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Supporting Information

Sequential Bottom-Up and Top-Down Processing for the Synthesis of Transition Metal Dichalcogenide Nanosheets: The Case of Rhenium Disulfide (ReS_2)

Naktal-Al Dulaimi,[a] Edward A. Lewis,[b] David J. Lewis,[a,b] Simon K. Howell,[c] Sarah J. Haigh[b] and Paul O'Brien.[a,b,*]

[a]*School of Chemistry, University of Manchester, Manchester, M13 9PL, U.K.*

[b]*School of Materials, University of Manchester, Manchester, M13 9PL, U.K.*

[c]*School of Physics, University of Manchester, Manchester, M13 9PL, U.K.*

General Considerations

Reagents were purchased from Sigma-Aldrich and solvents from Sigma-Aldrich or Fisher. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques.

Instrumentation

Elemental analysis was performed by the University of Manchester micro-analytical laboratory. Seiko SSC/S200 model from 10 to 600 was used for TGA measurements with a heating rate of 10 ˚C/min under nitrogen. Bruker D8 AXE diffractometer was used to record the p-XRD patterns, which used Cu-K_α source (1.5406 Å) in range from 2θ = 10 - 80° with step size of 0.02° and a dwell time of 3 s. SEM was performed using a Zeiss Sigma VP SEM at an accelerating voltage of 10 kV (for thin films) or 6 kV (for nanosheets). HAADF STEM imaging and EDX spectrum imaging were performed on holey carbon grids using a probe side aberration corrected FEI Titan G2 80-200 ChemiSTEM microscope operated at 200 kV with a probe current of ~180 pA, a convergence semi-angle of 18.5 mrad, and a HAADF inner angle of 54 mrad. EDX data was acquired with all of the microscope four silicon drift detectors (SDDs) turned on and the sample untilted. STEM images were acquired using FEI TIA software, EDX data was acquired and processed using Bruker Esprit Software. AFM was performed using a Bruker Multimode 8 instrument equipped with a silicon nitride cantilever tip. Raman spectroscopy was performed using a Renishaw 1000 microscope system equipped with a 50 × objective, with solid-state diode laser excitation (514.5 nm, 20%

power). The incident light was linearly polarized in the sample plane with scattered light left unanalyzed for collection by the air cooled CCD.

Synthesis of *bis*(perthiobenzoato)(dithiobenzoato)Rhenium(III) ($[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$)

The compound $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$ was synthesised as previously described (McConnachie et al. *Inorg. Chem.* **1997**, *36*, 6144-6145). Anal. Calc for $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$ (%) C, 35.56 ; H, 2.13; S, 36.06; Found (%) C, 35.56; H, 2.52; S, 35.79. ^{1}H NMR (400 MHz, dichloromethane -d_2) δ / ppm 1.18 (s, 1 H) 1.26 (tt, J=7.31, 1.77 Hz, 9 H) 3.28 (q, J=7.31 Hz, 6 H) 7.24 - 7.41 (m, 9 H) 7.41 - 7.53(m, 7 H) 7.56 - 7.69 (m, 3 H) 7.88 - 8.07 (m, 7 H). ^{13}C NMR 13C NMR (101 MHz, dichloromethane-d_2) δ ppm 124.59 (s, 1 C) 127.60 (s, 1 C) 128.34 (s, 2 C) 131.78 (s, 2 C) 133.26 (s, 1 C) 134.79 - 135.02 (m, 1C).

AACVD of ReS_2 thin films.

The setup has been described previously (Lewis et al. *Chem. Mater.* **2015**, *27*, 1367). Rhenium sulfide (ReS_2) thin films were deposited by using Aerosol-Assisted Chemical Vapor Deposition (AA-CVD). A 0.1 mmol solution of $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$ in THF (20 mL) was used at 550 °C. The aerosol was carried by Argon, which had flow rate 180 sccm controlled by a Platon flow gauge. in to the furnace where the precursor decomposed and deposits ReS_2 on the glass substrates (1 x 2 cm). Substrates were cleaned prior to deposition by sonication in deionized water for 15 min, then sonicated with isopropanol for 15 min, finally with acetone for 15 min to remove any contamination. A Platon flow gauge is used to control argon gas flow rate.

