Electronic Supplementary Material (ESI) for Nanoscale.

Low-temperature plasma-enhanced atomic layer deposition of 2-D MoS_2: large area, thickness control and tuneable morphology

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S1: ALD saturation curves

The self-limiting growth characteristic for the ALD process was investigated at growth temperature of 250°C and 450°C. The plots in Figure S1 (a) & (b) show the self-limiting behaviour of the process (at 250°C) for both half cycles. The growth per cycle (GPC) saturates to a value of 0.1 nm/cycle after 6 s of Mo precursor dose while keeping a constant plasma exposure time of 20 s for varying precursor dose. Likewise, a plasma exposure time of 20 s is required before the GPC saturates (Figure S1 (b)). The Mo precursor dose was fixed at 6s in first half-cycle in the latter case. In addition, no growth was observed when each half ALD cycle was performed in absence of either Mo precursor or H_2S based plasma co-reactant respectively (i.e. Mo precursor dose / H_2S plasma exposure time = 0 s), confirming the exclusion of any possibility of uncontrolled thermal decomposition of either of the reactants. Further, the optimum sequential dosing for each half cycle (Mo dose = 6 s, plasma exposure time = 20 s) yielded a linear relationship between thickness and number of ALD cycles as depicted in Figure S1 (c) which shows an Å level control over film thickness. Additionally, the film growth shows no nucleation delay during the initial cycles which is a highly valuable attribute for reproducible synthesis of mono-layer to thick MoS_2 films. The 2-D materials including MoS_2 are generally seen as an inert flat land with no out-of-plane dangling bonds and therefore intuitively should be unavailable for any chemisorption reactions necessary for ALD process to proceed. However, surface chemistry studies for general ALD of sulphides have shown that the surface thiols (-SH) mimic the role of surface hydroxyls (-OH) as in oxide ALD and are mainly responsible for driving the ALD process mechanism[1]. In our case, we believe that the plasma chemistry is accountable for inducing the surface thiols which are facilitating the chemisorption of metal precursor in the subsequent steps. The adsorption of precursor species however can be anisotropic on the basal planes or edge planes of the film grown as discussed in the main text.

