Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Influence of Organic Promoter Gradient on the MoS_2 Growth Dynamics

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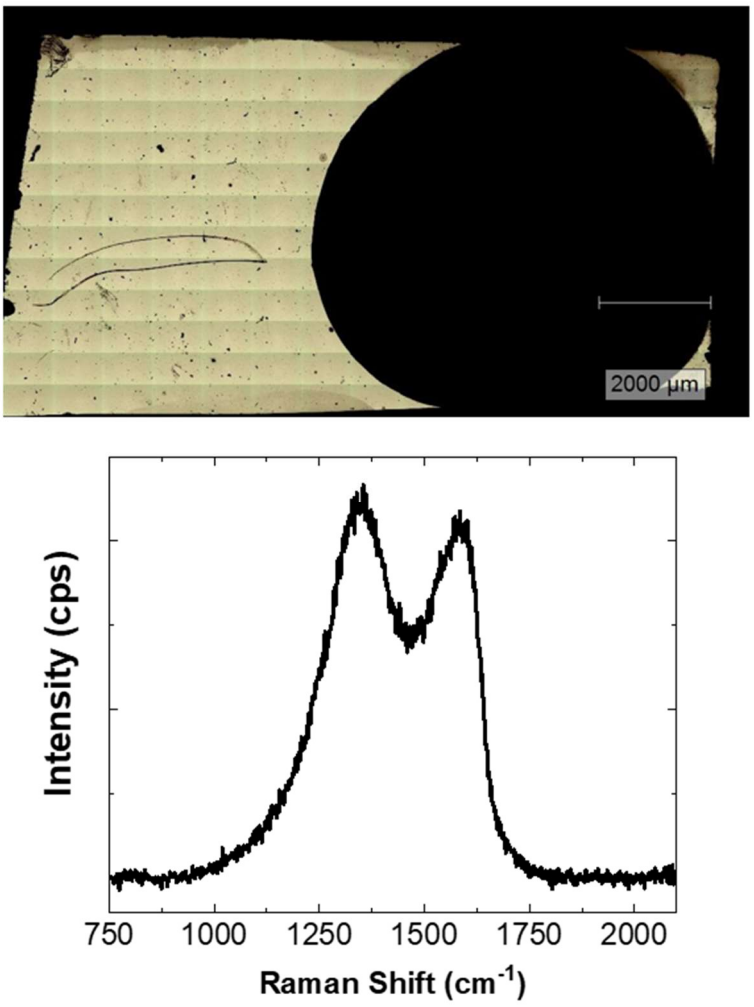

Figure S1 Optical Image of a representative PTCDA sacrificial substrate and the Raman spectrum of the PTCDA drop after the growth process.

In standard growth the silicon substrate is totally covered with PTCDA, in this case we deposited only a drop in order to show the difference between the carbonized layer and silicon. The Raman analysis demonstrates a complete carbonization of the organic promoter with no residuals of the organic molecules, after the growth process.

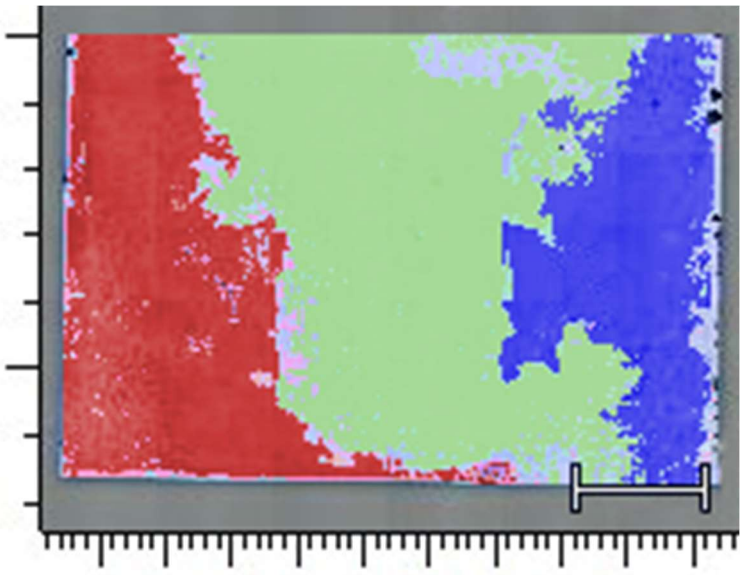

Figure S2 False color image of the whole substrate, highlighting the area with similar optical contrast, (±5% of the average value).

