Supplementary Information

Sulfonic acid/Sulfur trioxide (SO$_3$H/SO$_3$) functionalized two-dimensional MoS$_2$ nanosheets for high-performance photocatalysis of organic pollutants

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S1. Experimental

Chemicals: The as-purchased chemicals were ultra-pure and used as received without further purification. Ammonium molybdate tetrahydrate ($H_{24}Mo_7N_6O_{24}.4H_2O$) and bulk molybdenum (IV) sulfide (MoS_2) powder (<2μm, 99%, CSA 1317-33-5) were bought from Sigma Aldrich, India. Thiourea (H_2NCSNH_2) was bought from Merck Specialties Pvt. Ltd (India). Methylene blue ($C_{16}H_{18}CIN_3S.xH_2O$) was bought from S D Fine chem. Ltd (India). DI water used throughout all experiments was purified through a Millipore system.

Synthesis of SO_3H/SO_3 functionalized MoS_2 Nanosheets: The SO_3H/SO_3 functionalized MoS_2 Nanosheets were synthesized by hydrothermal process. In the typical process, about 2.067 g ammonium molybdate tetrahydrate ($H_{24}Mo_7N_6O_{24}.4H_2O$) and 8.9 g thiourea ($H_2NCSNH_2$) were first dissolved in 60 ml DI water. After that, the solution was constantly stirred for 20 min at 400 rpm to get a transparent solution. Then the solution was transferred to 100 ml Teflon lined stainless steel autoclave tightly sealed and maintained at 180 ˚C for 24 h in an electric oven. Afterward, the Teflon autoclave was naturally cooled down to room temperature (RT). After cooling to RT naturally, the resulting black solution was separated by centrifugation at 8000 rpm followed by washing three times with ethanol and deionized water (DI) respectively and dried at 80 ˚C for 12 h in a vacuum oven to obtain a SO_3H/SO_3 functionalized MoS_2 nanosheets.

Material characterization: Raman spectra was recorded using a α-300 Access (WITec focus innovation, Germany) Raman spectrometer with an UHTS spectrometer inbuilt with 532 nm laser excitation at 1.5-2 mW power and 600 nm grating. The infrared spectrum of the samples was obtained by using an FT-IR spectrometer (Nicolet iS5, ThermoFisher Scientific,

USA) and spectra ranging from 4000 to 400 cm^{-1} acquired. The X-ray photoelectron spectroscopy (XPS) spectra were obtained on XPS dispersive spectrometer (K-Alpha, Thermo Fisher Scientific, USA) with an Al Kα monochromatic X-ray beam of energy 4000 eV. The morphology of SO_3H/SO_3 was characterized by a scanning electron microscope (Nova Nano SEM 450, FEI, Inc. USA). The phase and morphology of the catalysts were observed by using transmission electron microscopy (TEM) (TECNAI G2 20 TWIN, FEI, USA) techniques. All the TEM/HRTEM data were analyzed in GATAN (GATAN Inc., USA) software. UV-Visible (UV-Vis) spectral analysis was done by UV-Vis spectrophotometer (Model No: V-770, JASCO, Japan) operating in the spectral range of 200-800 nm. Phase and crystal structure was analyzed by Rigaku Miniflex (Rigaku Corporation, Japan) desktop X-ray diffraction (XRD) system with Cu K_{α} radiation (1.54 Å) and a 2θ scan range of 5°-80°. To evaluate the surface area, we performed the (Brunauer, Emmett and Teller) BET (Model- Autosorb IQ2, Quantachrome Instruments USA) measurement technique.

Photocatalytic degradation of methylene blue under visible light: Photocatalytic degradation was conducted with different initial methylene blue (MB) concentrations and different MoS_2. About 5 mg of catalyst was added to an aqueous solution of MB dye (5 ml of 10 ppm). The entire assembly was kept inside of a laboratory-based closed light chamber with visible while LED source (light intensity: 2 W/m^2, and light spectrum: 360 to 700 nm). Before irradiation, the mixture was stirred in dark for a few minutes to attain adsorption-desorption equilibrium. In the defined intervals of time some amount of sample was taken, centrifuged and then the adsorption spectrum changes of MB were measured to monitor the MB photodegradation using JASCO V-770 UV-Vis Spectrophotometer. A similar

