Electronic Supporting Information for

Tungsten disulfide thin films via electrodeposition from a single source precursor

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Experimental

Syntheses of precursors

Syntheses were performed by using standard Schlenk and glove-box techniques under a dry N_2 atmosphere. $[N^nBu_4]OH$ (40% aqueous solution), $S(SiMe_3)_2$, $[Et_4N]Cl$, $[N^nBu_4]Cl$, $[Ph_4P]Cl$ were obtained from Sigma Aldrich and $[NH_4]_2[WS_4]$ from Alfa Asear and were used as received. $WSCl_4$ was made as described previously.[1] Solvents were dried by distillation from CaH_2 (CH_2Cl_2) or Na/benzophenone ketyl (n-hexane).

Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer in the range 4000–200 cm^{-1}, with samples prepared as Nujol mulls between CsI plates. ^1H NMR spectra were recorded using a Bruker AV 400 spectrometer and referenced to the residual protio-resonance of the solvent. Microanalyses on new compounds were undertaken by London Metropolitan University.

$[N^nBu_4]_2[WS_4]$: Following the literature method,[2] ammonium tetrathiotungstate (0.490 g, 1.41 mmol) was dissolved in deionised water (10 mL) to form a yellow solution. A solution of tetrabutylammonium hydroxide (40% wt., 1.83 g, 2.82 mmol) in water (10 mL) was slowly added dropwise, a yellow solid immediately precipitated. The solution was filtered and the solid washed with water (1 x 2 mL) and cold ^iPrOH (1 x 2 mL) and dried *in vacuo*. Yield: 0.513 g, 45 %. Required for $C_{32}H_{72}N_2WS_4$ (797.02): C: 48.22, N: 3.51, H: 9.11 %. Found: C: 48.17, N: 3.55, H: 9.18 %. IR spectrum (Nujol, v / cm^{-1}): 448s W=S. ^1H NMR ($CDCl_3$): δ/ppm = 1.0 (t, [3H], J_{HH} = 7.34 Hz, CH_3), 1.44 (m, [2H], J_{HH} = 7.38 Hz, CH_2), 1.6 - 1.7 (m, [2H], CH_2), 3.2 - 3.4 (m, [2H], CH_2).

$[Et_4N]_2[WS_2Cl_4]$: A solution of tetraethylammonium chloride (0.185 g, 1.12 mmol) was dissolved in dichloromethane (3 mL) and slowly added to a solution of $WSCl_4$ (0.200 g, 0.56 mmol) in dichloromethane (5 mL). The green solution was stirred for 30 mins., then a solution of hexamethyldisilathiane (0.100 g, 0.56 mmol) in dichloromethane (1 mL) was slowly added and the reaction was left to stir for 1 h. A brown precipitate was observed, and supernatant filtered and the beige solid isolated and dried *in vacuo*. Yield: 0.250 g, 68 %. Required for $C_{16}H_{40}Cl_4N_2S_2W$ (650.28): C: 29.55, H: 6.20, N: 4.31 %. Found: C: 29.19, H: 6.06, N: 4.33 %. IR spectrum (Nujol, v / cm^{-1}): 498s W=S, 289s W-Cl. ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.30 (br s, [3H], Me), 3.23 (br s, [2H], CH_2). UV/Vis (diffuse reflectance)/cm^{-1}: 27,770, 24,630, 20,000sh.

$[PPh_4]_2[WS_2Cl_4]\cdot CHCl_3$: A solution of tetraphenylphosphonium chloride (0.420 g, 1.12 mmol) in dichloromethane (5mL) was added to a solution of $WSCl_4$ (0.200 g, 0.56 mmol) in dichloromethane (5mL). turning green. The solution was allowed to stir for 30 minutes then a solution of hexamethyldisilathiane (0.100 g, 0.56 mmol) in dichloromethane (1 mL) was added, when the solution darkened and then turned a deep red. The solution was stirred for 30 mins. and concentrated under vacuum, after which the brown solid was precipitated out with n-hexane (10 mL), filtered and washed with chloroform (5 mL) before drying *in vacuo*. Yield: 0.50 g, 75%. Required for $C_{49}H_{41}Cl_4P_2S_2W$ (1187.94): C: 49.54, H: 3.48 Found: C: 49.45, H: 3.34%. IR Spectrum (Nujol/cm^{-1}): W=S – obscured by cation modes, 296s, 233m W-Cl. ^{1}H NMR (CD_2Cl_2) δ = 7.85 (br s, [2H]), 7.70 (br s, [2H]), 7.56 (br s, [H]). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ/ppm = +23.3 (s).

