

Supporting Information

Room Temperature Synthesis of an Amorphous Molybdenum Sulfide Based Composite: Characterization and Photocatalytic Hydrogen Evolution.

Felix Niefind, John Djamil, Wolfgang Bensch,* Bikshandarkoil R. Srinivasan, Ilya Sinev, Wolfgang Grünert, Mao Deng, Andriy Lotnyk, Lorenz Kienle, Laura Dura, Sven Hansen, Torsten Beweries

1. Raman measurements

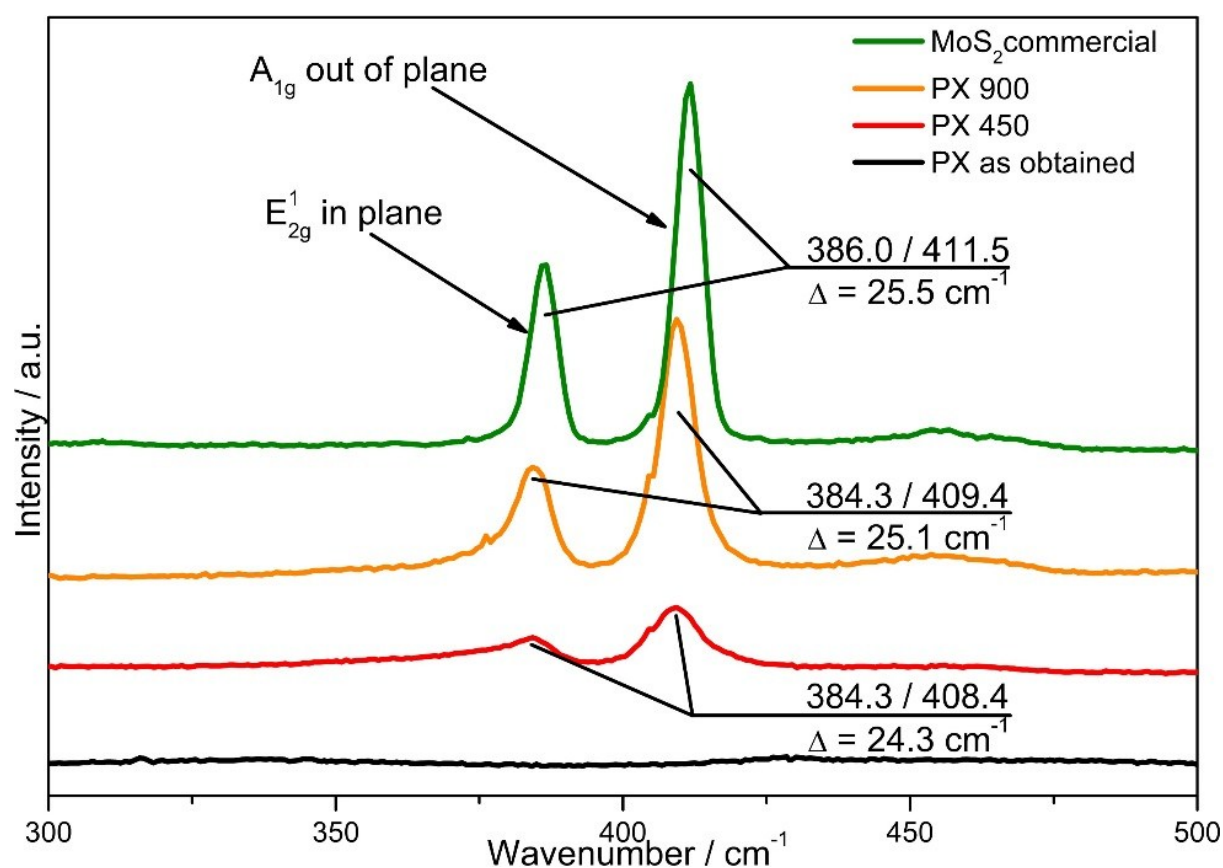


Figure S1. Raman spectra of PX (black trace), PX450 (red trace), PX900 (orange trace) and commercial MoS₂ (green trace).

2. Infrared measurements

Figure S2 shows the MIR spectra of PX, ATM, hydrazine and ammonia for comparison. If residues of the starting material ATM are still in the sample vibrations of NH_4^+ in the MIR and MoS_4^{2-} in the MIR and FIR regions should be observable. Comparison of the MIR spectra of ATM and PX demonstrates that the intense absorption of the MoS_4^{2-} ion is absent in PX. But some other broad bands can be observed although not very intense and quite broad which renders the assignment rather difficult: the band at 1580 cm^{-1} can be assigned as the deformation vibration of a N-NH_2 group, 1400 cm^{-1} fits with the deformation vibration of H-N-H , and the weak band at 986 cm^{-1} may be assigned to the N-N vibration of a $\text{Mo-NH}_2\text{NH}_2$ group.¹ Note that the intensities of the absorptions in Figure 8 are normalized (against the peak with the highest intensity) and without this normalization the bands of PX were not visible due to a very low intensity indicating a low concentration of N species in PX.

