Supporting Information

Enhancement of visible light driven dye degradation and photocatalytic H_2 evolution over MoS_2 through combination with perylene diimide aggregates

Yongshan Ma *, Jingcheng Cui, Mengmeng Yin, Xuemei Li, Tianyi Jiang, Fengxia Zhang *, Yanyan Zhu, Yuanyuan Liu

School of Municipal and Environmental Engineering, Shandong Jianzhu University, Jinan 250101, Shandong, China.

* *Corresponding author. E-mail addresses: mlosh@sdjzu.edu.cn (Y. Ma), zhangfengxia19@sdjzu.edu.cn (F. Zhang).*

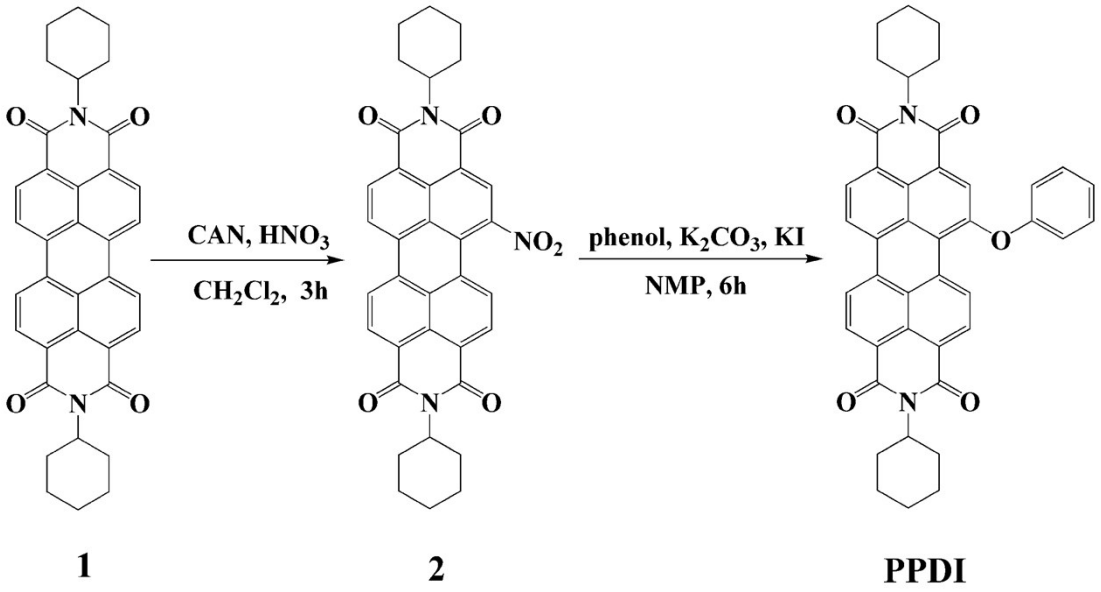


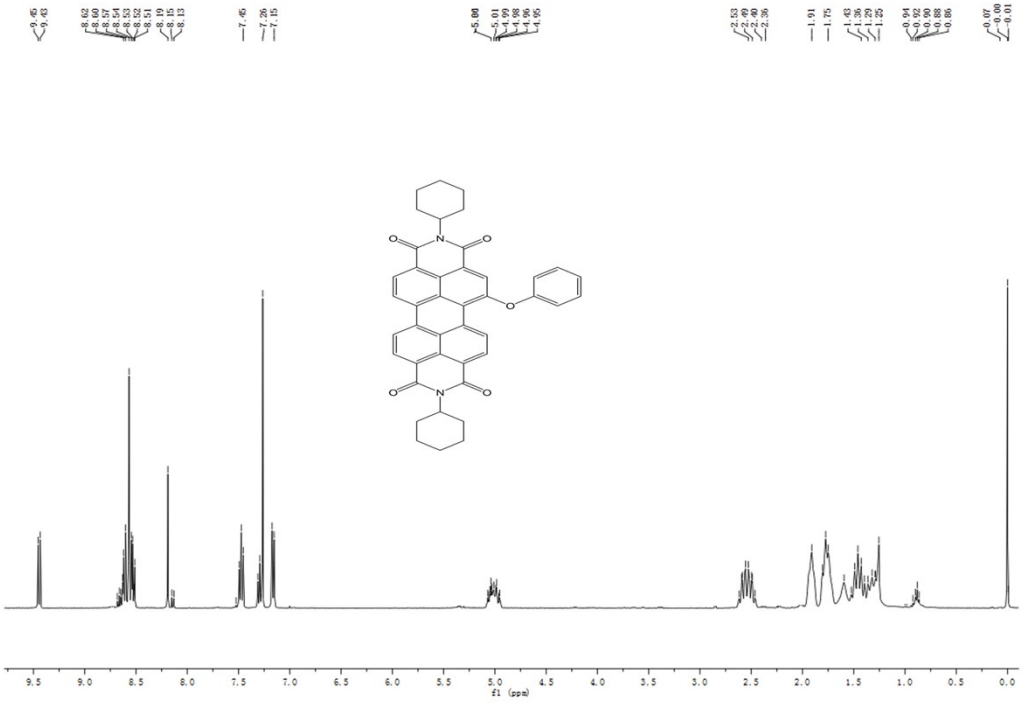
Fig.S-1 Synthesis route of PPDI.

