Supporting Information

Atomic Layer Deposition of Crystalline Epitaxial MoS_2 Nanowall Networks Exhibiting Excellent Performance in Thin-film Rechargeable Na-ion Batteries

M. B. Sreedhara,[a] Subhra Gope,[b] Badri Vishal,[a] Ranjan Datta,[a] Aninda J. Bhattacharyya[b] and C. N. R. Rao*[ab]

[a]Chemistry and Physics of Materials Unit, International Centre for Materials Science and Sheikh Saqr Laboratory, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P. O., Bangalore-560064, India.

[b]Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore- 560012, India.

*E-mail: cnrrao@jncasr.ac.in

Experimental section

Deposition of crystalline epitaxial MoS_2 thin films

Crystalline epitaxial hexagonal 2H MoS_2 thin films were grown by atomic layer deposition on single crystalline *c*-sapphire (0001) substrates using a flow type ALD reactor (Beneq, TFS 200 Finland Oy). Prior to the deposition, the substrates were cleaned thoroughly using H_2SO_4 and H_2O_2 in the ratio 4:1 at 120 °C followed by ultrasonication in acetone and isopropanol and dried under nitrogen. High purity molybdenum pentachloride ($MoCl_5$, 99.9%) and hydrogen sulfide (Bhuruka gases, 97.5%) were employed as Mo and S sources respectively. Ultra high pure N_2 (Chemix, 99.9995) was used as a carrier and purging gas at the flow rate of 600 sccm throughout the deposition. The chamber and reactor were pumped down to 10 and 1 mbar respectively before the starting recipe for the deposition. The reaction chamber was heated to 300 °C and hold 30 min for temperature stabilization. $MoCl_5$ was kept in the hot source HS-300 bubbler

(Beneq, Oy) and heated slowly to 120 °C to vaporize it. The hot source head and precursor lines from the hot source to the reactor were maintained at a slightly higher temperature than that the hot source to avoid condensation of $MoCl_5$. The films were deposited by sequential pulsing of $MoCl_5$ and H_2S. The hot source was boosted with high purity nitrogen for 1s before pulsing $MoCl_5$ to the reactor, to make sure enough vapor pressure of the precursor. The optimized pulse and purge times for $MoCl_5$ were 2s and 3s respectively, whereas the pulse and purge times for H_2S were 1s and 3s. A variation in the reactor pressure between 1-3 mbar was observed during pulsing and purging, the chamber pressure is almost intact. The complete ALD sequence for MoS_2 growth was pulse $MoCl_5$/purge//pulse H_2S/purge for 2s/3s//1s/3s. The deposition was carried out for 10, 100, 500, 1000, 1500 and 2000 cycles at 300 °C and the films cooled down to room temperature under vacuum. The as-obtained films were used for further characterization without post annealing. To ascertain the ALD temperature window and the self-terminating nature of ALD process, depositions were carried out at different reactor temperatures and pulse times and purge times.

TEM Sample preparation

TEM cross-sectional specimens are prepared first by mechanical polishing and then Ar ion milling to perforation to generate large electron thin transparent area. All the high-resolution transmission electron microscopy (HRTEM) imaging was carried out in a double aberration corrected TITAN 80-300 kV microscope under Cs ~ 40 µm and a positive defocus ~ 8 nm, which gives direct interpretation of images.

Characterization of MoS_2 thin films

X-ray diffraction (XRD) patterns of the as-deposited films were recorded with a Panalytical diffractometer (Empyrean) with θ-2θ scan using monochromatic Cu $K\alpha_1$ radiation (λ = 1.5404Å) to confirm the crystallinity. Raman optical modes of MoS_2 were recorded in using a 514 nm Ar

laser with a Jobin Yvon LabRam HR spectrometer in backscattering geometry. X-ray photoelectron (XP) spectra were recorded using an Omicron nanotechnology spectrometer with Mg Kα X-ray source (E = 1253.6 eV). Optical transmission spectra were recorded on a PerkinElmer UV−Vis spectrometer from 200 to 800 nm range. Optical microscope images were captured using Leica DM2700 M microscope fitted with bright universal LED illumination. Field emission scanning electron microscope (FESEM) Nova NanoSEM 600 FESEM equipped with an Energy Dispersive X-ray (EDX) analysis system (FEI Company) was employed to ascertain the film thickness (in cross-section mode) and surface morphology. The surface roughness and topography of the films were determined using atomic force microscopy (AFM) in contact mode (Bruker Innova) using high-resolution SNL-10 Bruker AFM probe with tip radium of 2 nm. The sample for transmission electron microscopy (TEM) was prepared by the by mechanical polishing and Ar ion milling. Cross-sectional high-resolution TEM (HRTEM) was performed using double aberration corrected FEI TITAN 80−300 operated at 300 kV. Room-temperature carrier concentration and mobility were determined using Ecopia HMS-3000 Hall effect measurement system.

Electrode fabrication and electrochemical measurements

Electrochemical stability and Lithium and Sodium battery performance studies are tested in coin-cells (CR-2032). For the Sodium ion cell, Na-foil (Aldrich, thickness = 0.75 mm) is used as a counter and a reference electrode, Whatman glass fiber as a separator and 1M $NaPF_6$ in EC:DEC (1:1 v/v) as the electrolyte. For the Lithium-ion cell, Li-foil (Aldrich, thickness = 0.75 mm) is used as a counter and reference electrode, Whatman glass fiber as separator and 1M $LiPF_6$ in EC:DMC (1:1 v/v) as electrolyte. For electrochemical measurements, the ALD grown MoS_2 layers on the stainless steel current collector of the coin cell is used directly as the working electrode. In this case, the working electrode is devoid of acetylene black (CB) or polyvinylidene fluoride (PVDF) which is conventionally used as electron conductor and binder

respectively during electrode casting. The mass loading per electrode on the current collector is about 120 µg obtained after running 2000 ALD cycles. All cell assembly is done at 25 °C in an Argon filled glove box (MBraun) (H_2O <1, O_2< 1 ppm).