Attempted Preparation of $[N^nBu_4]_2[WS_2Cl_4]$: A solution of tetrabutylammonium chloride (0.558 g, 2 mmol) in dichloromethane (5 mL) was added to a solution of $WSCl_4$ (0.400 g, 1 mmol) in dichloromethane (5 mL) which turned green. The solution was allowed to stir for 30 minutes then a solution of hexamethyldisilathiane (0.215 g, 1 mmol) in dichloromethane (2 mL) was added. The solution darkened and then turned a deep red. The solution was stirred for 30 min and concentrated under vacuum. The resulting sticky brown solid was precipitated out with diethyl ether (10 mL). IR spectrum (Nujol/ cm^{-1}): 498s W=S, 295s, 235m W-Cl.

X-ray experimental

Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K (N_2 cryostream). Crystallographic parameters are presented in Table S1. Structure solution and refinement were performed using SHELX(T)-2018/2, SHELX-2018/3 through Olex2[3] and was mostly straightforward but showed significant residual electron peaks near to the tungsten, which are attributed to absorption correction problems. The CCDC reference number for the crystallographic information file in cif format is CCDC 2084213.

Electrochemistry

All the electrolyte preparations, electrochemical characterisations and electrodeposition were performed inside an N_2 filled recirculating glove box (Belle Technology, UK) with sub-10 ppm O_2 and H_2O levels. Electrolyte solutions were prepared in anhydrous CH_2Cl_2 (Sigma-Aldrich, 95%), dried and degassed by refluxing with CaH_2 followed by distillation. The water content in dried CH_2Cl_2 was *ca.* 18

ppm determined by Karl Fischer titration. 0.1 M $[N^nBu_4]Cl$ (Sigma-Aldrich, ≥99.0%, as-received) was used as the supporting electrolyte. Trimethylammonium chloride (Sigma-Aldrich) was used as the proton source for electrodeposition trials with the $[N^nBu_4]_2[WS_4]$ precursor.

All cyclic voltammetry and electrodeposition experiments were carried out in a three-electrode system using an Autolab potentiostat (µAUT70706). A Pt mesh was used as the counter electrode and the reference electrode was Ag/AgCl (0.1 M $[N^nBu_4]Cl$ in CH_2Cl_2). The Pt mesh counter electrode was cleaned by rinsing with de-ionised water and heating in a butane/propane mix flame (70% butane, 30% propane). A 0.4 cm diameter titanium nitride (TiN) substrate (200 nm TiN on Si) was employed as the working electrode. The EQCM (QCM 200, SRS) system used 5 MHz AT-cut quartz crystal (1.3 cm diameter) with Pt coatings. After the electrodeposition, the substrates were cleaned with fresh CH_2Cl_2 solvent followed by rinsing with isopropyl alcohol and dried prior to characterisation. The samples were annealed in a tube furnace under an N_2 atmosphere by applying 100 °C for 10 min followed by 500 °C for 2 h in the presence of a small amount of elemental sulfur.

Film characterisation

A scanning electron microscope (SEM, Philips XL30 ESEM) was used to image the deposits after electrodeposition. The elemental composition was obtained by energy dispersive X-ray spectroscopy (EDX) coupled to SEM, using a Thermo Scientific NORAN System 7 X-ray Microanalysis System. Wavelength dispersive X-ray spectroscopy (WDX) was employed for obtaining higher spectral resolution. The calibration of the EDX/WDX quantification was confirmed by comparison to a standard WS_2 single crystal sample (Ossila Technologies). Raman spectra were obtained using Renishaw Inc. spectrometer with 532 nm laser excitation. X-Ray diffraction (XRD) patterns were collected in grazing incidence mode ($\theta_1 = 1°$) using a Rigaku SmartLab diffractometer (Cu-K_α, $\lambda = 1.5418$ Å) with parallel X-ray beam and a Hypix detector used in 1D mode.

