Supporting Information for

Aerosol-assisted chemical vapor deposition of WS_2 from the single source precursor $WS(S_2)(S_2CNEt_2)_2$

*Nathaniel E. Richey, Chandler Haines, Jessica L. Tami, Lisa McElwee-White**

Department of Chemistry, University of Florida, Gainesville, Florida, 32611, United States

*Address correspondence to: lmwhite@chem.ufl.edu

Table of contents

Experimental details

General Procedure. Reagents were purchased from Sigma Aldrich or Fisher Scientific; $CDCl_3$ was purchased from Cambridge Isotopes. Nitrogen gas (99.999%) was purchased from AirGas. Toluene was purified using an MBraun MB-SP solvent purification system and stored over activated 3 Å molecular sieves for at least 48 h prior to experiments. All other reagents were used as received. NMR spectra were recorded on a Varian Mercury 300BB (300 MHz) spectrometer using residual protons from deuterated solvents for reference. IR spectra were obtained on a Bruker Vertex 80V equipped with an ATR diamond crystal stage. Thermogravimetric analysis (TGA, TA Discovery5500) was performed under N_2 gas with a heating rate of 10 °C/minute. TGA coupled to a mass spectrometer (TGA-MS, Discovery Mass

Spectrometer) was used to determine the masses of byproducts between 1-300 atomic mass units (AMU).

Depositions were carried out using a Blue Wave Semiconductors CVD reactor with a Liquifog ultrasonic liquids atomizer from Johnson Matthey Piezoproducts. The elemental compositions of tungsten disulfide deposits were determined by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI XPS). Adventitious carbon was used as an internal standard for XPS and referenced to 284.8 eV. The crystallinities and morphologies were measured by X-ray diffraction (XRD, Panalytical X'pert Pro) and field emission scanning electron microscope (FESEM, FEI Nova NanoSEM 430). Raman spectroscopy (LabRAM Aramis) was performed using a 532 nm laser with 40× objective lens.

$WS(S_2)(S_2CNEt_2)_2$. This compound was synthesized using a modification of a previously reported procedure.[1] To a flame dried flask was added $(NH_4)_2WS_4$ (500 mg, 0.144 mmol) and tetraethylthiuram disulfide (1.08 g, 3.64 mmol). The flask was then purged three times with N_2 and anhydrous acetonitrile (approximately 30 mL) was added by cannula while stirring. A green color appeared immediately and the solution was stirred for an additional two hours. The solution was chilled in an ice bath for 10 min and then filtered. The resulting green solid was washed with twice with 5 mL acetonitrile, 10 mL water, 5 mL 95% ethanol, and 10 mL pentane. The green solid was then dried under vacuum to afford the product in 86% yield. The product was identified by comparison to literature data.[1] ^{1}H NMR ($CDCl_3$) δ 1.12 (t, 3H, J = 7.2 Hz), δ 1.41 (m, 9H), δ 3.42 (m, 2H), δ 3.84 (m, 6H). IR 543.9 cm^{-1} (m), 496.6 cm^{-1} (s).

Deposition of WS_2. Silicon with native silicon dioxide (Si/SiO_2, n-type, <100>) was cut into squares of approximately 1 cm^2 and cleaned in boiling isopropanol, acetone, and methanol for three min each. The substrates were then placed onto the heating stand, placed under vacuum

(200-300 mTorr), and heated to the desired temperature (300-500 °C). In a glovebox, 250 mg of $WS(S_2)(S_2CNEt_2)_2$ (0.43 mmol) was dissolved in 20 mL toluene and added to a glass trap. The trap was then removed from the glovebox and connected to the N_2 inlet of the reactor, N_2 was flowed through the trap for 10 min before connecting to the transfer line. The pressure of the reaction chamber was increased to 350 Torr and the transfer line was heated to 50 °C. The trap was then opened to the reaction chamber and nebulization of the solution was started. During the course of the deposition (typically 60-75 min), N_2 flow was maintained at 200 sccm and the pressure was maintained at 350 Torr. Once all of the solution had been nebulized, the pressure of the reaction chamber was increased to atmospheric pressure and the substrates were cooled to room temperature.