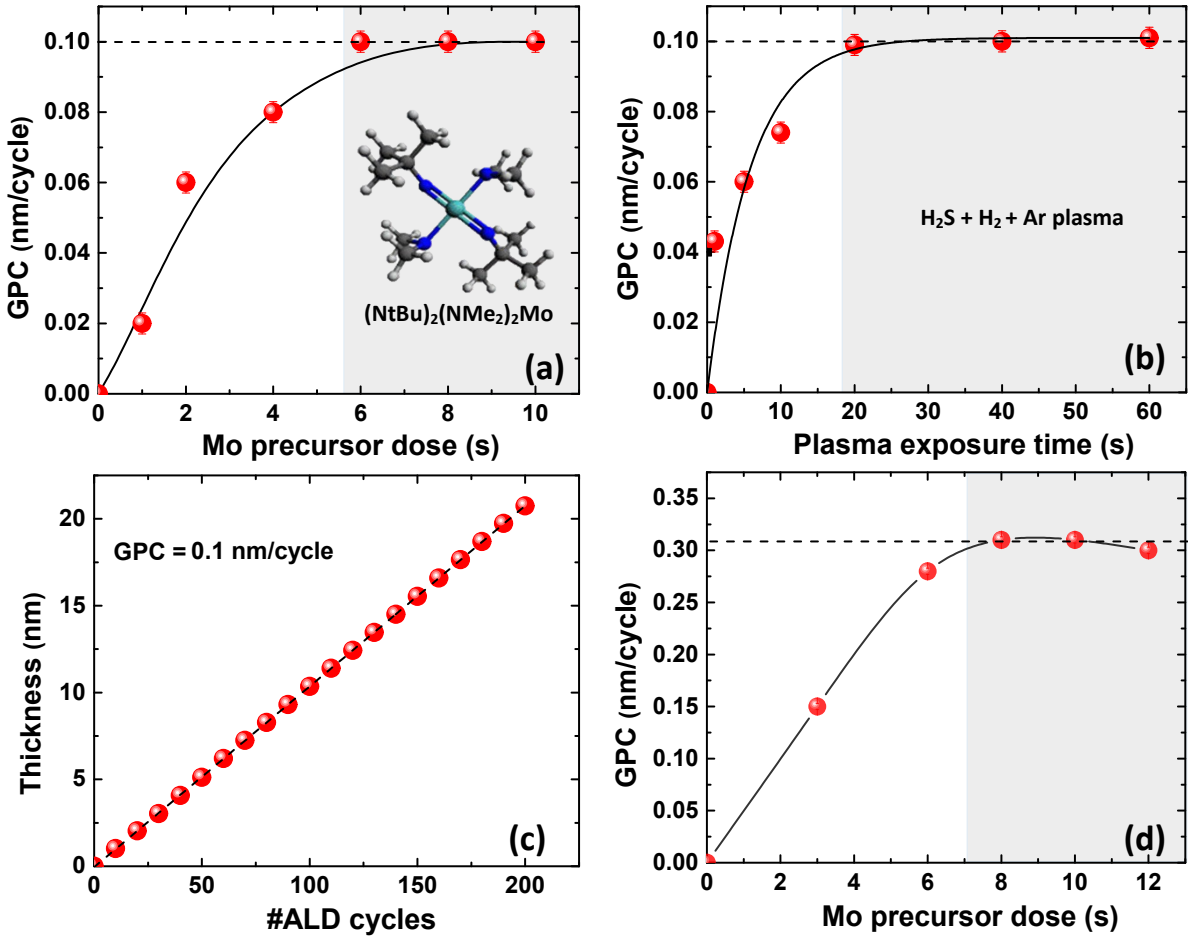

Figure S1 Typical ALD saturation curves (for growth temperature of 250°C) showing the growth per cycle (GPC) as a function of (a) Mo precursor dose (the precursor molecule is shown in inset) and, (b) H_2S based plasma exposure. The saturated regimes for both half cycles are highlighted in grey, the saturation levels are indicated by horizontal dashed black lines and the solid black lines serve as a guide to the eye in both cases. (c) Linear relation between thickness and number of ALD cycles demonstrating precise control over film thickness (d) Half cycle saturation curve for Mo precursor dosing showing a clear saturated growth-per-cycle after a finite dosing time indicating the typical self-limiting ALD growth mode at a growth temperature of 450°C. A plasma exposure time of 20 s was used. The same description is valid for grey area, horizontal dashed and solid black lines in this case.

S2.1: XPS analysis of MoS_2 films

The X-ray photoelectron spectroscopy (XPS) has been used to determine the chemical composition of the MoS_2 films. Figure S2.1 shows the XPS surface scan and the resolved spectra for Mo3d, O1s and C1s regions respectively. A depth profile was recorded by using energetic Ar^+ ion beam (~200 eV) to etch the film and determine the content of contaminants (O, C) within the bulk of the film. It is found that a 50 s etch cycle results in the preferential sputtering of S from MoS_2 species leading to formation of additional metallic Mo component by ion bombardment as shown in Figure S2 (b).