The cyclic voltammogram is obtained in CH Instrument (CH 403), while the galvanostatic charge/discharge cycling are obtained on Neware Battery Cycler using TC53 software at different C-rates (1C = 167 mA g^{-1}) in two sets of the voltage ranges of 0.2 – 3.0 V and 1.0 – 3.0 V (versus Li^+/Li and Na^+/Na).

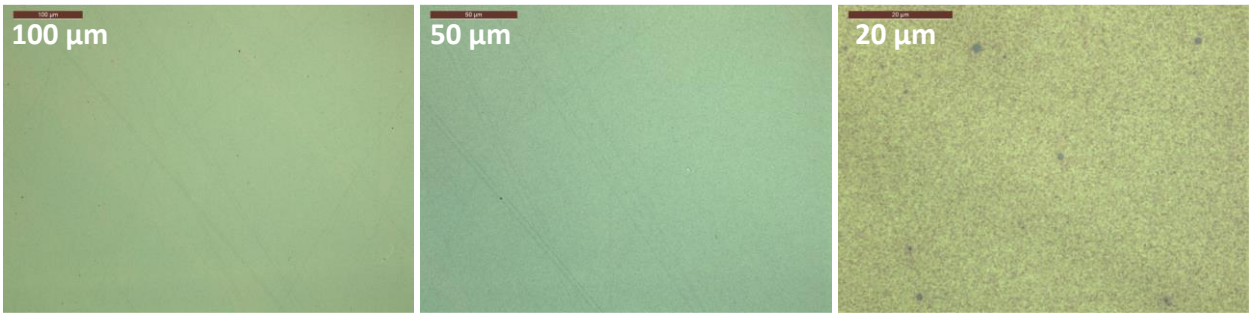

Fig. S1 Optical microscope images of MoS_2 thin film of 2000 ALD cycles grown on c-sapphire.

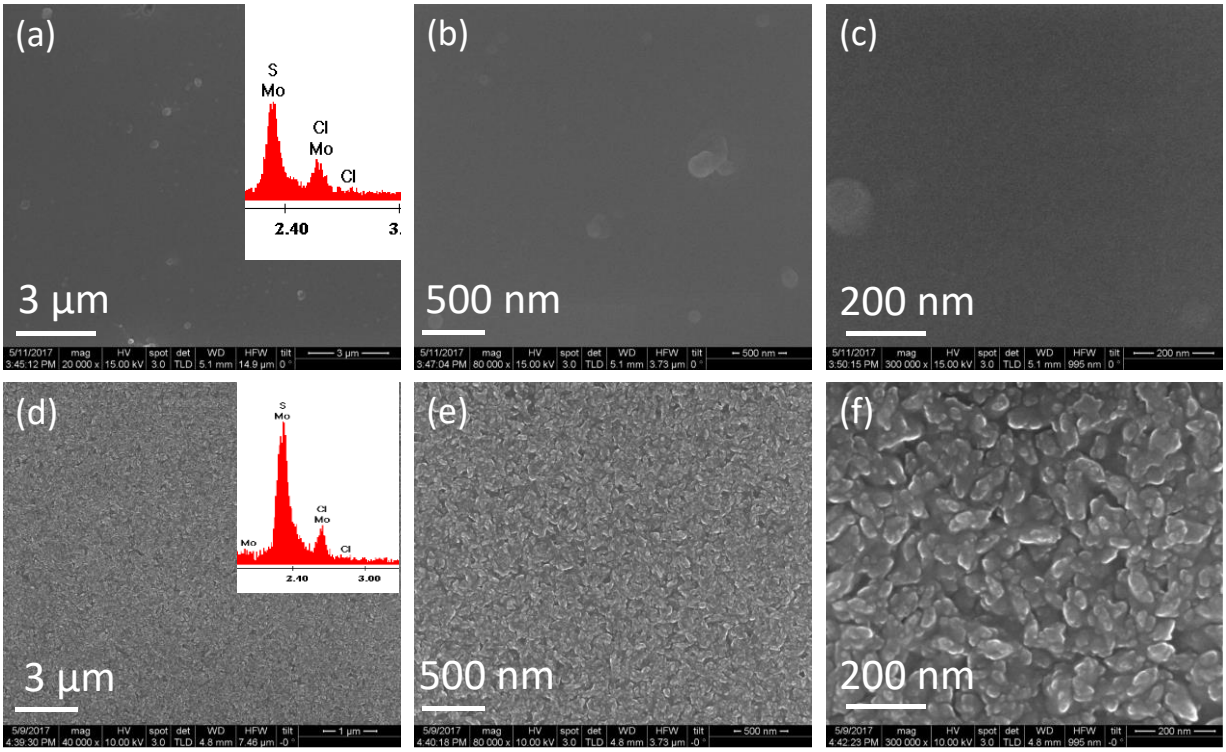

Fig. S2 FESEM images of as-deposited MoS_2 thin films at 150 °C (a-c) and 200 °C (d-f) on c-sapphire substrate. Inset of the Fig. (a) and (d) shows corresponding EDAX spectrum.

