Supporting Information

Solution-Phase Synthesis of Highly Conductive Tungsten Diselenide Nanosheets

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Experimental Details

General considerations. Tungsten(IV) chloride (WCl_4 , Strem, 97%), selenium powder (Alfa Aesar, 99.5%), trichloroethylene (TCE, Alfa Aesar, 99.5+%), tetra-*n*-octylammonium bromide (TOAB, Alfa Aesar, 98+%), 1,2-dichlorobenzene (DCB, Sigma-Aldrich, 99%), and tungsten(IV) selenide (WSe_2, Alfa Aesar, 99.8%) were all purchased and used without further purification. Both dodecylamine (Alfa Aesar, 98+%), dried from CaO, and tetramethylurea (TMU, Alfa Aesar, 99%) were distilled prior to use. Syntheses were performed using standard Schlenk techniques under nitrogen in the absence of water and oxygen.

Synthesis of WSe_2 nanosheets. In a typical synthesis, WCl_4 (150 mg, 0.46 mmol) was added to a three-neck round-bottom flask fitted with a reflux condenser, stir bar, and rubber septum inside a glove box. Deoxygenated, distilled dodecylamine (25 mL) was added to WCl_4 and then dissolved under nitrogen by alternating between heating and an ultrasonic bath (5-10 min); care was taken as to not overheat the reaction mixture as WCl_4 is known to be easily reduced in the presence of organics.[1] The dark bluish-black solution was then heated to 95 °C and degassed for 3 minutes, cycling between vacuum and nitrogen three times to eliminate adventitious water and dissolved oxygen. The reaction was further heated to 150 °C (10 °C min^{-1}), and $^tBu_2Se_2$ (185 μL, 0.92 mmol) was quickly injected to the reaction flask under nitrogen. The synthesis of $^tBu_2Se_2$ was carried out according to an improved version of a previously published method.[2,3] The temperature was increased to 225 °C (10 °C min^{-1}) and held at this temperature for 6 h while stirring. The reaction was stopped by removing the heating mantle and allowing the reaction to cool to room temperature, at which point 10 mL of a 20 mg mL^{-1} TOAB-DCM solution was used to disperse the reaction mixture. After vigorous mixing and sonication, the reaction mixture was divided into two centrifuge tubes, and ethanol (25 mL) was added. A black precipitate was obtained after centrifugation (6000 rpm for 1 min). Dispersion/precipitation was repeated three more times using 1) 5 mL of 20 mg mL^{-1} TOAB in DCM and 5 mL ethanol; 2) 5 mL of 40 mg mL^{-1} TOAB in TCE, left overnight, and 5 mL ethanol was added the next day; 3) 5 mL toluene and 5 mL ethanol to remove excess TOAB. The product was washed a total of 4 times and finally re-dispersed in *ca*. 5 mL toluene. Visually smooth films were drop-cast using *ca*. 40 mg mL^{-1} suspensions of WSe_2 in toluene.

Structural Characterization. *Powder X-ray diffraction (XRD).* Conventional XRD patterns were collected using a Cu Kα radiation source (λ = 1.5406 Å) on a Rigaku Ultima IV diffractometer. Diffraction patterns were recorded at room temperature in the range of 10-80°. *Scanning electron microscope energy dispersive X-ray spectroscopy (SEM-EDX).* SEM-EDX spectra were collected on a JEOL JSM-6610 scanning electron microscope operating at 5 kV and equipped with an EDAX Apollo silicon drift detector (SDD). Multiple regions of a sample deposited on a Si substrate were analyzed. *Elemental analysis (ICP-AES).* Elemental analysis of W and Se were performed by inductively coupled plasma atomic emission spectroscopy at Galbraith Laboratories (Knoxville, TN). *Raman spectroscopy.* Raman spectra were recorded under ambient conditions using a Horiba Jobin Yvon, Xplora Raman Microscope System. An excitation source of 532 nm from a diode laser was employed at a power level of 13.7 mW. *Transmission electron microscopy (TEM) and selected area electron diffraction (SAED).* TEM and SAED were performed on a JEOL JEM-2100 microscope at an operating voltage of 200 kV (or 100 kV for low resolution TEM images), equipped with a Gatan Orius CCD camera. Samples were prepared from dilute dispersions in toluene or TMU and deposited onto 300 mesh Formvar-coated copper grids (Ted Pella, Inc.).

