Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information to: A novel 2-step ALD route to ultra-thin MoS_2 films on SiO_2 through a surface organometallic intermediate

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1. Detailed experimental procedures

1.1 General

1,2-ethanedithiol (≥ 98% purchased on Sigma-Aldrich) was dried on molecular sieves 4Å and degassed by freeze-pump-thaw cycles. $Mo(NMe_2)_4$ was synthetized according to the novel procedure described in supplementary material, which is a modification of the previously reported routes.[1, 2] All sensitive reagents and samples were handled under strict oxygen and moisture-free atmosphere.

1.2 ALD on SiO_2/Si wafers

Preparation For the atomic layer deposition on silicon wafers, our substrates consist in 25x40 mm silicon plates with 275nm of thermally grown oxide. Before deposition, samples were calcined at 800°C for 4h to remove carbon contamination, fully rehydrated under water steam, and dehydrated at 200°C under vacuum for 30 min in the deposition chamber. The deposition was performed in a custom-built CVD-ALD reactor with chamber pressure at ca. 1 torr and sample holder at 50°C. $Mo(NMe_2)_4$ was placed in a sublimator (20°C; 1 torr) and brought to the reaction chamber in 40 sccm of argon. 1,2-ethanedithiol was saturated in 60 sccm of argon using a bubbler (20°C;

850 torr) and expanded to 1 torr at the inlet of the reaction chamber. The pulse time was 5 min for the two precursors. After each reactive pulse, the reaction chamber was purged by flowing pure argon (1 torr; 40 sccm) during 3 min. The thermal annealing was performed for 1h in a quartz tube under continuous flow (1 torr; 100 sccm) either at 800°C in pure argon or 450°C under hydrogen (20 v/v% in argon).

Raman Annealed samples have been characterized by Raman spectroscopy using a Renishaw In-Via spectrometer, equipped with a Peltier cooled CCD detector. Raman spectra were recorded in the backscattering geometry. The light was focused onto the sample surface thanks to a 100 x (0.85 numerical aperture) short working objective. The resulting spot diameter was around 0.7 µm. A 532 nm laser diode was used as light source with a typical laser power of 0.5 mW.

X-ray Photoelectron Spectroscopy (XPS) XPS Spectra were recorded with a PHI 5000 VersaProbe II spectrometer using monochromatic Al Kα radiation and with an overall energy resolution of 0.6 eV. The experimental line shapes were fitted with Gaussian-Lorentzian components.

Transmission Electron microscopy (TEM) Atomic resolution structural characterization has been done by a low voltage aberration corrected TEM (LVAC-TEM) imaging using Titan Ultimate (FEI) operating at 80 kV. For TEM observation, the same samples used for other analysis were transferred on the TEM grid. The samples were first spin coated by PMMA, then separated from substrate by a subsequent etching of the SiO_2 substrate in 10% hydrofluoric acid and transferred on a TEM grid supported with amorphous carbon membrane, allowing to observe the free-standing MoS_2 deposits in top view.

Wavelength dispersive X-Ray fluorescence (WDXRF) S/Mo atomic ratios have been determined by wavelength dispersive X-Ray fluorescence (WDXRF) on Rigaku AZX400 tool operated with 4 kW Rhodium source and Ge<111> crystal as monochromator. The S/Mo quantification was based on fundamental parameters approach applied to intensities of Mo(Lβ1) and S(Kα) fluorescence lines, after correction of Mo(Lα)/ S(Kα) overlap.

1.3 ALD on silica nano-beads

Starting material For the study performed on silica powder, our substrate consists in 40-60 mesh agglomerates of non-porous silica nanoparticles (AEROSIL® 200 fumed silica; 15-20 nm particles; 200 m^2/g surface area (BET method)) treated overnight at 500°C under high vacuum (10^{-5} torr). Grafting steps were performed under static vacuum in a 500 mL closed tubular reactor containing 500 mg of silica powder with 100 mg of $(Mo(NMe_2)_4$ or 0.2 ml of 1,2-ethanedithiol. The reactor was placed for 90 min in an oven pre-heated at 50°C, followed by the removal of by-products and excess reactants under high vacuum (10^{-5} torr).