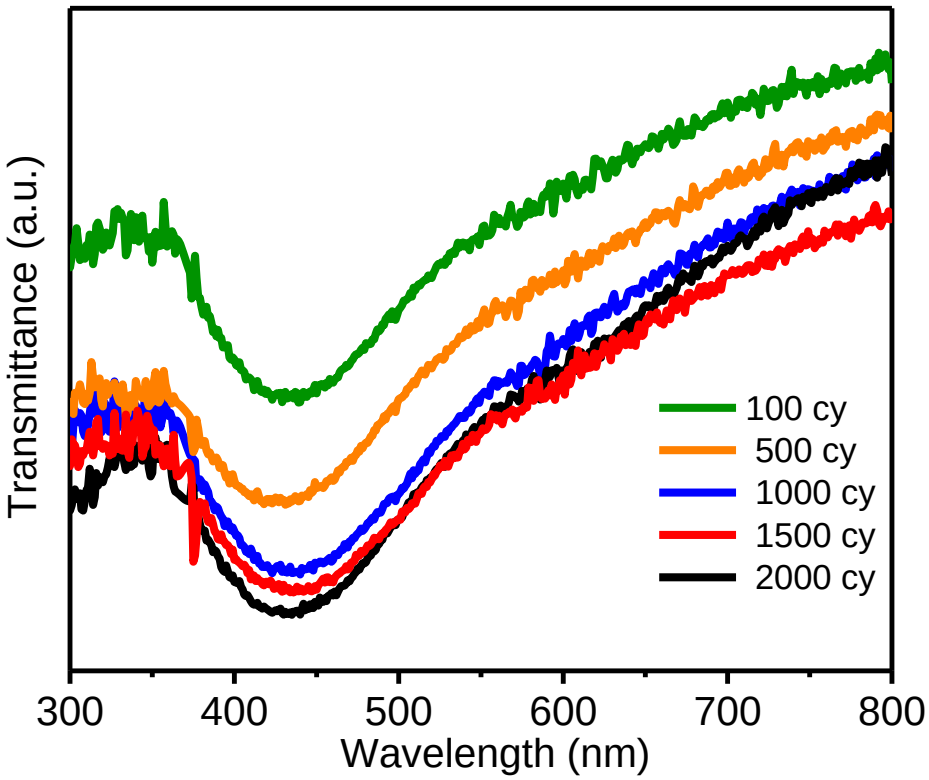

Fig. S3 Optical transmittance spectra of MoS_2 nanowall network on c-sapphire of varying thickness.

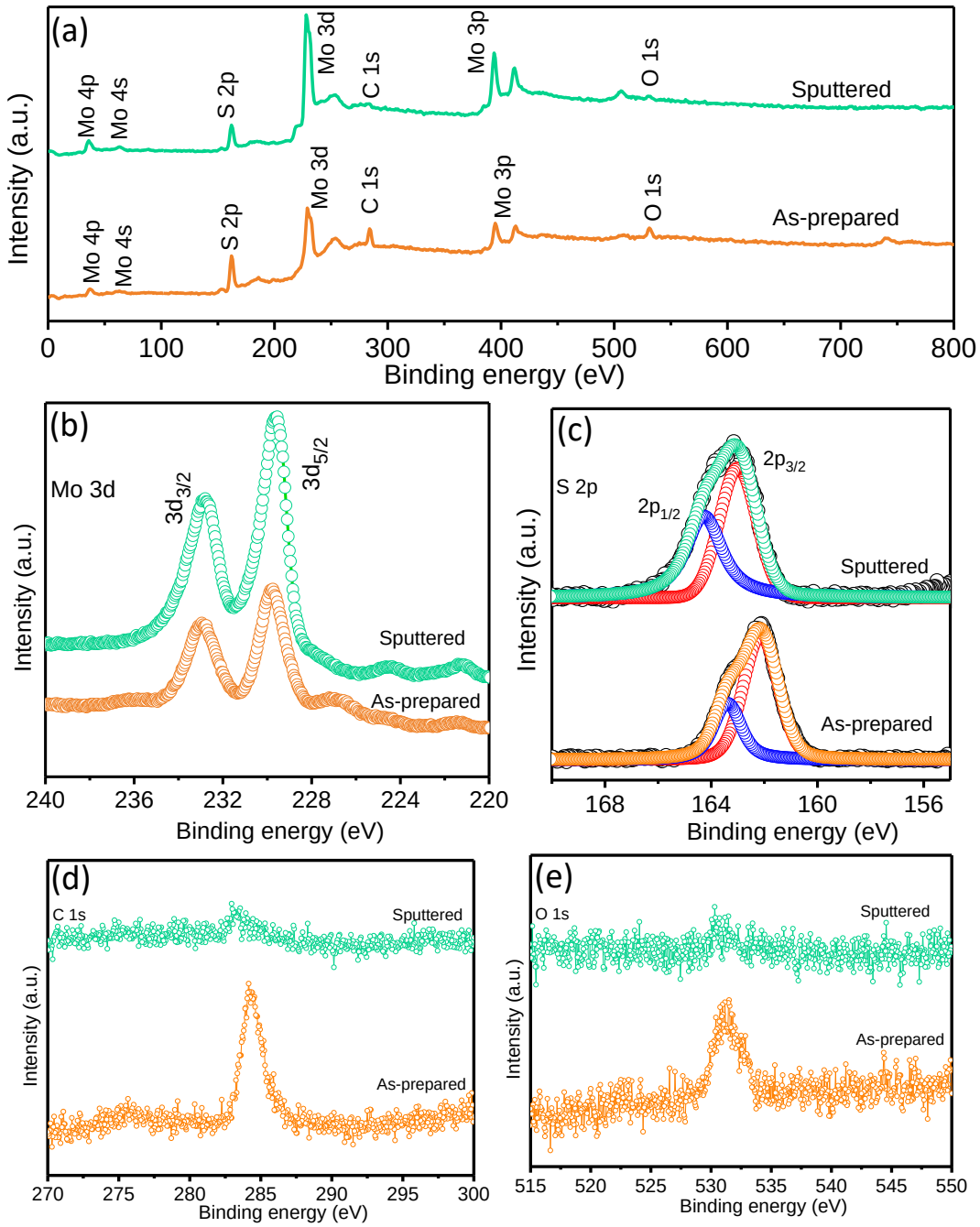

Fig. S4 (a) Survey scan XP spectra of MoS_2 thin films grown on c-sapphire and corresponding core-level spectrum of Mo 3d (d) and S 2p (e).Core-level XP spectra of (d) C 1s and (e) O 1s in as-prepared and sputtered thin films of MoS_2.