Device Characterization. *Current-voltage measurements.* The current dependence on applied test voltage measurements were performed in air at room temperature using a Keithley 2420 SourceMeter (sensitivity = 100 pA). Data was collected at an interval of 40 mV. The room temperature two-point *I-V* characteristics of the unannealed WSe_2 films were taken using two types of devices with different channel dimensions (0.85 mm × 5.87 mm × 75 nm and 0.63 cm × 2.51 cm × 150 nm) to verify the conductivity values obtained. The annealed WSe_2 films required a modified structure in which the material was annealed (475 °C) first and then the Al electrodes were vapor deposited on top of the WSe_2 to prevent contact failures. Assuming a uniform current flow along the film, we calculated the resistance of the film to be the inverse of the slope of the *I-V* curve. The channel conductivity (σ) for the unannealed films was estimated by assuming that the effective height of the channel was given by the Al electrodes ($\sigma = L/R \times A$, where L is the channel length, R is the measured resistance, and A the surface area of the Al electrodes facing each other). *Profilometry.* The electrode thickness for the unannealed devices was determined using a Sloan Dektak IIA profilometer. The channel conductivity (σ) for the annealed films was estimated in a similar manner by calculating the effective height of the channel by determining the concentration (20 mg mL^{-1}) and depositing a known volume of the WSe_2 sample in a 0.63 cm × 2.51 cm channel. A density of 9.32 g cm^{-3} for WSe_2 was used to derive channel thickness.

Additional Figures

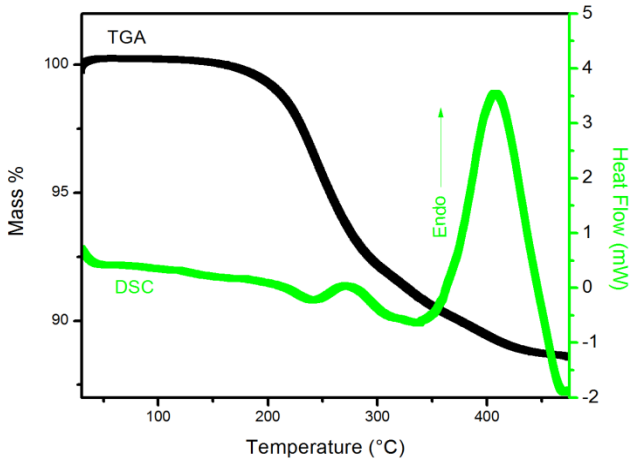

Figure S1. TGA analysis of WSe_2 nanosheets shows mass loss above 200 °C and leveling off below 500 °C (black curve). DSC shows two endothermic peaks that are likely due to loss of organic material (green curve).