Preparation and Characterisation of Nanosheets

Nanosheets were dispersed by sonication of the ReS_2 thin film immersed in NMP (2 mL) for 36 h using the ultrasonic bath setup described previously (Brent et al. *J. Am. Chem. Soc.* **2015**, *137*, 12689).

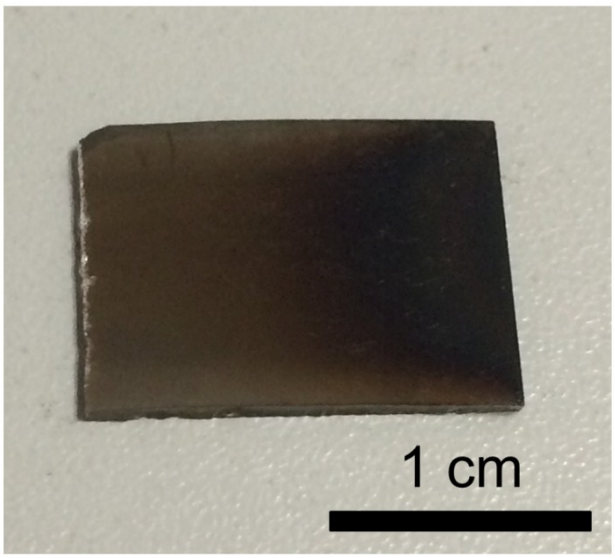

Fig. S1: Gross appearance of of ReS_2 film grown by AACVD at 550 °C on a glass substrate.

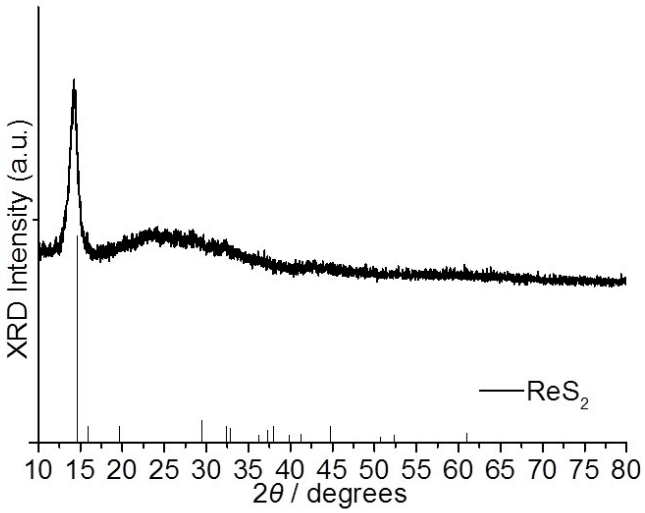

Fig. S2: Powder X-ray diffraction pattern of ReS_2 film grown on a glass substrate by AACVD at 550 °C. Black sticks represent the theoretical pattern for ReS_2 taken From cif file data from Zelikman A.N., Voronov B.K., Dudkin L.D., Teslitskaya M.V., Evstigneeva E.D.: *Effect of tantalum and rhenium on the electrical properties of MoS_2*. Inorganic Materials (translated from Neorganicheskie Materialy) **7** (1971) 381-384 (http://materials.springer.com/isp/crystallographic/docs/sd_0309035).