experiment is carried out with 5 ppm and 15 ppm MB dye. The Bulk MoS_2, Pristine 2D-MoS_2, and SO_3H/SO_3-MoS_2 were used as the photocatalyst.
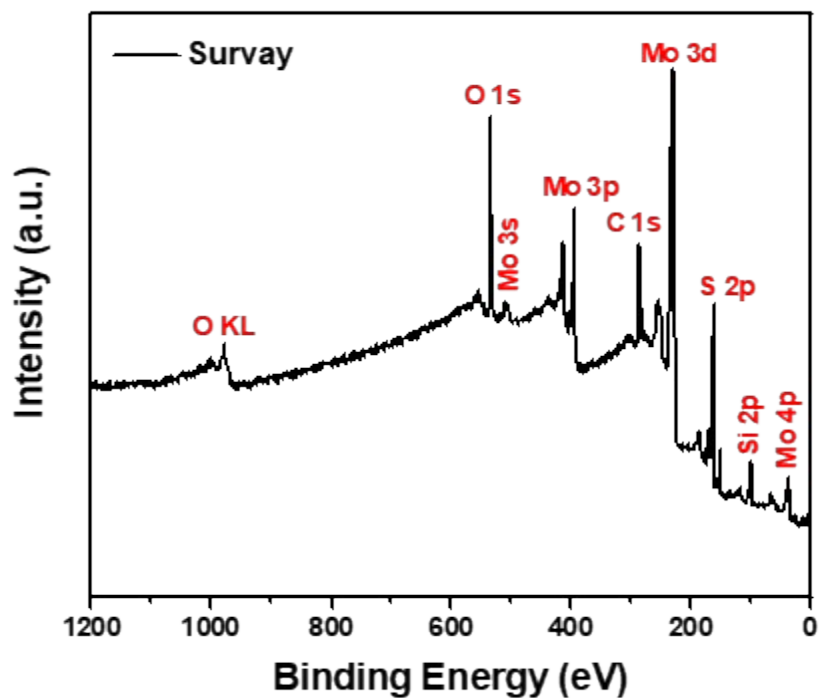
S2. X-ray photoelectron spectroscopy

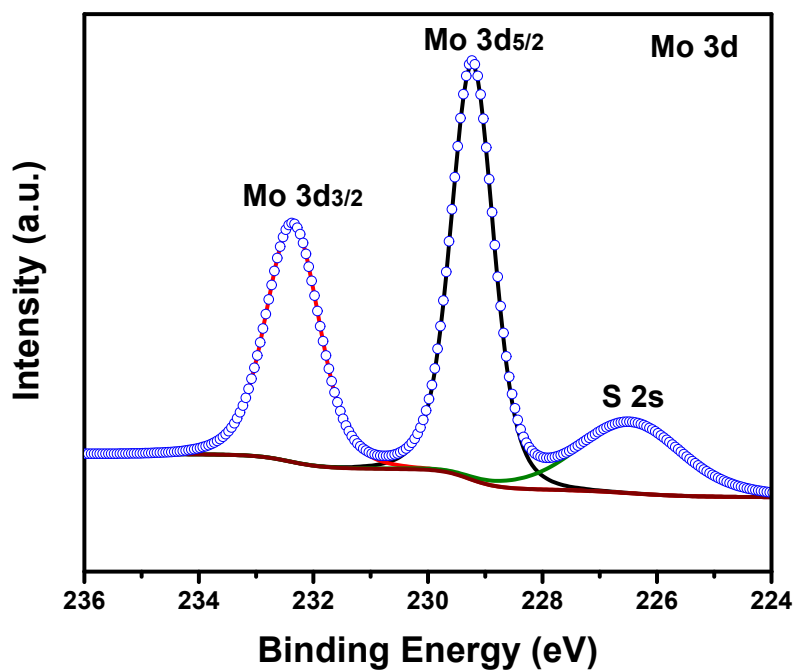*Figure S1: XPS survey spectrum obtained from the* SO$_3$H/SO$_3$-MoS$_2$ *sample.*

Figure S2: High-resolution XPS spectrum showing the characteristics Mo 3d peaks.