Spectroscopic and structural data for the precursors

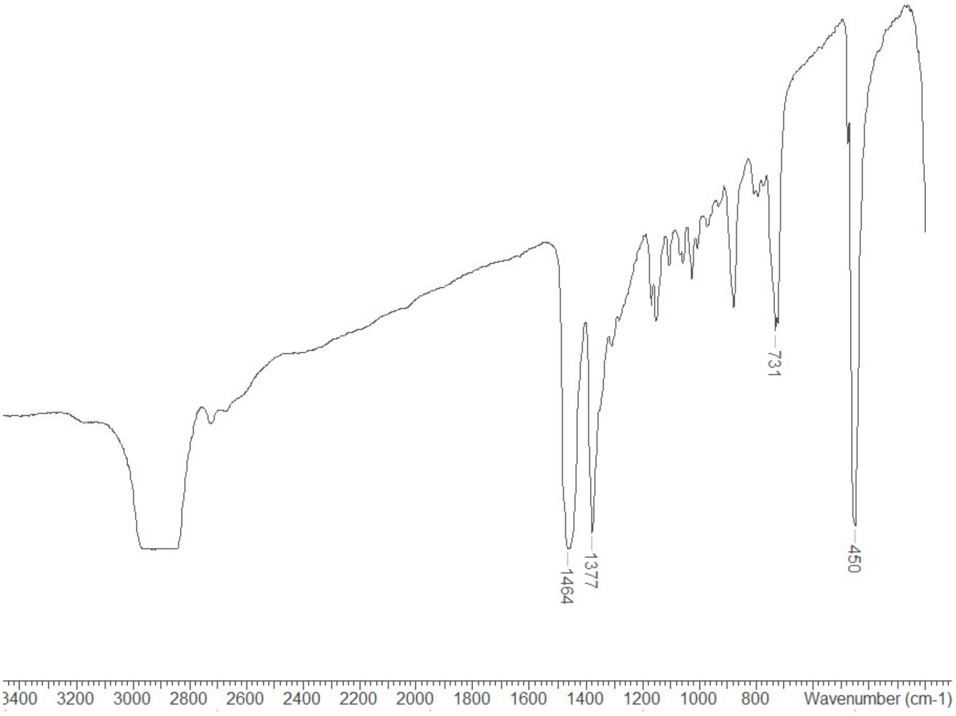

Fig. S1: IR spectrum of $[N^nBu_4]_2[WS_4]$ (Nujol mull)

