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Sequential bottom-up and top-down processing for the synthesis of transition metal dichalcogenide nanosheets: the case of rhenium disulfide (ReS₂)[†]

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Bottom-up (aerosol-assisted chemical vapor deposition, AACVD) and **top-down** (liquid phase exfoliation, LPE) processing methodologies are used in tandem to produce colloids of few-layer thick rhenium disulfide (ReS₂) in *N*-methyl pyrrolidone. The processing route we use is a potentially robust and scalable pathway to manufacture useful 2D materials.

Rheniite (rhenium disulfide, ReS₂) is a naturally occurring yet extremely rare transition metal dichalcogenide (TMDC).¹ Like other TMDCs it has a layered crystal structure (Fig. 1); with a preference for pinacoidal cleavage. In most common TMDCs such as molybdenum disulfide (MoS₂), the metal spacing is regular and can be simply described by conventional packing. However, the ReS₂ crystal structure is more complex because metal–metal interactions contribute significantly to the inter-layer bonding, leading to the formation of a repeating motif of Re-parallellograms of varying sizes within the metal layer.²

Very recently, there has been some interest in ReS₂ as a two-dimensional semiconductor. ReS₂ is a direct tunable band gap semiconductor, from 1.47 eV in the bulk to 1.61 eV as a monolayer and shows evidence of birefringent behavior.³ The band gap energy is predicted to be insensitive to strain, and thus the material may be tolerant to a range of processing methods.⁴ It has been proposed that these favourable properties arise from interlayer decoupling caused by Peierls distortion of the 1T structure of ReS₂, which precludes ordered stacking and minimizes wavefunction overlap.⁵ Raman spectra of ReS₂ have been shown to be both anisotropic and dependent on the

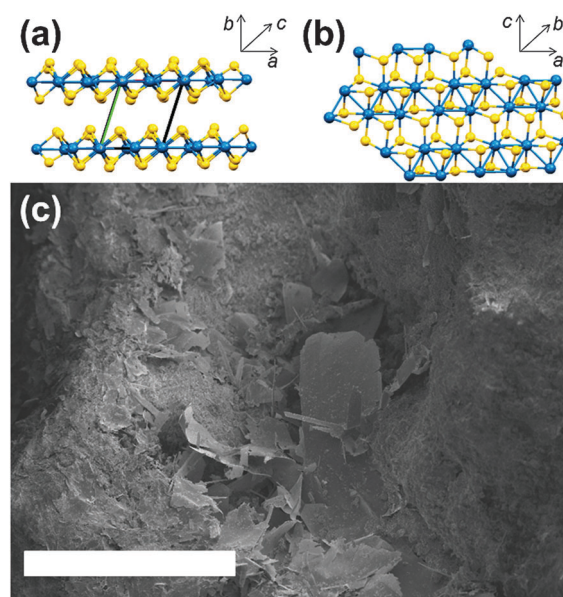


Fig. 1 Structure of rheniite (rhenium disulfide, ReS₂). (a) The crystal structure of ReS₂, showing the triclinic unit cell ($a = 6.378 \text{ \AA}$, $b = 6.417 \text{ \AA}$, $c = 6.461 \text{ \AA}$ with $\alpha = 91.62^\circ$, $\beta = 119.07^\circ$, $\gamma = 105.115^\circ$). (b) A monolayer of ReS₂ looking along the [010] zone axis. (c) Secondary electron SEM image (6 kV) of a sample of rheniite from Kudriavy volcano type locality showing the sheet-like crystals typical of the layered mineral. Scale bar represents 1 mm.

number of layers in the material.^{6,7} Current routes to ReS₂ monolayers are not ideal as they either rely on chemical vapor deposition processes requiring high vacuum,^{8,9} or harsh chemical exfoliation with organolithium species.¹⁰

Aerosol-assisted chemical vapor deposition (AACVD)¹¹ from single source precursors is a versatile route to produce pure metal chalcogenide thin films such as tin(II) sulfide (SnS),¹² cadmium sulfide (CdS),¹³ pyrite (FeS₂),^{14–16} molybdenum disulfide (MoS₂) as well as to produce related (*e.g.* Cr-doped) variants.^{17–19} Additionally a range of useful metal oxides^{6,7,20–24} and organohalide lead(II) perovskites have been reported.^{25–27} AACVD can take place at moderate temperature, at ambient pressure and is inherently