The surface chemical composition and oxidation states of the SO_3H/SO_3-MoS_2 were investigated using X-ray photoelectron spectroscopy (XPS) as shown in **Fig. 1c** and **1d** and **Fig. S1** and **S2** (ESI). The XPS survey scan shows the presence of Mo 3d, S 2p, and O 1s peaks, as illustrated in **Fig. S1** (ESI). The atomic percentage of SO_3H/SO_3 in MoS_2 was determined to be 3.45% from the XPS survey analysis and the atomic ratio of Mo (22.93%): S (47.70%) was obtained as 1:2. The high-resolution Mo 3d spectrum shown in **Fig. S2** (ESI) was deconvoluted into three different peaks and found that two characteristic peaks of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ are located at 229.45 and 232.60 eV suggesting the Mo^{4+} oxidation states in MoS_2. The peak at 226.66 eV confirms the S 2s peak, which is a typical signature of 2D-MoS_2.[1, 2]
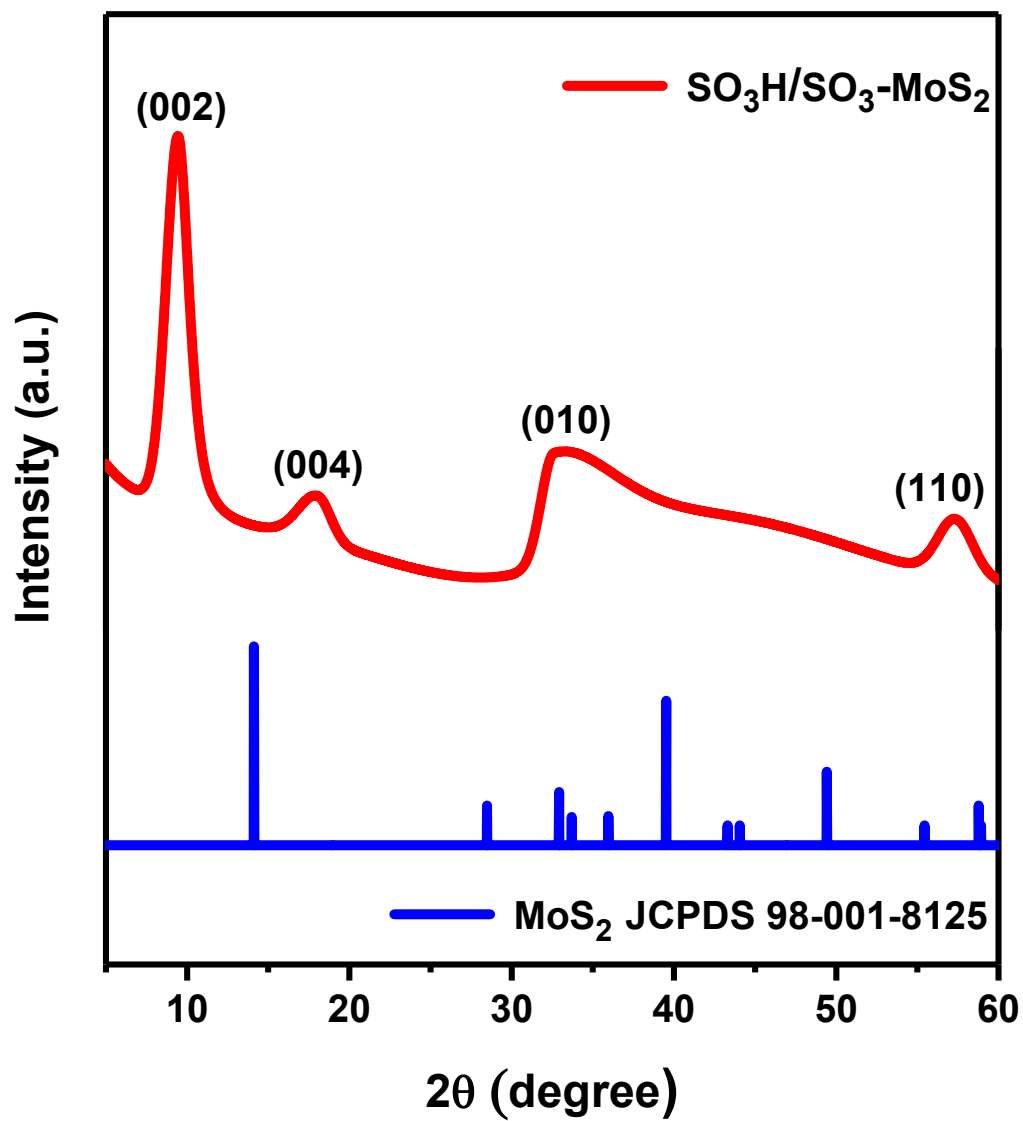
S3. X-ray diffraction