Control Experiment: Deposition Under Ambient Conditions. As a control experiment, a deposition was performed at 400 °C without drying the toluene and without maintaining rigorous air-free conditions. Under these conditions, deposition still resulted in WS_2 by Raman spectroscopy (Figure S5). However, note that exposure to the atmosphere has been shown in some cases to help with the formation of WS_2 through oxidation of sulfur byproducts.[2] All other depositions were carried out under an inert atmosphere.

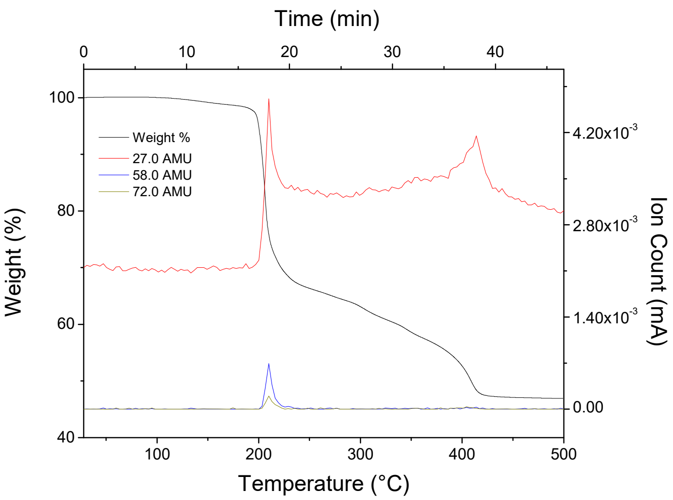

Figure S1. TGA-MS curves of $WS(S_2)(S_2CNEt_2)_2$ with detection of potential fragments from $EtNCS^+$. The fragments are HCN^+ (*m/z* 27.0), NCS^+ (*m/z* 58.0), and CH_2NCS^+ (*m/z* 72.0).

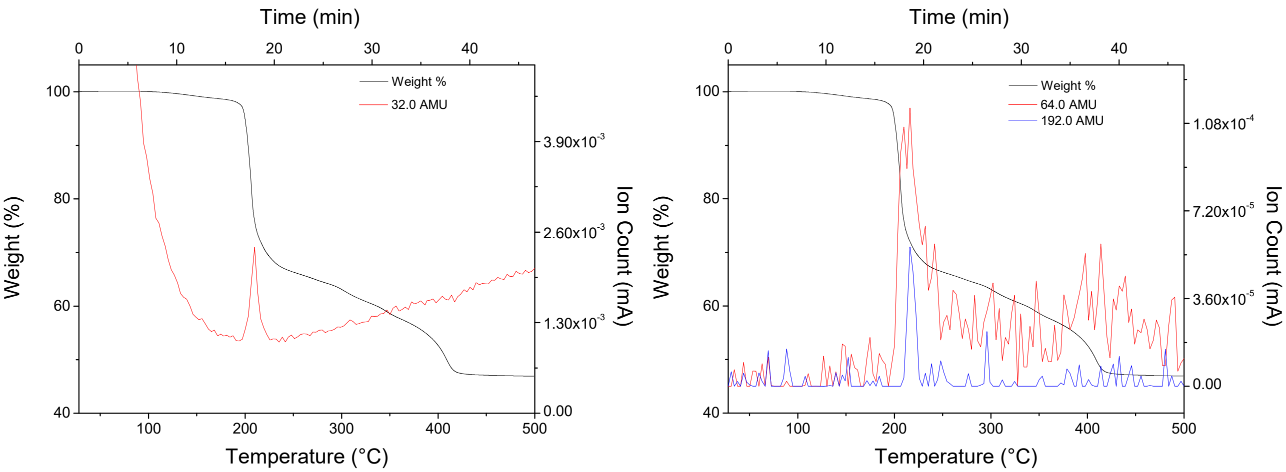

Figure S2. TGA-MS curves of $WS(S_2)(S_2CNEt_2)_2$ with detection of S^+ (*m/z* 32.0), S_2^+ (*m/z* 64.0), and S_6^+ (*m/z* 192.0).