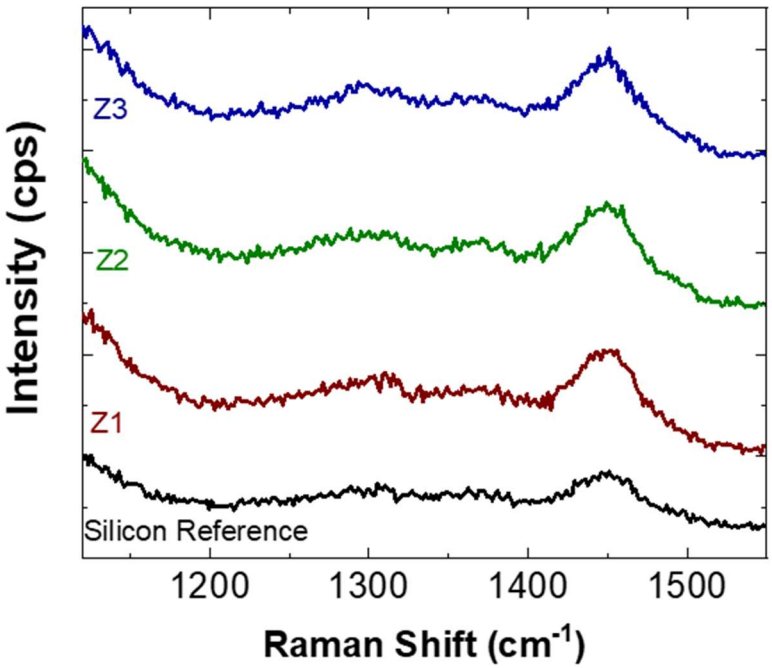

Figure S3 Raman analysis in the range of the amorphous carbon, revealing that no amorphous carbon or

PTCDA residuals are present in any analyzed areas of the sample. The peak at 1450 cm^{-1} is due to the third order of the silicon peak.

