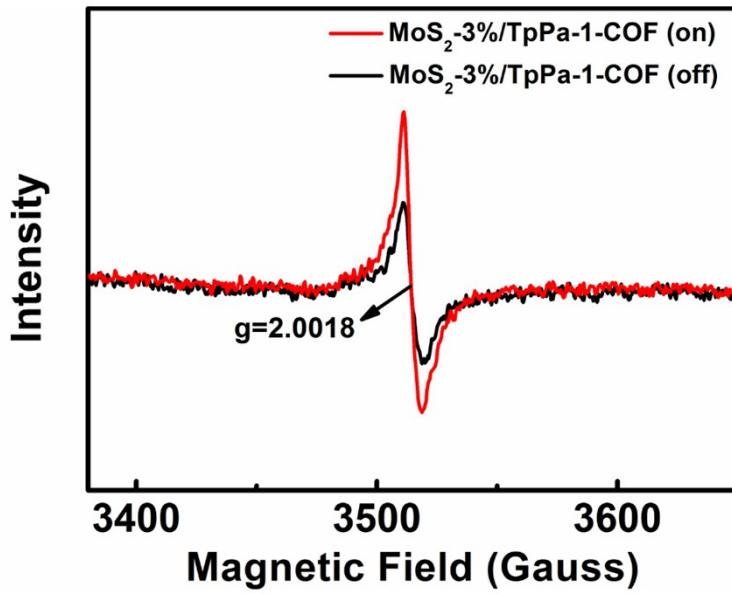


Figure S20. EPR spectra of MoS₂-3%/TpPa-1-COF with light on and off.

Table S1. Summary of H₂ evolution activity of photocatalysts.

Catalyst	Cocatalyst	Sacrificial agent	Illumination	Activity, $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	AQE	Ref
TpPa-1-COF	MoS ₂	Ascorbic acid	$\lambda > 420 \text{ nm}$	5585	0.76%	This work
TpPa-1	Pt	Ascorbic acid	$\lambda > 420 \text{ nm}$	5479	-	This work
TFPT-COF	Pt	Sodium ascorbate	$\lambda > 420 \text{ nm}$	230	-	¹
TFPT-COF	Pt	TEOA	$\lambda > 420 \text{ nm}$	1970	2.2-3.9%	²
N ₀ -COF	Pt	TEOA	$\lambda > 420 \text{ nm}$	23	0.001%	²
N ₁ -COF	Pt	TEOA	$\lambda > 420 \text{ nm}$	90	0.077%	²
N ₂ -COF	Pt	TEOA	$\lambda > 420 \text{ nm}$	438	0.19%	²
N ₁ -COF	Pt	TEOA	$\lambda > 420 \text{ nm}$	1703	0.44%	²
PTP-COF	Pt	TEOA	$\lambda > 420 \text{ nm}$	83.83	-	³
N ₂ -COF	Co-1 ^a	TEOA	AM 1.5	782	0.16%	⁴
N ₂ -COF	Co-2 ^b	TEOA	AM 1.5	414	-	⁴
N ₁ -COF	Co-1	TEOA	AM 1.5	100	-	⁴
N ₃ -COF	Co-1	TEOA	AM 1.5	163	-	⁴
COF-42	Co-1	TEOA	AM 1.5	233	-	⁴
g-C ₃ N ₄ nanosheets	Pt	TEOA	$\lambda > 420 \text{ nm}$	1860	3.75%	⁵
g-C ₃ N ₄	MoS ₂	Lactic acid	$\lambda > 420 \text{ nm}$	1030	2.1%	⁶
S-doped mpg-CN	Pt	TEOA	$\lambda > 420 \text{ nm}$	1360	5.8%	⁷
N-GQDs/g-C ₃ N ₄	Pt	TEOA	$\lambda > 420 \text{ nm}$	2180	5.25%	⁸
CdS	Ni(OH) ₂	TEOA	$\lambda > 420 \text{ nm}$	5084	28%	⁹
CdS	MoS ₂	Lactic acid	$\lambda > 420 \text{ nm}$	5530	79.7%	¹⁰
ZnS	CuS	Na ₂ S and Na ₂ SO ₃	$\lambda > 420 \text{ nm}$	4147	20%	¹¹
Zn _{0.8} Cd _{0.2} S	RGO	Na ₂ S and Na ₂ SO ₃	AM 1.5	1824	23.4%	¹²
Cu ₂ O	MoS ₂	Methanol	$\lambda > 420 \text{ nm}$	625	-	¹³
Mil-101/CdS	CDs	lactic acid	$\lambda > 420 \text{ nm}$	488	-	¹⁴
g-C ₃ N ₄	P	TEOA	$\lambda > 420 \text{ nm}$	1596	3.56%	¹⁵
g-C ₃ N ₄	CoP	TEOA	$\lambda > 420 \text{ nm}$	1924	12.4%	¹⁶
g-C ₃ N ₄ /CdS	NiS	TEOA	$\lambda > 420 \text{ nm}$	2563	-	¹⁷
CdS	Fe ₂ P	Ascorbic acid	$\lambda > 420 \text{ nm}$	186	15%	¹⁸