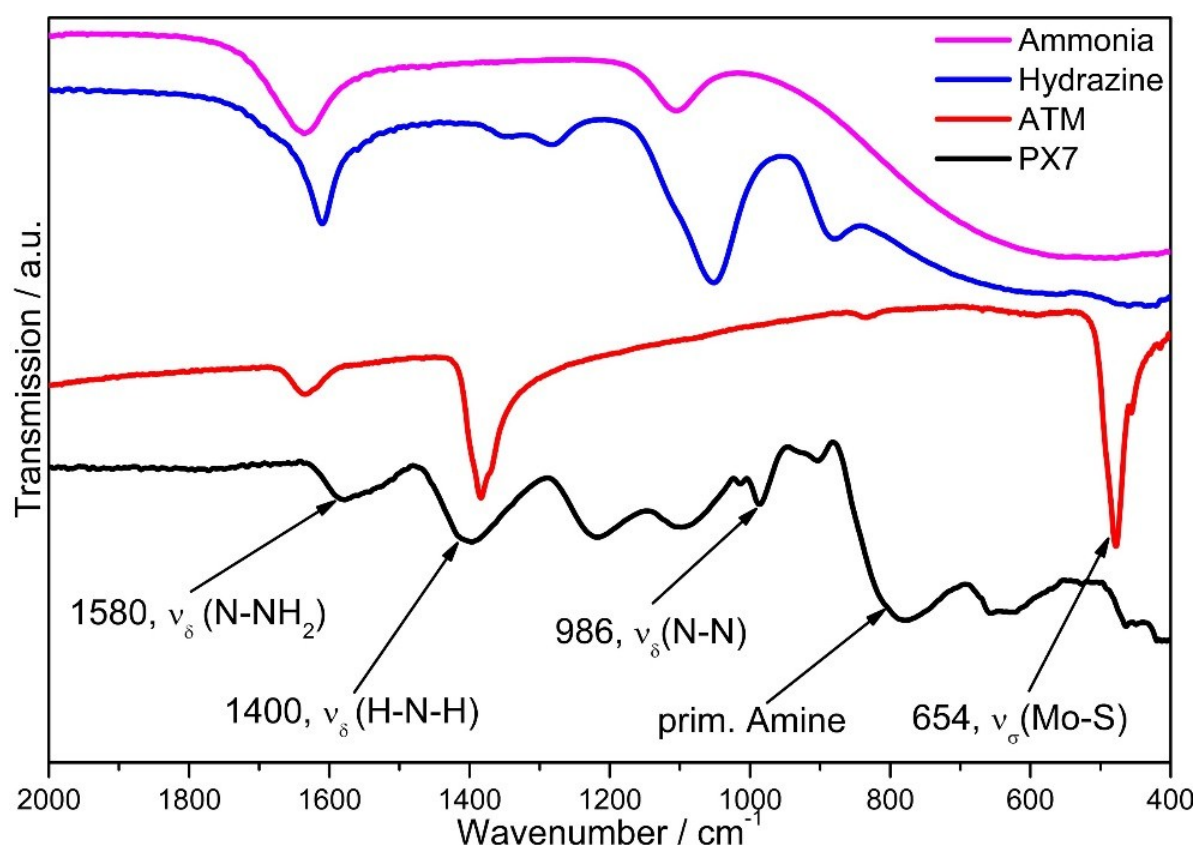


Figure S2. Comparison of the MIR spectra of PX (black trace), ATM (red trace), hydrazine (blue trace), and ammonia (purple trace).

A distinct assignment of the remaining absorptions is not straightforward due to the broadness of the bands. In any case, the vibrational spectroscopy data give clear evidences that no MoS_4^{2-} units are present in PX.

3. Far Infrared Measurements (FIR)

The FIR spectra (**Figure S3**) of PX heated to 450/900 °C and of commercial MoS_2 display the signals of the A_{2u} (out-of-plane) and the E_{1u} (in-plane) vibrations of the planes of MoS_2 at 468 and 383 cm^{-1} . The A_{2u} vibration exhibits a pronounced variation of the intensity. While commercial MoS_2 only shows a weak A_{2u} band, those of the materials heated to 450 and 900 are more intense. The other band can be assigned to the in plane vibration of MoS_2 which is present in all three samples - commercial MoS_2 , PX450 and PX900 – with more or less the same intensities which does not depend on the number of stacked MoS_2 layers. For the as prepared sample none of these absorptions can be seen in the spectrum, but two broad signals at about 480 and 340 cm^{-1} .

