Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

SII. Water contact angle measurements.

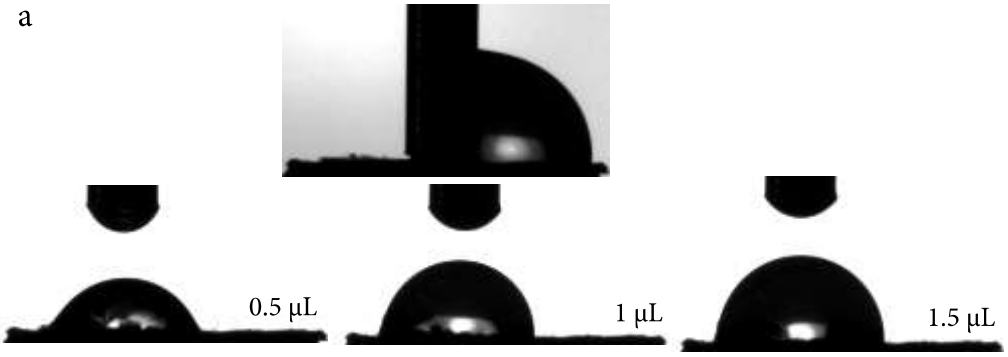
Advancing and receding water contact angle measurements were performed by the "add and remove volume" method in a Ramé-hart Model 200 Standard Goniometer with Dropimage Standard v2.3, equipped with an automated dispensing system. This device includes software as well as a fiber optic illuminator, 3-axis leveling stage, high-speed F4 Series digital camera, microsyringe fixture and assembly for manual dispensing. The system is improved with an automated dispensing system and manual tilting base.

a) Silhouettes of ultrapure H_2O drops of different volumes laid on the surface of a non-exfoliated large single crystal of TaS_2.

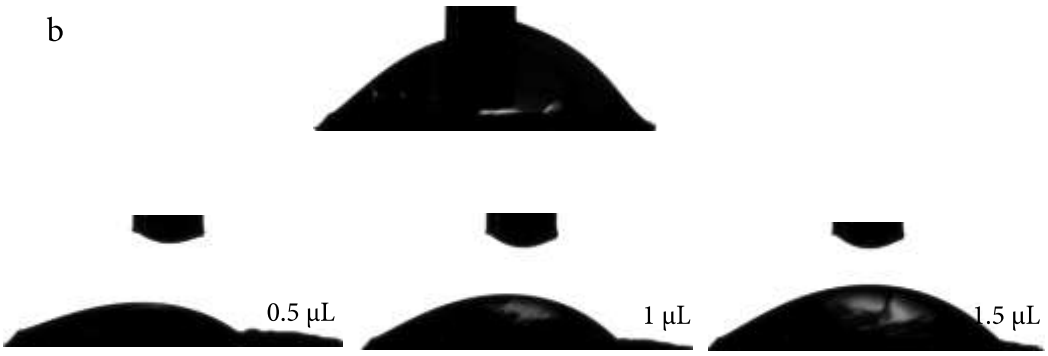
b) Same experiment performed on a freshly cleaved surface of the same TaS_2 crystal. The leading pictures in both cases show the silhouette of the drop at the end of an advancing contact angle run.

c) Advancing/receding contact angle cycles performed on non-cleaved and on exfoliated TaS_2 surfaces.