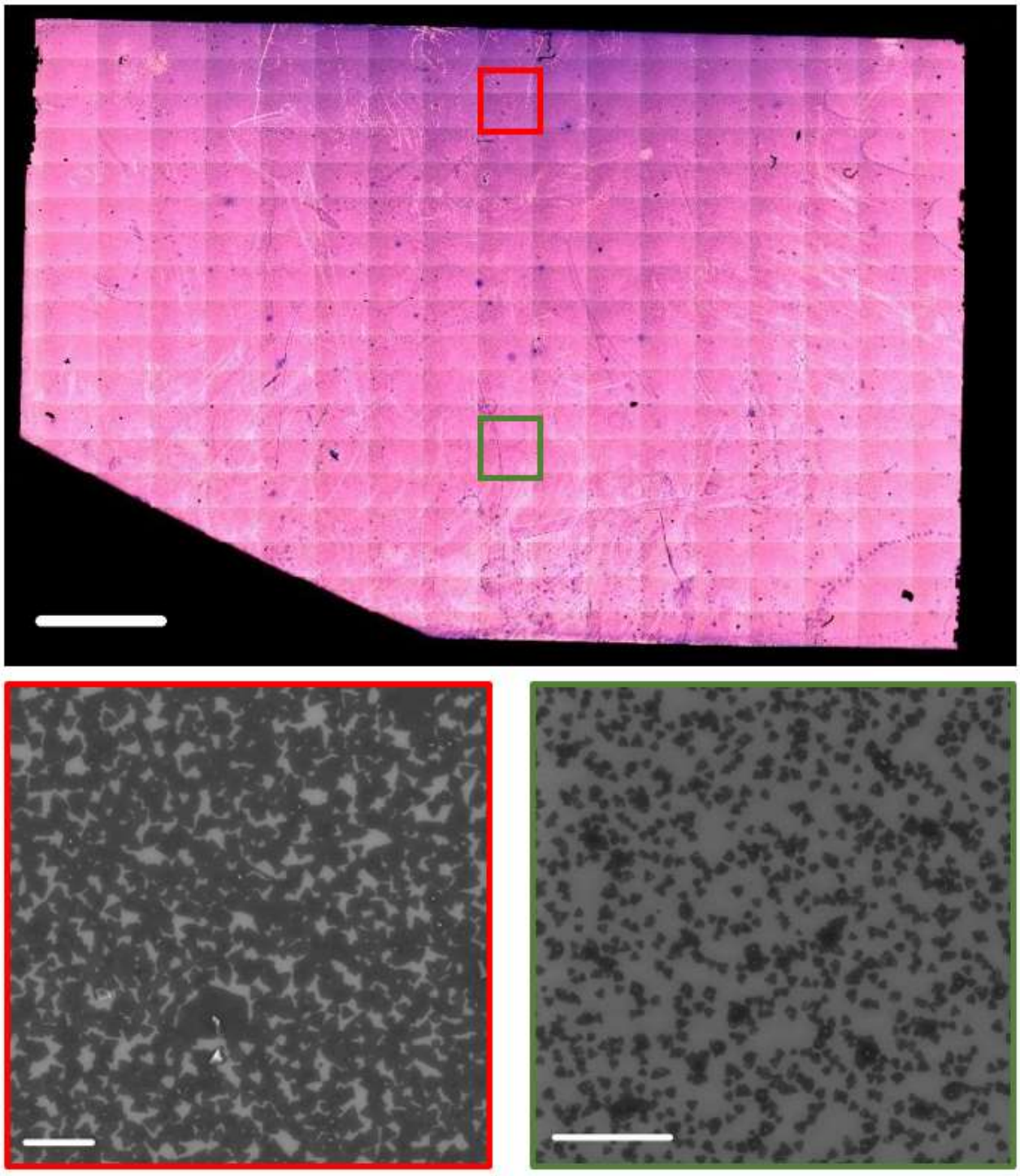

Figure S4 Growth process outcome without the PTCDA sacrificial substrate. Optical image of the whole substrate, the scale bar is 2000 μm. SEM migrographs of the two highlighted areas, the scale bar is 2 μm. It is worth noting that in the case of a growth process without the PTCDA sacrificial substrate, the main difference along the growth substrate, mainly due to the different Mo/S ratio, is the size and density of the MoS_2 triangular crystals. No dendritic structures are found on the whole substrate.