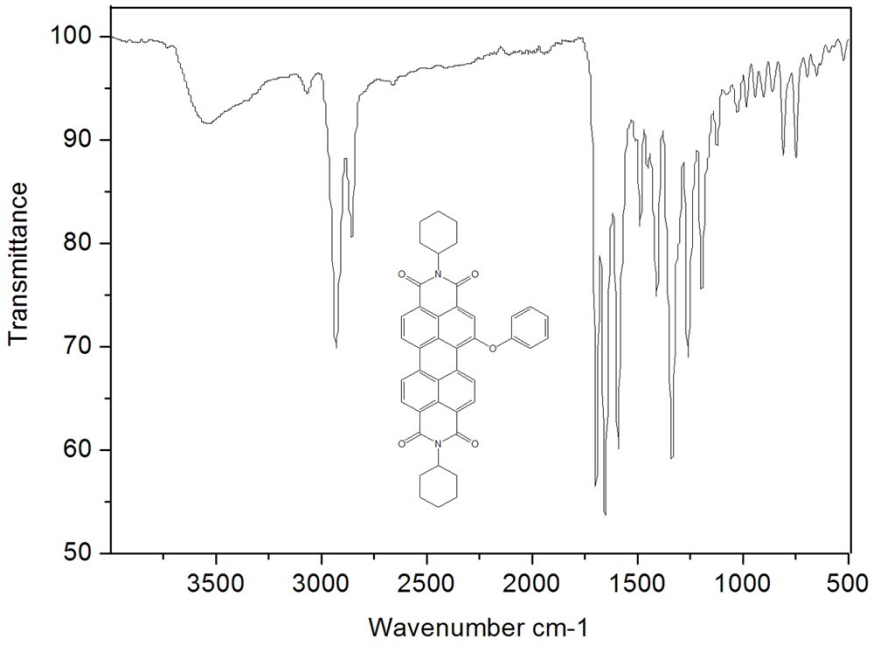
General procedure for the synthesis of PPDI

Compound 1 (1.0 g, 1.8 mmol), cerium (IV) ammonium nitrate (CAN) (1.2 g, 2.2 mmol), nitric acid (2.0 g, 31.7 mmol), and dichloromethane (100 mL) were stirred at 25 ℃ in an atmosphere of argon for 3 h. The mixture was neutralized with 10% KOH and extracted with dichloromethane. After the solvent was removed, the crude product was purified by silica gel column chromatography with eluent dichloromethane, and the compound 2 (1.1g) was obtained with a yield of 95%. Then compound **2** (0.6 g, 0.5 mmol), phenol (0.57 g, 5.0 mmol), 1.0 g K_2CO_3 and catalyzed KI were suspended in 20 mL anhydrous N-methylpyrrolidone (NMP). The resulting mixture was stirred under argon atmosphere at 25 ℃ for 6 h, and then HCl (2 mlo/L, 50 mL) and MeOH (20 mL) were added. The precipitate was collected by vacuum filtration, washed by methanol and dried in vacuum. The crude product was further purified by silica gel column chromatography with eluent dichloromethane/petroleum

ether (volume 4:1). After the solvent was removed, a red solid of PPDI (0.58 g) was obtained with a yield of 90%. ^{1}H-NMR (300 MHz, $CHCl_3$, TMS, ppm): δ = 9.44 (d, J = 6.0 Hz, 1H), 8.62-8.51 (m, 5H), 8.19 (s, 1H), 7.45 (m, 2H), 7.30 (m, 1H), 7.15 (m, 2H), 5.01 (m, 2H), 2.53-2.36 (m, 4H), 1.91-1.75 (m, 8H), 1.43-1.25 (m, 8H). FT-IR (KBr, cm^{-1}): v = 2931, 2849, 1696, 1649, 1601, 1482, 1402, 1338, 1251, 1187, 813, 757. MS (MALDI-TOF): m/z 647.2 $[M+H]^+$.