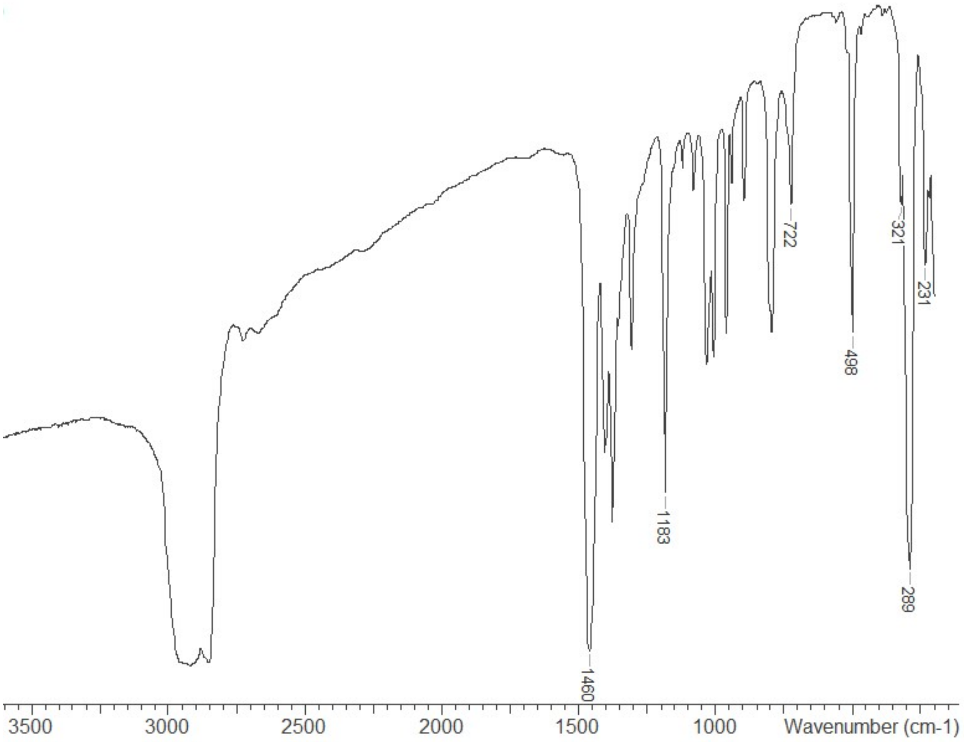

Fig. S2: IR spectrum of $[NEt_4]_2[WS_2Cl_4]$ (Nujol mull)

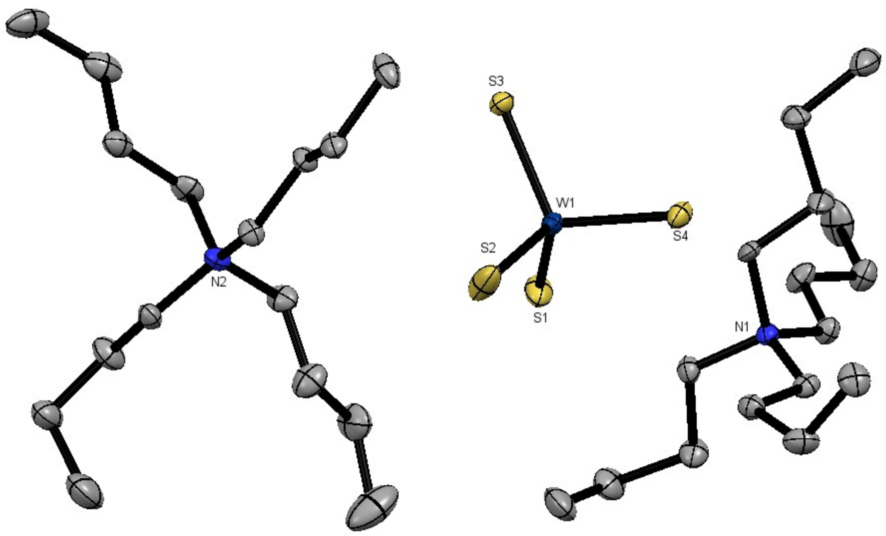

Fig. S3: View of the structure of $[N^nBu_4]_2[WS_4]$ with numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W1–S1 = 2.192(3), W1–S2 = 2.182(2), W1–S3 = 2.192(2), W1–S4 = 2.201(2), S3–W1–S4 = 110.09(9), S1–W1–S3 = 108.59(10), S1–W1–S4 = 110.09(9), S2–W1–S3 = 107.97(11), S2–W1–S4 = 110.51(9), S2–W1–S1 = 109.55(12).

Table S1: Crystallographic parameters[a]

Compound	$[N^nBu_4]_2[WS_4]$
Formula	$C_{32}H_{72}N_2S_4W$
M	797.00
Crystal system	Orthorhombic
Space group (no)	Fdd2 (43)
a/Å	35.5546(5)
b/Å	28.7261(4)
c/Å	15.5575(3)
α/°	90
β/°	90
γ/°	90
$U/Å^3$	15889.6(4)
Z	16
μ(Mo-Kα)/mm^{-1}	3.140
F(000)	6656
Total Reflns.	10806
R_{int}	0.050
Unique Reflns.	9094
Parameters/restraints	360, 1
GOF	1.011
R_1, wR_2 ($I>2\sigma I$)[b]	0.054, 0.112
R_1, wR_2 (all data)[b]	0.065, 0.115

[a] T = 100 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°; [b] $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR_2=[\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4]^{1/2}$