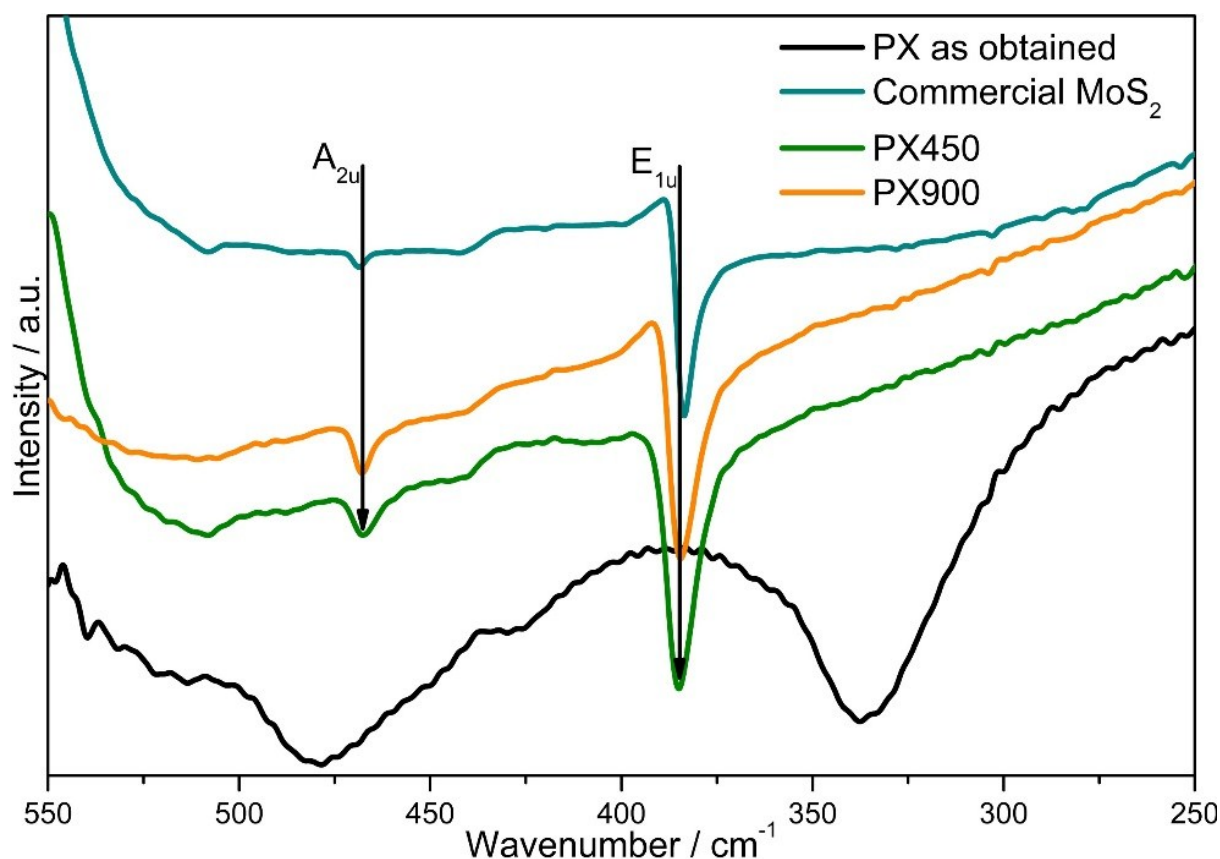


Figure S3. FIR of PX (black trace) in comparison with PX450 (green trace), PX900 (orange trace) and commercial MoS_2 (light blue trace).

Figure S4 again depicts the FIR of PX in comparison with ATM and commercial MoS₂. The absorption at 480 cm⁻¹ may be caused by a Mo-H₂O vibration (477 cm⁻¹) due to contamination with water from the air, but in this case two more bands at about 511 cm⁻¹ and 551 cm⁻¹ should be seen which are not present. The XPS measurements (see SI Figure S2) in the O 1s region give no hints for the presence of H₂O. According to literature the signal can be assigned to the Mo-N vibration of a Mo-NH₂-NH₂ coordination.^{1,2} The second band at 334 cm⁻¹ can be assigned to a bridging S₂-S²⁻ ligand between two Mo atoms. This band was assigned to imperfections in the arrangement of MoS₂ sheets which have defects in their basal sulphur atom arrangement or in other words interconnections of two layers by Mo-S-Mo bridges.³

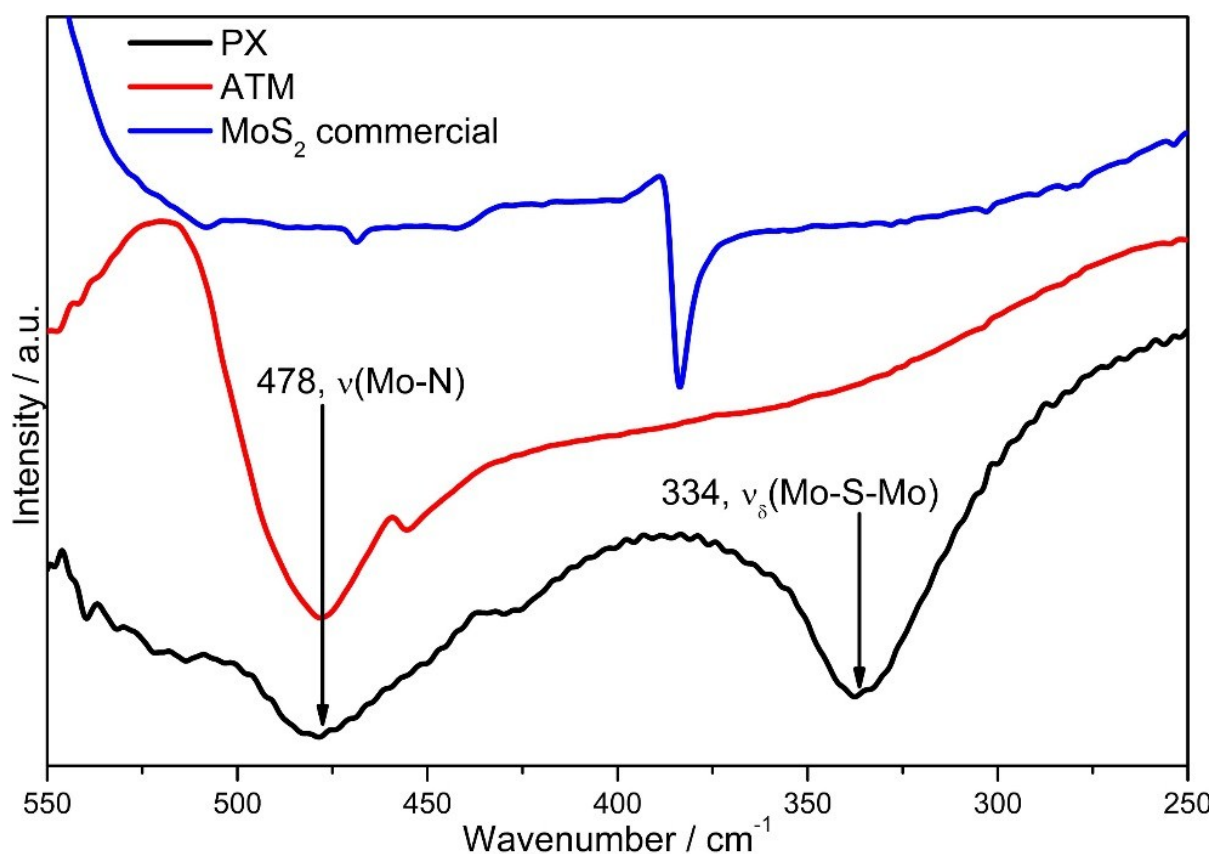


Figure S4. FIR of PX (black trace) in comparison with ATM (red trace) and commercial bulk MoS₂ (blue trace).