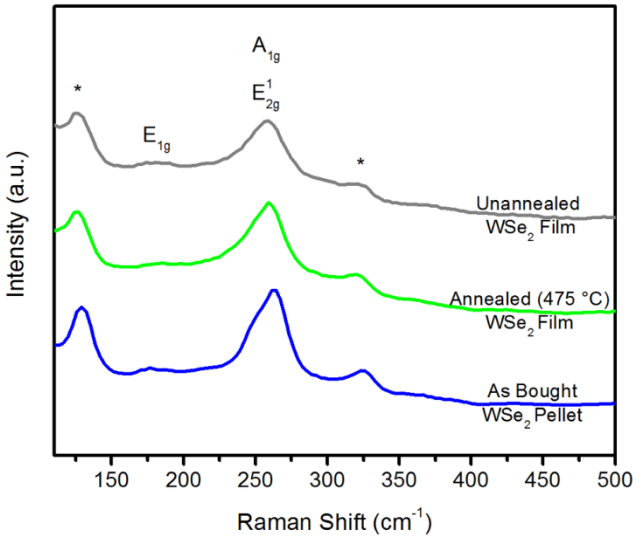

Figure S2. Raman spectra of a WSe_2 powder from Alfa Aesar (blue), annealed (green) and unannealed (gray) WSe_2 nanosheet films on glass; peaks highlighted by asterisks match both the spectrum of the "as bought" material and that of reported single crystal WSe_2.[4]

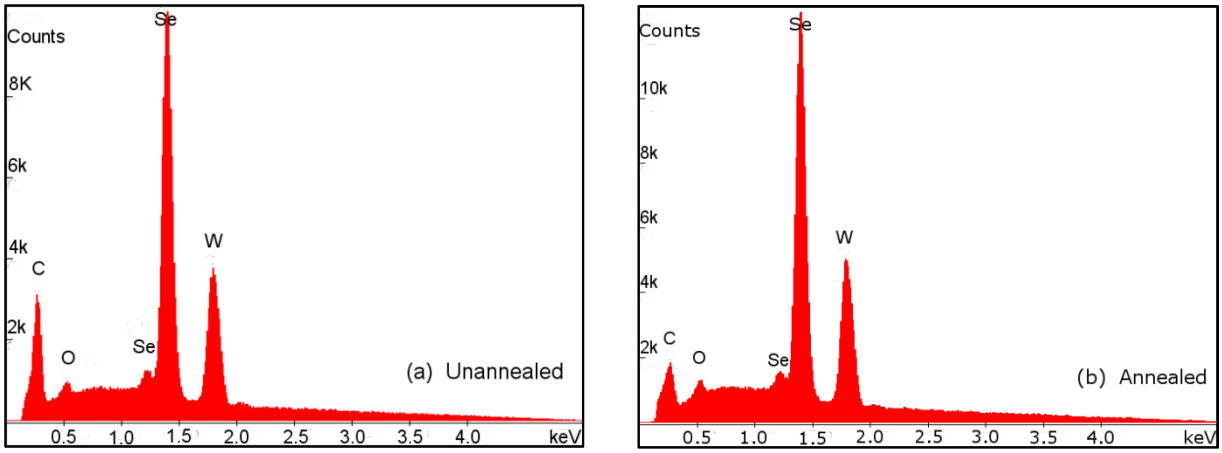

Figure S3. SEM-EDX elemental analysis of a WSe_2 nanosheet sample on a Si substrate. (a) unannealed and (b) annealed to 475 °C. The at% for the unannealed sample was 10.9% Se and 5.4% W, while the at% for the annealed sample was 18.7% Se and 10.4% W.