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[†] Electronic supplementary information (ESI) available: Characterization of [Re(S₂CC₆H₅)(S₃CC₆H₅)₂]. Characterization of ReS₂ thin film produced by AACVD by pXRD, SEM and Raman spectroscopy. Additional atomic-resolution HAADF STEM images, summed energy dispersive X-ray (EDX) spectrum from elemental imaging of nanosheets. See DOI: 10.1039/c6cc03316d

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scalable. We have recently reported the production of polycrystalline thin films of ReS_2 using AACVD from a single source precursor.²⁸

In general, two-dimensional (2D) materials such as graphene²⁹ and 2D TMDCs³⁰ are produced for demonstrative studies using mechanical (scotch tape) exfoliation. More recently, liquid-phase exfoliation (LPE) has emerged as a more scalable and versatile solution-phase processing methodology to produce industrially

significant quantities of nanomaterials ranging from graphene,³¹ TMDCs,³² phosphorene³³ and 2D tin(II) sulfide.³⁴ Negatively charged ReS_2 nanosheets have been reported by Chen and co-workers using lithium intercalation-exfoliation.³⁵ In this paper we present the marriage of a scalable bottom-up process (AACVD) with top-down LPE as a new scalable processing route to produce atomically thin materials, in this case few-layer ReS_2 .

ReS_2 thin films were produced by AACVD on glass substrates at 550 °C using the single source precursor $[\text{Re}(\text{S}_2\text{CC}_6\text{H}_5)(\text{S}_3\text{CC}_6\text{H}_5)_2]$.³⁶ Characterization of the films by Raman spectroscopy agreed with the previously reported spectra for ReS_2 ^{5,28} and powder X-ray diffraction (pXRD) measurements showed a preferred orientation in the (010) plane whilst scanning electron microscopy (SEM) revealed the lamellar morphology of the individual crystallites within the thin film. EDX spectrum mapping of the Re L_{α} (8.6 keV) and S K_{α} (2.3 keV) lines demonstrated the homogeneous co-localisation of both elements in the thin film. Atomic force microscopy (AFM) at the film-edge was used to measure the thickness of the film as 150 ± 50 nm. The above evidence for ReS_2 film formation is given fully in the ESI.† All of the characterisation data from the thin films were consistent with that observed previously for ReS_2 films produced by AACVD.²⁸ The thin films were then immersed in *N*-methyl-2-pyrrolidone (NMP) and ultrasonicated for 36 h, using similar

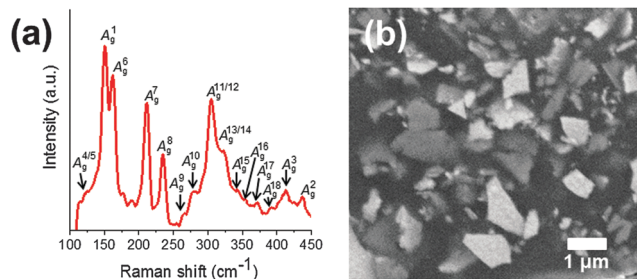


Fig. 2 Characterization of ReS_2 nanosheets exfoliated from thin films of ReS_2 grown by AACVD at 550 °C. (a) Raman spectrum of exfoliated nanosheets drop cast from NMP on Si@SiO_2 substrates with peaks labelled using the scheme proposed by Pradhan *et al.*²¹ (b) Secondary electron SEM image (6 kV) of ReS_2 nanosheets drop cast from NMP onto Si@SiO_2 substrates.