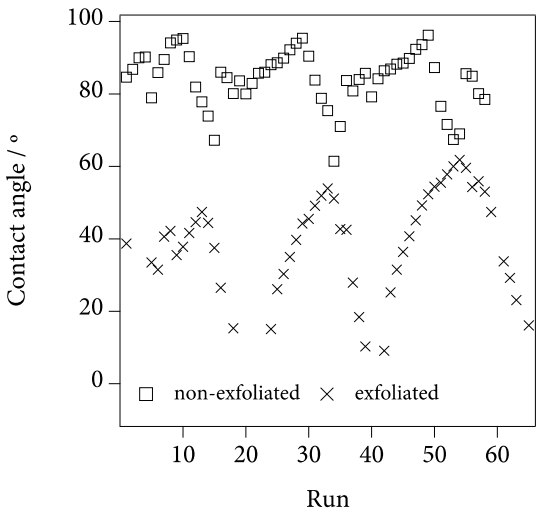
a



b



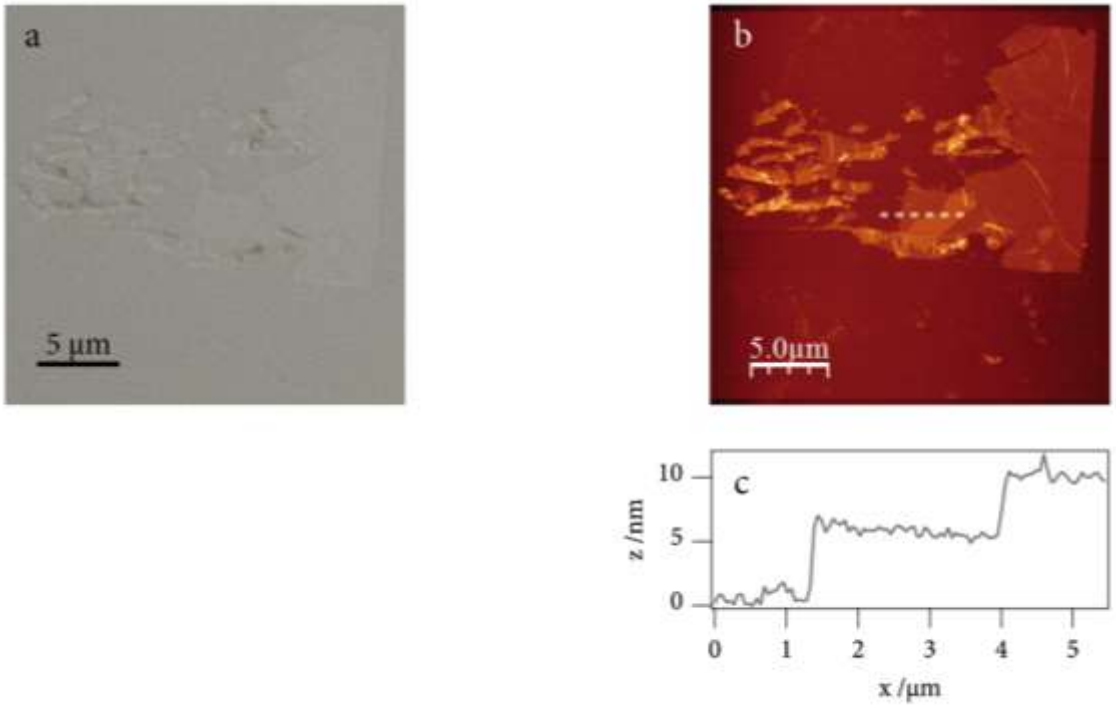
c



SI2. Optical microscopy Nomarski-DIC image of a 5 nm flake on Si/native SiO_2

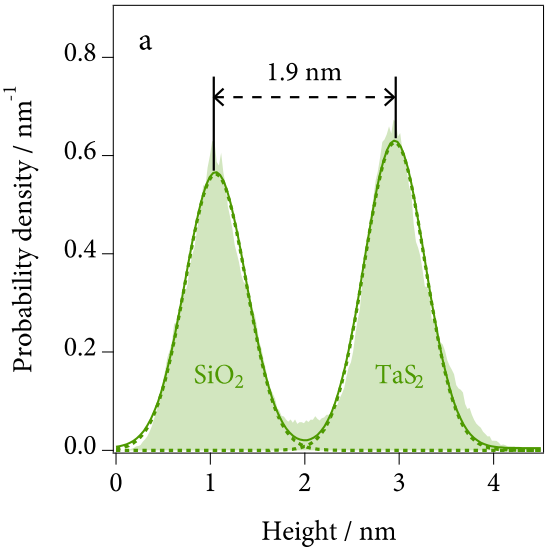
Optical microscopy images were taken using a Nikon D-600 SLR camera mounted on a Nikon LV-100 optical microscope. The microscope was equipped with a Nomarski prism for DIC contrast imaging.

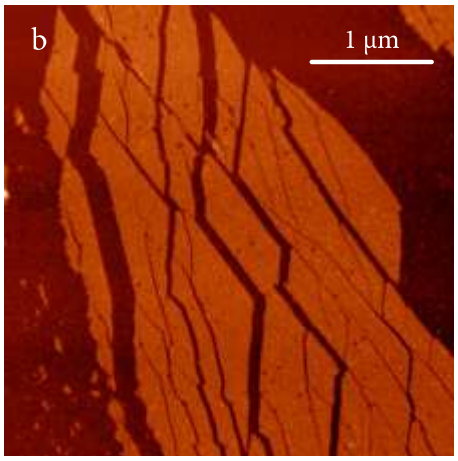
Comparison of the optical microscopy image (a) with the AFM topography image (b) confirms the visibility of 5 nm flakes (height profile along dashed line showed in (c)) on bare Si to the naked eye.



SI3. Determination of the thickness of ultrathin TaS_2 flakes (< 5 nm).

