Supplementary Information

Long-term stability and tree-ring oxidation of WSe_2 using phase-contrast AFM

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1. Time evolution of the WSe_2 flake

Fig. 1 shows a collection of optical micrographs of the WSe_2 flake recorded over a period of 75 months. The degradation of the flake is optically visible already after three months where holes in the single layer in the top left have developed. After six months, degradation at the edges and exposed steps starts to be optically visible. The single layer was inspected by AFM just after exfoliation, revealing small second layers of co-oriented triangles, see Fig. 2. The degradation of the single layer commences at the edges, while the triangular oxidative structures are most like a result of defects originating from the defects created during synthesis of the WSe_2 crystals used for exfoliation. Fig. 2 shows the topography of the as-exfoliated and aged single layer WSe_2 with a clear correlation between the initial triangles and the holes in the single layer of the aged crystal. Full phase-contrast and topography AFM scans of the initial flake and 68 months after exfoliation are seen in Fig. 3 along with topography AFM from the mean time in Fig. 3c.

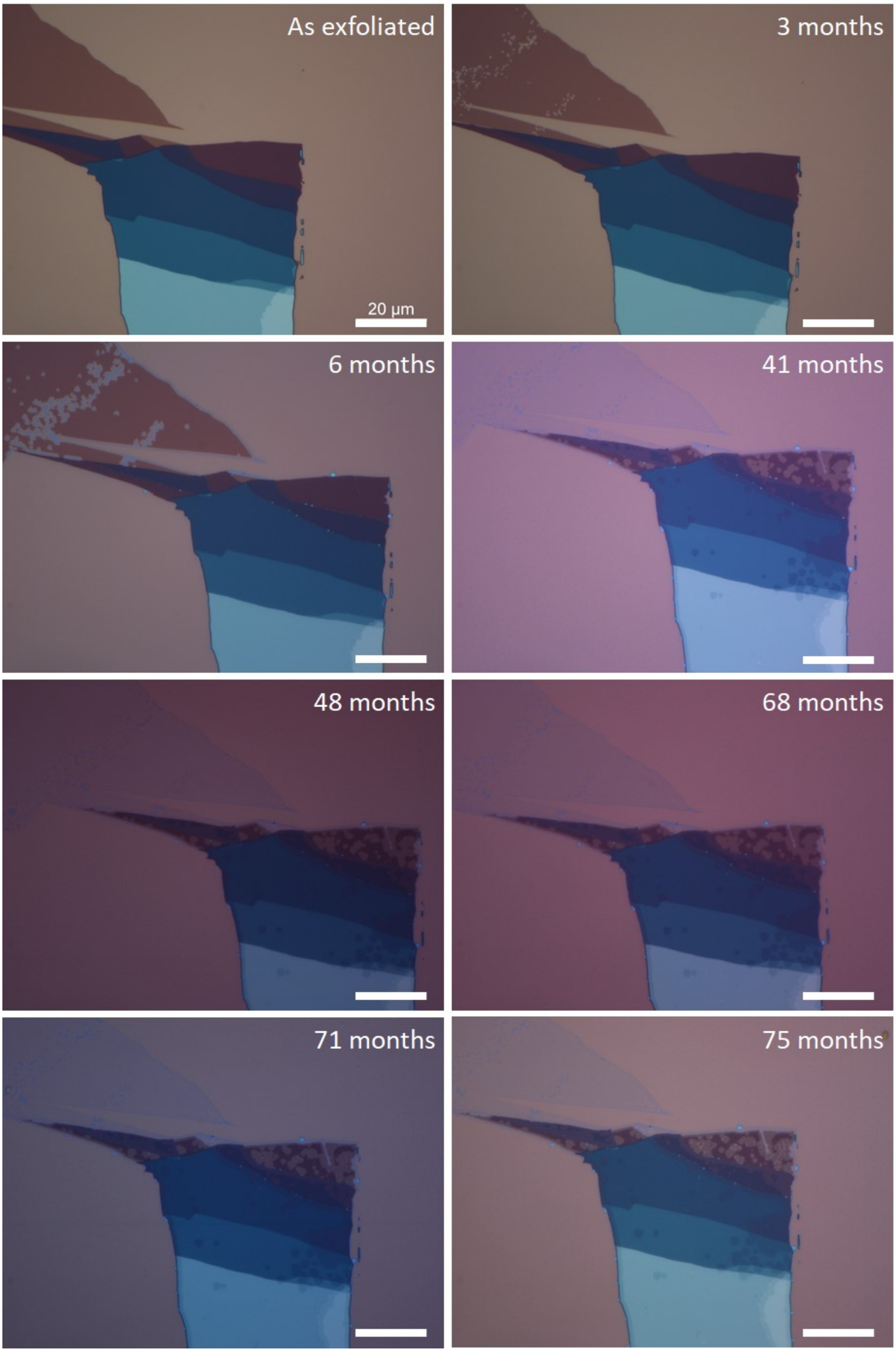

Figure *1*. Optical micrographs of the WSe_2 flake over a period of 75 months. All scale bars are 20 µm. Variations in microscope settings leads to minor differences in colour and contrast.

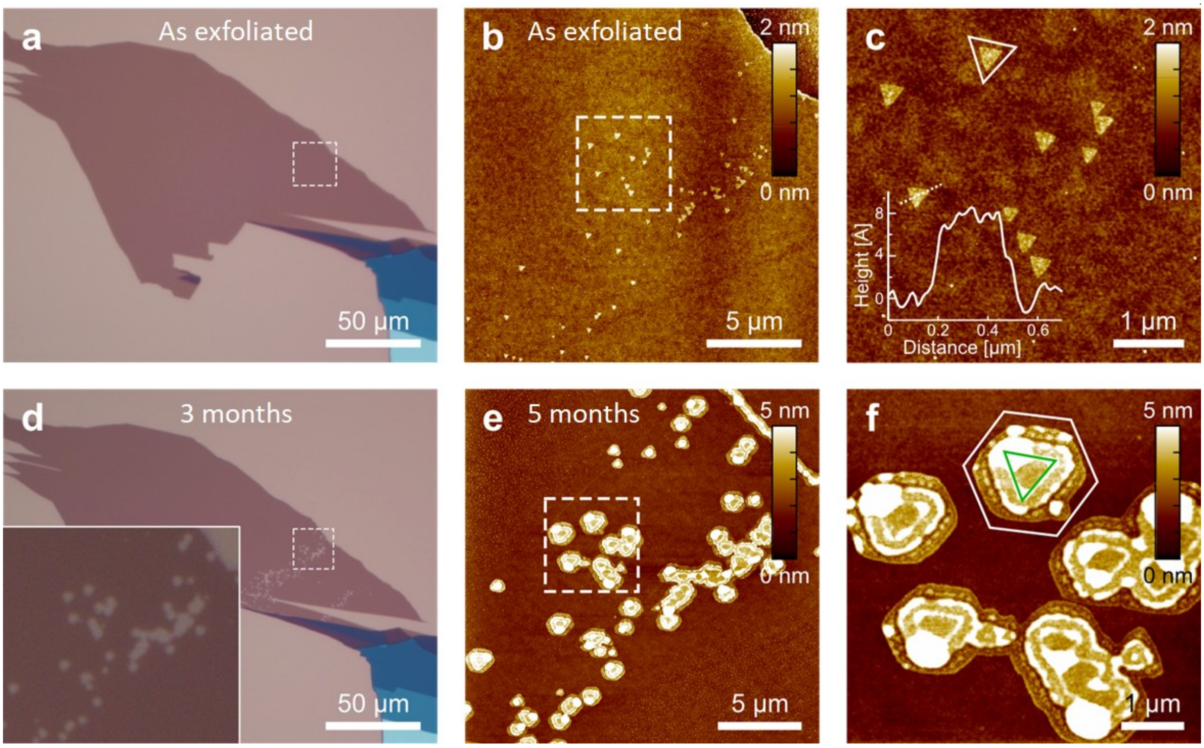

Figure *2*. (a)-(c) Optical micrographs and topographical AFM of the as-exfoliated flake in a single-layer region. Panel (c) is a magnified view of the box in (b). (d) Optical micrographs three months after exfoliation and (e)-(f) AFM micrographs after five months. Small triangular areas were observed within (or on top of) the large single layer. A line scan across a triangle is included as in inset in (c). The triangles evolve into larger hexagonal hole over time.