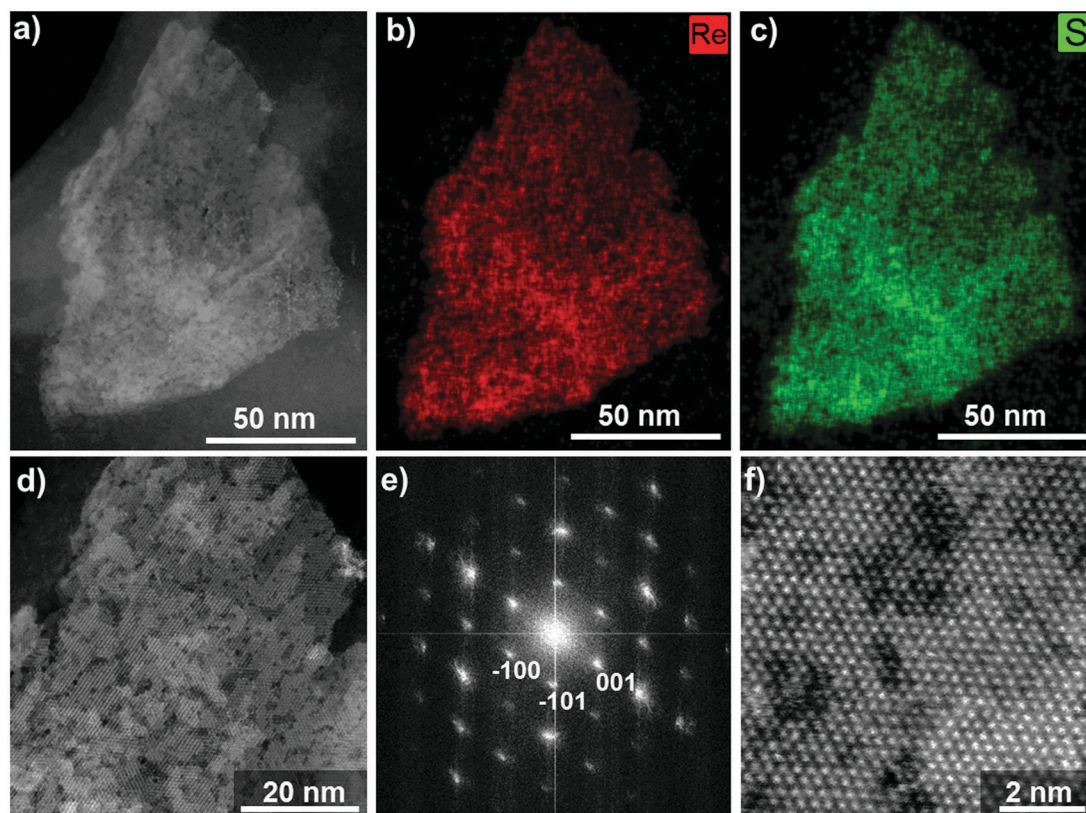


Fig. 3 (a) HAADF STEM image of a representative LPE flake of ReS_2 grown by AACVD at 550 °C. Corresponding EDX elemental maps showing (b) Re L_{α} (8.6 keV) and (c) S K_{α} (2.3 keV) X-ray counts demonstrate co-localisation of Re and S, the summed EDX spectrum can be found in the ESI.† (d) Atomic resolution HAADF STEM image of a region of the flake shown in (a). (e) Fourier transform of (d), confirming the expected crystal structure for ReS_2 viewed down the [010] zone axis and demonstrating that the entire nanosheet is a single crystal. (f) Shows a higher magnification image of the same flake so that the atomic structure can be clearly seen.



conditions to that reported previously for liquid exfoliation of other 2D materials.^{33,34} The resulting colloidal suspension of nanosheets was drop-casted onto silicon wafers coated with 300 nm of silicon dioxide (Si@SiO₂) for analysis.

Raman spectroscopy of ReS₂ nanosheets on Si@SiO₂ substrates showed signals of a weak intensity associated with ReS₂; optical phonon modes are observed at *ca.* 150, 163, 212, 235 and 305 cm⁻¹ (Fig. 2a), as previously reported. A total of 18 phonon modes, which have previously been attributed to vibrations of A_g symmetry,²¹ were identified. As all the modes were observed at once, we conclude that a number of randomly orientated flakes were sampled during the measurement, as the Raman response from ReS₂ has been shown to be anisotropic for large mechanically exfoliated flakes.^{6,21} There are some subtle differences in the Raman spectrum of the nanosheets compared to that of the bulk thin film: the A_g¹ mode shifts from 148.5 cm⁻¹ to 150.4 cm⁻¹ whilst the A_g² mode shifts from 207.8 to 211.6 cm⁻¹ in going from bulk to nanosheet form. These shifts are consistent with those found by Hone and co-workers for micromechanically exfoliated ReS₂ compared with bulk ReS₂.⁶ Secondary electron scanning electron microscopy (SEM) images at 6 kV reveal nanosheets of up to 1 μm in length/width (Fig. 2b), though there are many smaller nanosheets found in the sample, typically < 500 nm. The smaller sheet size from LPE sols is typical for TMDCs produced by this method compared to mechanical exfoliation, where sheet size can be in the micron range.¹⁰