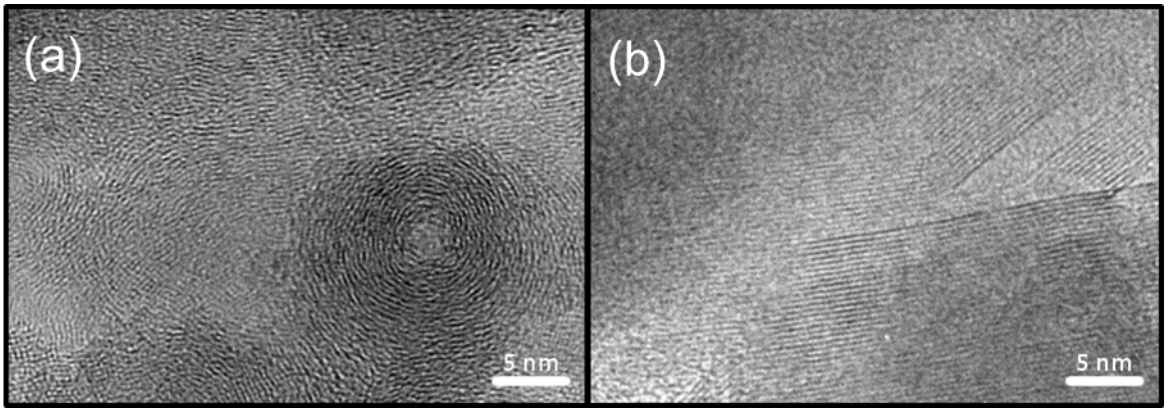

Figure S4. HR-TEM of unannealed TEM samples dried from toluene showing some agglomerates that formed (a) nano-onion structures, and (b) long, aligned plates.

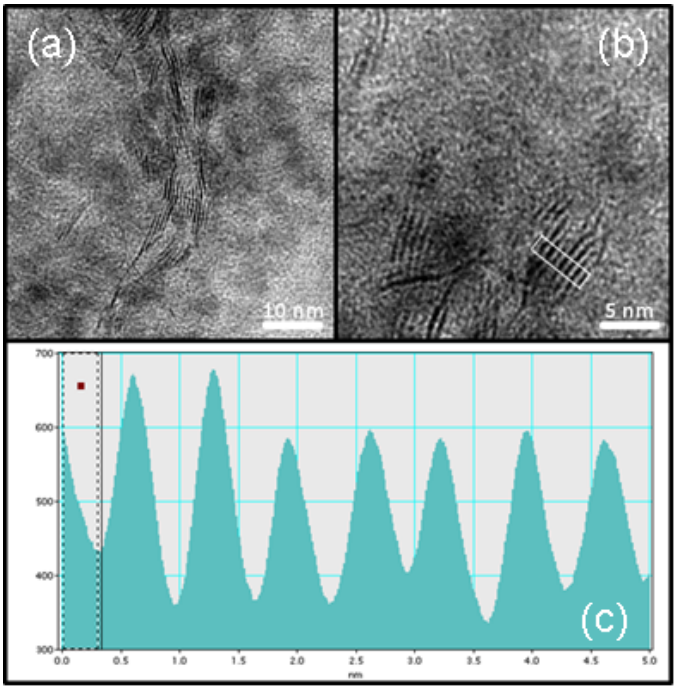

Figure S5. (a) Typical TEM image of WSe_2 nanosheets dried from TMU. (b) TEM image showing the lattice fringes measured and averaged inside the white box. (c) The average spacing of the fringes depicted within the box in (b) is d = 6.6 Å, corresponding to the (002) lattice plane.

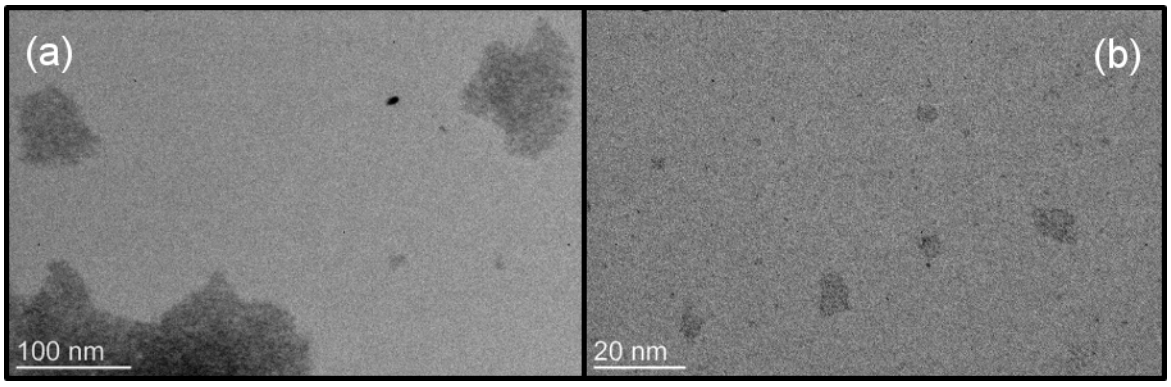

Figure S6. Low resolution TEM of isolated, unannealed WSe_2 nanosheets. (a) Unannealed WSe_2 nanosheets dispersed and dried from toluene with excess TOAB. (b) Unannealed WSe_2 nanosheets dispersed and dried from toluene.

