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 \(\text{N}_2\) atmosphere. \([\text{N}^n\text{Bu}_4]\text{OH}\) (40% aqueous solution), \(\text{S(SiMe}_3\text{)}_2\), \([\text{Et}_4\text{N}]\text{Cl}\), \([\text{N}^n\text{Bu}_4]\text{Cl}\), \([\text{Ph}_4\text{P}]\text{Cl}\) were obtained from Sigma Aldrich and \([\text{NH}_4]_2[\text{WS}_4]\) from Alfa Aesar and were used as received. \(\text{WSCl}_4\) was made as described previously.\(^1\) Solvents were dried by distillation from Ca\(\text{H}_2\) (\(\text{CH}_2\text{Cl}_2\)) or Na/benzophenone ketyl (n-hexane).

Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer in the range 4000–200 \(\text{cm}^{-1}\), with samples prepared as Nujol mulls between CsI plates. \(^1\)H 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.

**[\text{N}^n\text{Bu}_4]\_2[\text{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 \(\text{iPrOH}\) (1 x 2 mL) and dried \textit{in vacuo}. Yield: 0.513 g, 45 %. Required for \(\text{C}_{32}\text{H}_{72}\text{N}_2\text{WS}_4\) (797.02): C: 48.22, N: 3.51, H: 9.11 %. Found: C: 48.17, N: 3.55, H: 9.18 %. IR spectrum (Nujol, \(\nu\) / \(\text{cm}^{-1}\)): 448s W=S.

\(^1\)H NMR (CDCl\(_3\)): \(\delta/\text{ppm} = 1.0\) (t, \([3\text{H}]\), \(J_{\text{HH}} = 7.34\) Hz, \(\text{CH}_3\)), 1.44 (m, \([2\text{H}]\), \(J_{\text{HH}} = 7.38\) Hz, \(\text{CH}_2\)), 3.2 - 3.4 (m, \([2\text{H}]\), \(\text{CH}_2\)).

**[\text{Et}_4\text{N}]_2[\text{WS}_2\text{Cl}_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 \(\text{WSCl}_4\) (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 \textit{in vacuo}. Yield: 0.250 g, 68 %. Required for \(\text{C}_{16}\text{H}_{40}\text{Cl}_4\text{N}_2\text{S}_2\text{W}\) (650.28): C: 29.55, H: 6.20, N: 4.31 %. Found: C: 29.19, H: 6.06, N: 4.33 %. IR spectrum (Nujol, \(\nu\) / \(\text{cm}^{-1}\)): 498s W=S,
289s W-Cl. $^1$H NMR (CD$_2$Cl$_2$): $\delta$/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.

$[\text{PPh}_4]_2[\text{WS}_2\text{Cl}_4]\cdot\text{CHCl}_3$: A solution of tetrphenylphosphonium chloride (0.420 g, 1.12 mmol) in dichloromethane (5 mL) was added to a solution of WSCl$_4$ (0.200 g, 0.56 mmol) in dichloromethane (5 mL). 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$_4$P$_2$S$_2$W (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$_2$Cl$_2$): $\delta$ = 7.85 (br s, [2H]), 7.70 (br s, [2H]), 7.56 (br s, [H]). $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$): $\delta$/ppm = +23.3 (s).

Attempted Preparation of [N$^\text{Bu}_4]_2[\text{WS}_2\text{Cl}_4]$: 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 ($\lambda = 0.71073$) 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$^1$ 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$_2$O levels. Electrolyte solutions were prepared in anhydrous CH$_2$Cl$_2$ (Sigma-Aldrich, 95%), dried and degassed by refluxing with CaH$_2$ followed by distillation. The water content in dried CH$_2$Cl$_2$ was ca. 18
ppm determined by Karl Fischer titration. 0.1 M [N\textsubscript{n}Bu\textsubscript{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\textsubscript{n}Bu\textsubscript{4}]\textsubscript{2}[WS\textsubscript{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\textsubscript{n}Bu\textsubscript{4}]Cl in CH\textsubscript{2}Cl\textsubscript{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\textsubscript{2}Cl\textsubscript{2} solvent followed by rinsing with isopropyl alcohol and dried prior to characterisation. The samples were annealed in a tube furnace under an N\textsubscript{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\textsubscript{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 (θ\textsubscript{1} = 1°) using a Rigaku SmartLab diffractometer (Cu-K\textsubscript{α}, λ = 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 $[\text{N}^\text{Bu}_4\text{S}]_2[\text{WS}_4]$ (Nujol mull)

Fig. S2: IR spectrum of $[\text{NEt}_4]_2[\text{WS}_2\text{Cl}_4]$ (Nujol mull)
Fig. S3: View of the structure of \([\text{N}^4\text{Bu}_4]_2[\text{WS}_4]\) 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

| Compound | [N\textsubscript{n}Bu\textsubscript{4}]\textsubscript{2}[WS\textsubscript{4}] |
|----------|----------------------------------|
| Formula  | C\textsubscript{32}H\textsubscript{72}N\textsubscript{2}S\textsubscript{4}W |
| 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\textsuperscript{3} | 15889.6(4)                |
| Z        | 16                              |
| μ(Mo-K\textalpha)/mm\textsuperscript{-1} | 3.140                          |
| F(000)   | 6656                            |
| Total Reflns. | 10806                       |
| R\textsubscript{int} | 0.050                        |
| Unique Reflns. | 9094                         |
| Parameters/restraints | 360, 1                         |
| GOF      | 1.011                           |
| R\textsubscript{s}, wR\textsubscript{s} (I>2σI)\textsuperscript{b} | 0.054, 0.112                  |
| R\textsubscript{s}, wR\textsubscript{s} (all data)\textsuperscript{b} | 0.065, 0.115                  |