Spectra of NMR, FTIR and MALDI-TOF-MS of PPDI




Transmittance
100
90
80
70
60
50
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

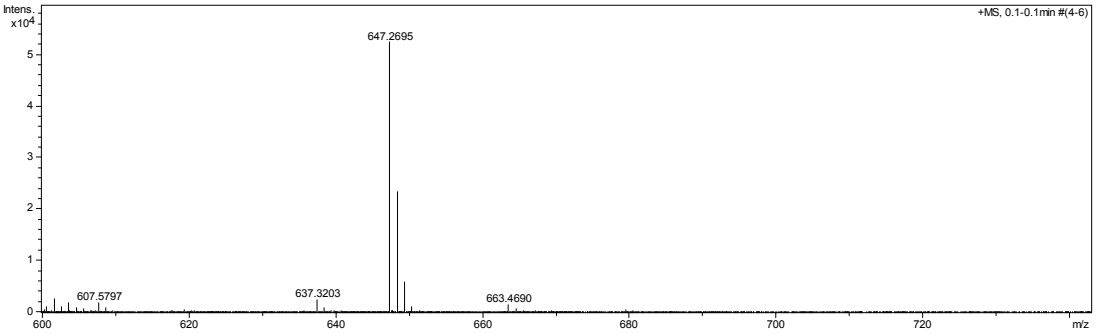

Intens.
x10^4
+MS, 0.1-0.1min #(4-6)
647.2695
607.5797
637.3203
663.4690
0
1
2
3
4
5
600
620
640
660
680
700
720
m/z

Fig. S-2 EDX spectrum of MoS_2/PPDI HSs.

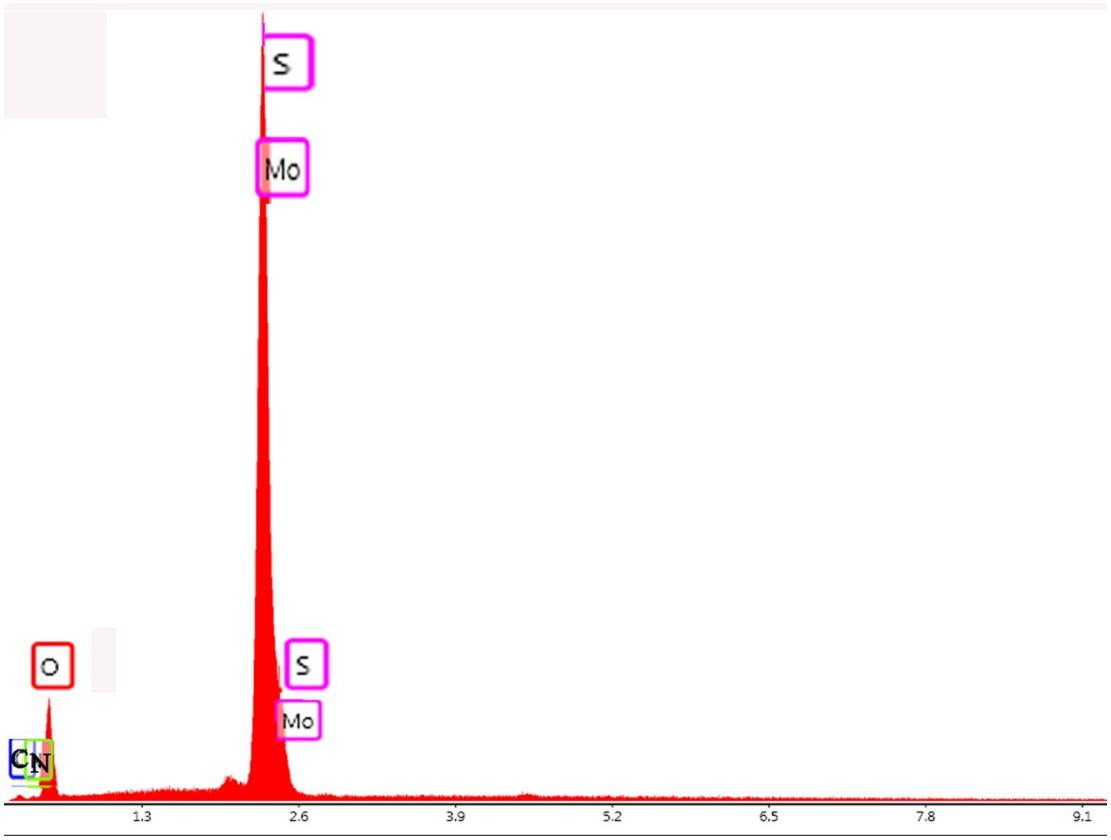


Fig. S-3 Raman spectra of MoS_2, PPDI, and MoS_2/PPDI.