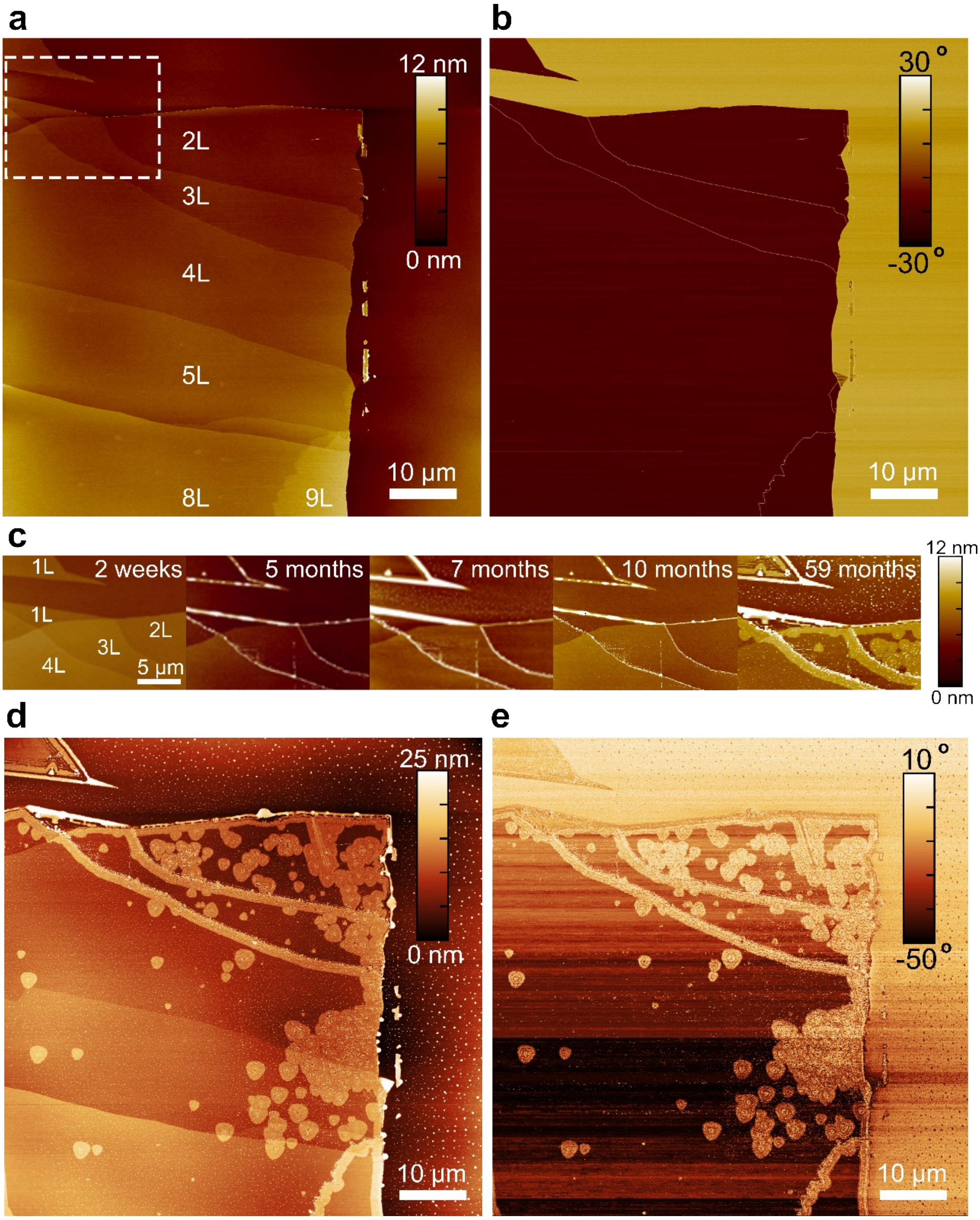

Figure *3*. AFM inspection over time. (a) Initial topography (b) and phase shift AFM, (c) topographic AFM of the area indicated with a dashed-line box in panel a, measured across a timespan from 2 weeks to 59 months after exfoliation. (d) Topography and (e) phase shift AFM of the flake at 68 months after exfoliation.