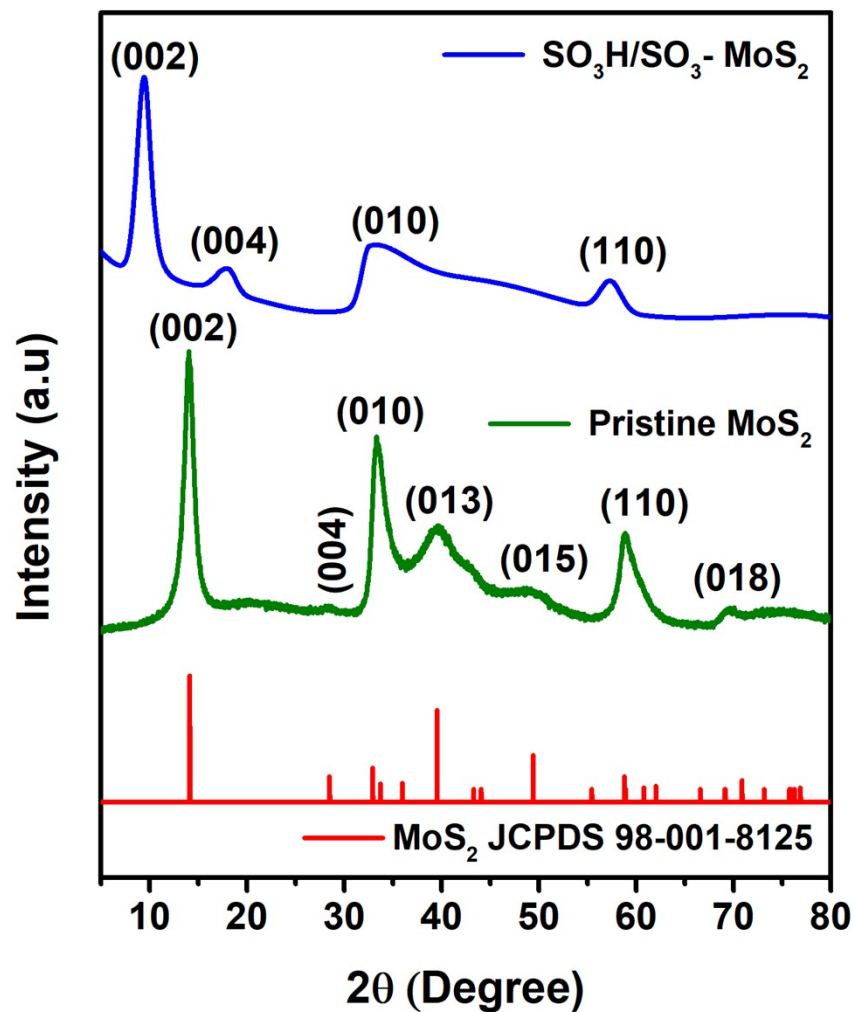*Figure S3A. Shows the XRD patterns of SO$_3$H/SO$_3$ functionalized 2D-MoS$_2$*