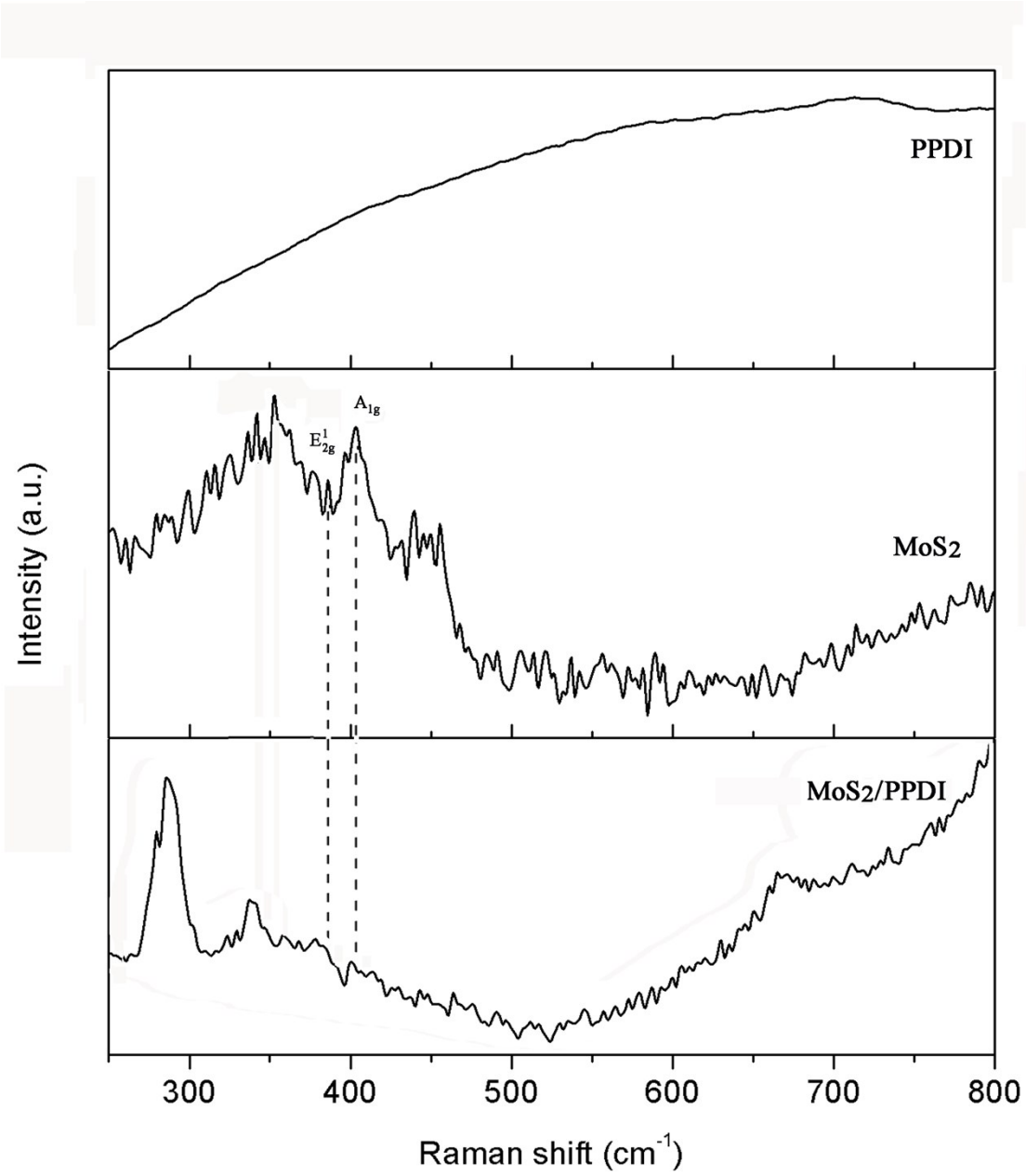


Fig. S-4 N_2 adsorption-desorption isotherms for (a) MoS_2 NFs and (b) MoS_2/PPDI HSs.