2. Estimating the edge oxidation from optical micrographs

Optical microscopy (OM) was used to estimate the width of the oxidised edge at point in time where no AFM scans were available. To do so, the contrast and saturation of an images recorded with a 100x objective were increased to obtain a large grayscale contrast between the oxidised step and the layers beside it. Fig. 4a shows an optical micrograph of the WSe_2 flake 48 months after exfoliation. The grey value of a line with a width of five pixels across the step from 2L to 3L, indicated with the dotted line in Fig. 4a, was extracted, this is the same location where the width is measured by AFM. The normalised grey value along the dotted line is plotted in Fig. 4b, the oxidised 3L appears as an increase in the grey value compared to the 2L and 3L region.

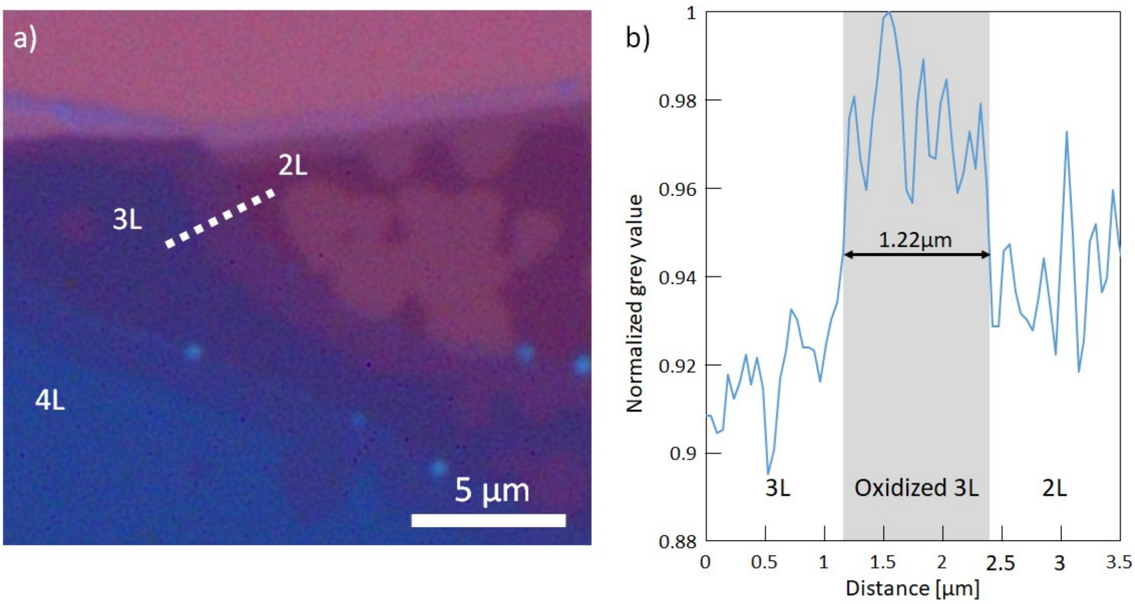

Figure *4*. (a) Optical micrograph after 48 months, the colours of the optical micrograph have been changed to increase the grayscale contrast of the step from 2L to 3L this was done by increasing the contrast and saturation. (b) Normalised grayscale values versus distance of a five-pixel wide line at the location indicated by the dotted line in (a).

To verify the method, the width of the oxidised edge measured on optical micrographs for the 68 months, 71 months, and 75 months where AFM scans also are available. The width measured by OM is consistently overestimating the width by 80 nm compared to the AFM scans. In Fig. 5, all OM and AFM measurements of the width of the oxidised edge versus months since exfoliation are included. The OM values of the main text Fig. 4d calibrated to the more accurate AFM values by subtraction of 80 nm, compared to the Fig. 5 below.