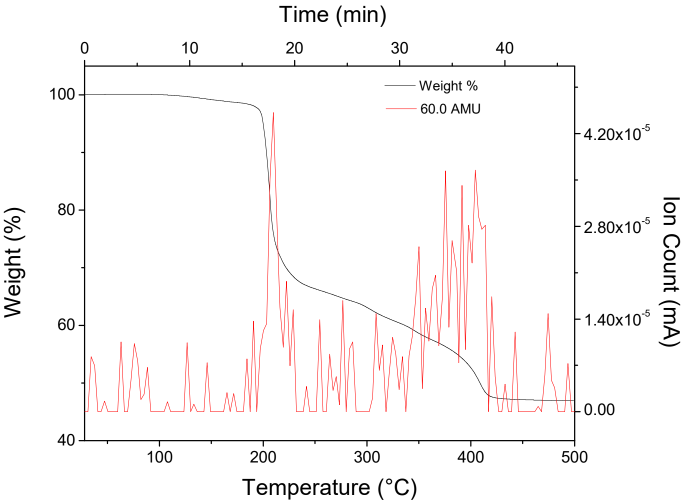

Figure S3. TGA-MS of $WS(S_2)(S_2CNEt_2)_2$ with detection of $C_2H_4S^+$ (*m/z* 60.0).

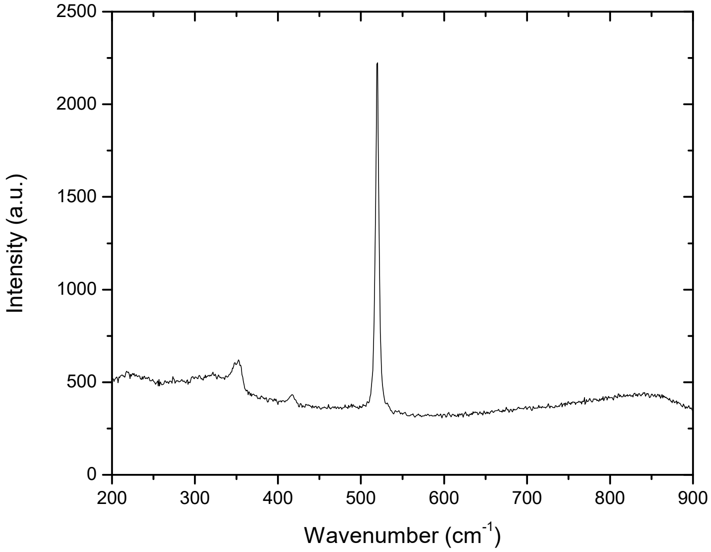

Figure S4. Raman spectrum taken at a spot of visibly bare substrate from the deposits grown at 350 °C

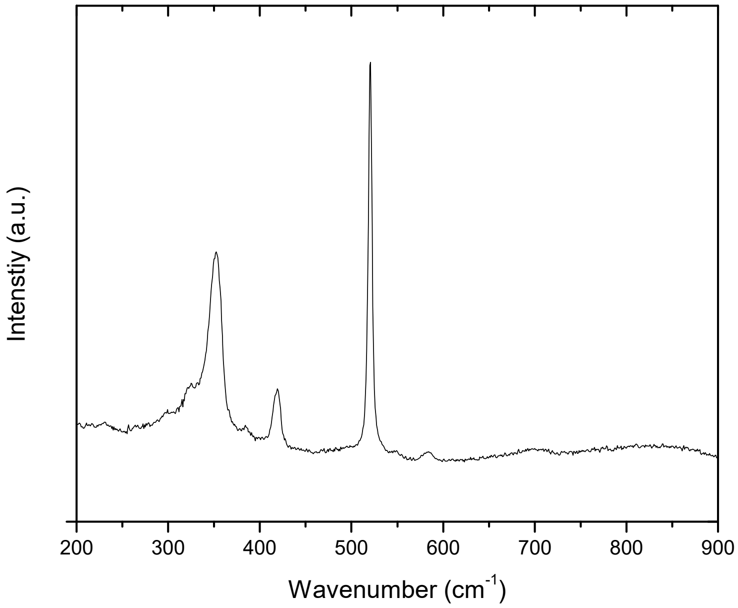

Figure S5. Raman spectrum of deposits grown from $WS(S_2)(S_2CNEt_2)_2$ at 400 °C without exclusion of air or water.

References

(1) Pan, W. H.; Halbert, T. R.; Hutchings, L. L.; Stiefel, E. I. *J. Chem. Soc., Chem. Commun.* **1985**, 927.
(2) Hunyadi, D.; Vieira Machado Ramos, A. L.; Szilagyi, I. M. *J. Therm. Anal. Calorim.* **2015**, *120*, 209.