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## Sequential bottom-up and top-down processing for the synthesis of transition metal dichalcogenide nanosheets: the case of rhenium disulfide (ReS<sub>2</sub>)<sup>†</sup>

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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 (ReS<sub>2</sub>) in *N*-methyl pyrrolidone. The processing route we use is a potentially robust and scalable pathway to manufacture useful 2D materials.

Rheniite (rhenium disulfide, ReS<sub>2</sub>) is a naturally occurring yet extremely rare transition metal dichalcogenide (TMDC).<sup>1</sup> 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 (MoS<sub>2</sub>), the metal spacing is regular and can be simply described by conventional packing. However, the ReS<sub>2</sub> 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.<sup>2</sup>

Very recently, there has been some interest in ReS<sub>2</sub> as a two-dimensional semiconductor. ReS<sub>2</sub> 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.<sup>3</sup> The band gap energy is predicted to be insensitive to strain, and thus the material may be tolerant to a range of processing methods.<sup>4</sup> It has been proposed that these favourable properties arise from interlayer decoupling caused by Peierls distortion of the 1T structure of ReS<sub>2</sub>, which precludes ordered stacking and minimizes wavefunction overlap.<sup>5</sup> Raman spectra of ReS<sub>2</sub> have been shown to be both anisotropic and dependent on the

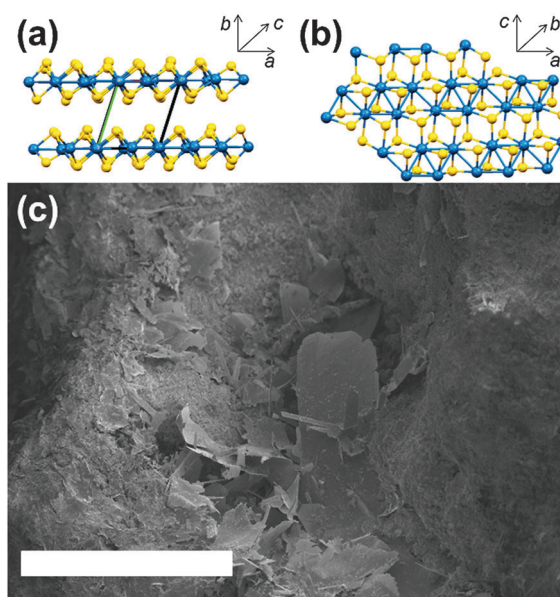


Fig. 1 Structure of rheniite (rhenium disulfide, ReS<sub>2</sub>). (a) The crystal structure of ReS<sub>2</sub>, showing the triclinic unit cell ( $a = 6.378 \text{ \AA}$ ,  $b = 6.417 \text{ \AA}$ ,  $c = 6.461 \text{ \AA}$  with  $\alpha = 91.62^\circ$ ,  $\beta = 119.07^\circ$ ,  $\gamma = 105.115^\circ$ ). (b) A monolayer of ReS<sub>2</sub> 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.<sup>6,7</sup> Current routes to ReS<sub>2</sub> monolayers are not ideal as they either rely on chemical vapor deposition processes requiring high vacuum,<sup>8,9</sup> or harsh chemical exfoliation with organolithium species.<sup>10</sup>

Aerosol-assisted chemical vapor deposition (AACVD)<sup>11</sup> from single source precursors is a versatile route to produce pure metal chalcogenide thin films such as tin(II) sulfide (SnS),<sup>12</sup> cadmium sulfide (CdS),<sup>13</sup> pyrite (FeS<sub>2</sub>),<sup>14–16</sup> molybdenum disulfide (MoS<sub>2</sub>) as well as to produce related (*e.g.* Cr-doped) variants.<sup>17–19</sup> Additionally a range of useful metal oxides<sup>6,7,20–24</sup> and organohalide lead(II) perovskites have been reported.<sup>25–27</sup> AACVD can take place at moderate temperature, at ambient pressure and is inherently