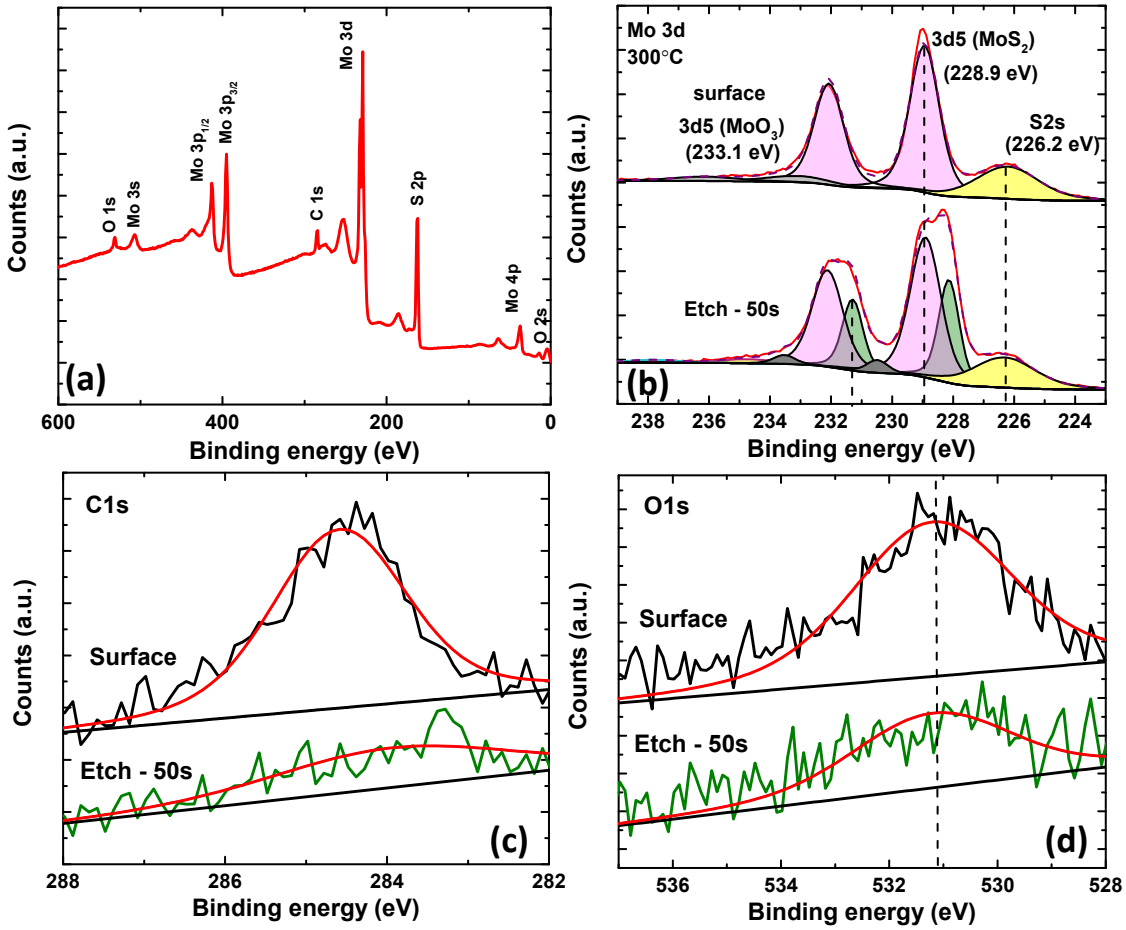

Figure S2.1 (*upper panel*) (a) XPS spectrum scan of ca. 20 nm thick MoS_2 film deposited at 300°C. (b) Resolved spectrum of the Mo3d region showing predominant peaks corresponding to MoS_2 as highlighted. The peak corresponding to S2s is also visible. A small doublet peak corresponding to MoO_3 species is also observed. The red curve is the experimental data while the dashed line represents the fitted data. (*lower panel*) (c, d) Individual scans for C1s and O1s regions; almost complete removal of both species was observed after a 50 s sputter cycle (peak at bottom) confirming the confinement of C and O contaminants to the surface region and with only a trace amount within bulk.

S2.1: RBS analysis of MoS_2 films

The RBS analysis was performed to study the absolute stoichiometry of MoS_2 films grown at different temperatures. Figure S2.2 shows the RBS spectra in which two peaks are assigned to sulphur and molybdenum respectively. The steep edges represent the Si substrate.