Elemental analyses Grafted silica samples were characterized by elemental analyses (CHNS analysis by combustion and Mo determination by ICP-AES) at "Mikroanalytisches Labor Pascher" in Germany.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) DRIFT spectra were acquired on a Nicolet FTIR 6700 spectrophotometer under inert conditions. Infrared spectra were recorded in the 400-4000 cm^{-1} range with a resolution of 2 cm^{-1} (256 scans), subtracted with a background spectrum of dry KBr taken under the same conditions, and normalized relative to the peak height of the 1860 cm^{-1} peak corresponding to a combination vibration of the SiO_2 lattice.

Transmission Electron spectroscopy (TEM) Transmission electron micrographs on annealed powdered samples were recorded at the "Centre Technologique des Microstructures", UCBL, Villeurbanne, on a Jeol 2100F transmission electron microscope.

1.4 In-situ DRIFT coupled GC-MS monitoring of the annealing step

The *in operando* DRIFT experiment was carried out in an integrated system comprising Brooks mass flow controllers, Harrick's high-temperature reaction chamber with ZnSe windows, Nicolet FTIR 6700 spectrophotometer equipped with MCT detector and online GC-MS (Agilent 6850/5975C). During the FTIR acquisition, 10 ml/min of argon (99.999% from Air Liquide) or dihydrogen was constantly flowing through the sample. The sample was heated from 20°C to 450 °C at 2 °C/min. A resolution of 4 cm^{-1} was applied. Each spectrum was recorded with 64 scans, subtracted with a background spectrum of dry KBr taken under the same conditions, and normalized relative to the peak height of the 1860 cm^{-1} peak corresponding to a combination vibration of the SiO_2 lattice. The output gas was separated with a 25 m Agilent PoraBOND Q column at a constant temperature of 40°C and analysed with a mass spectrometer (see Figure S1 and S2).

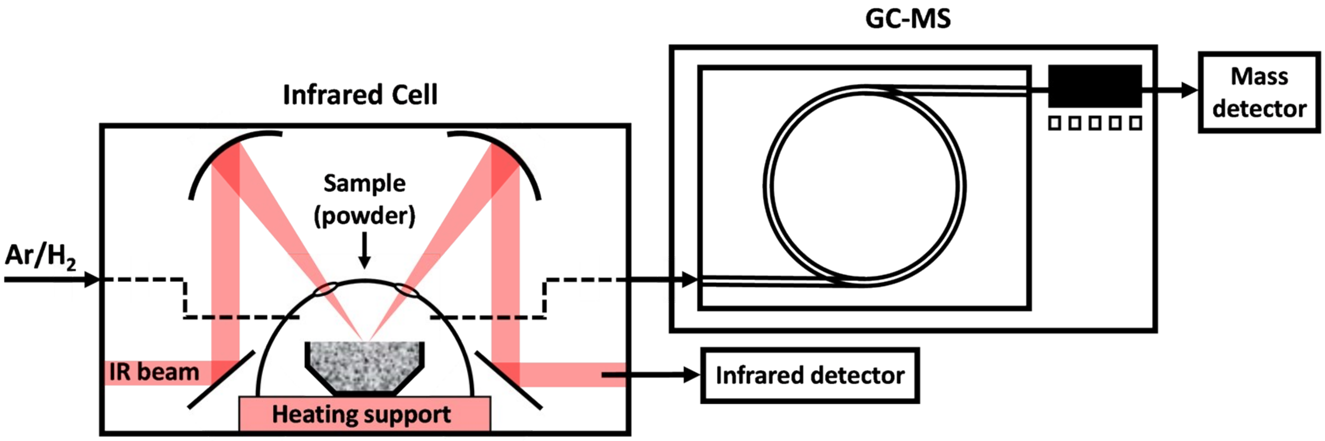

Figure S1: Schematic representation of the experimental setup used for *in-situ* DRIFT and GC-MS monitoring of the thermal decomposition of our ALD-deposited molybdenum thiolate on silica nano-beads.