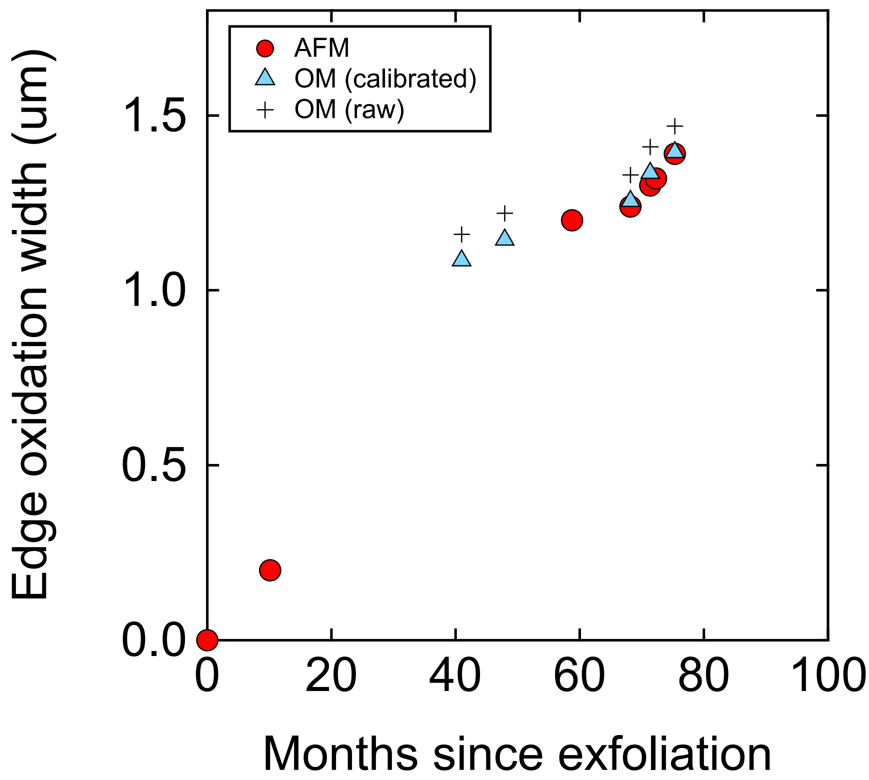

Figure 5. Edge oxidation width (µm) versus months since exfoliation. The crosses represent the estimated width of the oxidation regions from optical microscopy, while the blue triangles show the same OM data that has been adjusted to match the values extracted from AFM images (red circles) at, by a constant offset of 80 nm.