X-ray photoelectron (XP) spectral analyses

X-ray photoelectron (XP) spectroscopy was adapted to understand the chemical bonding nature of the deposited films. Fig. S4a shows the survey scan XP spectra of epitaxial MoS_2 thin film on sapphire. As deposited film shows all the characteristic signals corresponding to Mo and S. In addition to all the characteristic peaks, we also observed C and O peak which are may be due to surface contamination. In order to know proper bulk composition, we sputtered the sample with high pure argon for 10s to remove few nanometer from the surface. C and O signals are diminished in the sputtered sample, which represents the pure MoS_2 without any contamination. The core-level XP spectra of Mo 3d shows the characteristic peak of $3d_{5/2}$ and $3d_{3/2}$ at 229.5 and 232.8 eV respectively, which are attributed to Mo^{4+} bonding with S (Fig. S4b). There no peak observed for Mo-O bonding (Mo^{6+}, 236.2 eV) in the collected spectrum of Mo 3d, indicates high-quality MoS_2. The core-level XP spectrum of S 2p levels is shown in Fig. 1e. The asymmetry and broad peak in S 2p spectra is not only due to the chemical environment but also overlapping of S $2p_{3/2}$ and S $2p_{1/2}$ signal. Therefore, S 2p spectrum deconvoluted into two peaks and were appear at 162.9 and 163.4 eV corresponding S $2p_{3/2}$ and S $2p_{1/2}$ of MoS_2 bonding respectively. The core-level spectra of sputtered sample show more prominent and distinguishable signals compared to as-deposited films. We have also collected the C 1s and O 1s core-level spectra before and after sputtering (Fig. S4 d and e), reveals there is no contamination of C and O in the films.

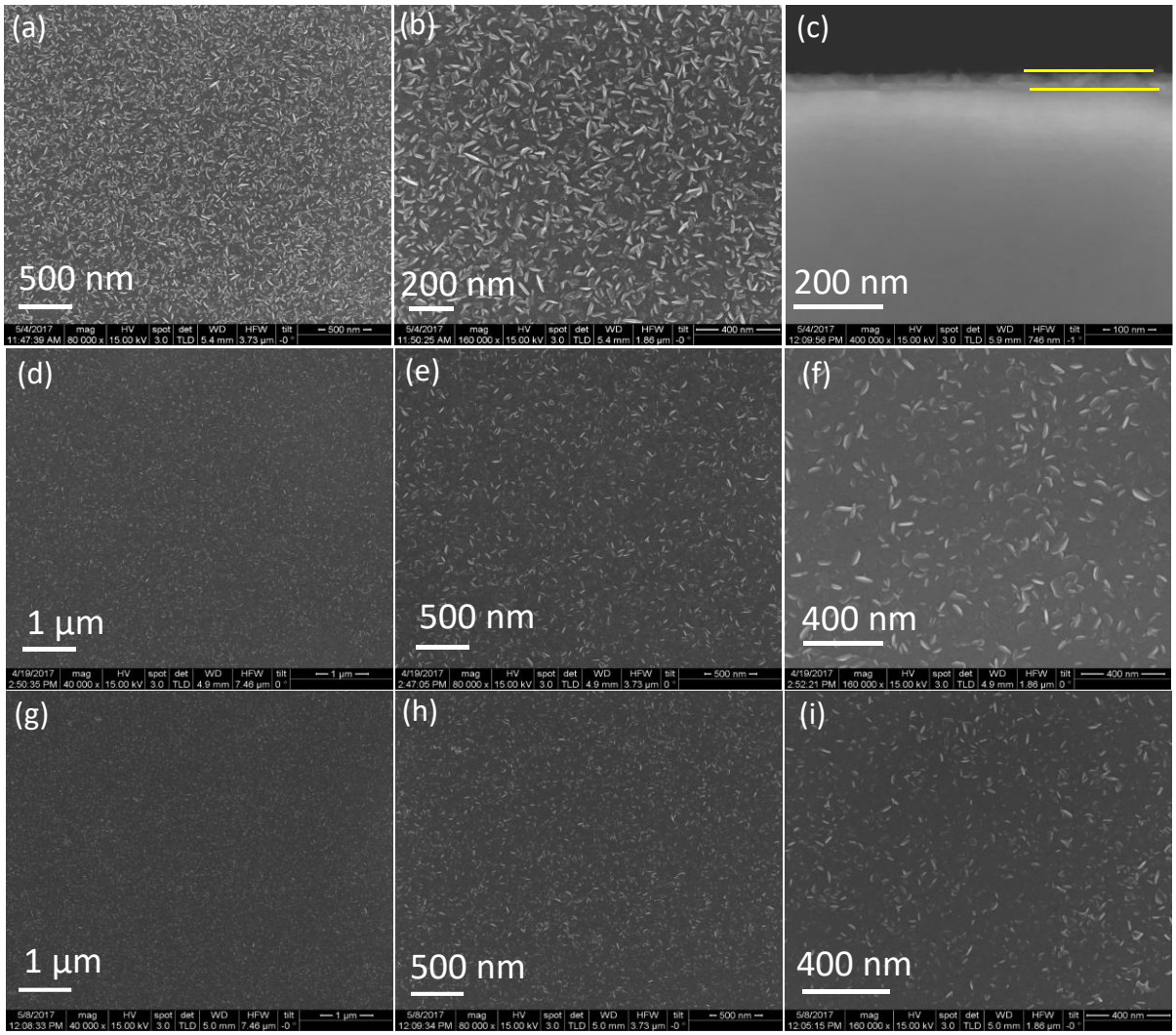

Fig. S5 FESEM images showing surface morphology of as-deposited (a-c) 1500 (d-f) 1000 and (g-i) 500 cycles epitaxial MoS_2 films.

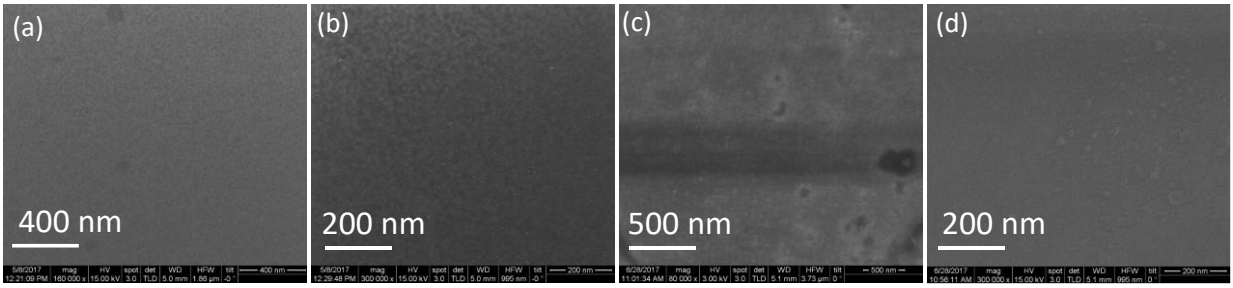

Fig. S6 FESEM images showing surface morphology of as-deposited (a, b) 100 and (c, d) 10 cycles epitaxial MoS_2 films.