Electrochemistry of $[N^nBu_4]_2[WS_4]$

Our experiments showed that the simple ammonium salt, $[NH_4]_2[WS_4]$, is not sufficiently soluble in either CH_2Cl_2 or MeCN and therefore it is not suitable as an electrolyte precursor to deposit WS_2. Several experiments were performed to electrodeposit WS_2 using the much more soluble $[N^nBu_4]_2[WS_4]$ precursor in CH_2Cl_2. The black curve in Fig. S4 shows the cyclic voltammogram (CV) of 5 mM $[N^nBu_4]_2[WS_4]$ with 0.1 M $[N^nBu_4]Cl$ (supporting electrolyte) in CH_2Cl_2. In comparison to the background CV (red curve in Fig. S4), no significant reduction current related to the reduction of $[WS_4]^{2-}$ is observed and attempts at potentiostatic electrodeposition failed to produce WS_2 thin films.

While our previous studies on MoS_2 electrodeposition indicated that the addition of a proton source (Me_3NHCl) facilitated the electroreduction of $[MoS_4]^{2-}$ from the analogous $[N^nBu_4]_2[MoS_4]$ precursor,[4] the addition of Me_3NHCl to $[N^nBu_4]_2[WS_4]$ was not successful in depositing WS_2. Although the CV of 5 mM $[N^nBu_4]_2[WS_4]$ with 0.2 M Me_3NHCl (Fig. S5) shows large reductions currents, these are due to the decomposition of Me_3NHCl only. The role of the proton source in electrodepositing MoS_2 from $[N^nBu_4]_2[MoS_4]$ is the removal of excess sulfur from the $[MoS_4]^{2-}$ ions. However, it is noted that the addition of proton sources to the electrolyte makes the electrochemical mechanism complex due to the early breakdown of Me_3NHCl. Additionally, the as-deposited MoS_x thin films electrodeposited from $[N^nBu_4]_2[MoS_4]$ were slightly sulfur-rich due to the inclusion of residual S or S^{2-} in the films.

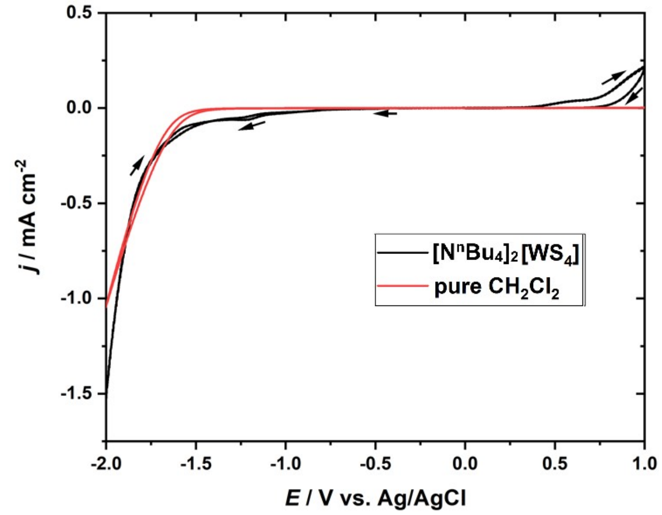

Fig. S4: Cyclic voltammogram of 5 mM $[N^nBu_4]_2[WS_4]$ in CH_2Cl_2 on TiN electrode. The red line shows the background CV for CH_2Cl_2. The supporting electrolyte is 0.1 M $[N^nBu_4]Cl$ and the scan rate is 50 mV s^{-1}. Arrows indicate the direction of potential scanning and the starting potential is 0 V.