$\text{g-C}_3\text{N}_4$	MoS_2	TEOA	$\lambda > 400 \text{ nm}$	252	-	19
$\text{g-C}_3\text{N}_4$	WS_2	Methanol	$\lambda > 420 \text{ nm}$	101	-	20
$\text{CdS/g-C}_3\text{N}_4$	NiS	TEOA	$\lambda > 420 \text{ nm}$	2563	-	21
$\text{g-C}_3\text{N}_4$	Ni_{12}P_5	TEOA	$\lambda > 420 \text{ nm}$	126.6	-	22

^bCo-1: $[\text{Co}(\text{dmgH})_2\text{pyCl}]$. ^cCo-2: $[\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)_2]$

Table S2. The fitting data of electrochemical impedance spectroscopy (EIS).

	TpPa-1-COF	MoS_2 -3%/TpPa-1-COF
Rs	34.56	36.16
Rt	12666	5337
CPE-P	0.95	0.90
CPE-T	3.45E-5	4.39E-5

Reference

1. L. Stegbauer, K. Schwinghammer and B. V. Lotsch, *Chem. Sci.*, 2014, **5**, 2789-2793.
2. V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld and B. V. Lotsch, *Nat. Commun.*, 2015, **6**, 8508.
3. F. Haase, T. Banerjee, G. Savasci, C. Ochsenfeld and B. V. Lotsch, *Faraday Discuss.*, 2017, **201**, 247-264.
4. T. Banerjee, F. Haase, G. k. Savasci, K. Gottschling, C. Ochsenfeld and B. V. Lotsch, *J. Am. Chem. Soc.*, 2017, **139**, 16228-16234.
5. S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang and P. M. Ajayan, *Adv. Mater.*, 2013, **25**, 2452-2456.
6. Y. Hou, A. B. Laursen, J. Zhang, G. Zhang, Y. Zhu, X. Wang, S. Dahl and I. Chorkendorff, *Angew. Chem. Int. Ed*, 2013, **52**, 3621-3625.
7. J. Hong, X. Xia, Y. Wang and R. Xu, *J. Mater. Chem.*, 2012, **22**, 15006-15012.
8. J.-P. Zou, L.-C. Wang, J. Luo, Y.-C. Nie, Q.-J. Xing, X.-B. Luo, H.-M. Du, S.-L. Luo and S. L. Suib, *Appl. Catal. B*, 2016, **193**, 103-109.
9. J. Ran, J. Yu and M. Jaroniec, *Green Chem.*, 2011, **13**, 2708-2713.
10. K. Zhang, J. K. Kim, B. Park, S. F. Qia, B. Ji, X. W. Sheng, H. Zeng, H. Shin, S. H. Oh, C. L. Lee and J. H. Park, *Nano Lett.*, 2017, **17**, 6676-6683.
11. J. Zhang, J. Yu, Y. Zhang, Q. Li and J. R. Gong, *Nano Lett.*, 2011, **11**, 4774-4779.
12. J. Zhang, J. Yu, M. Jaroniec and J. R. Gong, *Nano Lett.*, 2012, **12**, 4584-4589.
13. Y.-F. Zhao, Z.-Y. Yang, Y.-X. Zhang, L. Jing, X. Guo, Z. Ke, P. Hu, G. Wang, Y.-M. Yan and K.-N. Sun, *J. Phys. Chem. C*, 2014, **118**, 14238-14245.
14. X. B. Meng, J. L. Sheng, H. L. Tang, X. J. Sun, H. Dong and F. M. Zhang, *Appl. Catal. B*, 2019, **244**, 340-346.
15. J. R. Ran, T. Y. Ma, G. P. Gao, X. W. Du and S. Z. Qiao, *Energy & Environmental Science*, 2015, **8**, 3708-3717.

16. C. M. Li, Y. H. Du, D. P. Wang, S. M. Yin, W. G. Tu, Z. Chen, M. Kraft, G. Chen and R. Xu, *Adv. Funct. Mater.*, 2017, **27**.
17. J. Yuan, J. Wen, Y. Zhong, X. Li, Y. Fang, S. Zhang and W. Liu, *J. Mater. Chem. A*, 2015, **3**, 18244-18255.
18. Z. J. Sun, H. L. Chen, Q. Huang and P. W. Du, *Catalysis Science & Technology*, 2015, **5**, 4964-4967.
19. H. Zhao, Y. Dong, P. Jiang, H. Miao, G. Wang and J. Zhang, *J. Mater. Chem. A*, 2015, **3**, 7375-7381.
20. M. S. Akple, J. Low, S. Wageh, A. A. Al-Ghamdi, J. Yu and J. Zhang, *Appl. Surf. Sci.*, 2015, **358**, 196-203.
21. J. Yuan, J. Wen, Y. Zhong, X. Li, Y. Fang, S. Zhang and W. Liu, *J. Mater. Chem. A*, 2015, **3**, 18244-18255.
22. J. Wen, J. Xie, R. Shen, X. Li, X. Luo, H. Zhang, A. Zhang and G. Bi, *Dalton Trans.*, 2017, **46**, 1794-1802.