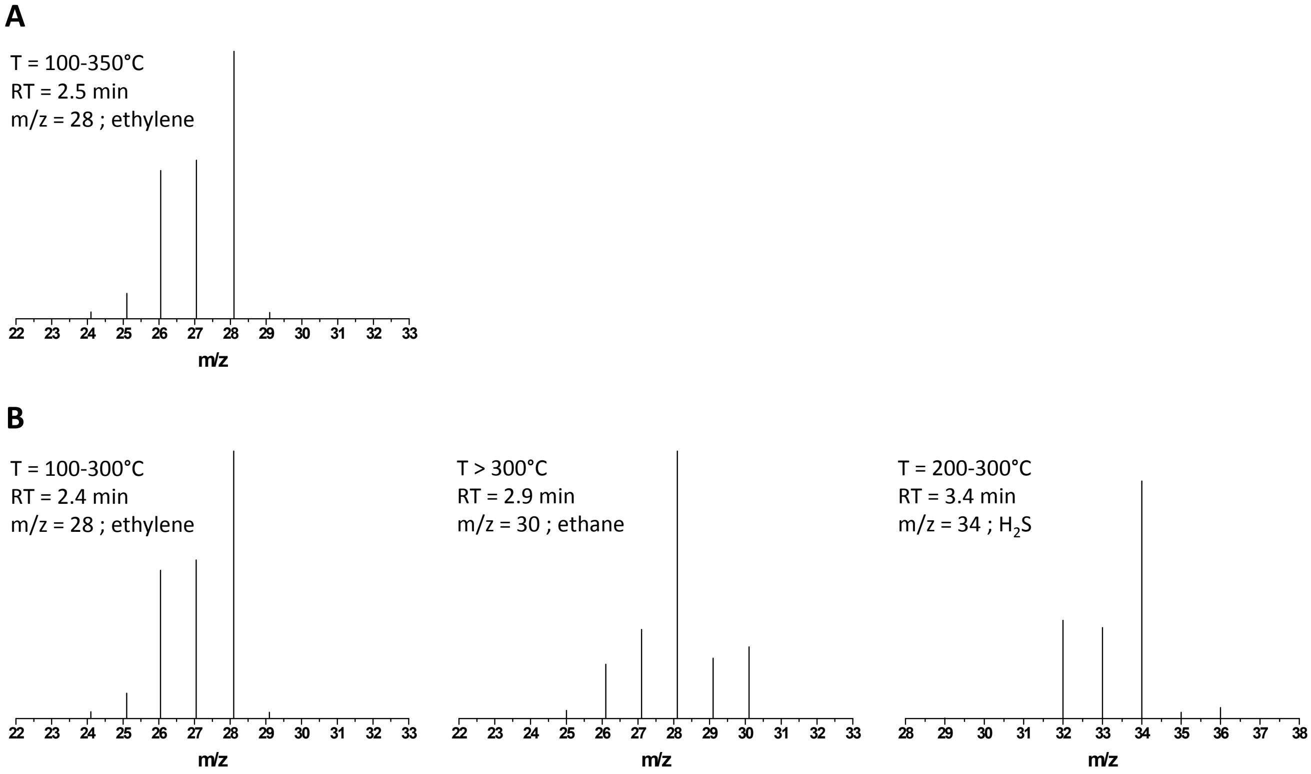

Figure S2: Fragmentation spectra of by-products collected during in-situ Drift coupled GC-MS monitoring of the annealing step: **A**: under argon and **B**: under hydrogen.