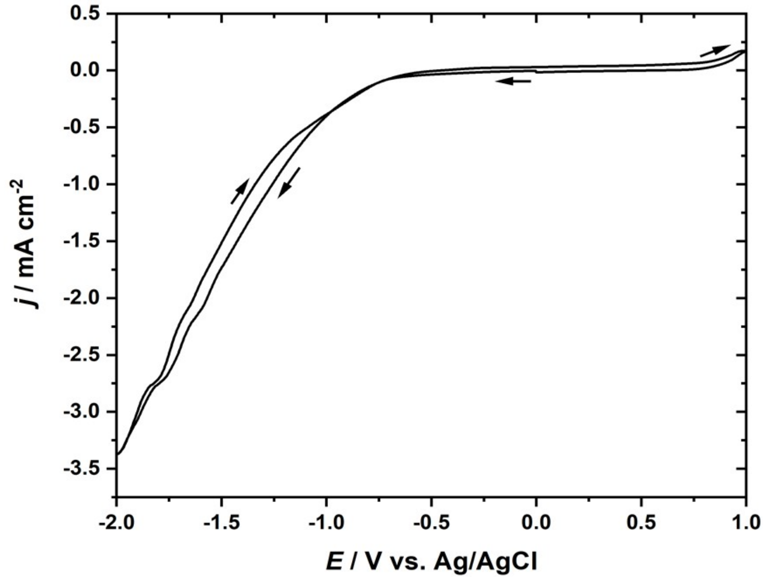

Fig. S5: Cyclic voltammogram of 5 mM $[N^nBu_4]_2[WS_2Cl_4]$ in CH_2Cl_2 with 0.2 M Me_3NHCl as proton source, recorded on TiN electrode. The supporting electrolyte is 0.1 M $[N^nBu_4]Cl$ and the scan rate is 50 mV s^{-1}. Arrows indicate the direction of potential scanning and the starting potential is 0 V.

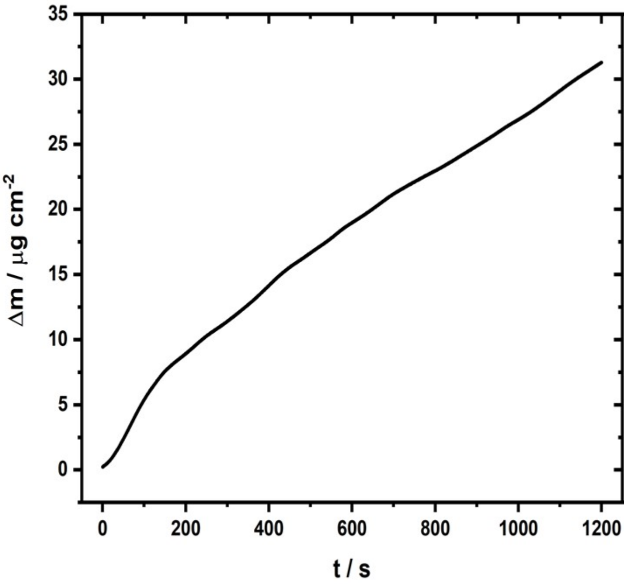

Fig. S6: Mass changes obtained from EQCM during the potentiostatic electrodeposition at -1.3 V for 20 minutes.

Calculation of Faradaic efficiency from EQCM

The faradaic efficiency of deposition is calculated using the Faraday equation; the mass of WS_2 deposited (m)

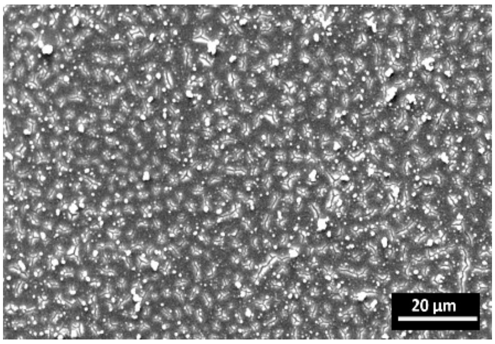

Fig. S7: Top-view SEM image of the as-deposited film obtained after potentiostatic deposition at -1.3 V for 60 minutes.

$$m = \frac{QM_w}{nF}$$

Where Q is the charge passed through the electrode in Coulomb, M_w is the molecular weight of WS_2 (247.98 g/mol), F is the Faraday constant (96485 C/ mol), and n is the number of electrons transferred. The mass estimated from the EQCM measurements is compared with the theoretical mass (assuming all the charge passed is used for WS_2 deposition, *i.e* 100% current efficiency) to obtain the faradaic efficiency of deposition.

$$Faradaic\ efficiency = \frac{mass\ from\ EQCM}{mass\ from\ charge} \times 100$$