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<sup>†</sup> Electronic supplementary information (ESI) available: Characterization of [Re(S<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)(S<sub>3</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]. Characterization of ReS<sub>2</sub> 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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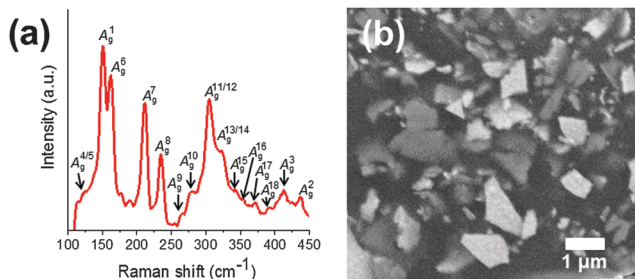


scalable. We have recently reported the production of polycrystalline thin films of  $\text{ReS}_2$  using AACVD from a single source precursor.<sup>28</sup>

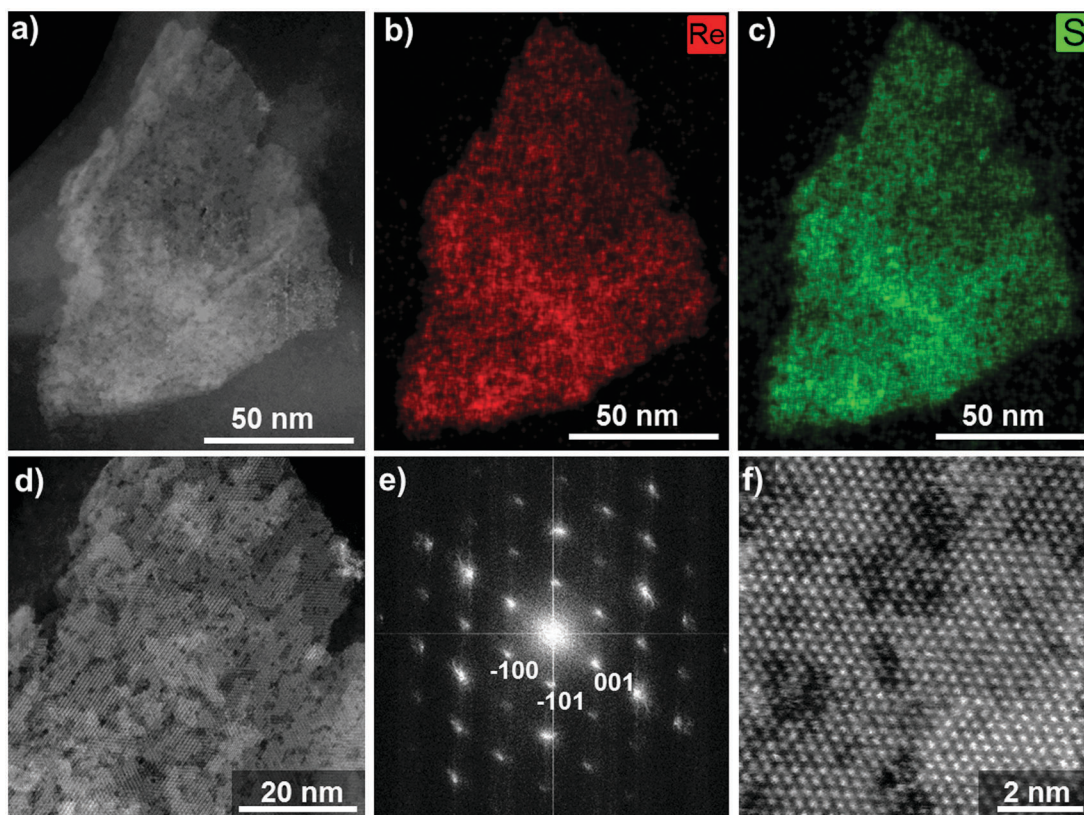
In general, two-dimensional (2D) materials such as graphene<sup>29</sup> and 2D TMDCs<sup>30</sup> are produced for demonstrative studies using mechanical (scotch tape) exfoliation. More recently, liquid-phase exfoliation (LPE) has emerged as a more scalable and versatile solution-phase processing methodology to produce industrially

significant quantities of nanomaterials ranging from graphene,<sup>31</sup> TMDCs,<sup>32</sup> phosphorene<sup>33</sup> and 2D tin(II) sulfide.<sup>34</sup> Negatively charged  $\text{ReS}_2$  nanosheets have been reported by Chen and co-workers using lithium intercalation-exfoliation.<sup>35</sup> 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  $\text{ReS}_2$ .