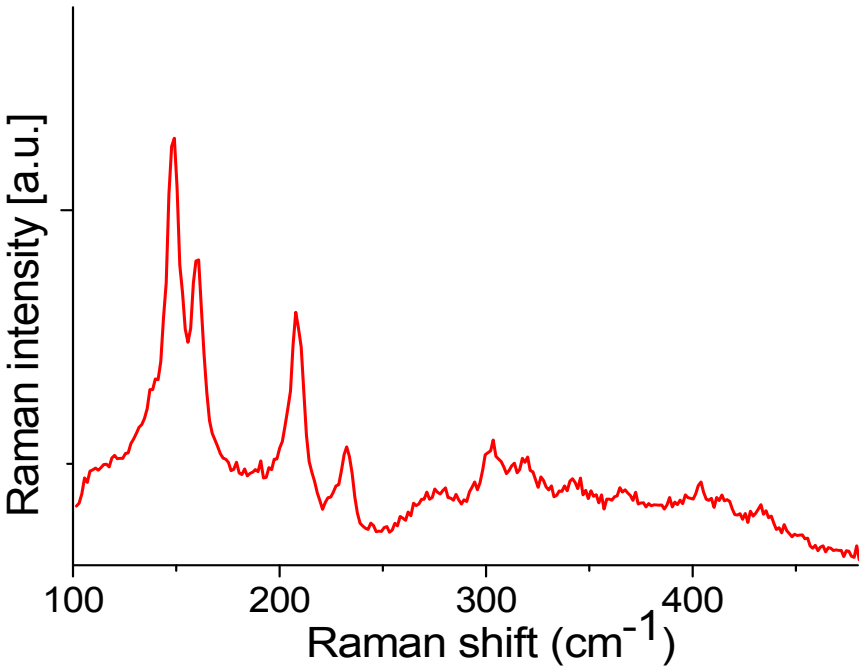

Fig. S3: Raman spectrum of ReS_2 film grown by AACVD at 550 °C on a glass substrate.