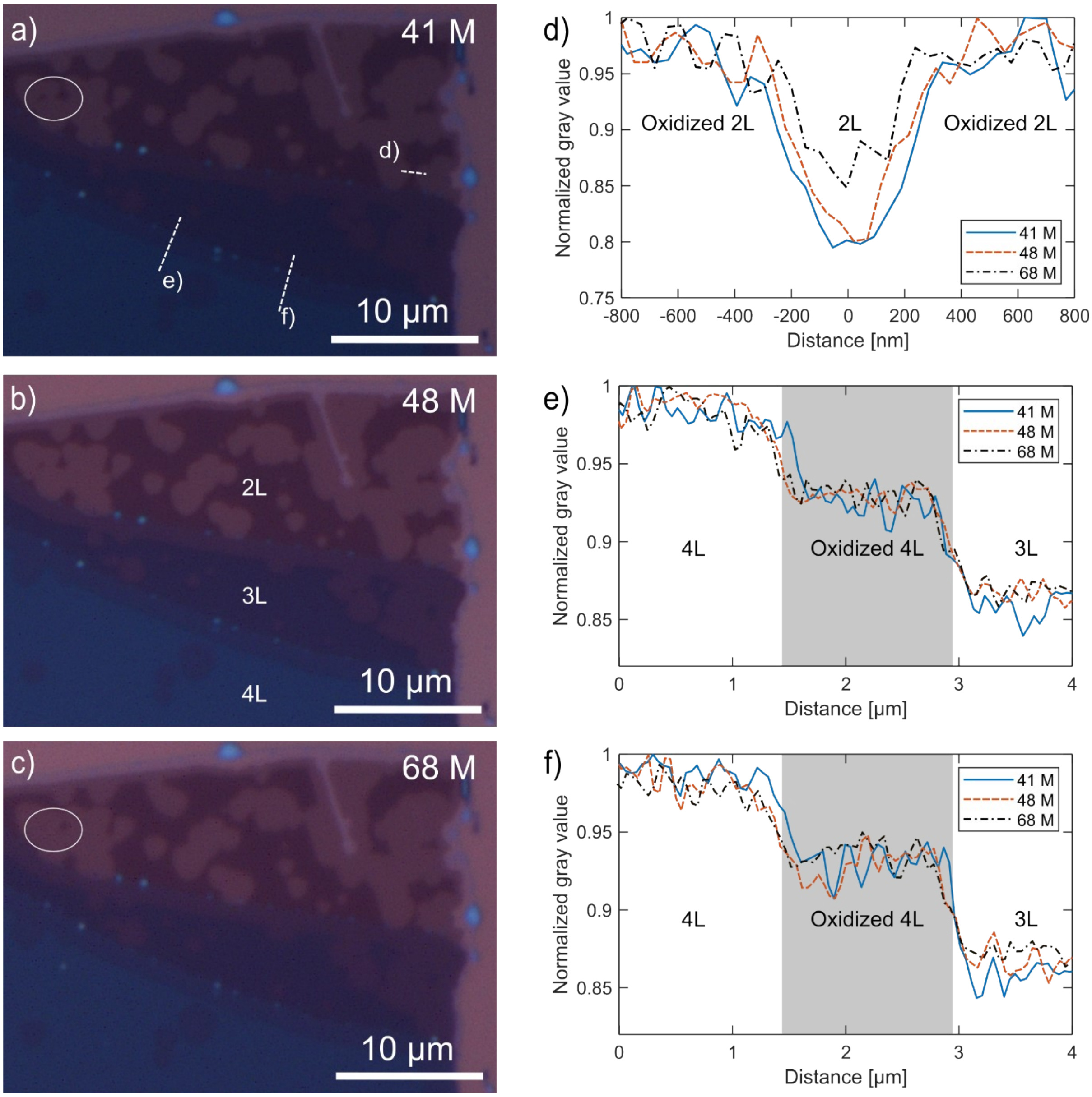

Figure *6*. (a)-(c) Optical micrographs of flake at 41, 48 and 68 months after exfoliation recorded during the period (M40-M69) where the flake was in dark storage. (d) Normalised grey value versus distance over a small constriction. The constriction gets narrower over time. (e) and (f) plots of the normalised grey value versus distance over the step from 3L to 4L at the two location indicated in (a). The width of the oxidised 4L region does not change significantly between months 41 and 68.

3. Cross-Sectional TEM

Fig. 7 displays cross-sectional TEM micrograph of the single step from six to seven layers in the WSe_2 flake displayed in main text Fig. 2. This step is as predicted from the phase-contrast AFM and exposed step.