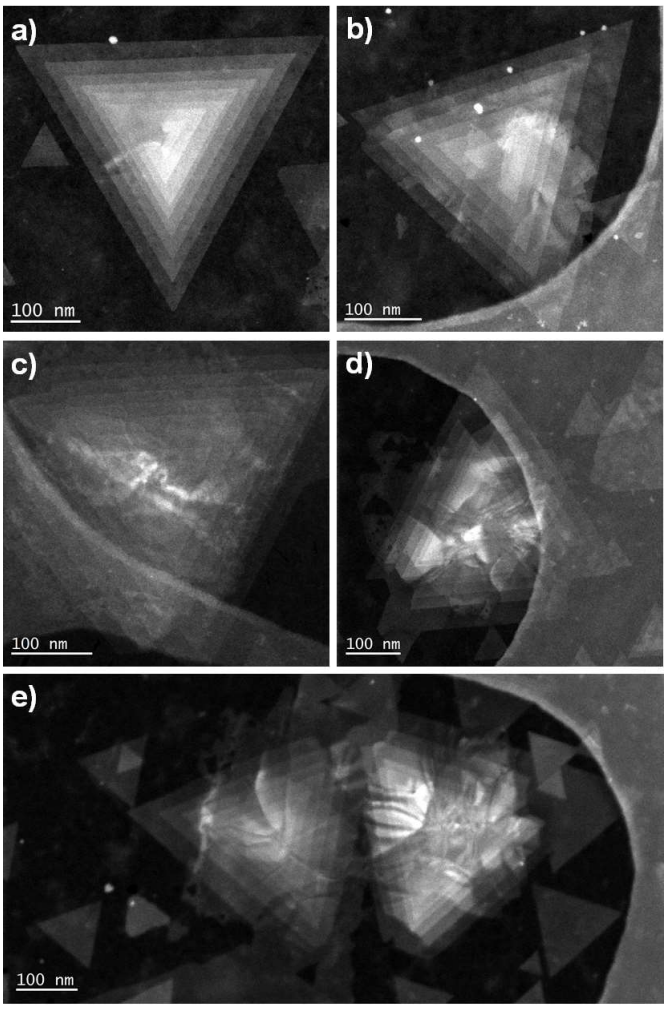

Figure S5: series of STEM images of the pyramidal structures. The overgrowth of pyramidal structures is often observed. These structures are typically several micrometers wide and consequently too thick for TEM observation. However, several small pyramids (few hundreds of nanometers) have been found. Even though they are not thin enough for a conclusive analysis, a defective structure can be clearly observed at the center of each one. The crystallographic nature of these defects remains unclear but it can be concluded that they can act as nucleation centers of dendritic structures.

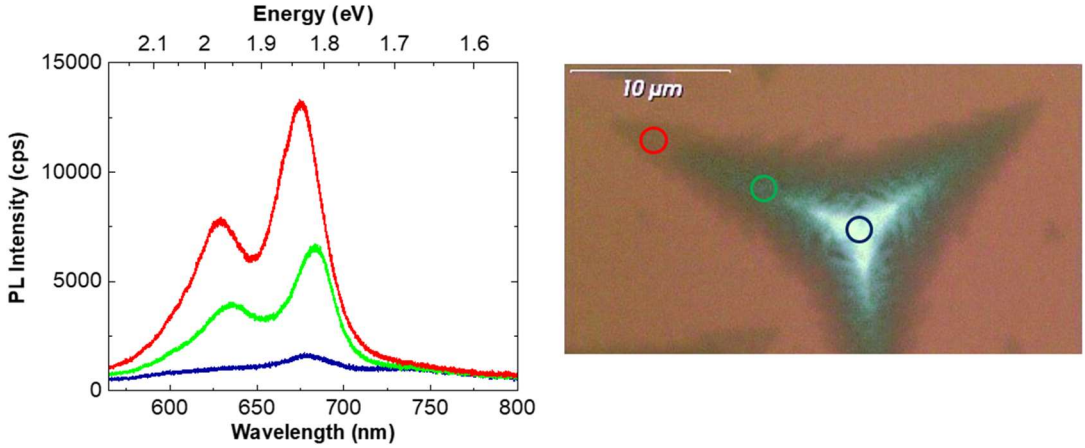

Figure S6 Representative PL spectra and the optical image of the area analyzed in Figure 2 of the manuscript.

The optical contrast demonstrates the increase of thickness in the central area of the dendritic structure.[1]It is worth noting that the same color code for the spot on the optical image and the PL spectra is used.

The PL spectroscopic analysis reveals that the integrated intensity decreases with increasing thickness, as expected due to the indirect-to-direct transition at the monolayer. Regarding the intensity of the single PL peaks, it is worth analyzing the ratio of the integrated intensities of the A and B excitons emission with increasing thickness. In the area defined by the red-spot, the ratio of the intensity results 1.68 and it decrease down to 1.61 in the green spot area. In case of the thicker area (blue spot) the B excitonic peak is not measurable due to the intensity decrease and an extreme broadening of the peak.

Considering the excitonic peak positions, the A exciton peak red-shifts from red spot (red spectrum) to the intermediate area (green spot), in fact the A exciton peak position in the red spot is 676 nm (1.83 eV) and it shifts up to 684 nm (1.81 eV) in the intermediate area. A similar shift is reported for the B exciton that The PL peak is set at 629 nm (1.97 eV) in the ML area and it shifts up to 635 nm (1.95 eV) in the intermediate area.