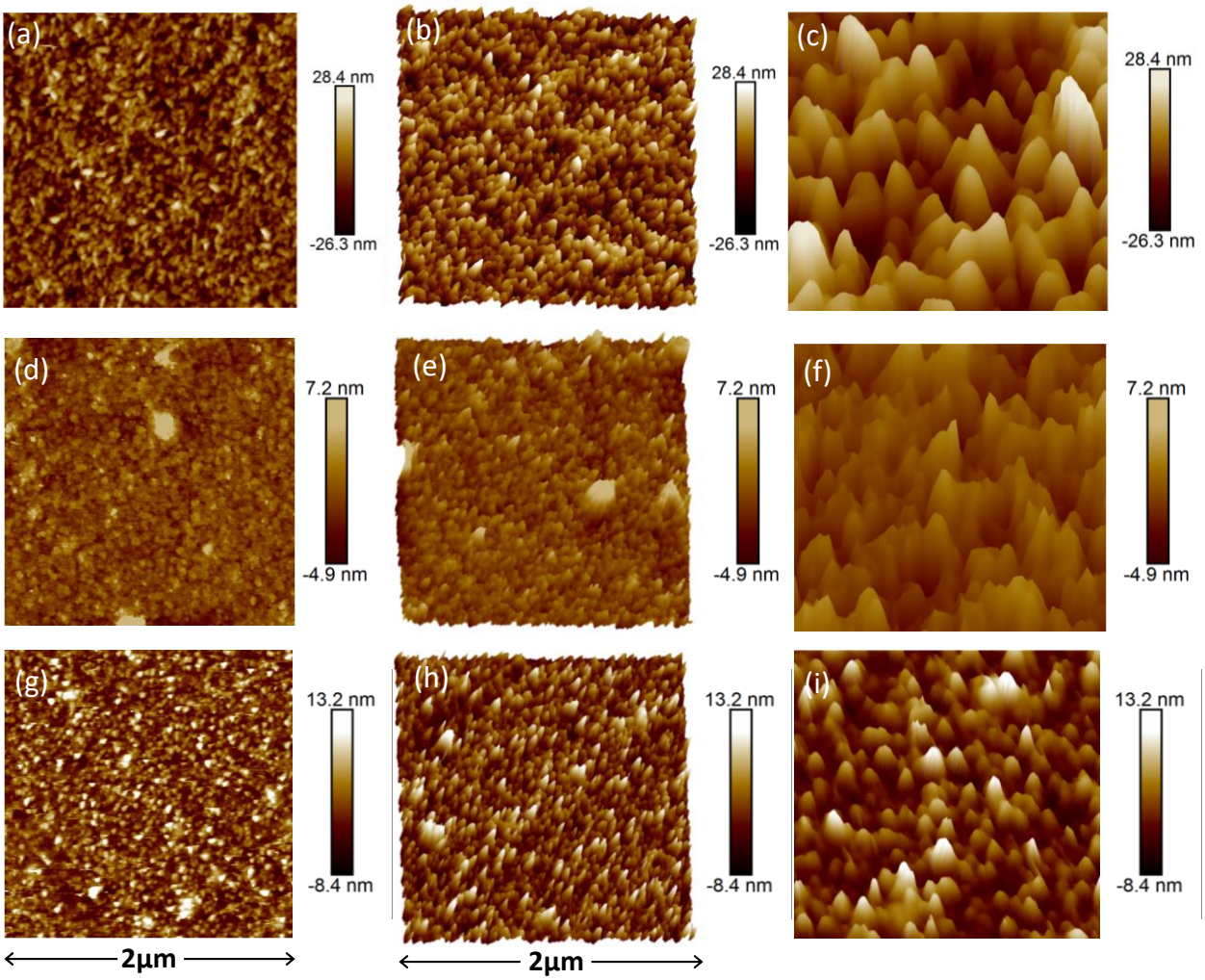

Fig. S7 AFM images of as-deposited (a-c) 1500, (d-f) 1000 and (g-i) 500 cycles epitaxial MoS_2 thin films on c-sapphire substrate. The images (b, e &h) shows 3D projection and (c, f & i) shows zoom in view image to distinguish individual wall.