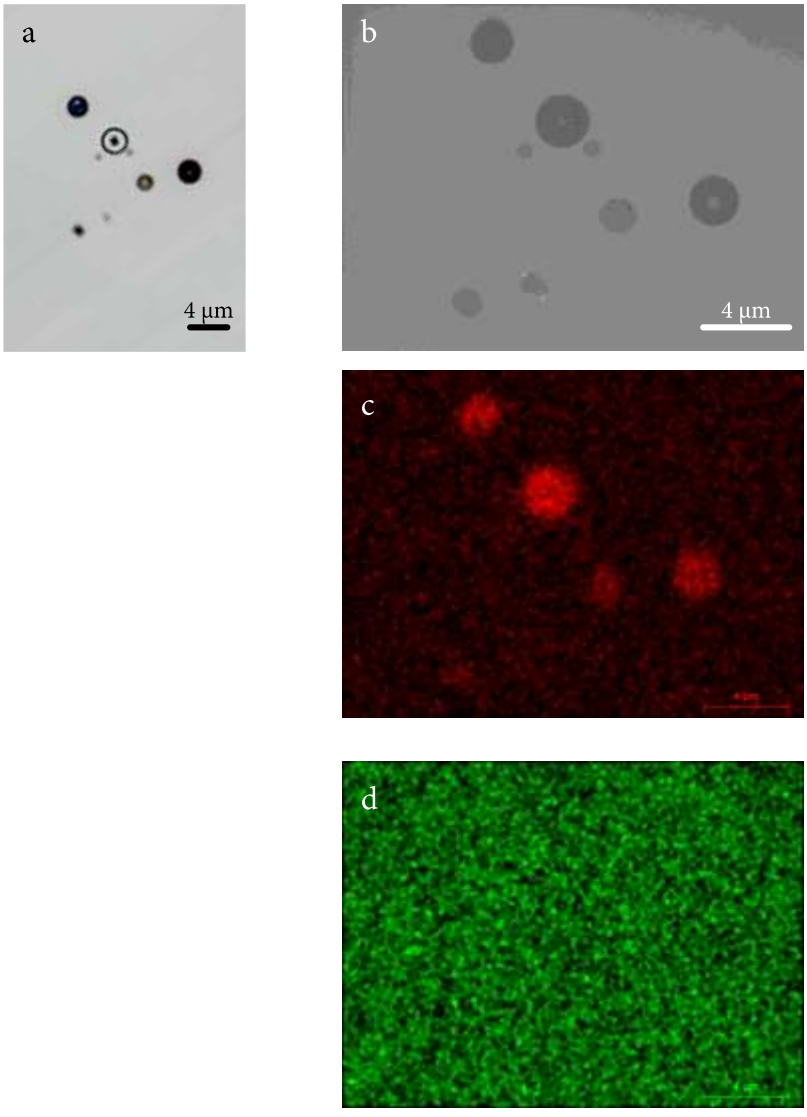
a) Height histogram of an AFM topography image of a region with a high density of ultrathin TaS_2 flakes of homogenous thickness (< 5 nm). (b) A multi-peak Gaussian fit has been carried out to determine the layer thicknesses. The data could be fitted to two Gaussian distributions corresponding to the SiO_2 (1.06 ± 0.46 nm) and the TaS_2 (2.95 ± 0.46 nm) surfaces. Thus, the calculated flake thickness is around 1.89 ± 0.46 nm.





SI4. SEM-EPMA mapping studies performed on a group of oxide motifs patterned on a thick TaS_2 flake.

a) Optical microscopy image of the group of oxide motifs. (b) Secondary electrons (SE) SEM image of the same region. (c) O K-shell SE channel. (d) Ta L-shell SE channel.



SI5. Technical specifications of the AFM-LON equipment and methodology.

Two different AFMs were used for the local oxidation nanolithography on TaS_2. One is a Nanoscope IVa (Bruker) interfaced with a home-made voltage amplifier. The other one is a Cervantes Fullmode AFM (Nanotec Electrónica) that provides powerful nanolithography software (WSxM)[1] that permits to plot customised pre-loaded patterns. All experiments were carried out at room temperature and the ambient relative humidity of 40-70% by employing a commercial bench-top humidifier.

In both AFMs, a vertical optical microscope is used to visualize the tip over the surface, being able to position the tip on top of the selected flake. The first part of the experiment consists on the topographic characterization of the surface in tapping mode, which is a non-invasive mode of operation. The same Silicon probes of fr ≈ 300 KHz and K ≈ 40 N/m (PPP-NCH, Nanosensors) were used for the morphological characterization as well as for performing the LON. Once the surface is scanned and the target area chosen, a set of pulses of increasing voltage and duration is carried out. This experiment patterns a set of consecutive oxidation features of different characteristics on the flake, allowing for the identification of voltage and time thresholds. To achieve a controlled and reproducible method to oxidise nano-structures it is also very important to control the tip-sample distance. The latter is checked by recording the so called force-distance curve. This distance can be adjusted by choosing the corresponding amplitude of oscillation and by fitting the set point in tapping mode. In general, a tapping set point of 1.5 V was initially tuned in order to achieve a reasonable surface proximity for LON

[1] I. Horcas, R. Fernandez, J.M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A.M. Baro, *Rev. Sci. Instrum.* **2007**,*78*,013705.

purposes. Fine adjusting of the tip-to-surface distance was performed prior to each LON event in order to control de oxidation outcome.