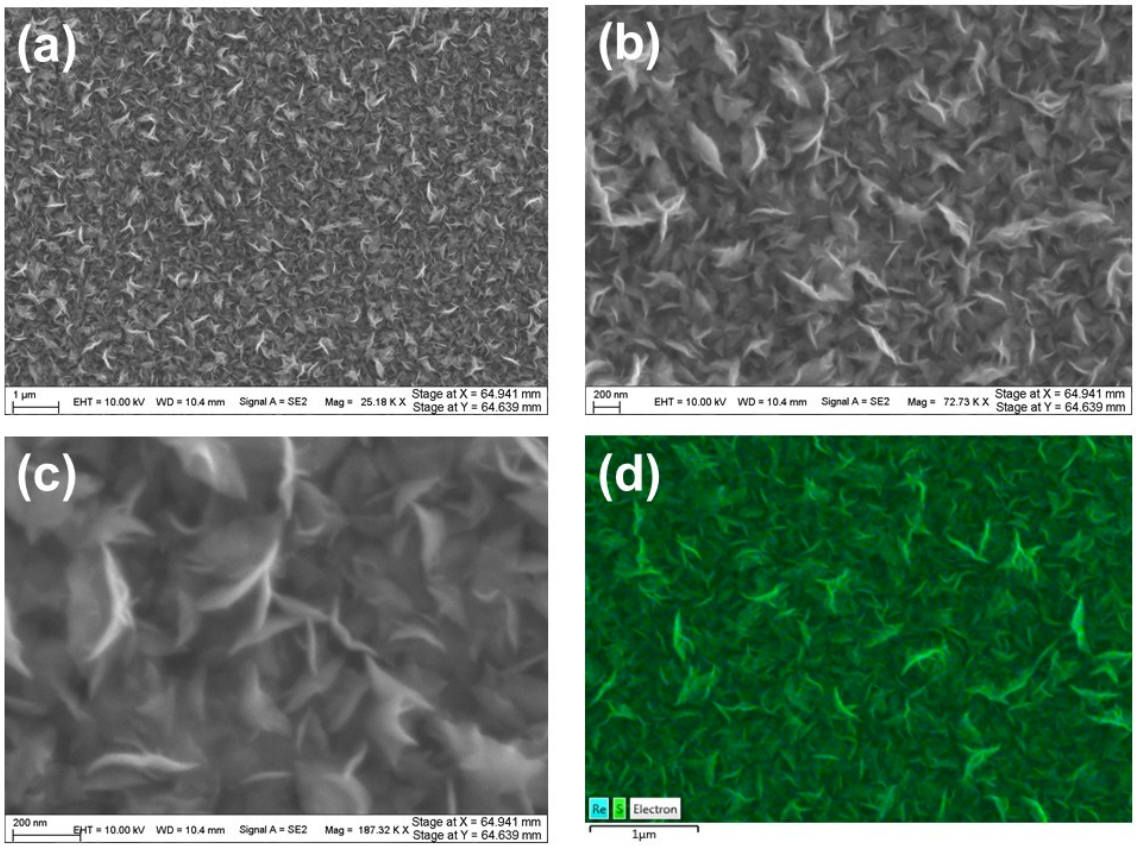

Fig. S4: Electron microscopy and elemental analysis of of ReS_2 film grown on a glass substrate by AACVD at 550 °C. (a - c) Secondary electron SEM images at various magnifications using an accelerating voltage of 10 kV and (d) EDX maps of Re L_α (8.65 eV) and S K_α (2.31 eV) overlayed on the SE image of an ReS_2 thin film at 20 kV accelerating voltage demonstrating the co-localisation of Re and S signals.