4. X-ray photoemission spectroscopy (XPS)

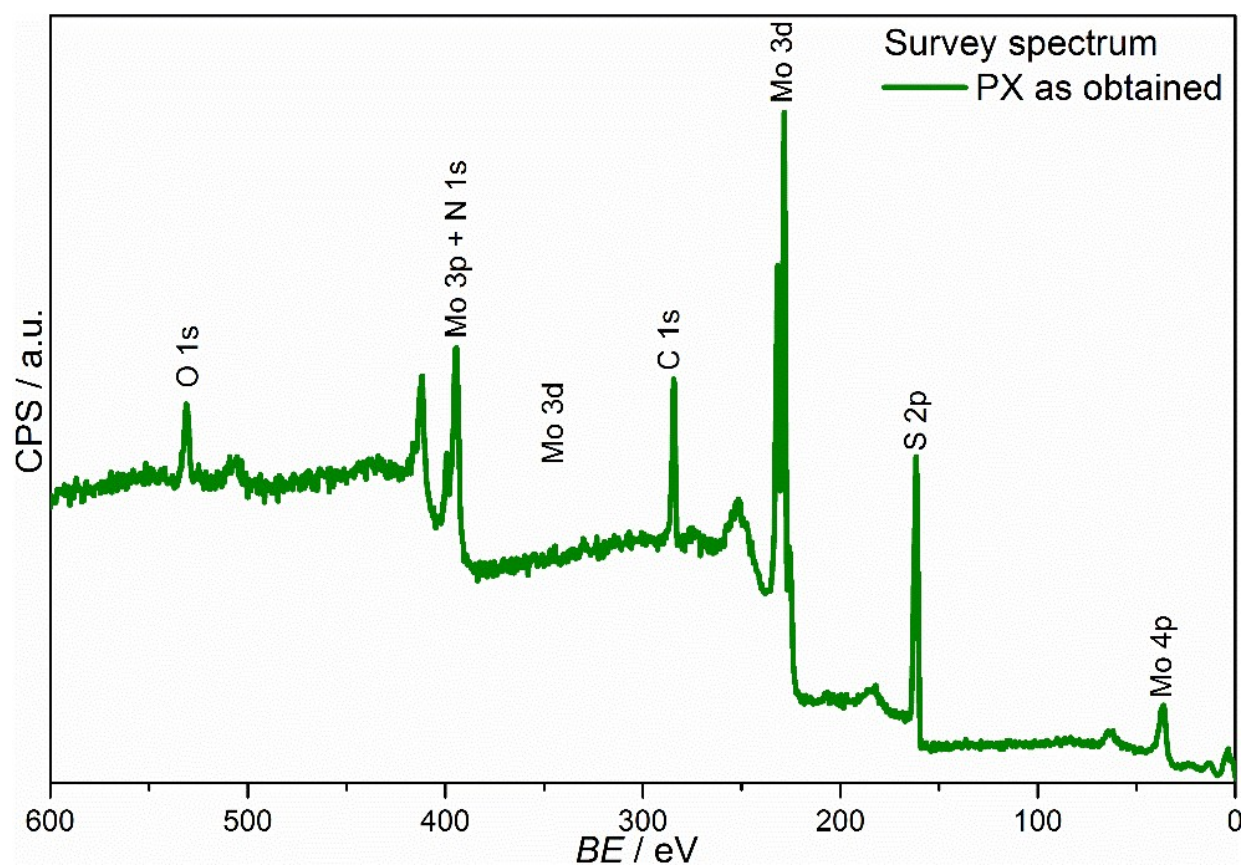


Figure S5. XPS survey spectrum of PX.