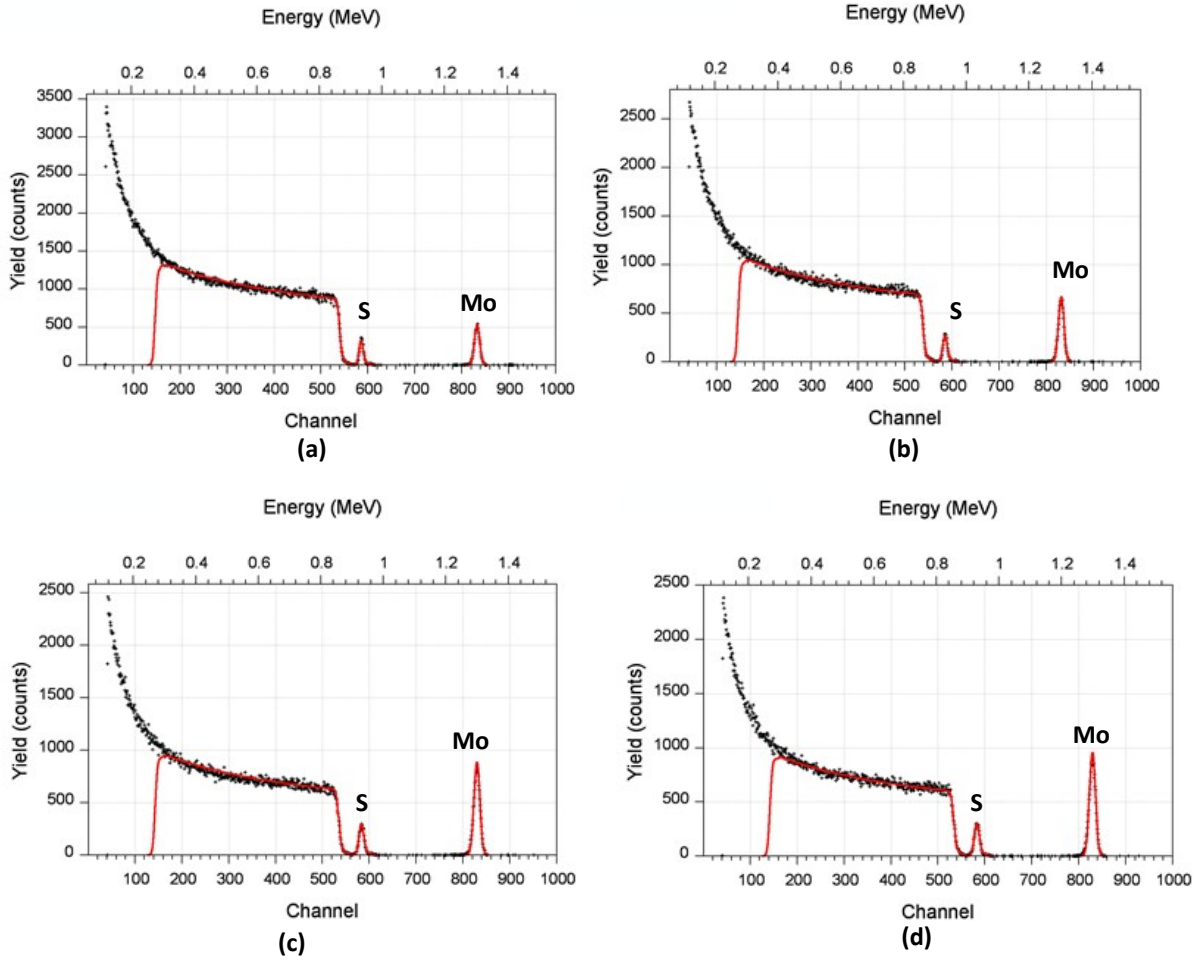

Figure S2.2 RBS spectra for MoS_2 films deposited at the growth temperature of (a) 150°C (b) 250°C (c) 350°C and (d) 450°C respectively. The black points in each case represent the experimental data while the red curves are the fitted curves. It can be seen that a good agreement is obtained between the experimental and fitted curves.