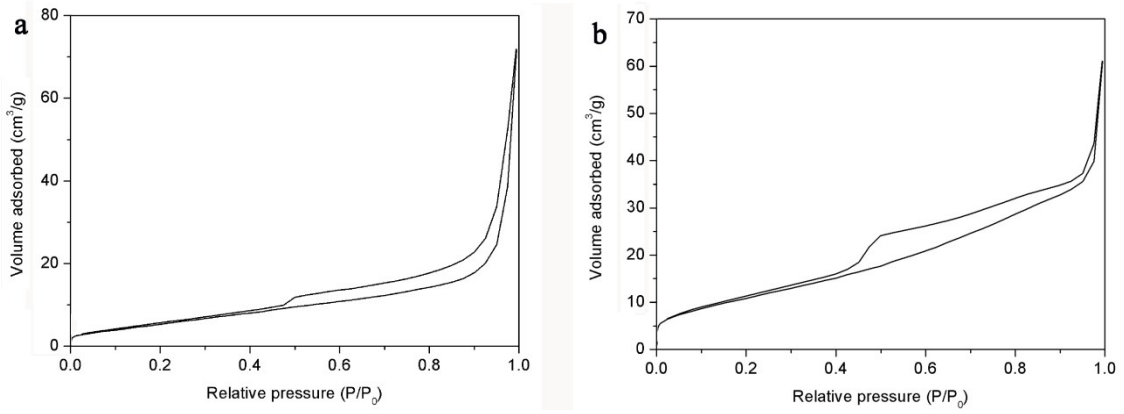


Fig. S-5 The activity diagram of (a) MB and (b) EBT degradation by different catalysts in visible light.

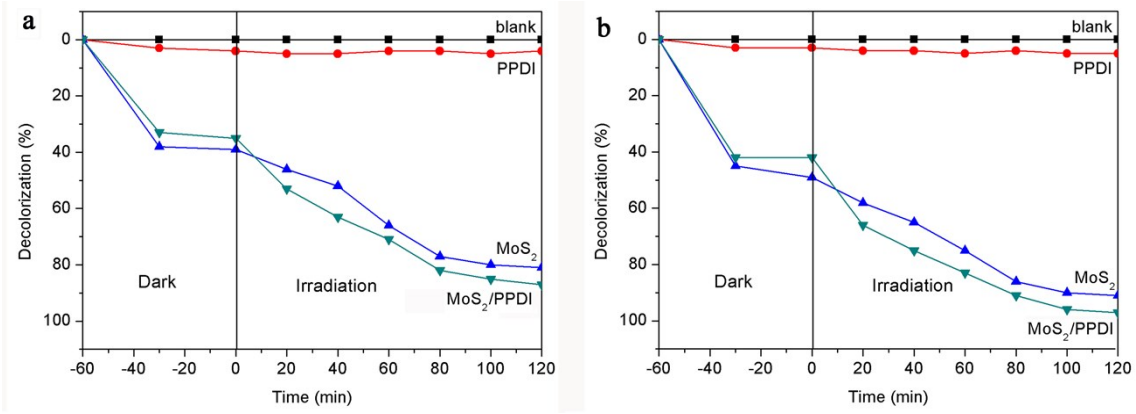


Figure S-6. The changes in UV-vis spectra of MB on irradiation with visible light in the presence of MoS_2/PPDI HSs. [MB] = 0.01g/L, pH = 7, catalyst suspended = 1g/L.