\textsuperscript{a} T = 100 K; wavelength (Mo-K\textalpha) = 0.71073 Å; θ(max) = 27.5\textdegree; \textsuperscript{b} R\textsubscript{s} = Σ||Fo|-|Fc||/Σ|Fo|; wR\textsubscript{s}=[Σw(Fo\textsuperscript{2}-Fc\textsuperscript{2})\textsuperscript{2}/ΣwFo\textsuperscript{4}\textsuperscript{1/2}}

**Electrochemistry of [N\textsubscript{n}Bu\textsubscript{4}]\textsubscript{2}[WS\textsubscript{4}]**

Our experiments showed that the simple ammonium salt, [NH\textsubscript{4}]\textsubscript{2}[WS\textsubscript{4}], is not sufficiently soluble in either CH\textsubscript{2}Cl\textsubscript{2} or MeCN and therefore it is not suitable as an electrolyte precursor to deposit WS\textsubscript{2}. Several experiments were performed to electrodeposit WS\textsubscript{2} using the much more soluble [N\textsubscript{n}Bu\textsubscript{4}]\textsubscript{2}[WS\textsubscript{4}] precursor in CH\textsubscript{2}Cl\textsubscript{2}. The black curve in Fig. S4 shows the cyclic voltammogram (CV) of 5 mM [N\textsubscript{n}Bu\textsubscript{4}]\textsubscript{2}[WS\textsubscript{4}] with 0.1 M [N\textsubscript{n}Bu\textsubscript{4}]Cl (supporting electrolyte) in CH\textsubscript{2}Cl\textsubscript{2}. In comparison to the background CV (red curve in Fig. S4), no significant reduction current related to the reduction of [WS\textsubscript{4}]\textsuperscript{2-} is observed and attempts at potentiostatic electrodeposition failed to produce WS\textsubscript{2} thin films.
While our previous studies on MoS\textsubscript{2} electrodeposition indicated that the addition of a proton source (Me\textsubscript{3}NHCl) facilitated the electroreduction of [MoS\textsubscript{4}]\textsuperscript{2-} from the analogous [N\text{\textsuperscript{4}Bu\textsubscript{4}}\textsubscript{2}][MoS\textsubscript{4}] precursor,\textsuperscript{4} the addition of Me\textsubscript{3}NHCl to [N\text{\textsuperscript{4}Bu\textsubscript{4}}\textsubscript{2}][WS\textsubscript{4}] was not successful in depositing WS\textsubscript{2}. Although the CV of 5 mM [N\text{\textsuperscript{4}Bu\textsubscript{4}}\textsubscript{2}][WS\textsubscript{4}] with 0.2 M Me\textsubscript{3}NHCl (Fig. S5) shows large reductions currents, these are due to the decomposition of Me\textsubscript{3}NHCl only. The role of the proton source in electrodepositing MoS\textsubscript{2} from [N\text{\textsuperscript{4}Bu\textsubscript{4}}\textsubscript{2}][MoS\textsubscript{4}] is the removal of excess sulfur from the [MoS\textsubscript{4}]\textsuperscript{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\textsubscript{3}NHCl. Additionally, the as-deposited MoS\textsubscript{x} thin films electrodeposited from [N\text{\textsuperscript{4}Bu\textsubscript{4}}\textsubscript{2}][MoS\textsubscript{4}] were slightly sulfur-rich due to the inclusion of residual S or S\textsuperscript{2-} in the films.

Fig. S4: Cyclic voltammogram of 5 mM [N\text{\textsuperscript{4}Bu\textsubscript{4}}\textsubscript{2}][WS\textsubscript{4}] in CH\textsubscript{2}Cl\textsubscript{2} on TiN electrode. The red line shows the background CV for CH\textsubscript{2}Cl\textsubscript{2}. The supporting electrolyte is 0.1 M [N\text{\textsuperscript{4}Bu\textsubscript{4}}][Cl] and the scan rate is 50 mV s\textsuperscript{-1}. Arrows indicate the direction of potential scanning and the starting potential is 0 V.
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. S6: Mass changes obtained from EQCM during the potentiostatic electrodeposition at -1.3 V for 20 minutes.

Fig. S7: Top-view SEM image of the as-deposited film obtained after potentiostatic deposition at -1.3 V for 60 minutes.
\[ m = \frac{Q M_w}{nF} \]

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.

\[
\text{Faradaic efficiency} = \frac{\text{mass from EQCM}}{\text{mass from charge}} \times 100
\]

Figure S8: AFM images and height profile of a WS\(_2\) deposit obtained at -1.7 V for 30 minutes.

Figure S9: XPS data for the annealed WS\(_2\) film showing the peaks associated with tungsten (left) and sulfur (right).

References
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