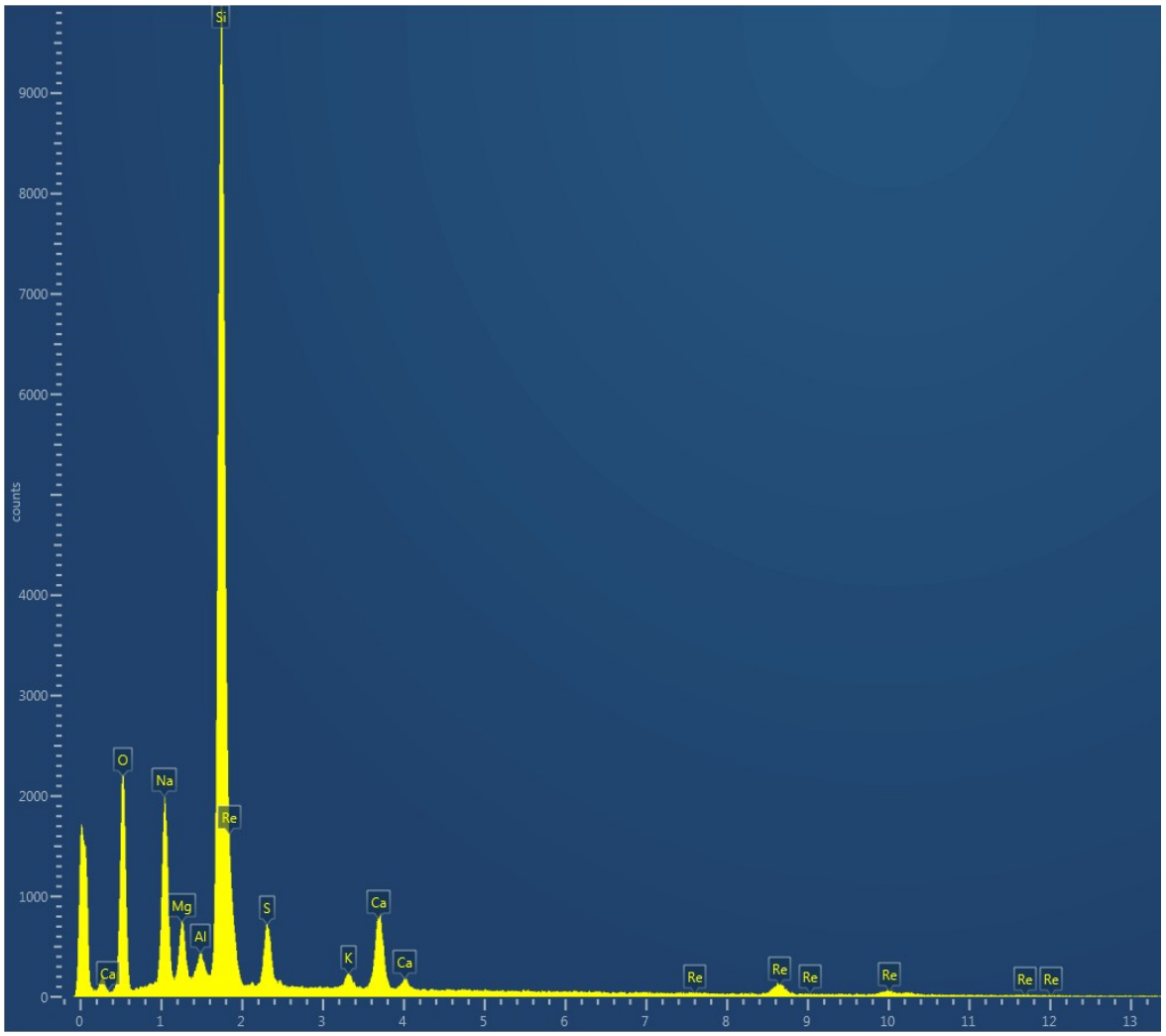

Fig. S5: EDX sum spectrum extracted from the EDX map of the ReS_2 ReS_2 film grown on a glass substrate by AACVD at 550 °C andpresented in Fig S3, taken at 20 kV. The signals for O, Si, Mg, Al, Na, K and Ca arise from the glass substrate.