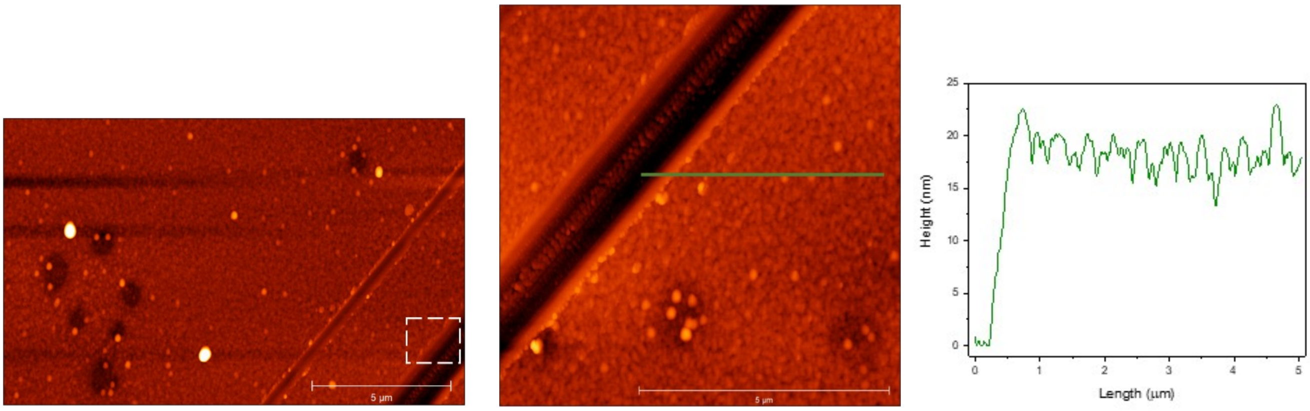

Figure S8: AFM images and height profile of a WS_2 deposit obtained at -1.7 V for 30 minutes.

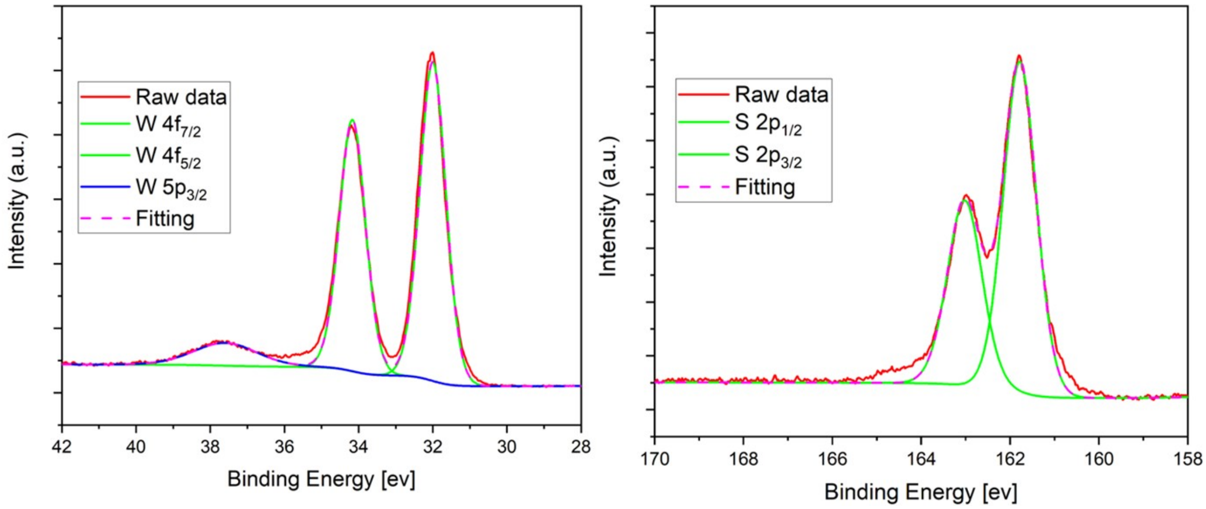

Fig. S9: XPS data for the annealed WS_2 film showing the peaks associated with tungsten (left) and sulfur (right).

References

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