1.5 Synthesis and characterization of $Mo(NMe_2)_4$

In a 500-ml Schlenk flask, dry diethyl ether (40 ml) and pentane (250 ml) were degassed by freeze-pump cycles. Cyclopentene (100 mmol, 7.1 g, 9.2 ml; 96% from Sigma Aldrich) were added together with 2 drops of NaK alloy and the mixture was stirred overnight at RT (mixture **1**).

$MoCl_5$ (18 g, 65 mmol) was introduced in another 500-ml Schlenk flask under argon and mixture **1** was integrally condensed with liquid N_2 in the $MoCl_5$-containing flask. The black-reddish solution obtained was allowed to rise RT and stirred for 30 min. After a slight exothermicity and some gas release, orange crystals of $MoCl_4(Et_2O)_2$ precipitated, accompanied by a decolouration of the solution (mixture **2**).

Mixture **2** was cooled to ca -50°C and $LiNMe_2$ (17.5 g, 325 mmol; 95% from Sigma Aldrich) was introduced in 1 portion under argon. The suspension was slowly allowed to rise RT (ice bath required to absorb exothermicity) and stirred at 25°C for 4h. A wine-like purple solution was obtained.

The solvent was finally removed under vacuum, leading to a sticky black solid. While the last drops of solvent are condensed, a violet product starts to co-distillate. The purple $Mo(NMe_2)_4$ is then sublimed under vacuum directly from the reaction mixture at 40°C and after 2h, the temperature is slowly allowed to rise 60°C to get the last traces of product. The Schlenk containing the product is placed under vacuum at RT to remove eventual traces of ether and the final product is stored in a glove-box. Isolated Yield: 1.42 g (8% vs. $MoCl_5$).

Elemental Analyses: Mo, 35.1%; C, 35.6 %; N, 20,3%; Required for $Mo(NMe_2)_4$: Mo, 35.2%; C, 35.3 %; N, 20,6%