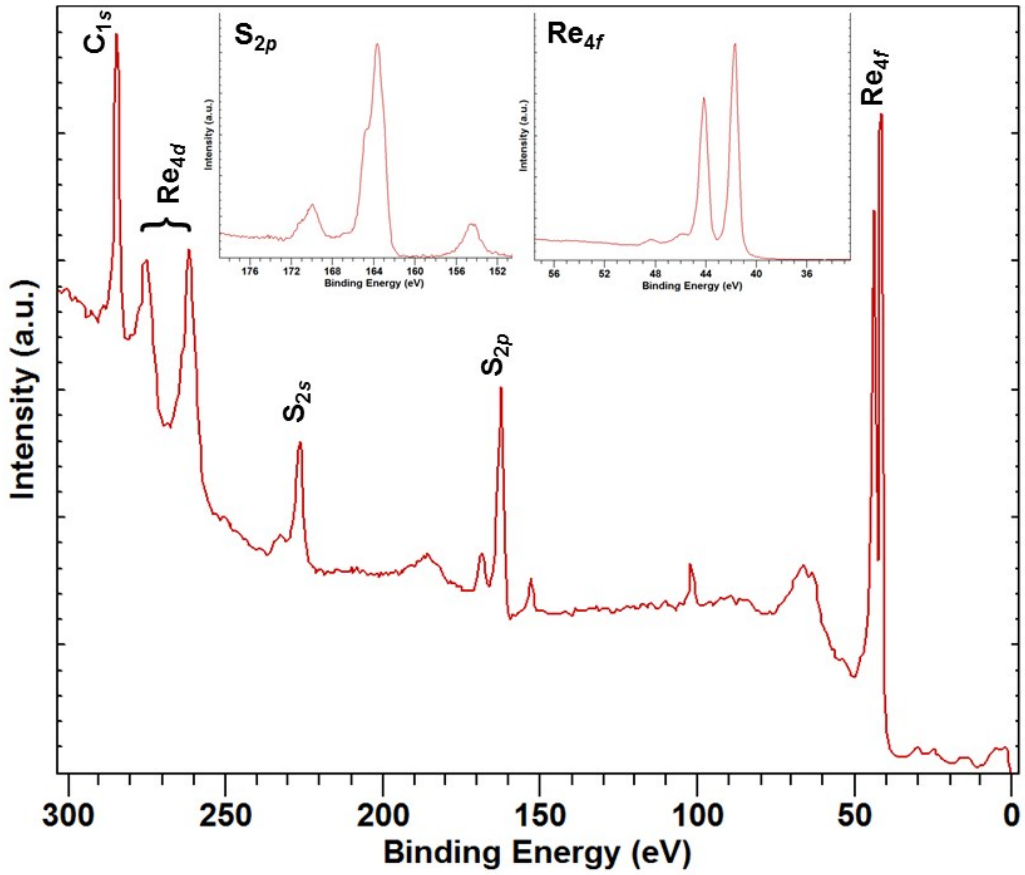

Fig. S6: Wide energy range XPS spectrum of the ReS_2 film ReS_2 film grown on a glass substrate by AACVD at 550 °C, showing the presence of Re and S at the surface of the thin film. Only adventitious carbon (C-C) was detected with no evidence of C-N or C-O contaminants. Insets: high-resolution S_{2p} and Re_{4f} spectra. All spectra are calibrated vs. the C_{1s} peak (284.8 eV).