In Table SI1, an estimation of stoichiometry obtained by XPS analysis and an absolute ratio (S/Mo) measured by RBS is given. For XPS, the surface compositions (in atomic%) were obtained by considering the integrated peak areas for Mo3d, S2p regions and the respective sensitivity factors. In case of RBS, the absolute concentrations of both sulfur and molybdenum were extracted by using a model, which were subsequently used to obtain S/Mo ratio. A good agreement between both measurement techniques is obtained showing almost the similar film stoichiometry as a function of growth temperature. At low growth

temperatures (150°C and 250°C), films are found to be over-stoichiometric which may be attributed to the presence of thiol groups on the film surface. Thus, the stoichiometry obtained at low growth temperatures may be rather inaccurate in absence of information regarding 'H' content in the films. On the contrary, at high growth temperatures (350°C and 450°C), the extracted stoichiometry indicates sulphur vacancies in the film which is expected for a polycrystalline MoS_2 film deposited with a bottom-up synthesis method.

Table SI1: The stoichiometry for as-deposited MoS_2 films obtained by XPS and RBS at various growth temperatures. The typical corresponding errors are indicated accordingly.

Growth temperature (°C)	Stoichiometry (S/Mo)	
	XPS	RBS
150	3.4 ± 0.1	3.47 ± 0.18
250	2.5	2.36 ± 0.12
350	1.8	1.95 ± 0.10
450	1.7	1.88 ± 0.09

S3: Deconvolution of Raman spectra

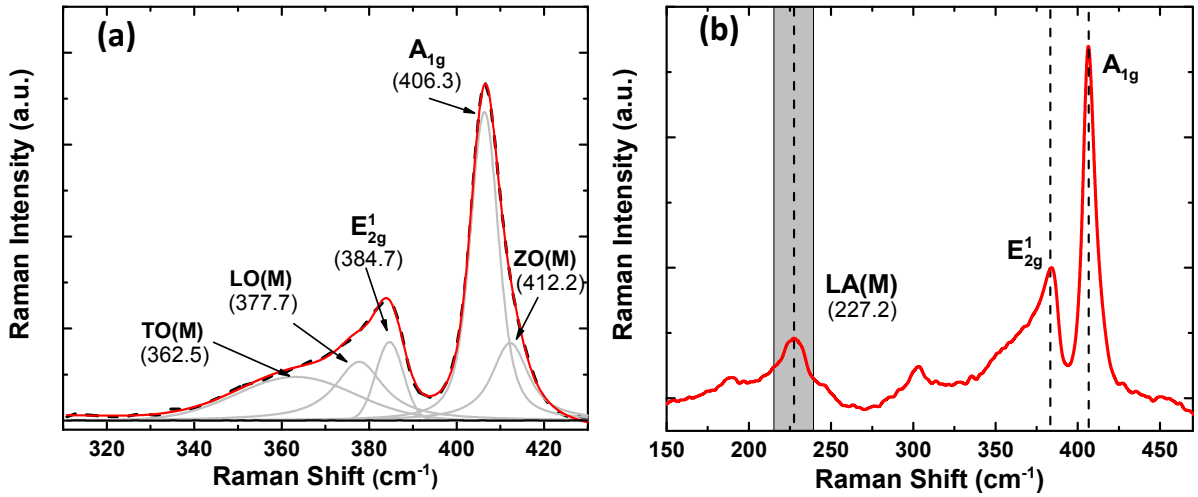

Figure S3 (a) The deconvoluted Raman spectrum for film deposited after 10 cycles at 450°C. The deconvolution reveals the presence of additional defects induced peaks (TO (M), LO (M), ZO (M)) other than the predominant in-plane and out-of-plane vibrational modes (E_{2g}^{1} and A_{1g}). The full width at half maximum (FWHM) values of the fitted peaks for the two components (E_{2g}^{1} and A_{1g}) were found to be 6.9 cm^{-1} and 8.6 cm^{-1} respectively. (b) The spectrum showing the low frequency region where a broad defect induced peak (LA(M)) is clearly visible at ~227 cm^{-1} (highlighted in grey).