^{1}H NMR (C_6D_6, 300 MHz): 3,28 ppm (s, 24H), see Figure S3

^{13}C NMR (C_6D_6, 75 MHz): 49,96 ppm, see Figure S4

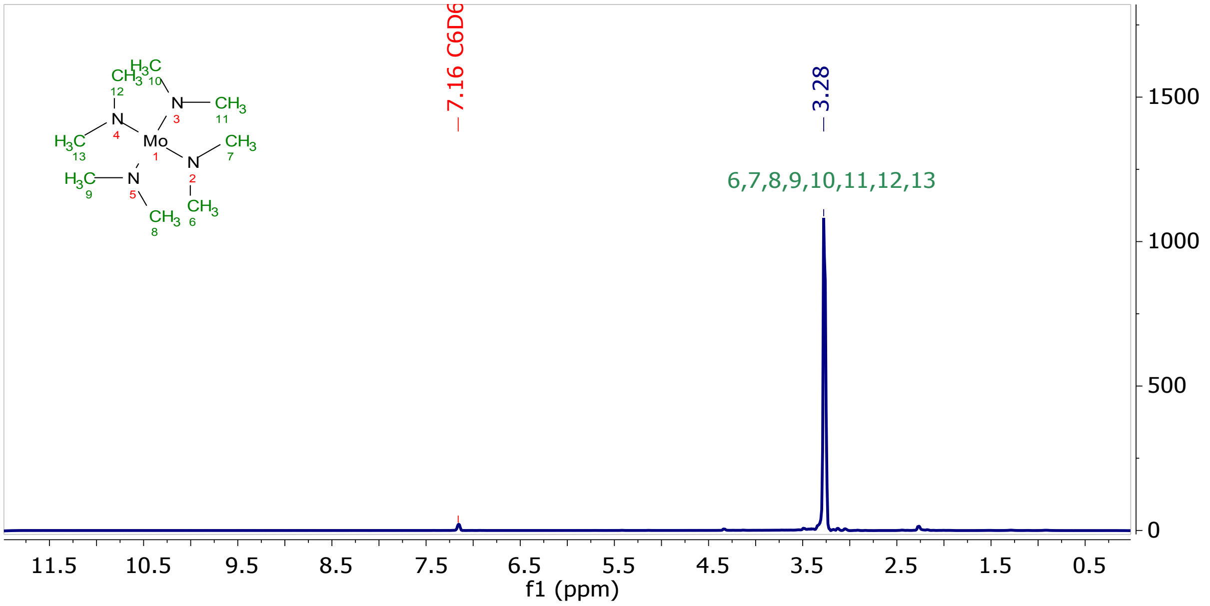

Figure S3: $Mo(NMe_2)_4$ ^1H NMR spectrum (C_6D_6, 300 MHz)

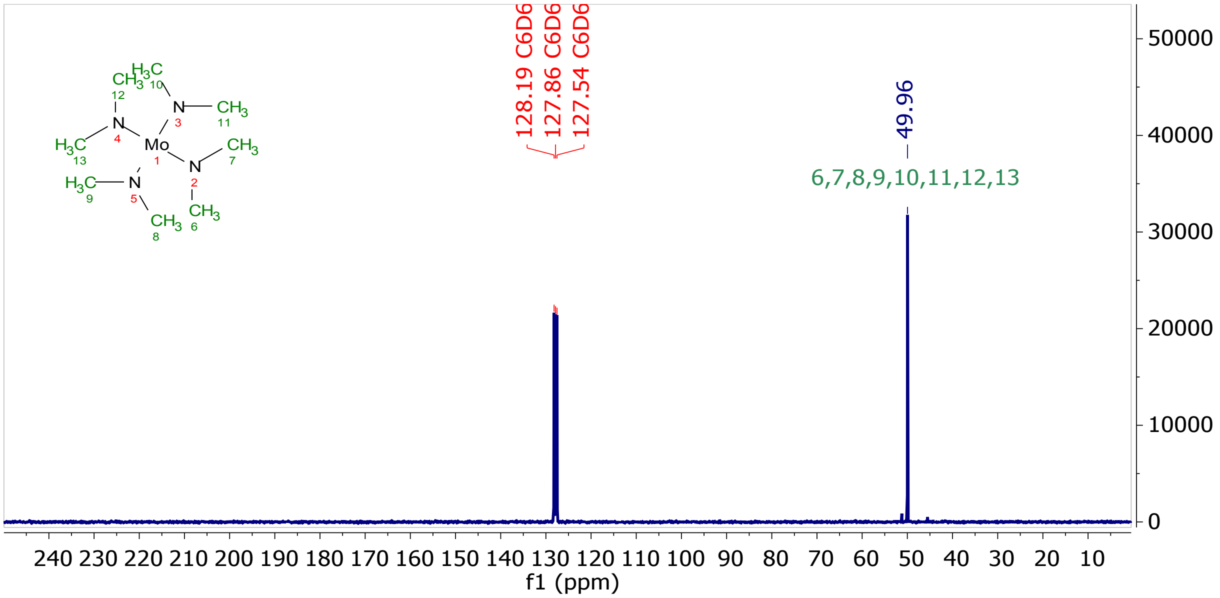

Figure S4: $Mo(NMe_2)_4$ ^{13}C NMR spectrum (C_6D_6, 75 MHz)