Figure S3B: XRD diffraction pattern of as-synthesized MoS$_2$ (Pristine MoS$_2$) with the interlayer spacing (d) of 6.3 Å and SO$_3$H/SO$_3$-MoS$_2$ with the interlayer spacing (d) of 9.4 Å.
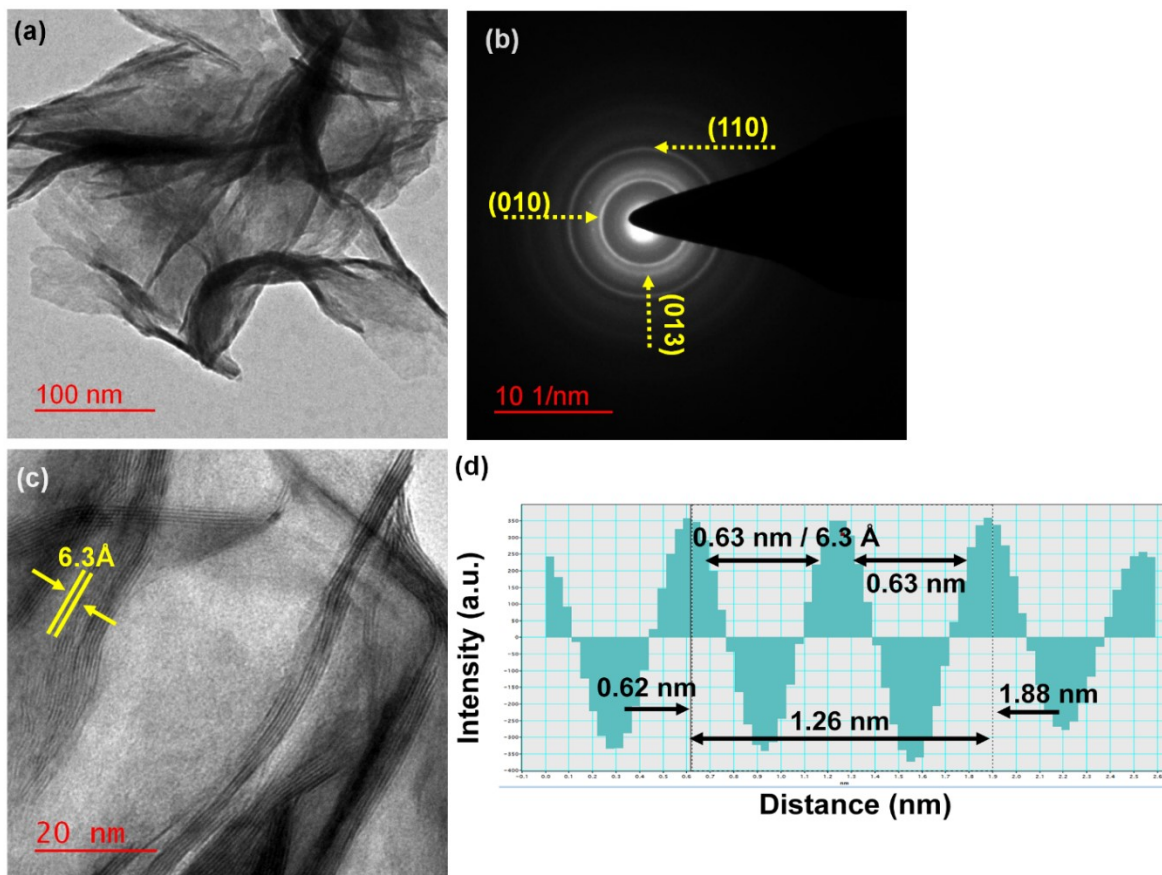
S4. TEM/HETRM

Figure S4: Shows (a) Transmission electron micrograph of pristine 2D-MoS$_2$ (i.e., P-MoS$_2$); (b) SAED pattern of pristine 2D-MoS$_2$ depicts characteristics crystal planes of (110), (013), and (010); (c) the HRTEM images of typical few-layered 2D-MoS$_2$ with an interplanar distance of 6.3 Å; (d) line intensity profile of the line drawn in the inverse FFT image(GATAN Inc., USA).