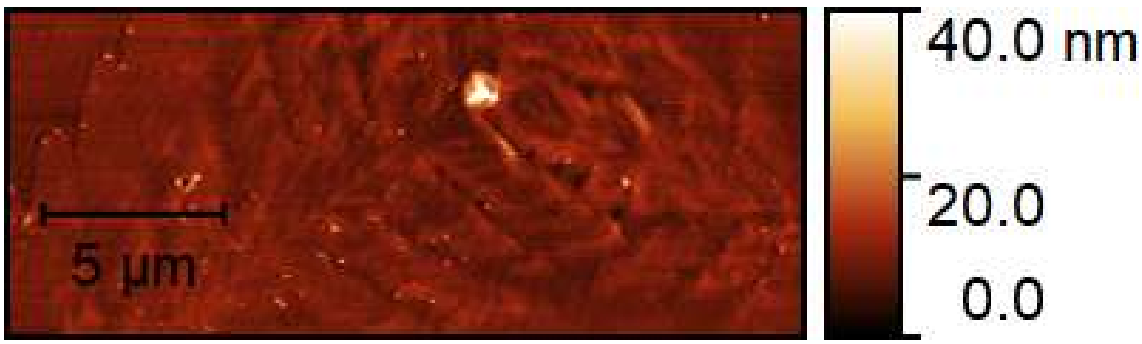

Figure S7 Atomic Force microscopic analysis of Z1 area. The central pyramid reach 10 nm thickness. The dendritic structures, close to the central pyramid, are 5 nm thick. Meanwhile the areas close to the edges are 2 nm thick, that are an indication for bilayer or trilayer.

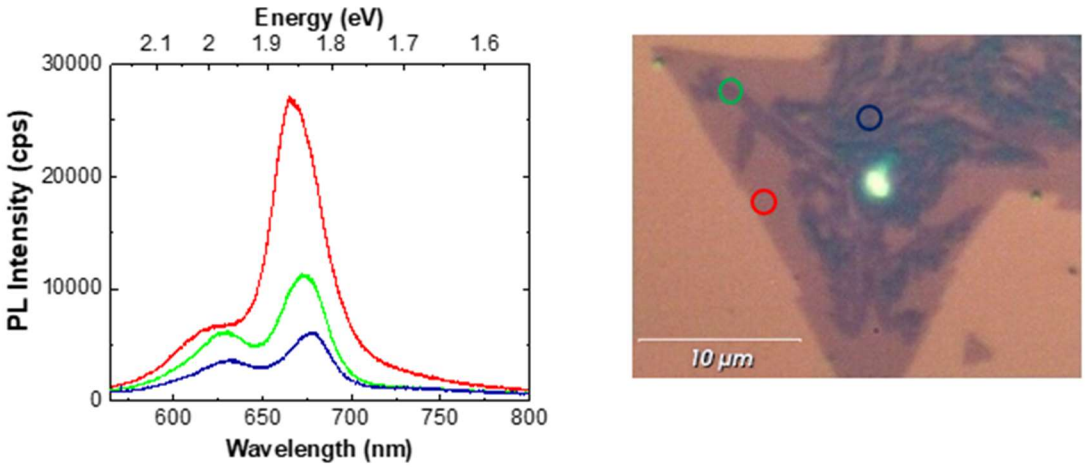

Figure S8 Representative PL spectra and the optical image of the area analyzed in Figure 3 of the manuscript.

The optical contrast demonstrates that the flake affected by dendritic overgrowth is bulk only in the central seeding point, meanwhile the dendritic overgrowth are few-layers structure.[1] Even the PL integrated intensity supports the optical contrast analysis. The analysis of the ratio of the A and B excitons emission intensity reveals that, in the red spot, the ratio of the intensity results 3.8 and it decrease down to 1.73 in the blue spot. It seems that also the ratio of the excitonic emission is a valuable benchmark method for the number of the layers.

Considering the excitonic peak positions, the A exciton peak red-shifts from the red spot (red spectrum) to the blue spot, in fact the A exciton peak position in the red spot is 668 nm (1.86 eV) and it shifts up to 678 nm (1.84 eV) in the blue spot. A similar shift is reported for the B exciton that The PL peak is set at 621 nm (2.00 eV) in red spot and it shifts up to 632 nm (1.96 eV) in the blue spot.