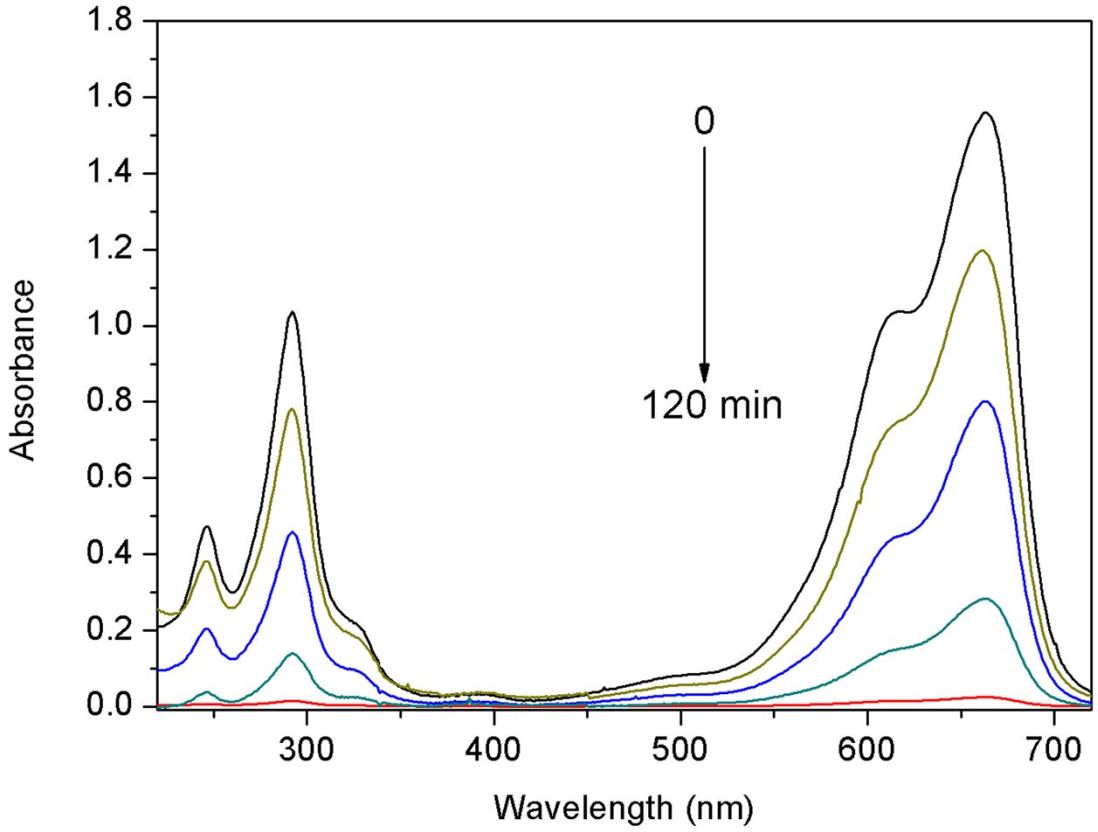


Figure S-7. Suggested mechanism for the decolorization of MB.