High-angle annular dark field scanning transmission electron microscope (HAADF STEM) images of the ReS₂ nanosheets show that they are highly crystalline (Fig. 3). The calculated rhenium positions of octahedral (T) ReS₂ as-viewed down the [010] zone axis of can be overlaid on the atomic resolution images and both match perfectly (ESI[†]). Fast Fourier transforms taken from these atomic resolution HAADF images of individual flakes demonstrate that the sheets are comprised of single crystals of ReS₂. Energy dispersive X-ray (EDX) elemental mapping of the Re L_α (8.6 keV) (Fig. 3b) and S K_α (2.3 keV) (Fig. 3c) X-ray counts show the expected co-localisation of Re and S within the boundary of the flakes.

Atomic force microscopy (AFM) was used to analyse the heights of the ReS₂ flakes produced by our novel method (Fig. 4). It was found that the flakes ranged in height from 1–20 nm. Significant populations of monolayer (*ca.* 1.7 nm), bilayer (3.9 nm) and trilayer (6.0 nm) flakes were observed along with larger flakes with heights up to *ca.* 20 nm, *i.e.* up to 10-layers, though the thinnest flakes do represent the majority of the population analysed under these conditions.

Hence, we conclude that the exfoliation procedure successfully produces ultrathin and crystalline ReS₂ sheets from ReS₂ thin films grown by AACVD. Our ReS₂ nanosheets are identical in phase to those reported previously by Chen and co-workers and have similar thickness,³⁵ but with the added advantage that there is no lithium associated with them (*i.e.* should be neutral compared to the negatively charged sheets produced by lithium intercalation-exfoliation) and do not require post-exfoliation modification.

In summary, we have coupled the bottom up processing of ReS₂ by AACVD with top-down LPE to produce ultrathin ReS₂,

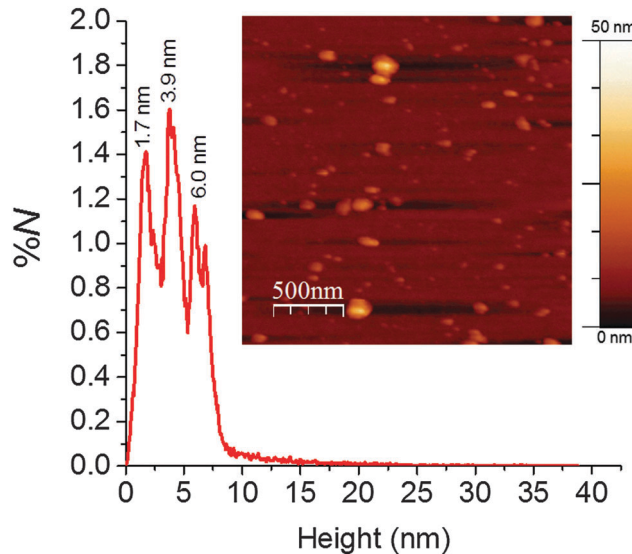


Fig. 4 Particle size distribution of ReS₂ nanosheets exfoliated from thin films of ReS₂ grown by AACVD at 550 °C as-measured by AFM showing significant peaks at 1.7, 3.9 and 6.0 nm. Inset: Representative height profile AFM image of exfoliated ReS₂ nanosheets spin coated from NMP suspension onto a Si@SiO₂ substrate.

nanosheets. In the case of ReS₂, which is a useful 2D semiconductor, this is important as natural sources are scarce and synthetic pathways are required. Additionally our processing methodology is potentially scalable and thus could be a route to commercial exploitation. Finally, the serial processing we report here is potentially applicable to a wide range of layered TMDC materials. It will be useful in the future for the production of a myriad of synthetic TMDC materials with interesting optoelectronic properties which are complementary to graphene. As it has been established that doping of TMDCs is possible by AACVD,¹⁸ there may also be scope to produce doped 2D materials in the future which are interesting for a range of applications.¹⁹

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