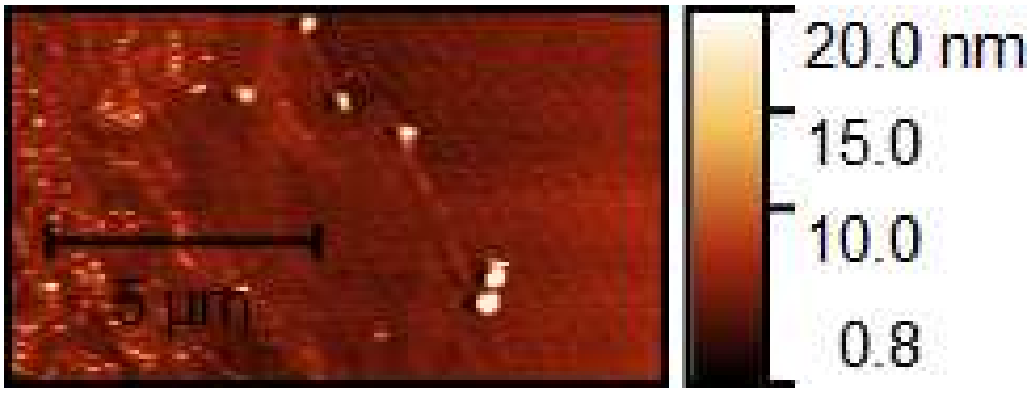

Figure S9 Atomic Force microscopic analysis of Z2 area. The dendritic structures have a thickness that varies between 2 and 3 nm, demonstrating a few-layer structures. The edges are 1 nm thick, that are an indication for monolayer.

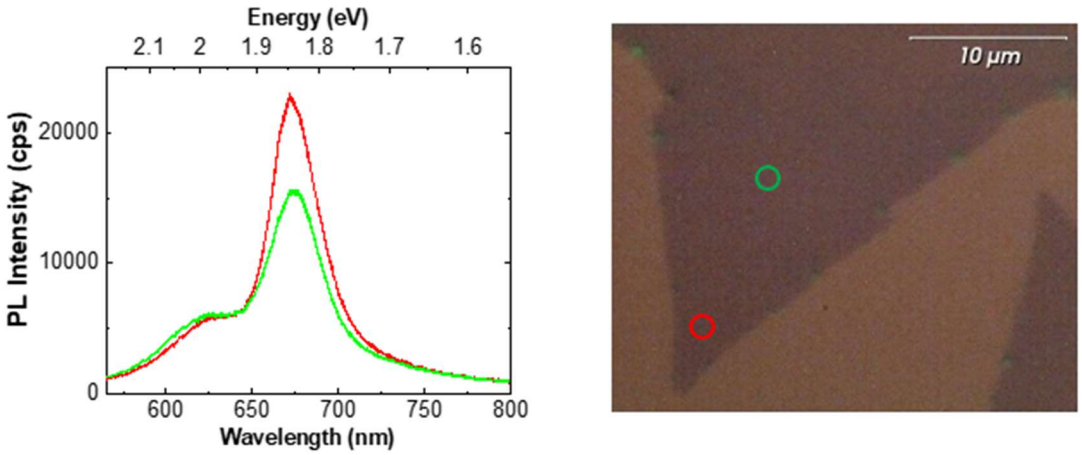

Figure S10 Representative PL spectra and the optical image of the area analyzed in Figure 4 of the manuscript.

In this particular area no optical contrast is detected. Even the PL integrated intensity supports the optical contrast analysis. In both the spots the A and B exciton appear at the same peak positions (A exciton 672 nm, 1.84 eV and B exciton 626 nm, 1.98 eV), however the B exciton has with a similar intensity meanwhile the A exciton emission looks quenched in the green spot compared to the red spot, where the Raman analysis (Figure 4 of the manuscript), suggest to have bi- tri-layer. The excitons intensity ratio varies from 3.75 (red spot) to 2.55 (green spot).