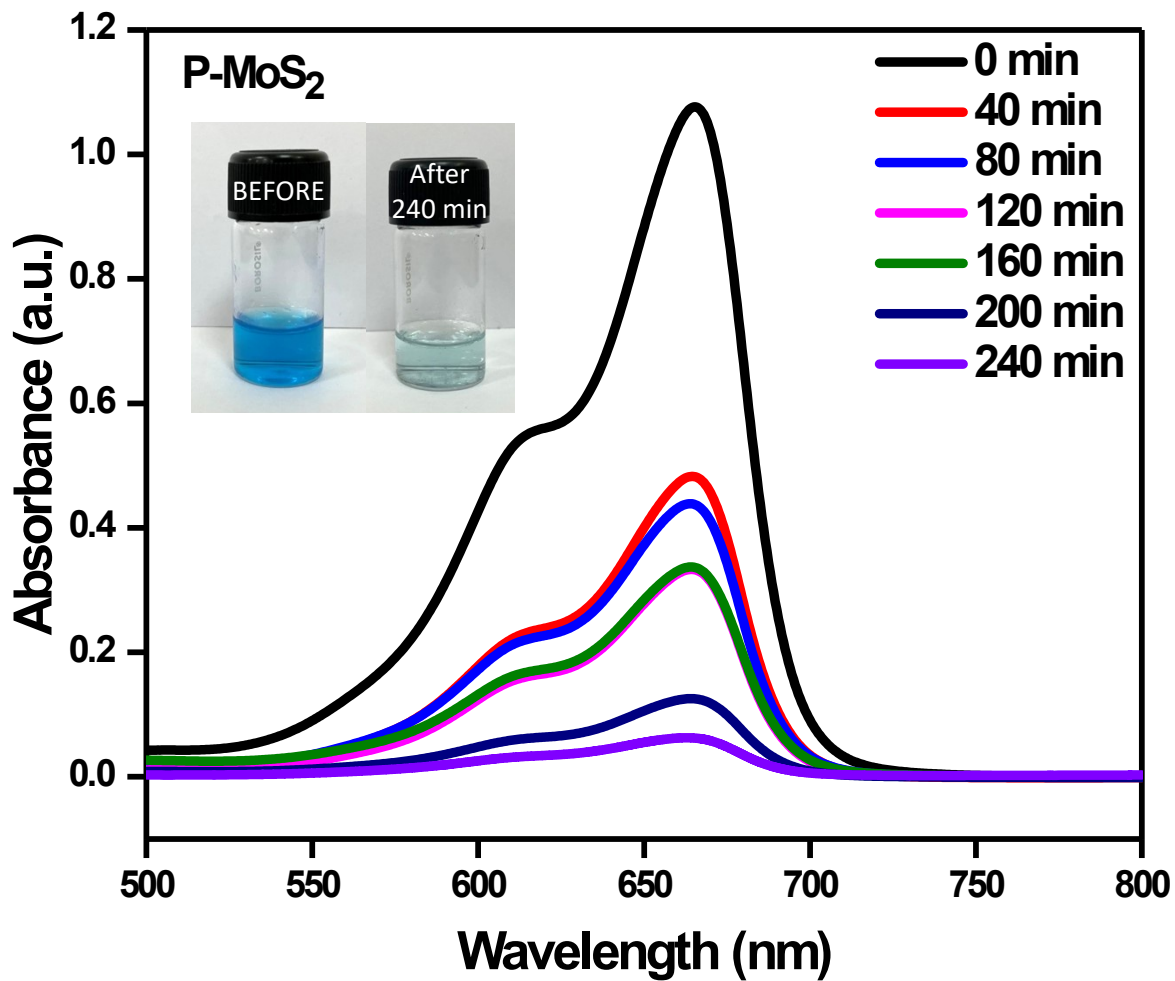## S5. Photocatalytic Dye-degradation

Figure S5: *UV-Vis absorbance spectra as a function of time of P-MoS₂ in 10 ppm MB dye.*
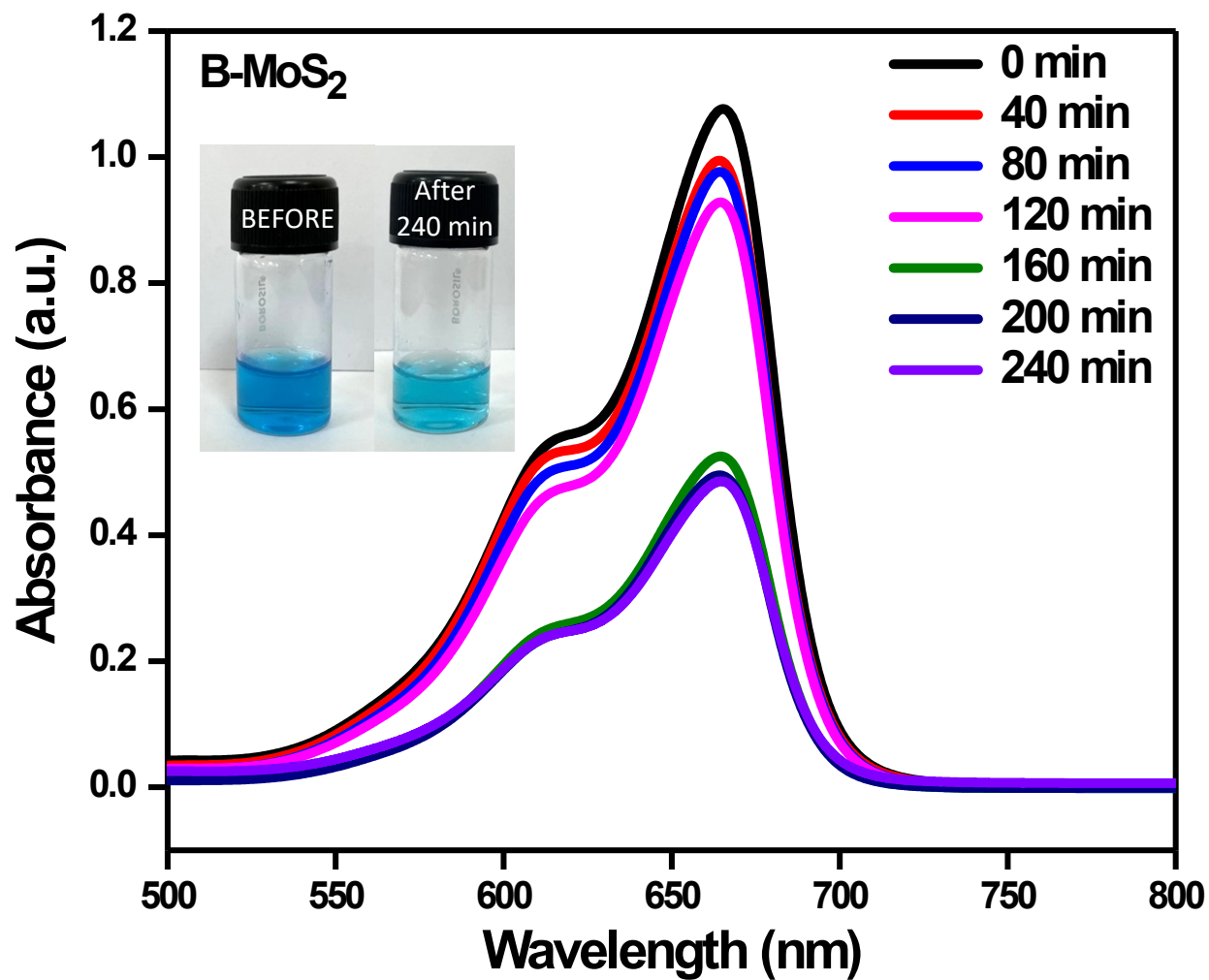