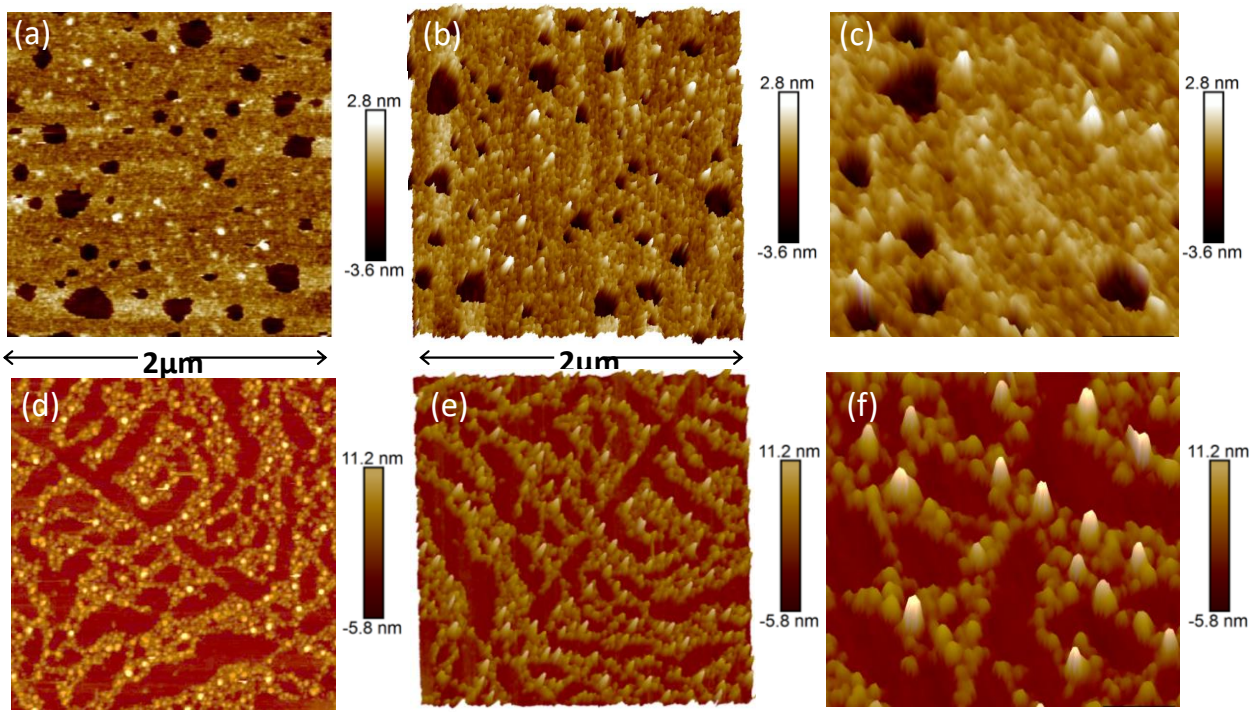

Fig. S8 AFM images of as-deposited (a-c)100 and 10 (d-f) cycles of epitaxial MoS_2 thin films.

The images (b) & (e) shows 3D projection, (c) & (f) shows zoom in view image.

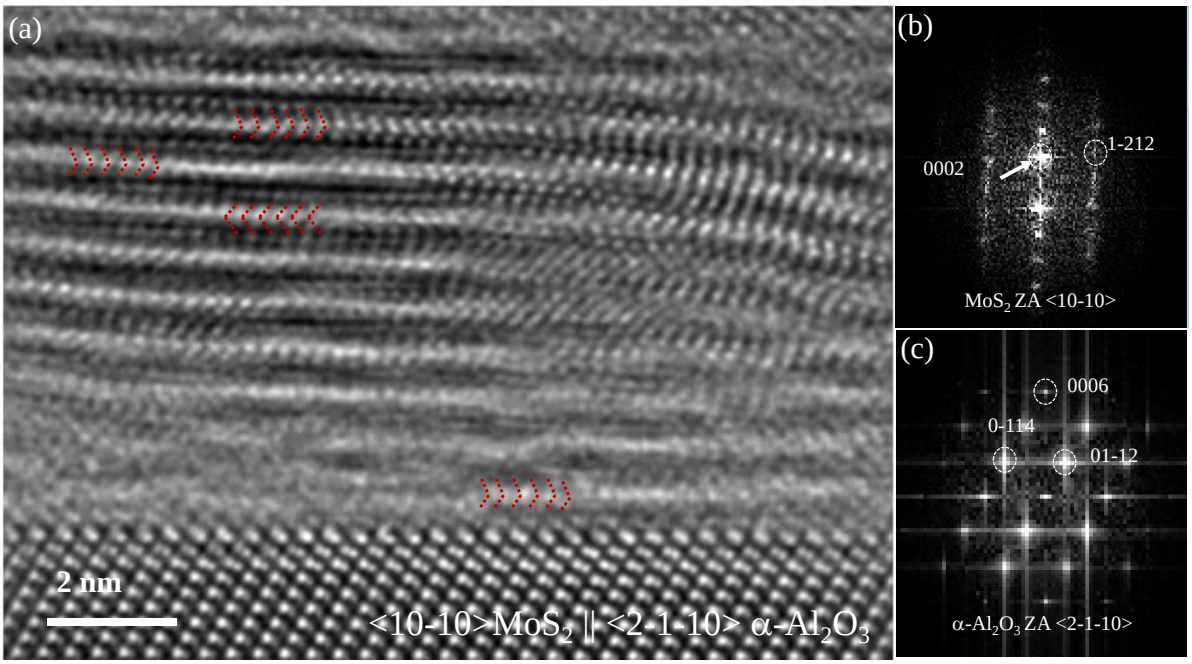

Fig. S9 HRTEM image of MoS_2 on c-sapphire along <11-20> of Al_2O_3. The epitaxial relationship between MoS_2 and sapphire is <10-10>MoS_2 || <2-1-10> Al_2O_3.