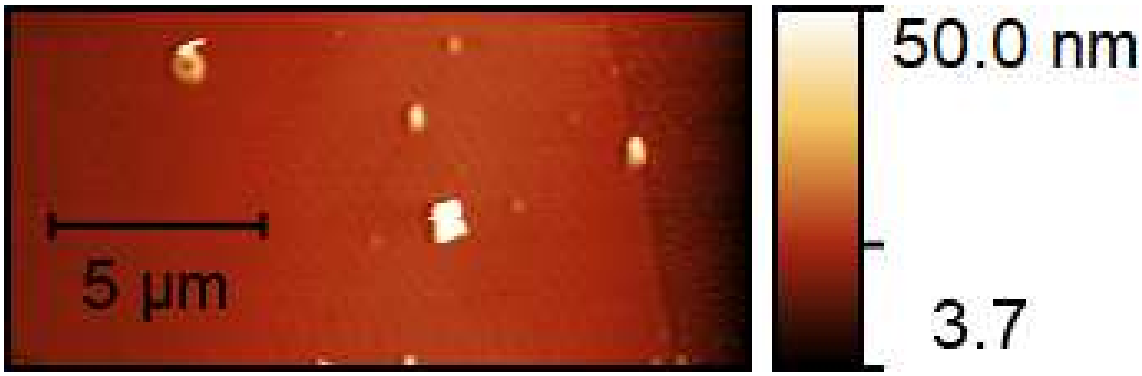

Figure S11 Atomic Force microscopic analysis of Z3 area. The edges are 1 nm thick, that are an indication for monolayer. It is possible to evidence a grain boundaries, the 20 nm thick grains along the grain boundaries is related to the oxidation of the monolayer MoS_2.[2]

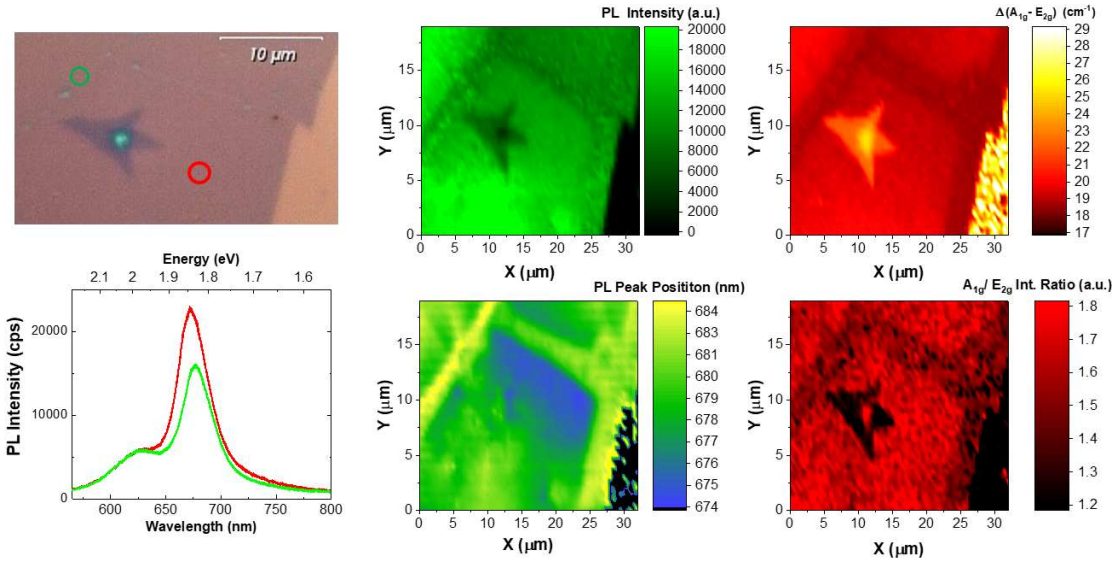

Figure S12 Optical Image of the polycrystalline MoS2 affected by grain boundaries. The area with darker contrast is related to the seeding point of the polycrystalline MoS_2. PL spectra taken in the highlighted positions of the polycrystalline MoS_2 monolayer depicted in the optical image. PL intensity and peak position maps of the MoS_2 A exciton. Raman map of the separation between the A_{1g} and E_{2g} modes, defined as Δ, Raman map of the A1g and E2g modes intensity ratio.