Figure S6: UV-Vis absorbance spectra as a function of time of bulk MoS$_2$ in 10 ppm MB dye solution.
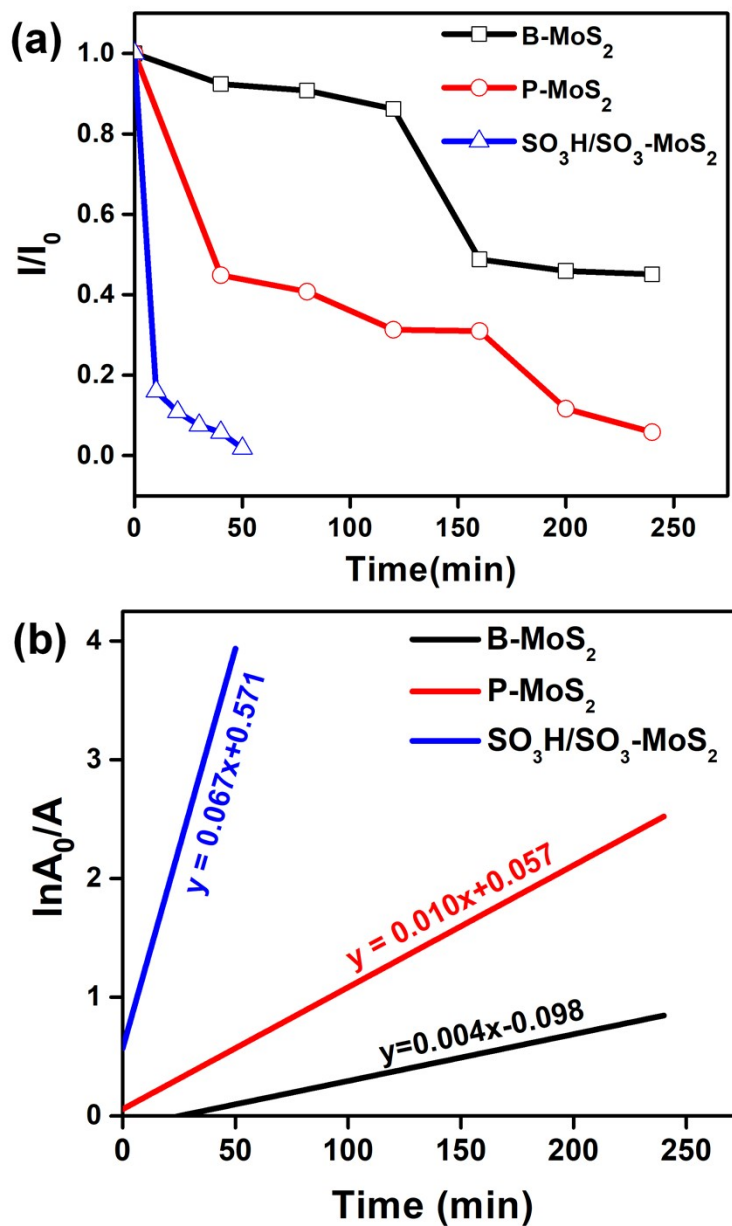
S6. Kinetics of Dye Degradation:

Figure S7: (a) Normalized intensity plots for SO_3H/SO_3-MoS_2, P-MoS_2, B-MoS_2 and as a function of time illustrating the MB dye degradation rate in 10 ppm dye solution; (b) demonstrates the rate kinetics plot of photocatalytic MB degradation using SO_3H/SO_3-MoS_2, P-MoS_2, and B-MoS_2.

S7. BET Surface Area:

In order to understand the better catalytic performance of SO_3H/SO_3 functionalized MoS_2, compared to pristine MoS_2, BET surface area and pore size distribution of both samples were evaluated by nitrogen adsorption isotherm measurements. Both the samples exhibited typical type IV isotherm with H_3 hysteresis loops attributing mesoscale pores in the materials. The BET surface area (SSA) for sulfonated MoS_2 is 23.532 m^2/g which is higher compared to pristine MoS_2 (19.719 m^2/g). The higher accessible surface area with additional surface functionality make the SO_3H/SO_3 functionalized MoS_2 catalytic more active for organic dye degradation compared to pristine MoS_2.

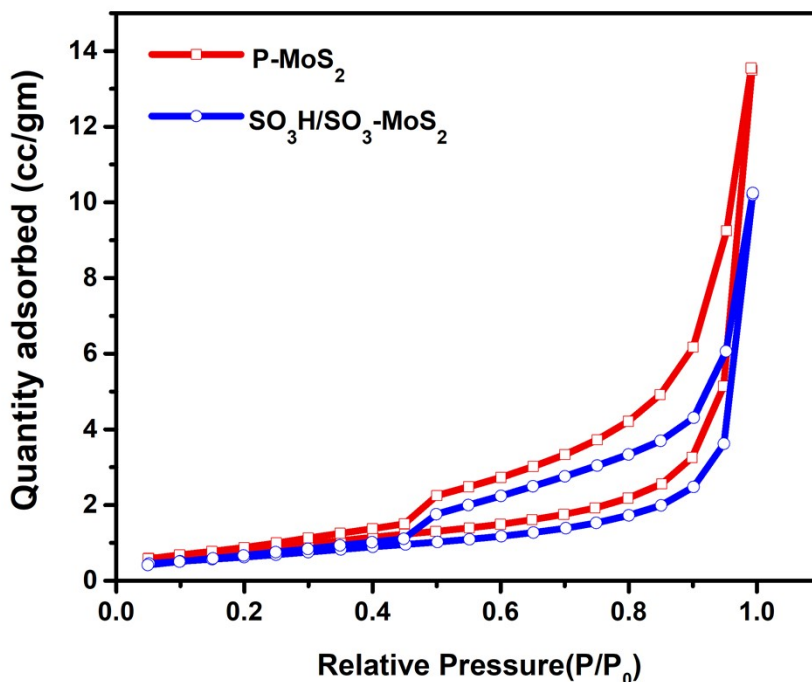*Figure S8: Illustrates the N_2 adsorption/desorption isotherms data of SO_3H/SO_3-MoS_2 obtained during the BET measurement*

References:

[1]   Y. Qi, Q. Xu, Y. Wang, B. Yan, Y. Ren, and Z. Chen, "CO2-Induced Phase Engineering: Protocol for Enhanced Photoelectrocatalytic Performance of 2D MoS2 Nanosheets," *ACS Nano,* vol. 10, no. 2, pp. 2903-2909, 2016/02/23 2016, doi: 10.1021/acsnano.6b00001.

[2]   Z. Liang *et al.*, "Facile preparation of metallic 1T phase molybdenum selenide as cocatalyst coupled with graphitic carbon nitride for enhanced photocatalytic H2 production," *Journal of Colloid and Interface Science,* vol. 598, pp. 172-180, 2021/09/15/ 2021, doi: https://doi.org/10.1016/j.jcis.2021.04.066.