S4: High resolution TEM and AFM images of OoPO film

The microstructure of OoPO films formed at 450°C is analysed by high angle annular dark field (HAADF) and high-resolution transmission electron microscope (HRTEM) imaging. Figure S4 shows the corresponding images revealing the out-of-plane oriented MoS_2 films deposited by PEALD on a SiO_2/Si substrate. Further, AFM analysis depicts the high roughness of the film deposited at growth temperature of 400°C.

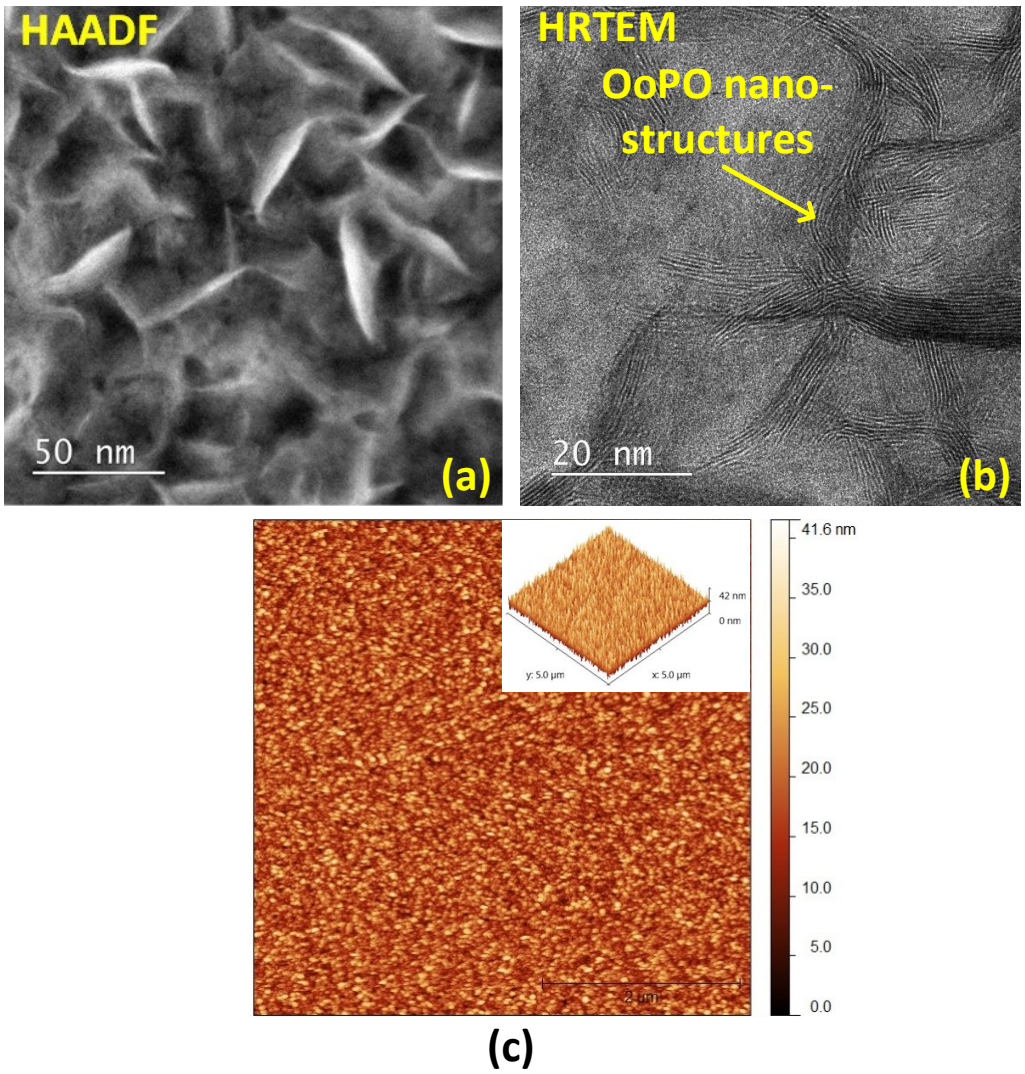

Figure S4 (a) The high angle annular dark field (HAADF) image of MoS_2 film deposited at PEALD growth temperature of 450°C clearly depicting the out-of-plane nanostructures. (b) High-resolution TEM image showing the mixed morphology of the film in the bulk. The distinctive flat regions correspond to the in-plane oriented film while the stripe-like structures correspond to the out-of-plane oriented MoS_2 film. (c) AFM image depicting the topography of ~25 nm thick film MoS_2 film deposited at 400°C. A high RMS roughness of 5.2 nm was observed. The 3-D view is also shown in the inset.

S5: Surface morphology of MoS_2 films on various substrates

Figure S5 shows the morphology of MoS_2 film deposited at 450°C (200 cycles each) on different substrates: Si substrate with 450 nm thermally grown SiO_2, Si substrate with 250 nm Al_2O_3 (deposited by thermal ALD), Si substrate coated with 100 nm Au (e-beam evaporation), SiO_2/Si substrate with mechanically exfoliated MoS_2 flakes from a natural MoS_2 single crystal (bought from Manchester Nanomaterials, UK) and glassy carbon substrate which is used for HER tests.