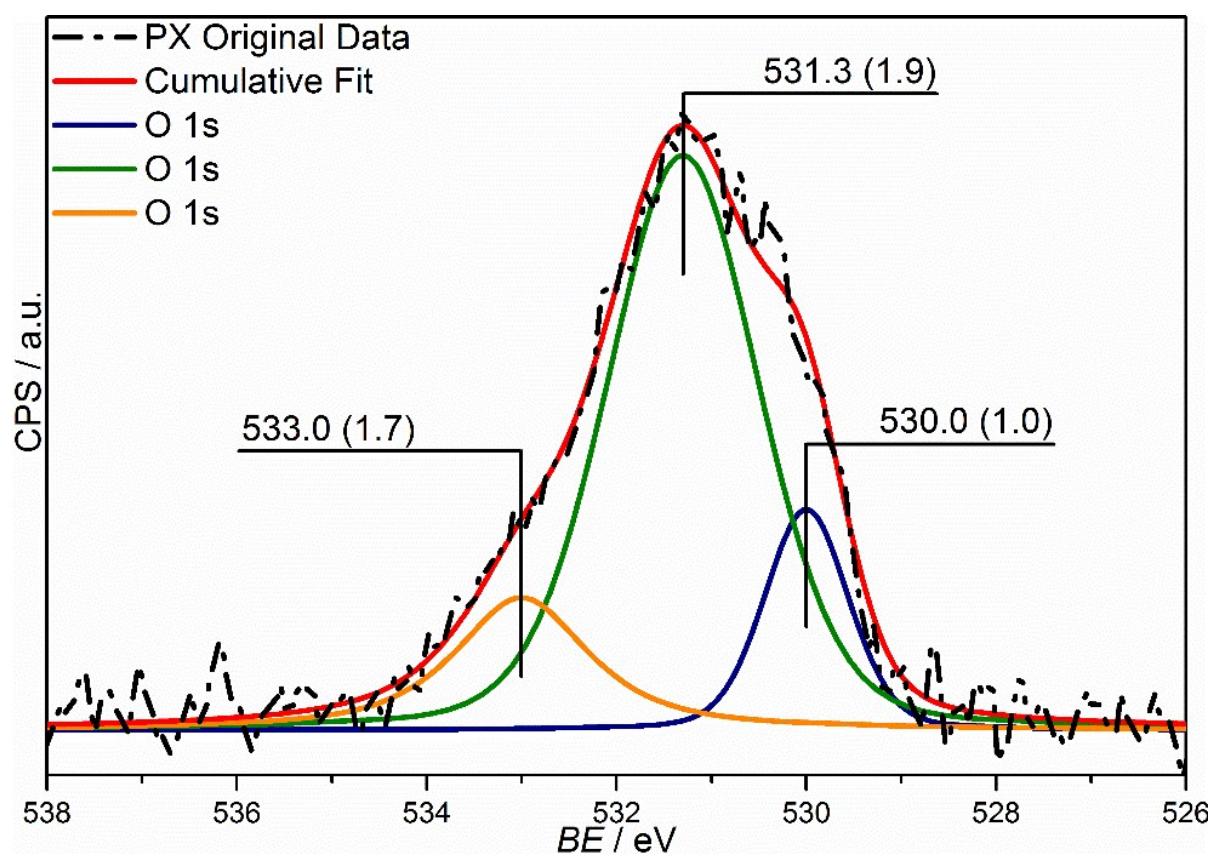


Figure S6. XPS measurement of the O 1s region of PX as obtained with the original data (black dash dotted trace), the cumulative fit (red trace) and the O 1s fitted curves (various colors).

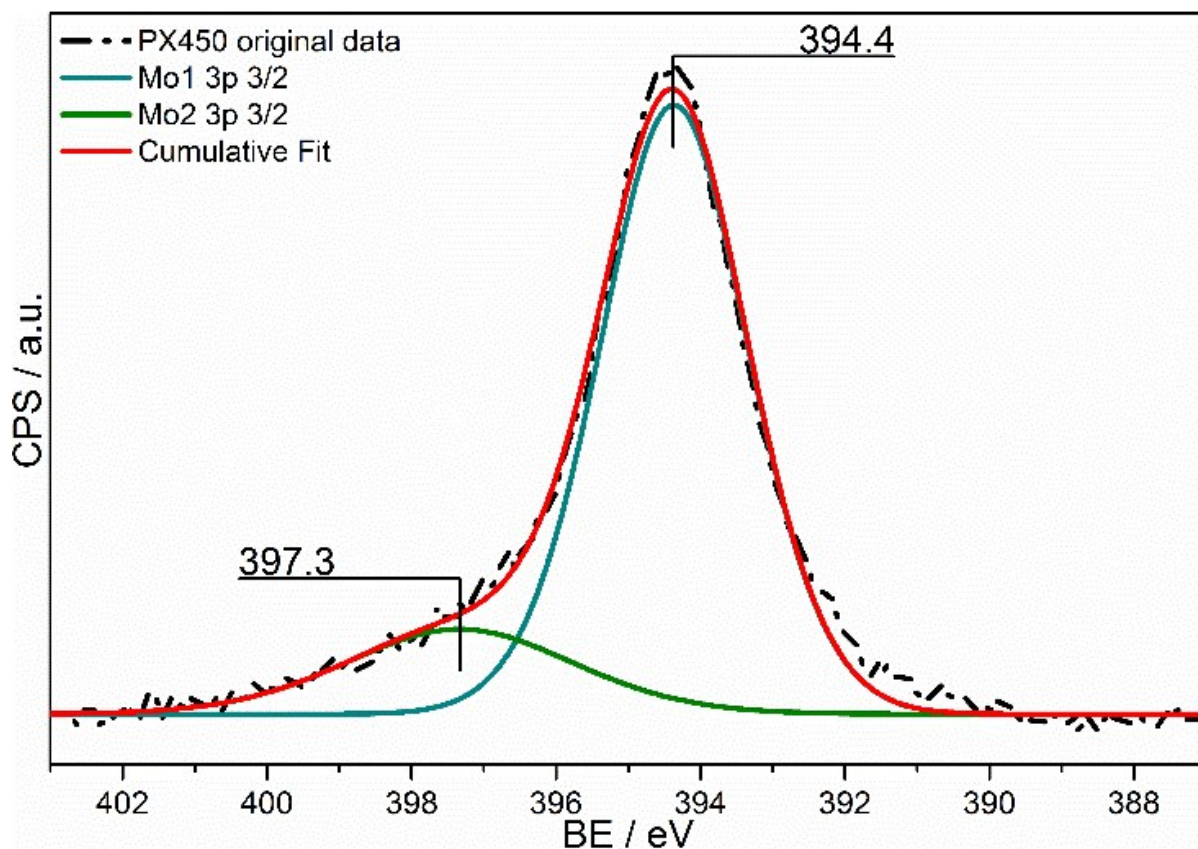


Figure S7. XPS measurement of the N 1s region of PX after heating to 450 °C (PX450) with the original data (black dash dotted trace), the cumulative fit (red trace) and the Mo 2p_{3/2} fitted curves (green and blue trace).