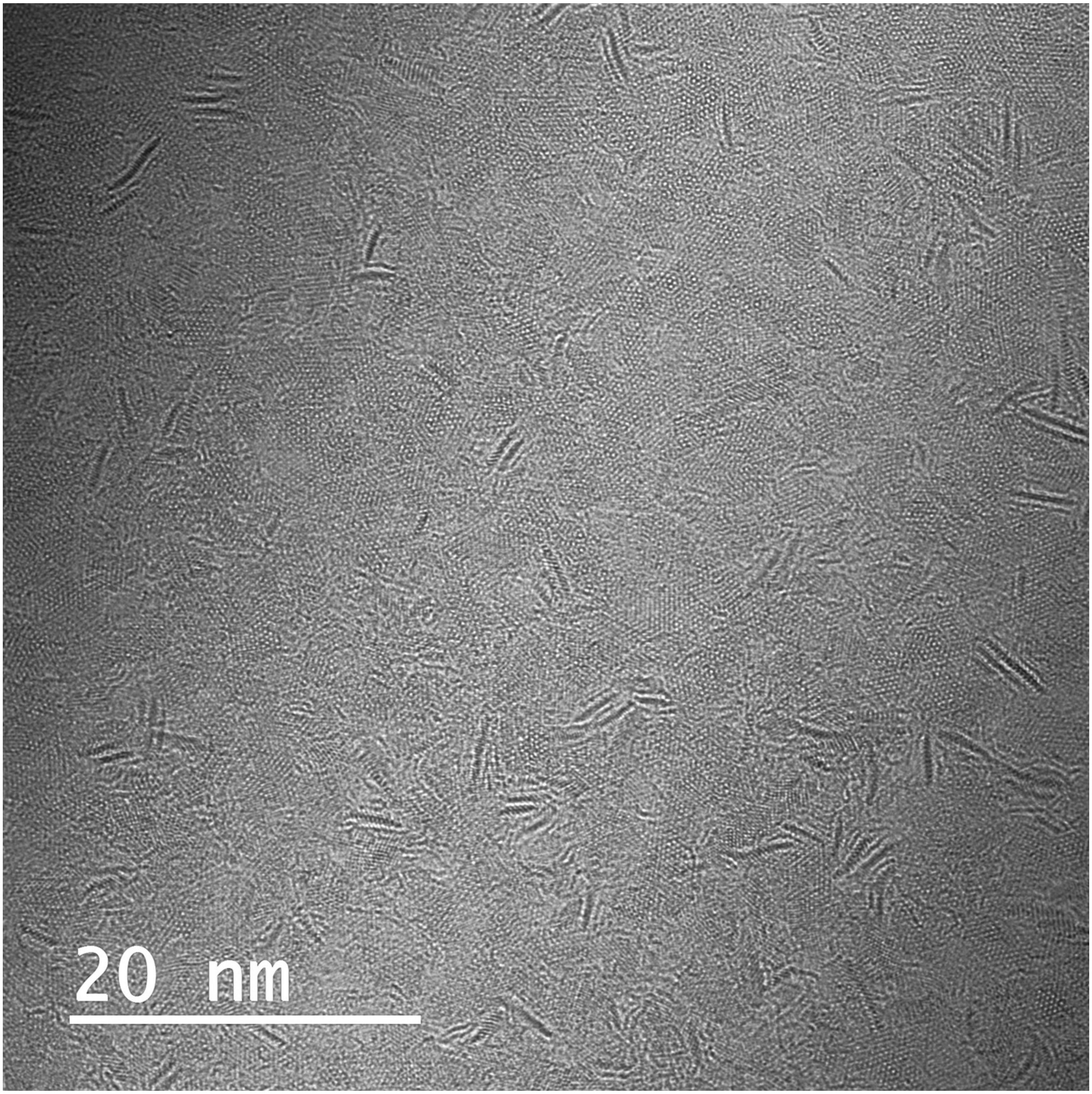

Figure S5: In-plane HRTEM image of the MoS_2 deposit obtained after 3 ALD cycles and annealing at 450°C under hydrogen for 30 min