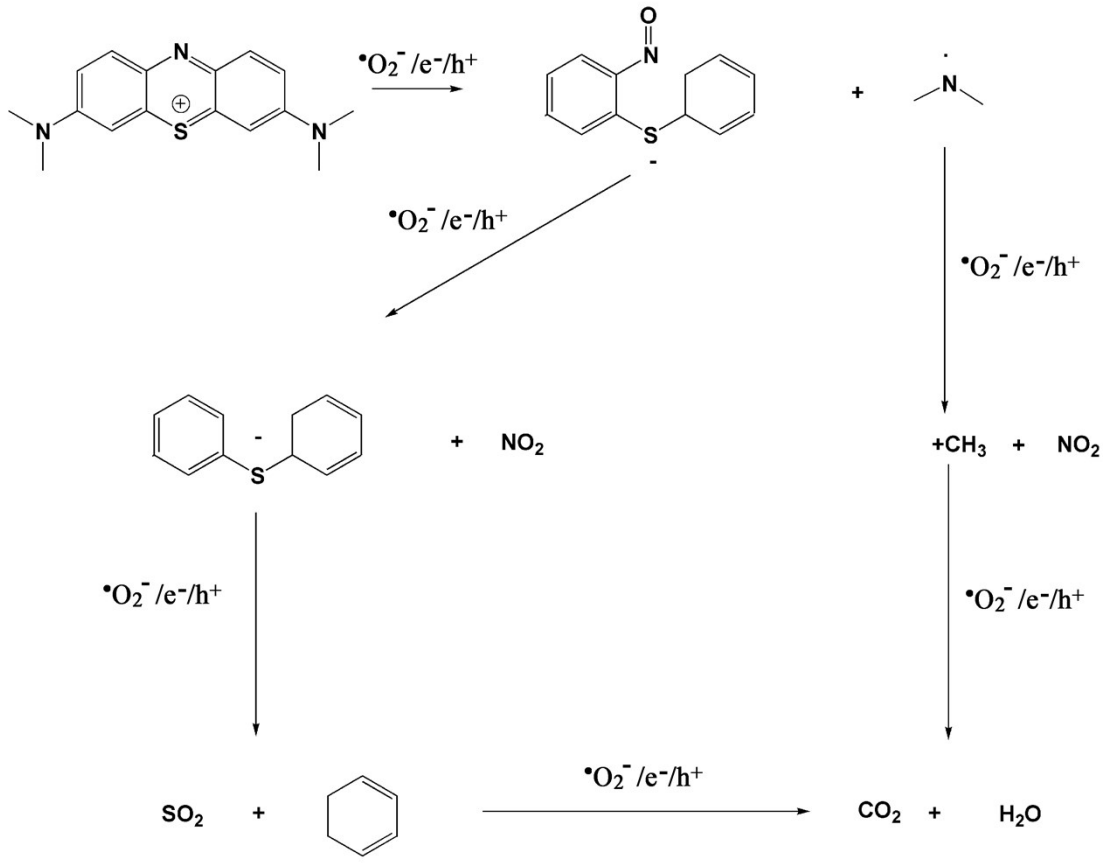


Fig. S-8 Kinetic study of the process based on the results of COD values of MB by catalyst MoS_2/PPDI HSs.

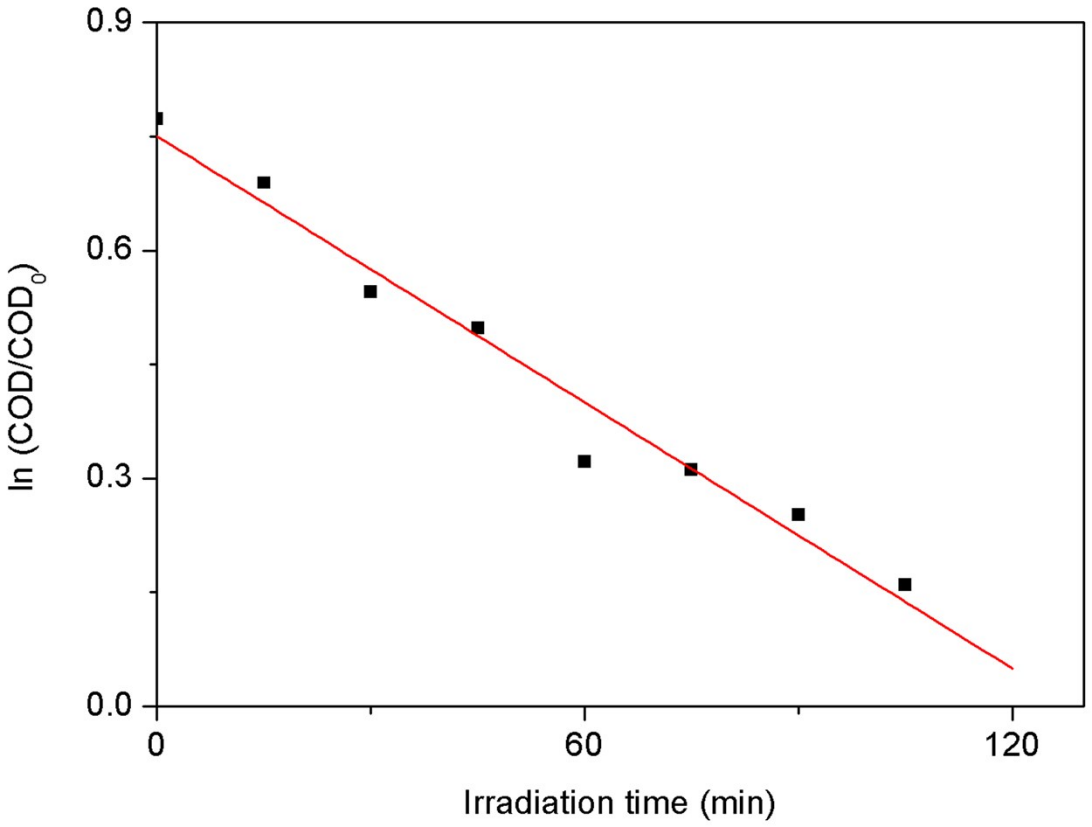


Fig. S-9 Removal rate of MB (10 mg/L), MO (10 mg/L) and EBT (25 mg/L) for MoS_2/PPDI HSs (1.0 g/L) under solar irradiation. (up: before solar irradiation; down: after solar irradiation. pH = 7).