6. TEM analysis

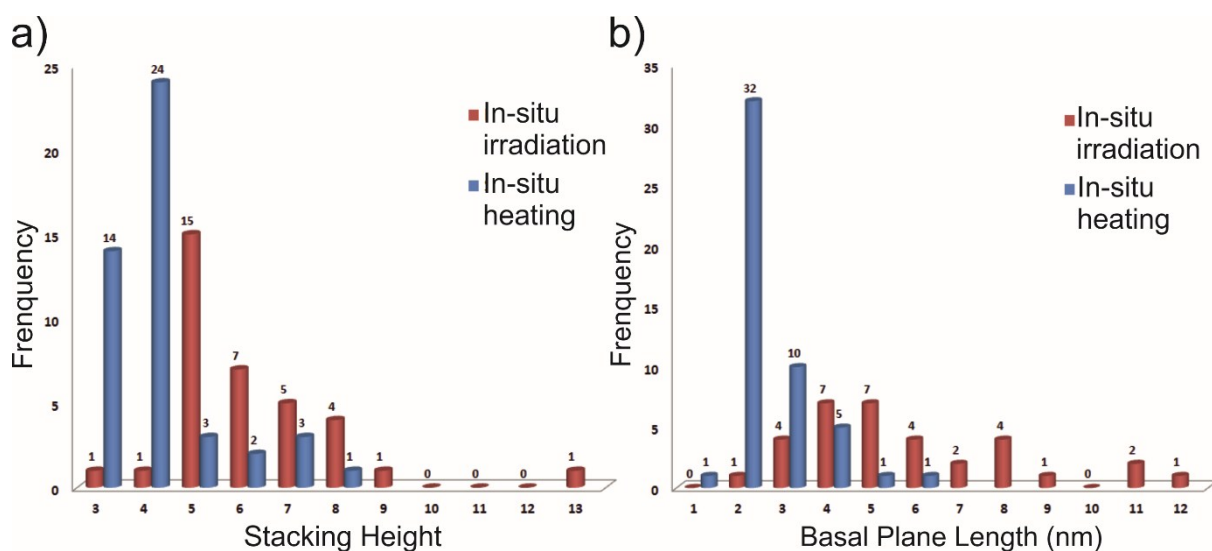


Figure S8. (a) Stacking height distribution counted from the HRTEM micrograph where PX was under in-situ irradiation after 1 hour (red column), and from the micrograph where the sample was in-situ heated to 500 °C (blue column). (b) Basal plane length distribution of the in-situ irradiated (red column) and in-situ heated (blue column) PX sample.

7. Thermal analyses (DTA/TG)

The thermal decomposition reaction of PX was studied with DTA-TG up to 900 °C in inert atmosphere (heating rate: 4 K/min; **Figure S9**). The weight loss starts at relatively low temperatures and a not well resolved step occurs at about 350 °C. During this decomposition reaction several N containing species such as NH_3 and N_2H_4 are emitted from the sample (MS spectra not shown here). Above about 350 °C another mass loss of about 3.3 % is accompanied by an exothermic event in the DTA curve indicative for the onset of crystallization of MoS_2 . For the thermal decomposition of ATM it is proposed that MoS_3 forms as an intermediate material^{4,5} followed by decomposition of MoS_3 and crystallization of MoS_2 which is also accompanied by an exothermic event. The XRD pattern of the compound heated to 450 °C (Fig. 2) shows the presence of highly disordered MoS_2 slabs supporting the assumption that the exothermic event is caused by the crystallization process. In the temperature range from 400 to 900 °C only a small weight loss of about 2 % occurs which may be due to the emission of material incorporated between the expanded van der Waals gaps (see discussion above). The formation of MoS_2 slabs also matches the XPS measurements of PX heated to 450 °C, where a new Mo species occurred with a binding energy matching with Mo in the oxidation state +IV while the two other species vanished.