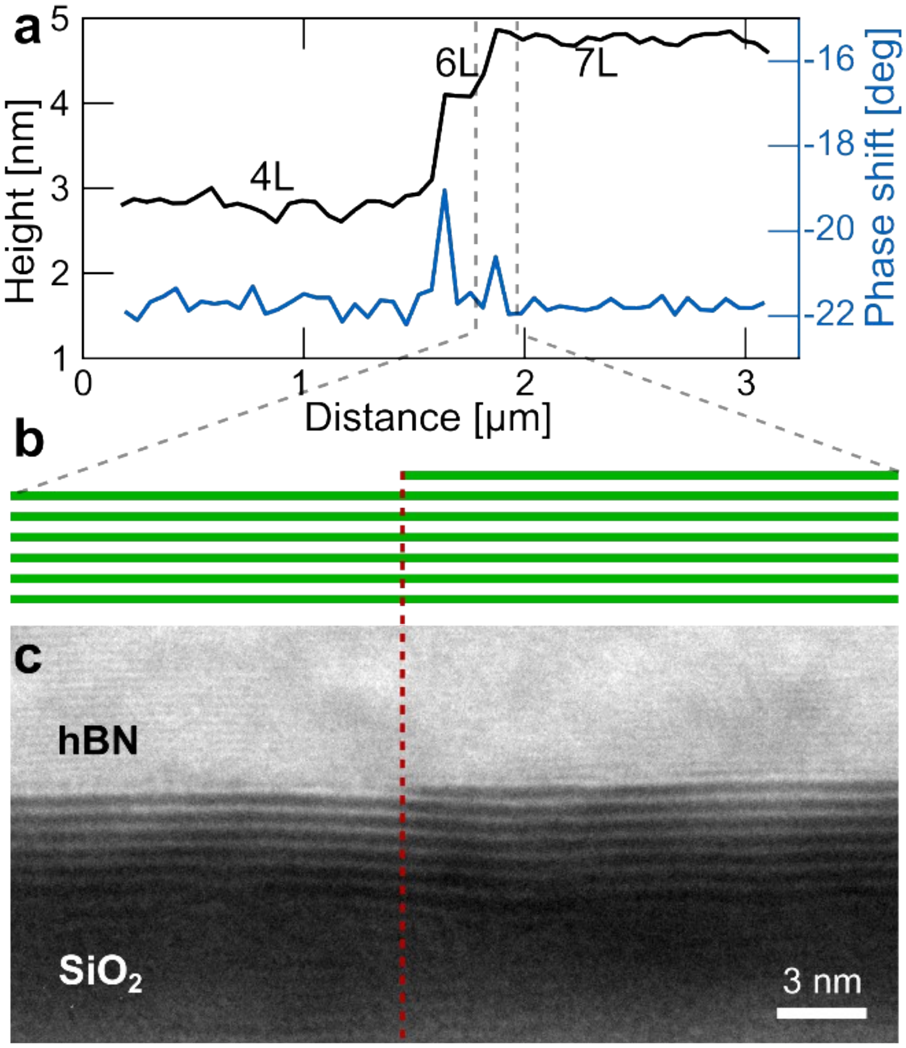

Figure 7. Topographical and phase shift AFM line-scans over step (ii) from Fig. 2 in the main text. Sketch (b) and cross-sectional TEM micrograph (c) show the exposed step transitioning from six to seven layers of WSe_2.

4. Phase contrast AFM on MoS_2 flakes

WSe_2 and $MoTe_2$, MoS_2 flakes were likewise inspected by AFM (see Fig. 8). Just as for WSe_2, some steps clearly emerge in the phase shift image for MoS_2, where others stay hidden. It is reasonable to assume that visible and hidden steps in the phase contrast AFM images for MoS_2 correspond to exposed and covered steps, respectively, exactly as for WSe_2.