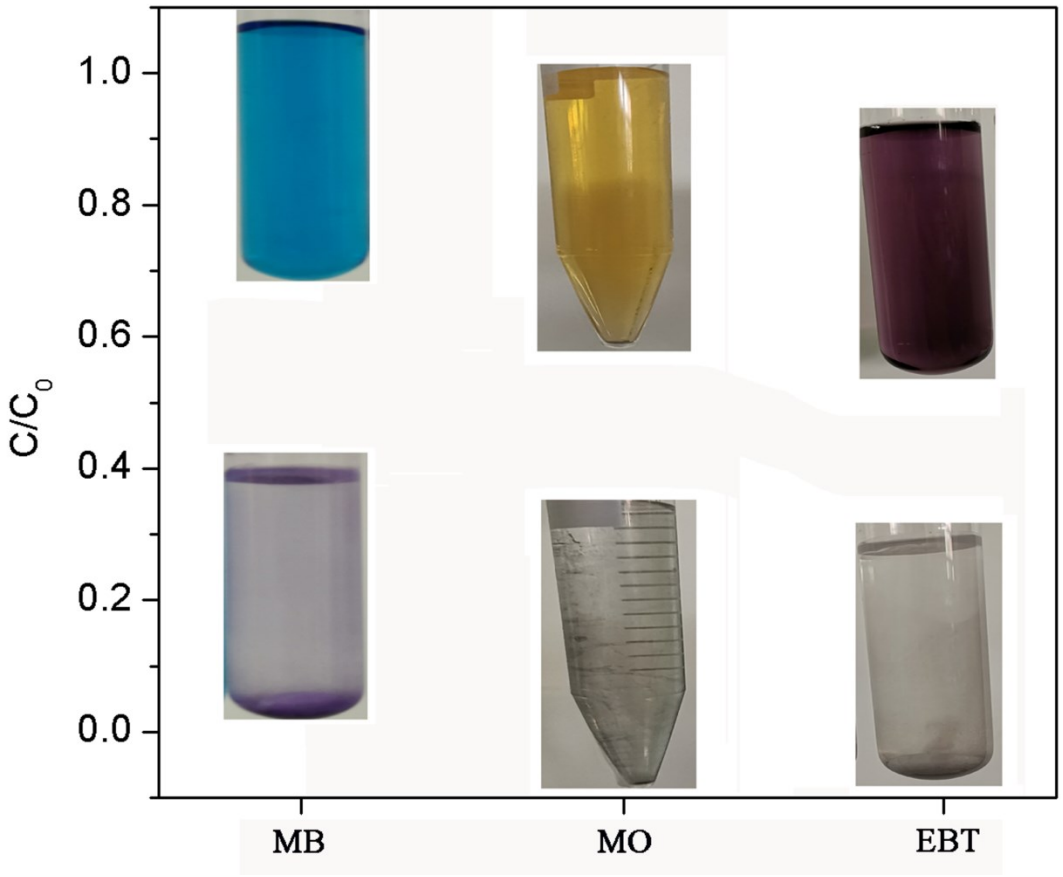


Table S-1 Comparison analysis of photocatalytic HER performance.

Photocatalysts	Sacrificial Reagent	H_2 Production Rate ($\mu mol \cdot h^{-1}$) [a]	Catalyst Dose	Ref.
MoS_2/CO-C_3N_4	Methanol/H_2O solution	1440	1 g	1
MoS_2/CdS/g-C_3N_4	Methanol/H_2O solution	956	1 g	2
CdS/MoS_2QDs/$ZnIn_2S_4$	Lactic acid aq.solution	2107.5	1 g	2
CeO_2@MoS_2/gC_3N_4	0.5 M Na_2SO_3 and 0.5 M Na_2S	1128	1 g	3
pyran-embedded PDIs	Methanol/H_2O solution	15-900	1 g	4
MoS_2/PPDI HSs (Present study)	Methanol/H_2O solution	286.2	0.1g	-

[a] Light source: 300 W Xe lamp $\lambda \geq 420$ nm.

References:

1 T. Zhao, Z. Xing, Z. Xiu, Z. Li, S. Yang and W. Zhou, *ACS Appl. Mater. Interfaces*, 2019, **11**, 7104-7111.

2 J. Zhang, C. Xing and F. Shi, *Int. J. Hydrogen Energy*, 2020, **45**, 6291-6301.

3 C. Zhu, Y. Wang, Z. Jiang, F. Xu, Q. Xian, C. Sun, Q. Tong, W. Zou, X. Duan and S. Wang, *Appl. Catal. B Environ.*, 2019, **259**, 118072.

4 R. Wang, G. Li, A. Zhang, W. Wang, G. Cui, J. Zhao, Z. Shi and B. Tang, *Chem. Commun.*, 2017, **53**, 6918-6921.