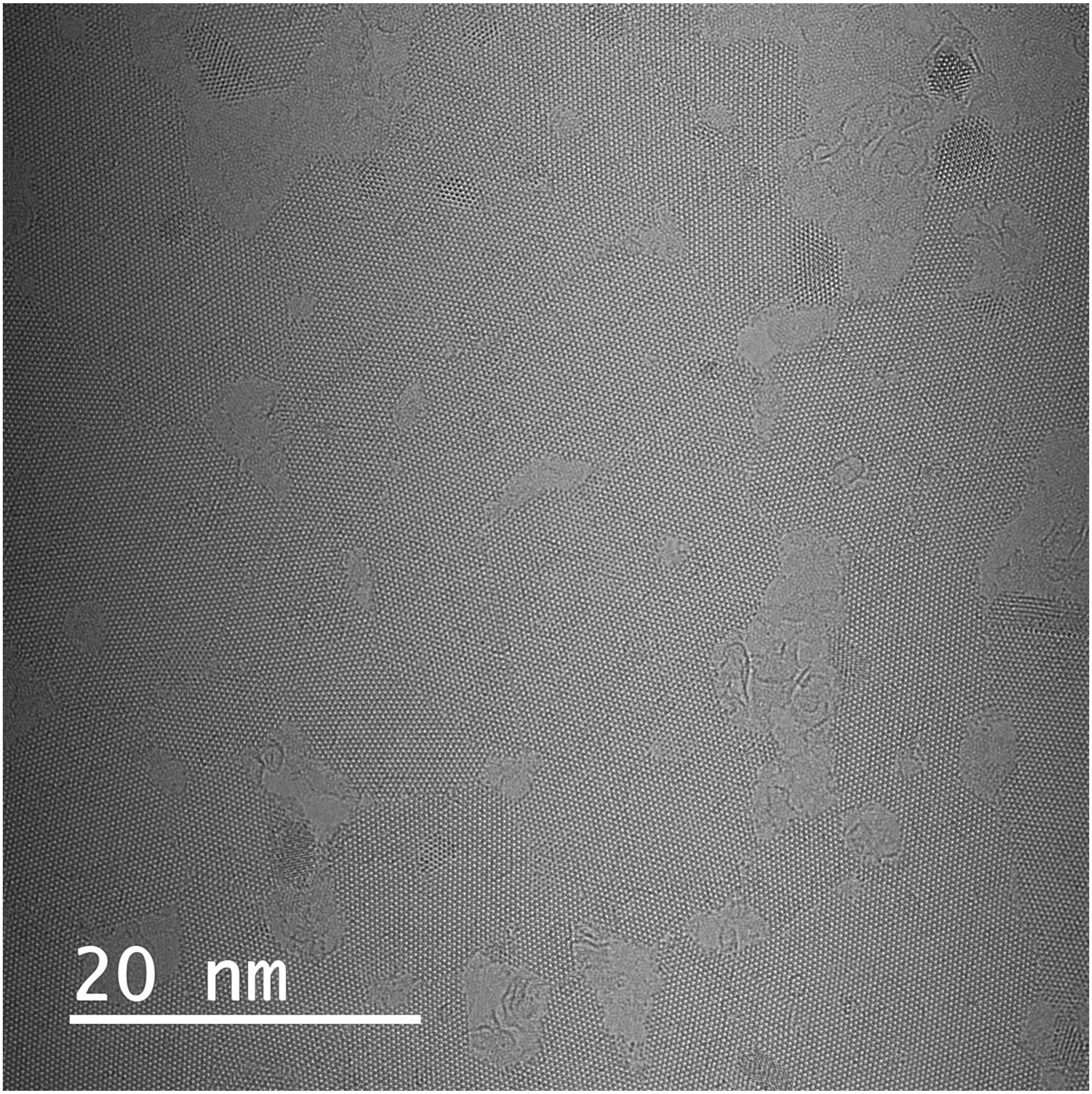

Figure S6: In-plane HRTEM image of the MoS_2 deposit obtained after 3 ALD cycles and annealing at 800°C under argon for 30 min

1. D. C. Bradley and M. H. Chisholm, *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 1971, 2741-2744.
2. D. S. Kuiper, P. T. Wolczanski, E. B. Lobkovsky and T. R. Cundari, *Inorganic Chemistry*, 2008, **47**, 10542-10553.