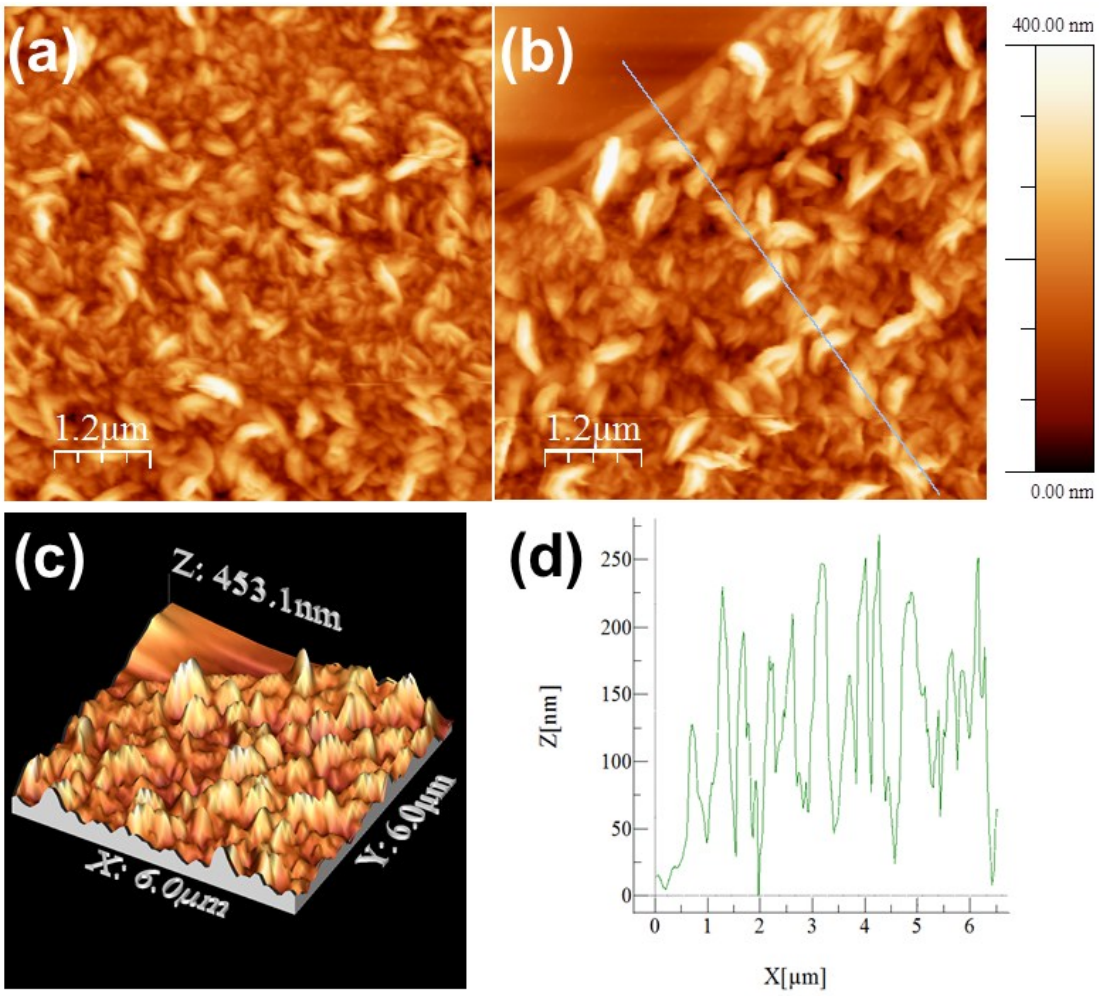

Fig. S7: AFM of the ReS_2 film grown on a glass substrate by AACVD at 550 °C. (a) Relief image on the bulk film (R_q = 61 nm, R_a = 49.6 nm). (b) Relief image of the film at the edge of a section scored-through with a scalpel to reveal the glass substrate below. (c) 3D image of the plan view image in (b), showing the film region and the glass substrate. (d) Line profile of the blue line in image (b); the film thickness is approximately 150 nm ± 50 nm.

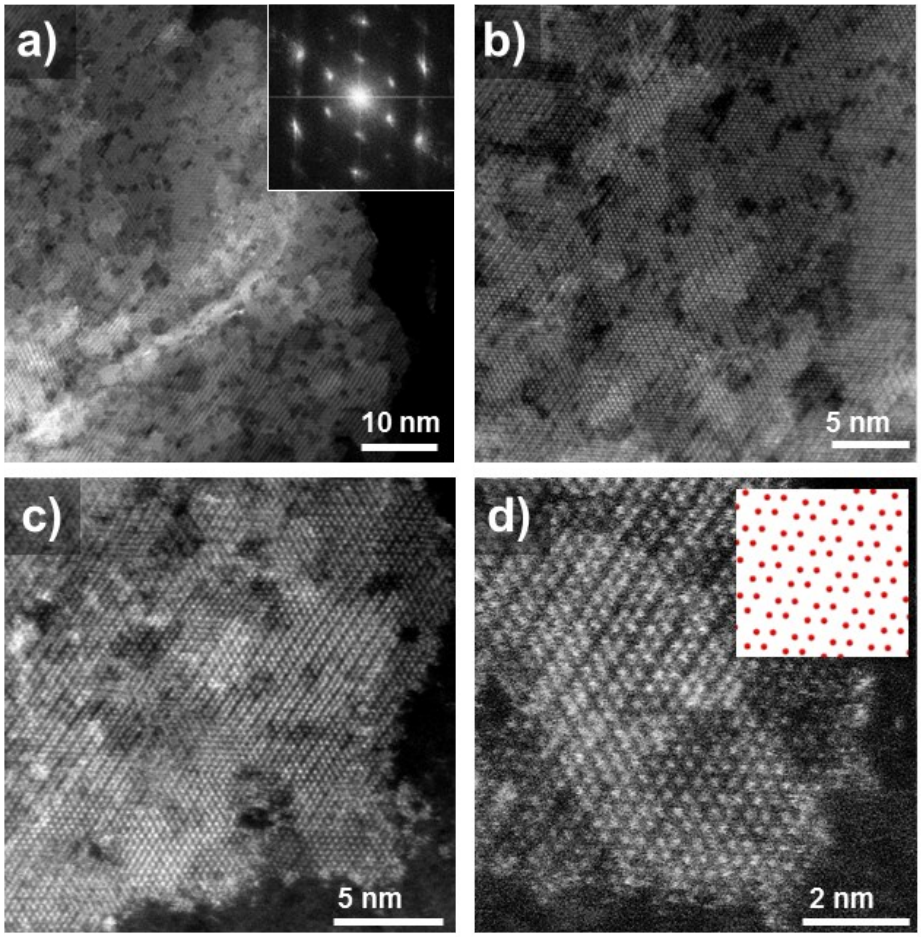

Fig. S8. Additional HAADF STEM images. (a) shows the edge of a flake, the Fourier transform is inset, (b-c) show higher magnification images of the area shown in (a), with (b) showing an internal region and (c and d) showing regions at the flake edge. The theoretical Re atomic positons for octahedral (*T*) ReS_2 viewed down the [010] zone axis are overlaid on (d), showing that the atomic positions observed in HAADF images are as expected.