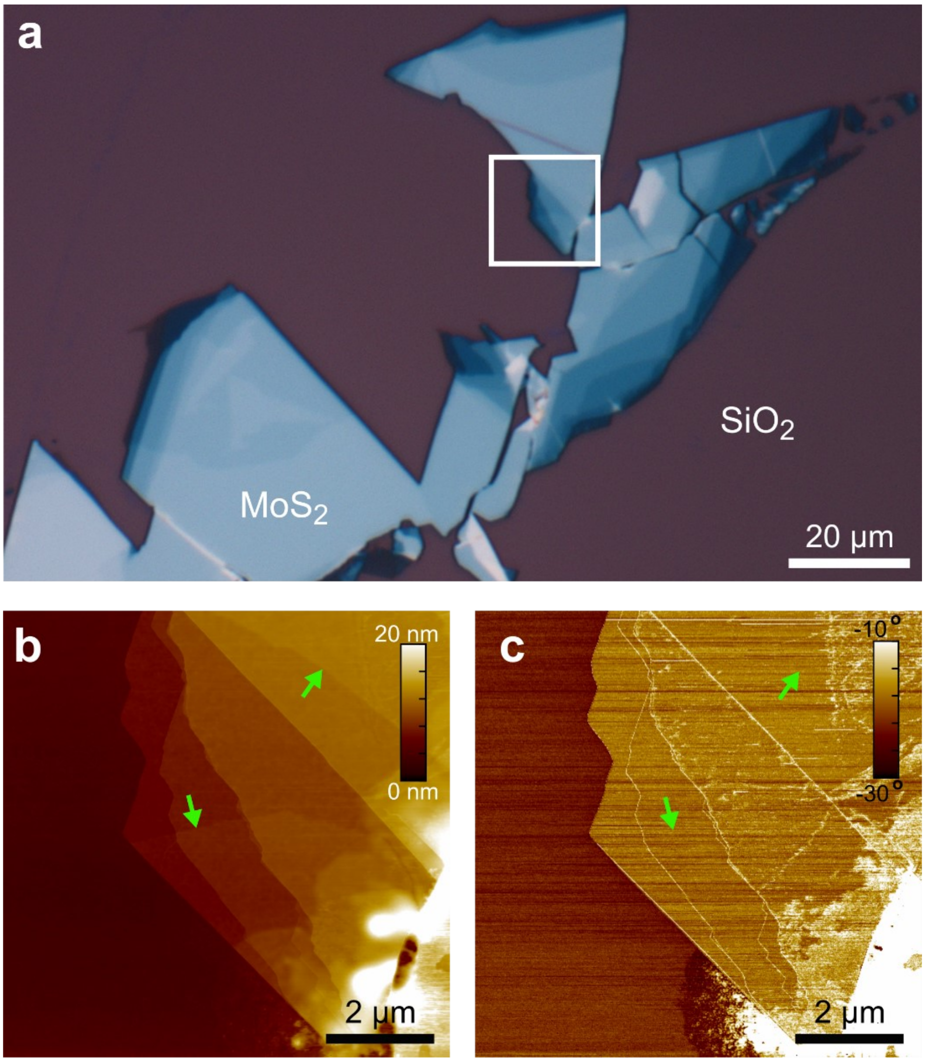

Figure *8*. AFM and optical inspection of an as-exfoliated MoS_2 flake. (a) Optical micrograph of the MoS_2, the white box indicate the area of the (b) AFM topography and (c) AFM phase shift images. The arrows in (d) and (c) indicate two covered edges.

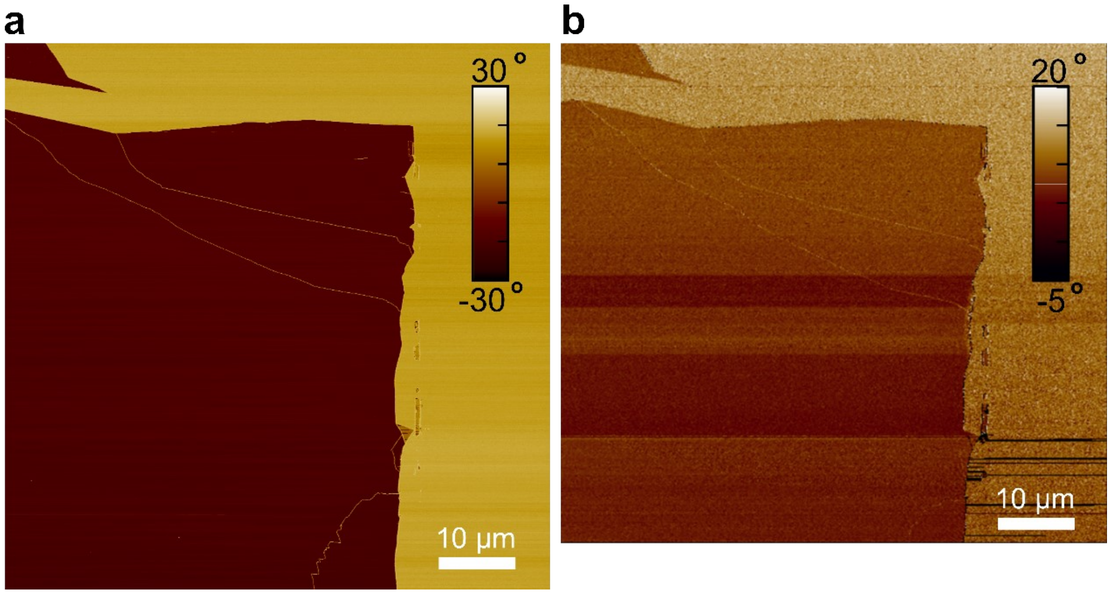

Figure 9. Phase-contrast images of same region of the WSe_2 flake after 2 weeks, with (a) the Bruker Dimension Icon-PT using Tap300Al-G probes from NanoAndMore GMBH and (b) the NT-MDT NTEGRA with MDT HA-HR probes. The two exposed edges are clearly visible in both images, however, the noise level is lowest in (a). See Experimental section for further information.