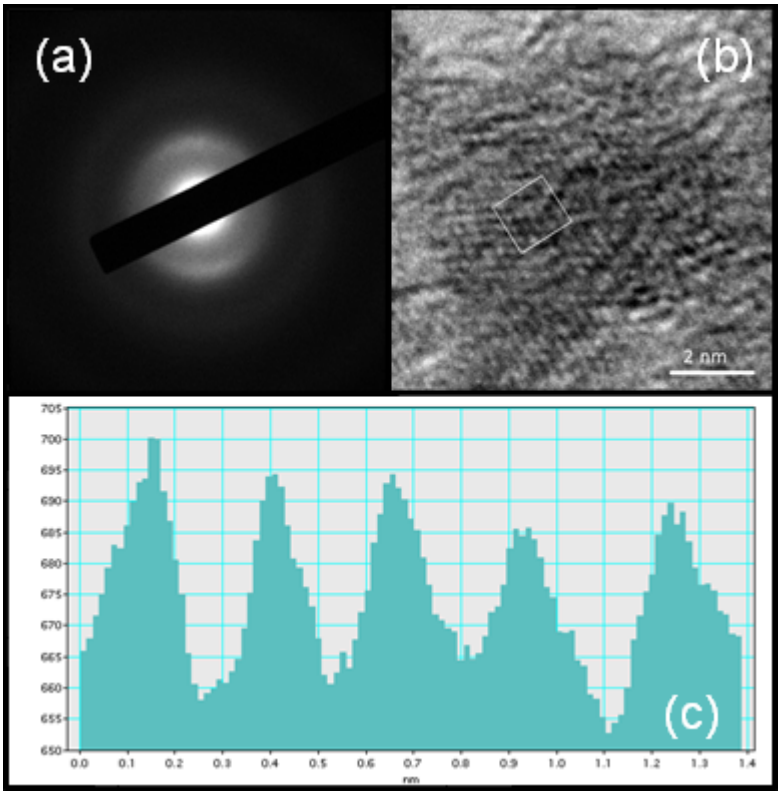

Figure S7. (a) SAED of unannealed WSe_2 nanosheets. (b) HR-TEM of unannealed WSe_2 nanosheets dispersed and dried from TMU. (c) Lattice fringe analysis with an average spacing of $d = 2.8$ Å, corresponding to the (101) lattice planes.

Supporting References

1. Blight, D. G.; Kepert, D. L., Pyridine Complexes of Tungsten(3) and Tungsten(4). *Journal of the Chemical Society a -Inorganic Physical Theoretical* **1968**, (3), 534.
2. Block, E.; Birringer, M.; Jiang, W. Q.; Nakahodo, T.; Thompson, H. J.; Toscano, P. J.; Uzar, H.; Zhang, X.; Zhu, Z. J., Allium chemistry: Synthesis, natural occurrence, biological activity, and chemistry of Se-alk(en)ylselenocysteines and their gamma-glutamyl derivatives and oxidation products. *Journal of Agricultural and Food Chemistry* **2001,** 49, (1), 458-470.
3. Webber, D. H.; Brutchey, R. L., Photochemical Synthesis of Bismuth Selenide Nanocrystals in an Aqueous Micellar Solution. *Inorganic Chemistry* **2011,** 50, (3), 723-725.
4. Galun, E.; Cohen, H.; Margulis, L.; Vilan, A.; Tsirlina, T.; Hodes, G.; Tenne, R.; Hershfinkel, M.; Jaegermann, W.; Ellmer, K., Crystallization of Layered Metal-Dichalcogenide Films on Amorphous Substrates. *Applied Physics Letters* **1995,** 67, (23), 3474-3476.