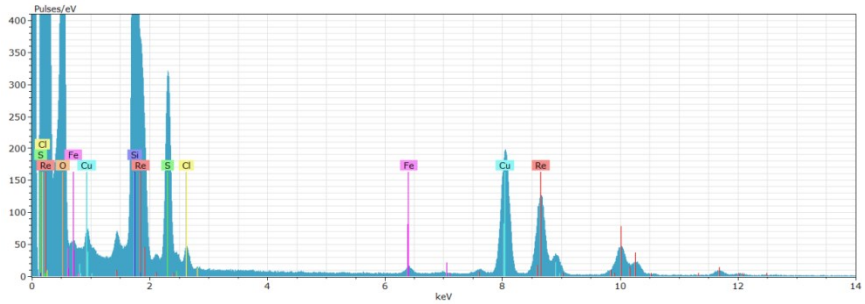

Fig S9. Summed EDX spectrum corresponding to spectrum image shown in Figure 3 of the main manuscript.

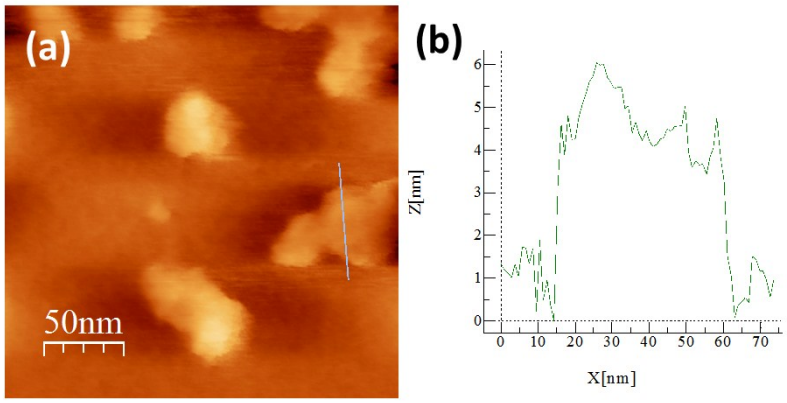

Fig S10. (a) High magnification AFM image of ReS_2 nanosheets. (b) Height profile along the blue line in image (a) which bisects potentially a trilayer ReS_2 nanosheet.

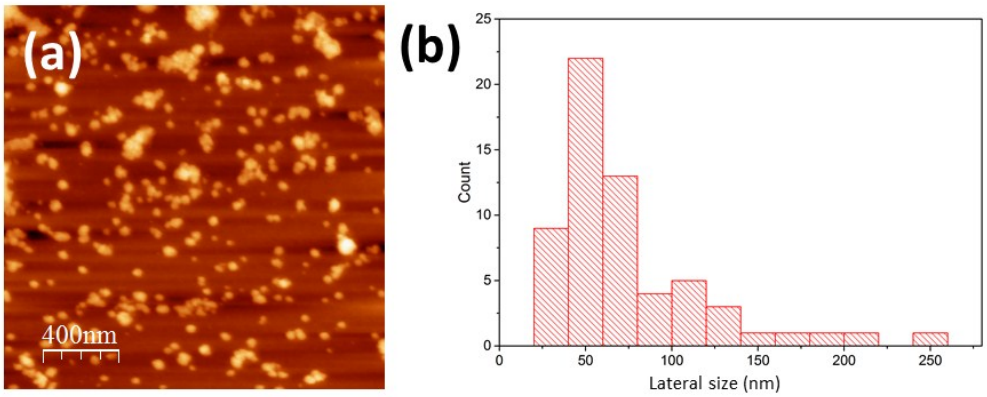

Fig S11. (a) Low magnification AFM image of ReS_2 nanosheets. (b) Histogram of lateral flake size from the image in (a).