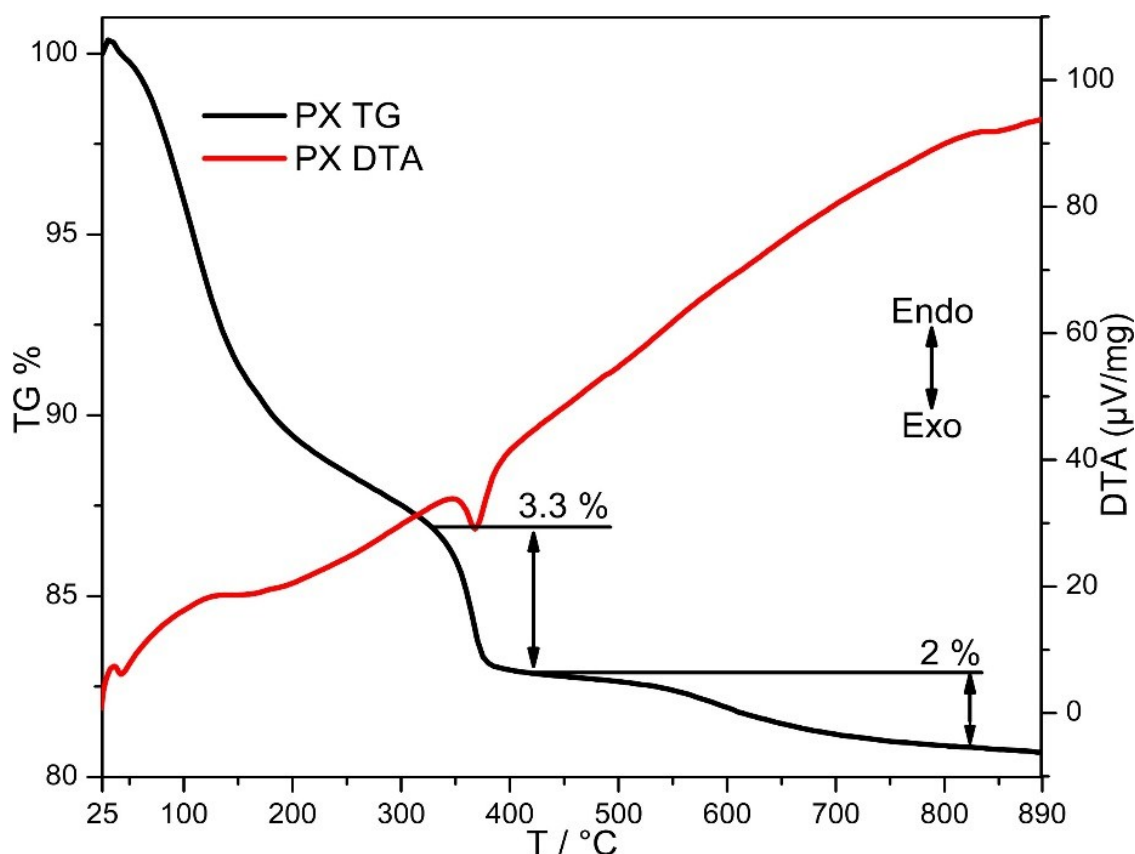


Figure S9. Thermal analysis (DTA/TG) of PX up to 900 °C.

Another set of heating experiments has been conducted where the temperature has been raised successively to specific values and the respective samples were directly examined via elemental analyses (Table S1).

Table S1. Heating experiments of PX to various temperatures and results of the elemental analyses.

Sample	Heating temperature / °C	N %	H %	N : H molar ratio
PX	---	various	various	Between 1 : 4 and 1:5
PX100	100	4.95	1.41	1 : 4.0
PX200	200	4.01	0.95	1 : 3.3
PX300	300	2.98	0.51	1 : 2.4
PX340	340	2.03	0.31	1 : 2.2
PX350	350	1.98	0.28	1 : 2.0
PX360	360	1.50	0.16	1 : 1.4

The as prepared PX contains ratios of N : H between 1 : 4 and 1 : 5. This depends on the sample as the nitrogen and hydrogen contents are varying. Upon heating the sample loses both N and

H, but H at a larger rate. Thus the molar ratio of N : H reaches 1 : 2.0 exactly at 350 °C, which is the temperature of crystallization. This ratio fits perfectly to hydrazine (N_2H_4) and gives another hint that up to that crystallization hydrazine is involved in the material. Another NH_x species seems to be present in the as prepared compound as well but is emitted upon heating prior to hydrazine.