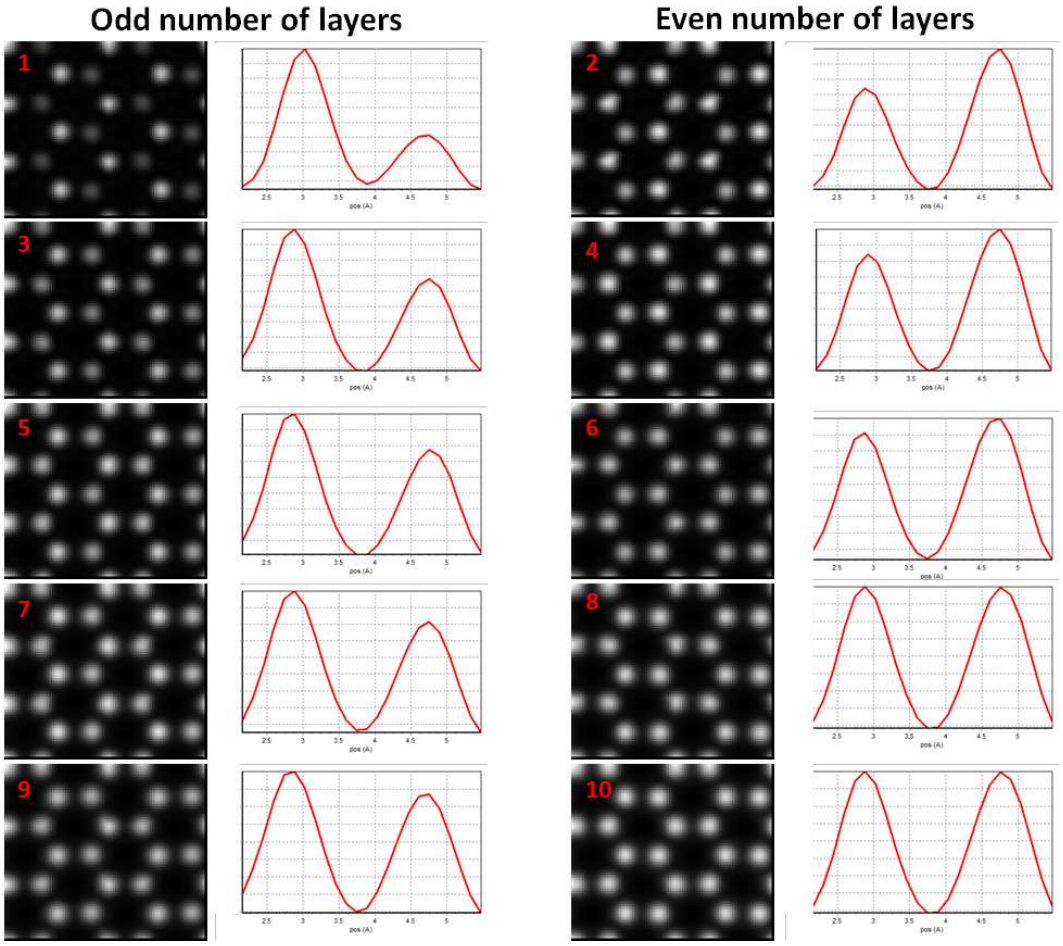

Figure S13: series of multislice STEM-HAADF simulations of a MoS2 flakes with varying number of layers. The intensity ratio between two adjacent columns directly relates to the number of layers.

References

(1) Li, H.; Wu, J.; Huang, X.; Lu, G.; Yang, J.; Lu, X.; Xiong, Q.; Zhang, H. Rapid and Reliable Thickness Identification of Two-Dimensional Nanosheets Using Optical Microscopy. *ACS Nano* **2013**, *7* (11), 10344–10353. https://doi.org/10.1021/nn4047474.

(2) Ly, T. H.; Chiu, M.-H.; Li, M.-Y.; Zhao, J.; Perello, D. J.; Cichocka, M. O.; Oh, H. M.; Chae, S. H.; Jeong, H. Y.; Yao, F.; et al. Observing Grain Boundaries in CVD-Grown Monolayer Transition Metal Dichalcogenides. *ACS Nano* **2014**, *8* (11), 11401–11408. https://doi.org/10.1021/nn504470q.