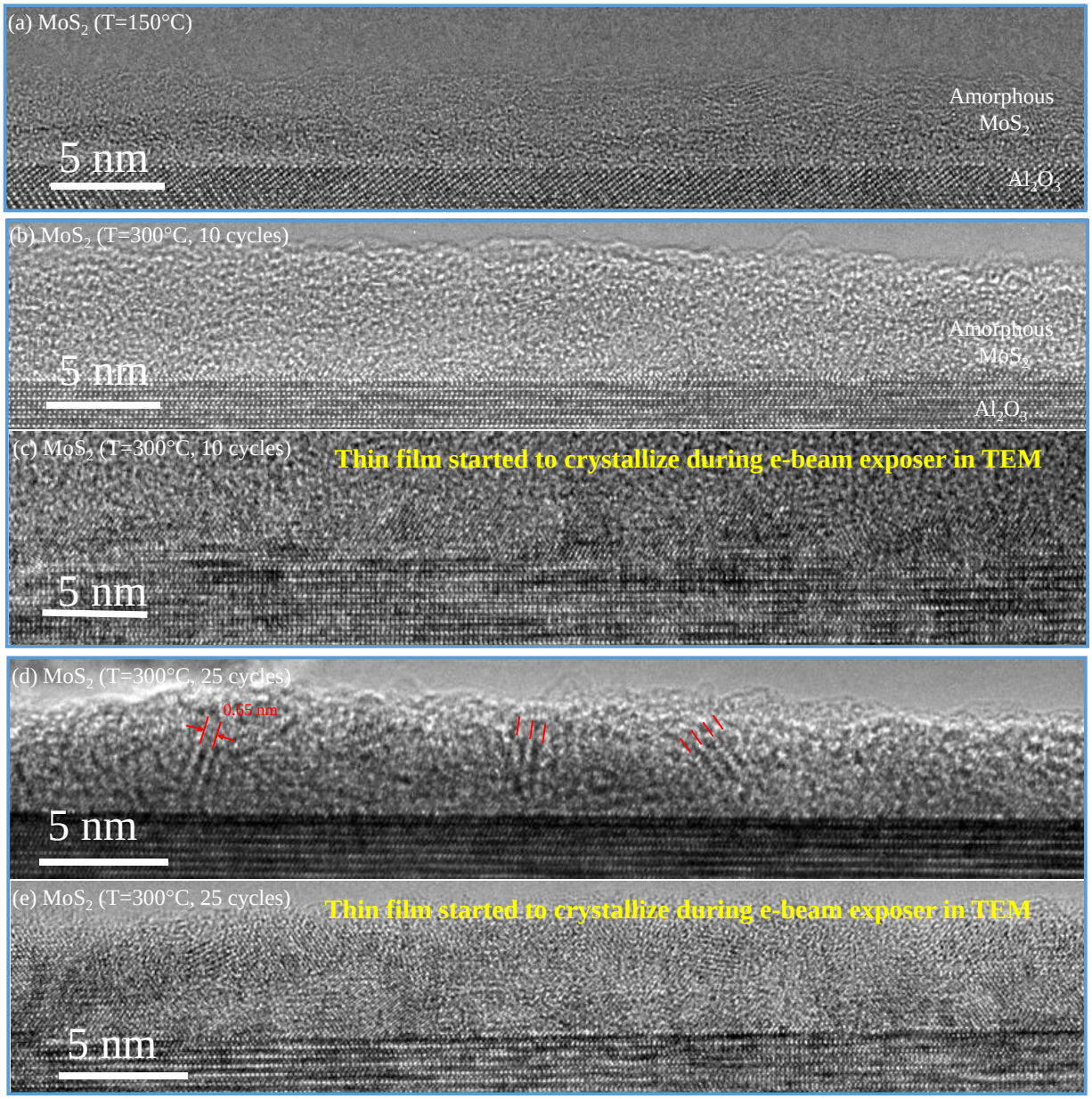

Fig. S10 Cross-section TEM images of MoS_2 on *c*-plane sapphire substrate grown by ALD at (a) 150 °C, (b and c) 300 °C for 10 cycles and (d and e) 300 °C for 25 cycles.

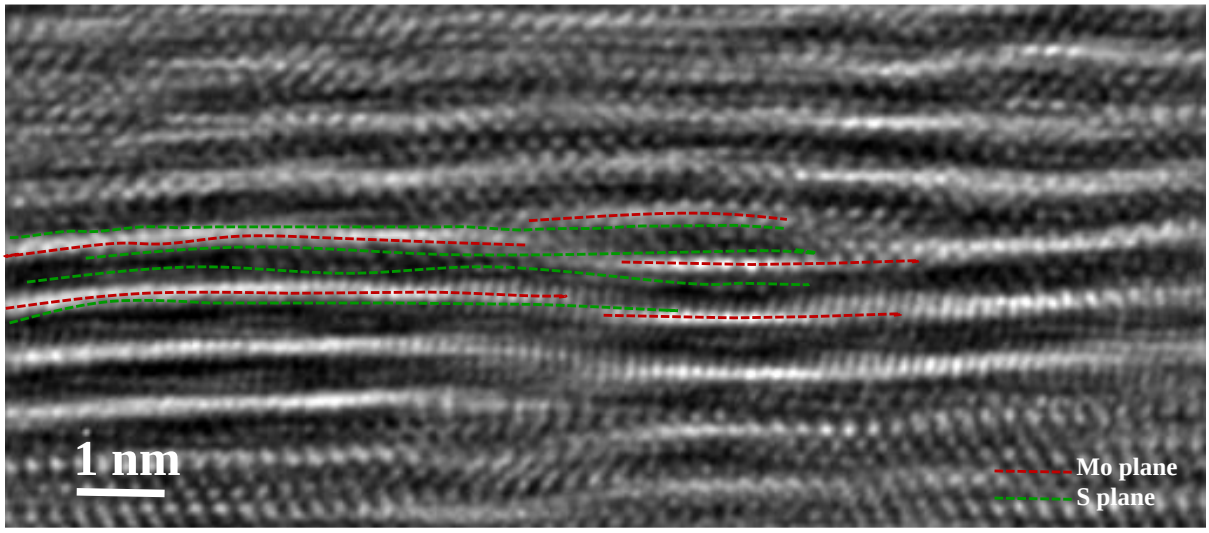

Fig. S11 Planer defects in MoS_2 van der walls epitaxial stacks. The origin of such fault due to discontinuous Mo layers, whereas the S atomic planes are continuous.

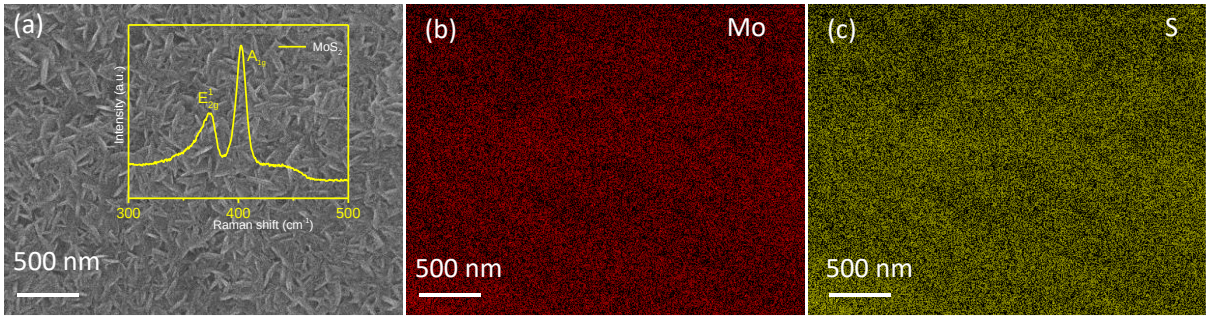

Fig. S12 (a) FESEM image of MoS_2 thin film deposited on stainless steel substrate for electrochemical measurements. Inset of (a) shows corresponding Raman spectra. (b and c) EDAX elemental mapping of MoS_2 thin film deposited on stainless steel substrate, Mo(red) and S (green).