8. Visible-light driven hydrogen evolution

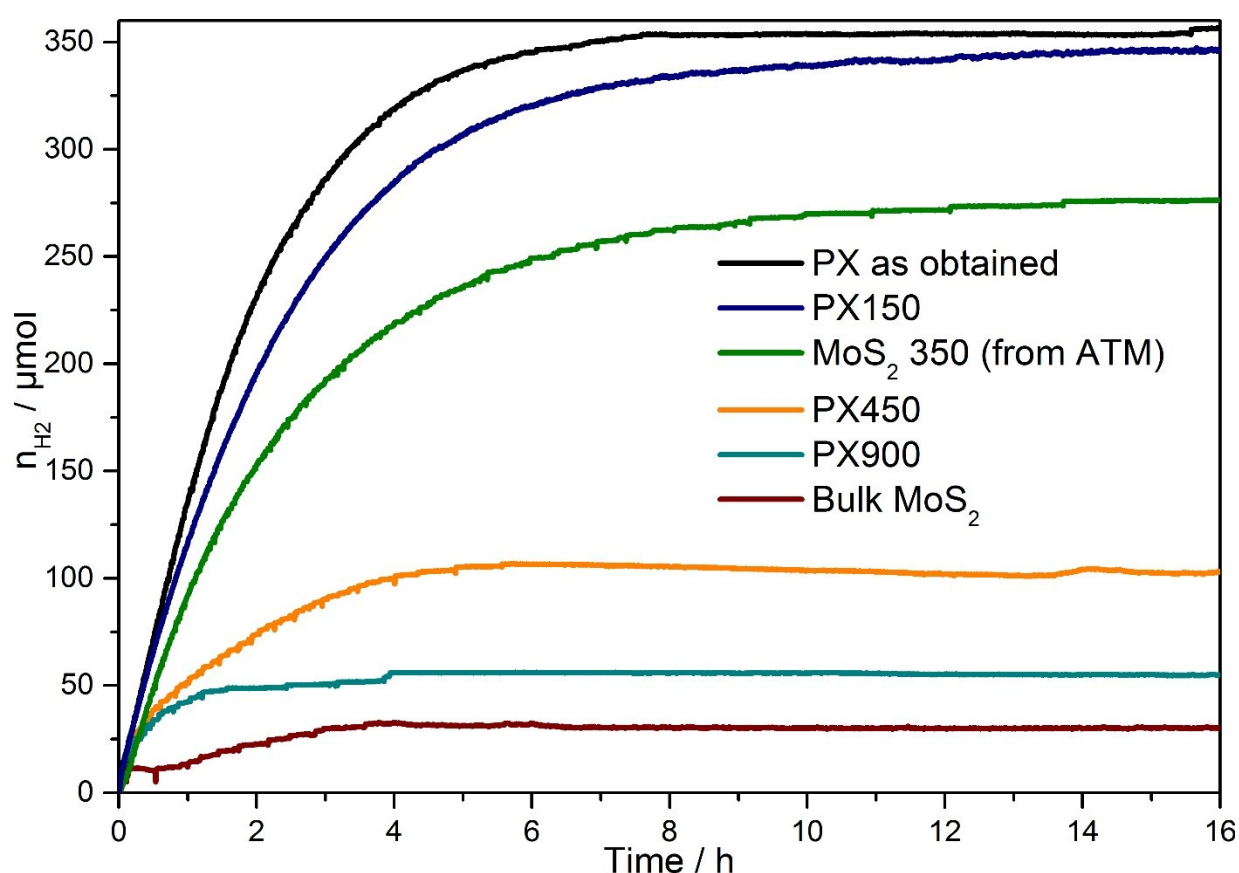


Figure S10. Development of the H_2 production during 16 hours of irradiation of PX as obtained (black trace), three heated samples (150 °C dark blue trace, 450 °C orange trace, 900 °C light blue trace), commercial bulk MoS_2 (dark red trace), and nanocrystalline MoS_2 prepared via a thermal decomposition of ATM at 350 °C for comparison (green trace).

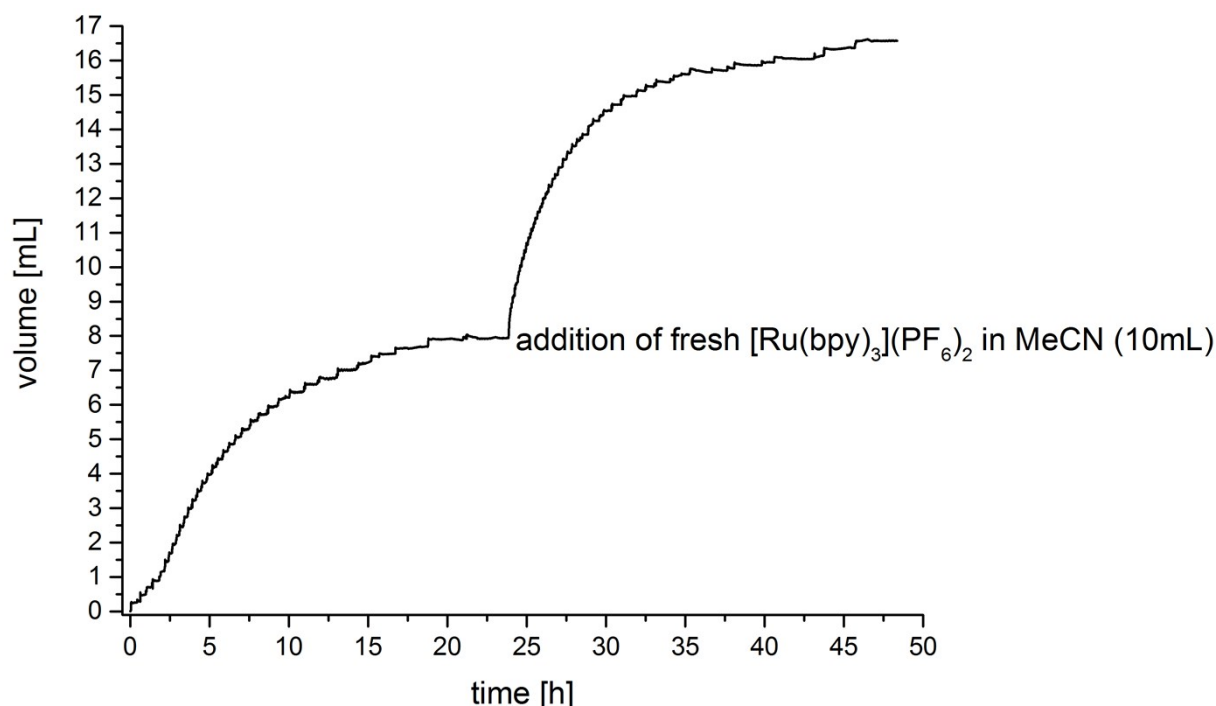


Figure S11. Depiction of a measurement of PX and the deactivation of the photosensitizer and addition of fresh PS to reinitialize the reaction.

The deactivation of the Ru dye leads to a retardation of the whole reaction. To proof that the photosensitizer is the weak component it was reapplied after the reaction had completely stopped after 25 h of reaction. After the PS was added, the system had time to equilibrate and then the reaction was reinitialized with light, which started the reaction immediately. This proofed that the catalyst is stable under the reaction conditions.

[1] S. Baskaran, C. Sivasankar, *J. Mol. Catal. A Chem.* **2013**, 370, 140-144.

[2] H. Vrubel, V. H. C. Verzenhassi, S. Nakagaki, F. S. Nunes, *Inorg. Chem. Commun.* **2008**, 11, 1040-1043.

[3] T. Weber, J. C. Muijsers, J. H. M. C. van Wolput, C. P. J. Verhagen, J. W. Niemantsverdriet, *J. Phys. Chem.* **1996**, 100, 14144-14150.

[4] A. Müller, T. P. Prasad, R. Menge, *Z. Anorg. Allg. Chem.* **1972**, 391, 107-112.

[5] T. P. Prasad, E. Diemann, A. Müller, *J. Inorg. Nucl. Chem.* **1973**, 35, 1895-1904.