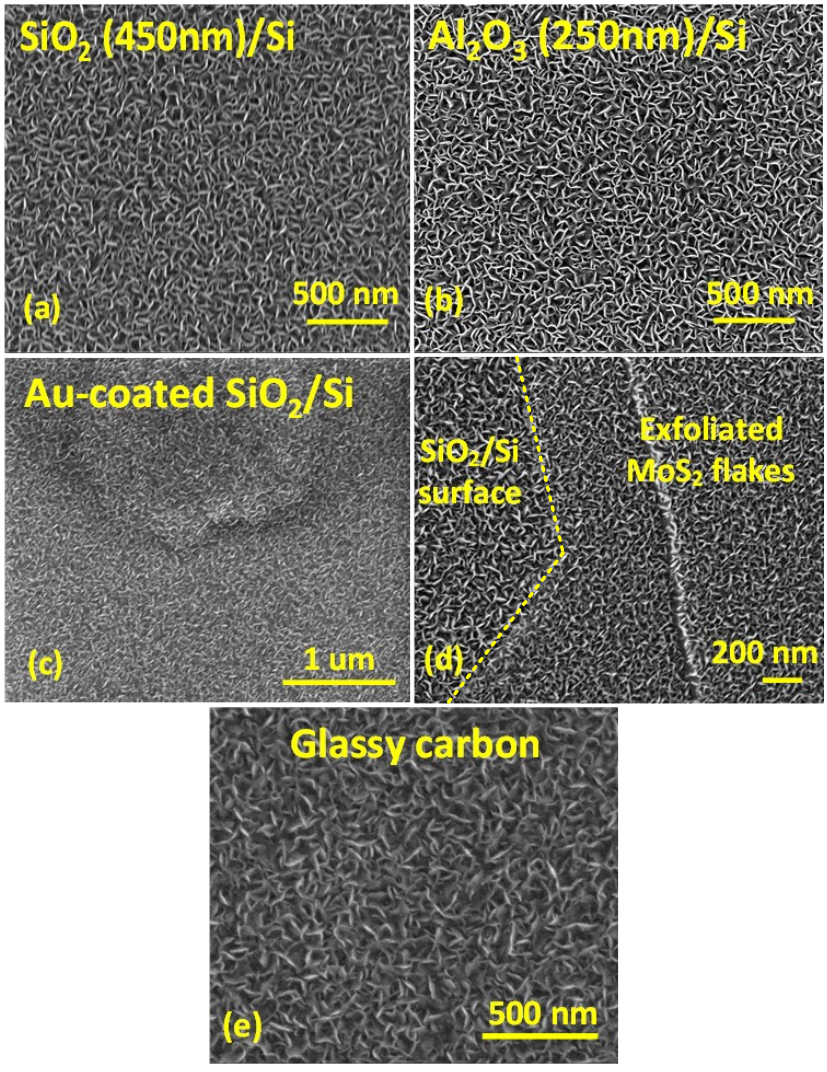

Figure S5 The top-view SEM images of the MoS_2 films grown at 450°C on different substrates. The development of out-of-plane nanostructures was observed irrespective of the substrate used (a) SiO_2/Si, (b) Al_2O_3, (c) Au-coated SiO_2, (d) Mechanically exfoliated MoS_2 flakes and (e) Glassy carbon.

S6: Electrochemical Impedance Spectroscopy of MoS_2 on glassy carbon

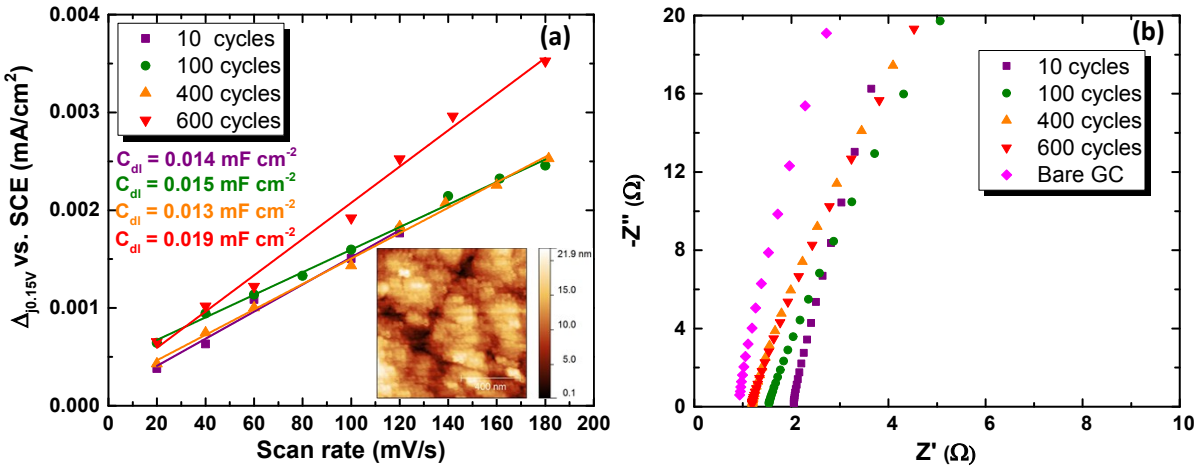

Figure S6 (a) The plot showing estimated double layer capacitance (C_{dl}) for the investigated samples at various scan rates (20 - 180 mVs^{-1}). The inset shows an AFM micrograph of a polished glassy carbon plate using Al_2O_3 polishing slurry (0.3 µm). It is evident that the post-polished surface becomes rough in nature with RMS roughness value of 3.6 nm. (b) Electrochemical impedance spectroscopy (EIS): Nyquist plots of bare glassy carbon substrate and as-deposited MoS_2 films with various ALD cycles collected at open circuit potential in 0.5 M H_2SO_4 electrolyte with an AC amplitude of 10 mV. The charge transfer resistances were evaluated to be 2.3 Ω (Bare GC), 2.1 Ω (10 cycles), 1.5 Ω (100 cycles), 1.2 Ω (400 cycles) and 1.2 Ω (600 cycles), respectively.

(1) N. P. Dasgupta, X. Meng, J. W. Elam, A. B. F. Martinson, *Accounts of Chemical Research* **2015**, 48, 341.