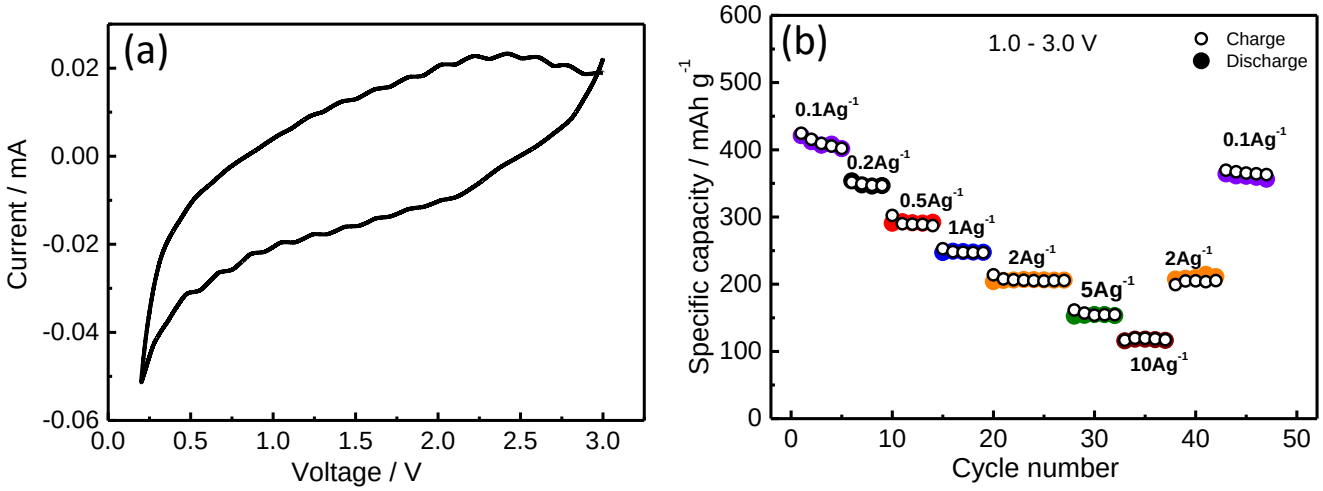

Fig. S13 (a) CV of MoS_2 nanowall versus Na (b) rate capability of MoS_2 nanowall versus Na for 1 – 3 V.

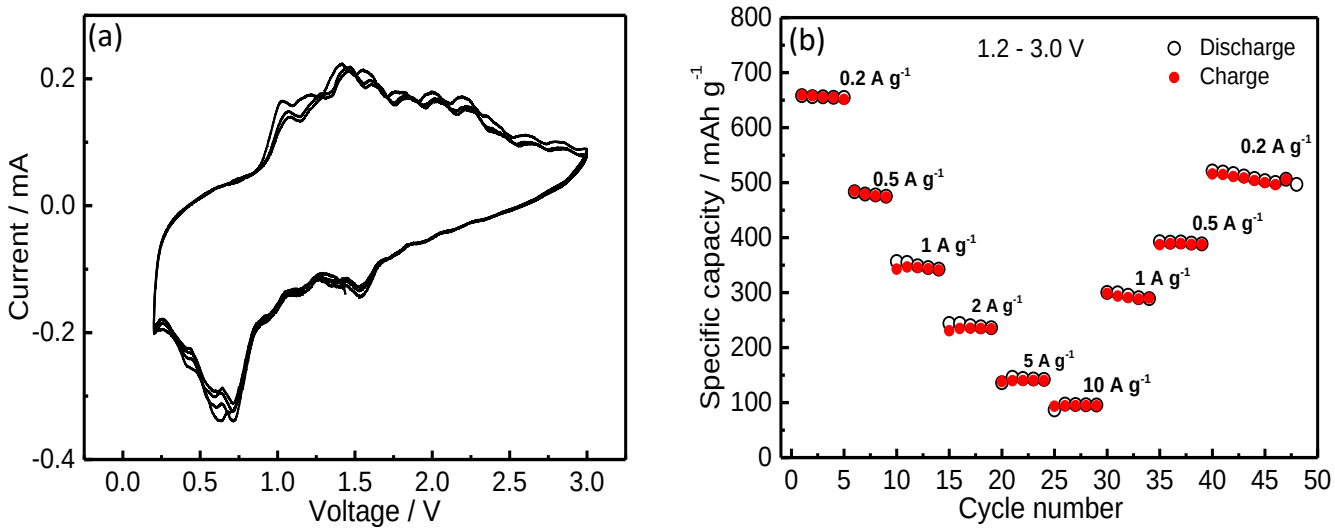

Fig. S14 (a) CV of MoS_2 nanowall versus Li for 0.2 – 3.0 V (b) rate capability of MoS_2 nanowall versus Li for 1.2 – 3.0 V.

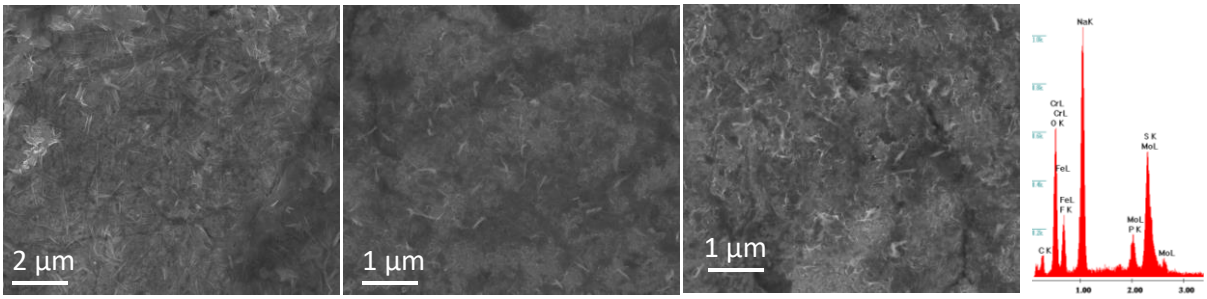

Figure S15. FESEM images of the surface of the MoS_2 thin films electrode after 100 cycles of Na battery test.