$\text{ReS}_2$  thin films were produced by AACVD on glass substrates at 550 °C using the single source precursor  $[\text{Re}(\text{S}_2\text{CC}_6\text{H}_5)(\text{S}_3\text{CC}_6\text{H}_5)_2]$ .<sup>36</sup> Characterization of the films by Raman spectroscopy agreed with the previously reported spectra for  $\text{ReS}_2$ <sup>5,28</sup> 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  $L_{\alpha}$  (8.6 keV) and S  $K_{\alpha}$  (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  $150 \pm 50$  nm. The above evidence for  $\text{ReS}_2$  film formation is given fully in the ESI.† All of the characterisation data from the thin films were consistent with that observed previously for  $\text{ReS}_2$  films produced by AACVD.<sup>28</sup> The thin films were then immersed in *N*-methyl-2-pyrrolidone (NMP) and ultrasonicated for 36 h, using similar



**Fig. 2** Characterization of  $\text{ReS}_2$  nanosheets exfoliated from thin films of  $\text{ReS}_2$  grown by AACVD at 550 °C. (a) Raman spectrum of exfoliated nanosheets drop cast from NMP on  $\text{Si@SiO}_2$  substrates with peaks labelled using the scheme proposed by Pradhan *et al.*<sup>21</sup> (b) Secondary electron SEM image (6 kV) of  $\text{ReS}_2$  nanosheets drop cast from NMP onto  $\text{Si@SiO}_2$  substrates.



**Fig. 3** (a) HAADF STEM image of a representative LPE flake of  $\text{ReS}_2$  grown by AACVD at 550 °C. Corresponding EDX elemental maps showing (b) Re  $L_{\alpha}$  (8.6 keV) and (c) S  $K_{\alpha}$  (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  $\text{ReS}_2$  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.<sup>33,34</sup> The resulting colloidal suspension of nanosheets was drop-casted onto silicon wafers coated with 300 nm of silicon dioxide (Si@SiO<sub>2</sub>) for analysis.

Raman spectroscopy of ReS<sub>2</sub> nanosheets on Si@SiO<sub>2</sub> substrates showed signals of a weak intensity associated with ReS<sub>2</sub>; optical phonon modes are observed at *ca.* 150, 163, 212, 235 and 305 cm<sup>-1</sup> (Fig. 2a), as previously reported. A total of 18 phonon modes, which have previously been attributed to vibrations of A<sub>g</sub> symmetry,<sup>21</sup> 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 ReS<sub>2</sub> has been shown to be anisotropic for large mechanically exfoliated flakes.<sup>6,21</sup> There are some subtle differences in the Raman spectrum of the nanosheets compared to that of the bulk thin film: the A<sub>g</sub><sup>1</sup> mode shifts from 148.5 cm<sup>-1</sup> to 150.4 cm<sup>-1</sup> whilst the A<sub>g</sub><sup>2</sup> mode shifts from 207.8 to 211.6 cm<sup>-1</sup> in going from bulk to nanosheet form. These shifts are consistent with those found by Hone and co-workers for micromechanically exfoliated ReS<sub>2</sub> compared with bulk ReS<sub>2</sub>.<sup>6</sup> 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.<sup>10</sup>

High-angle annular dark field scanning transmission electron microscope (HAADF STEM) images of the ReS<sub>2</sub> nanosheets show that they are highly crystalline (Fig. 3). The calculated rhenium positions of octahedral (T) ReS<sub>2</sub> as-viewed down the [010] zone axis of can be overlaid on the atomic resolution images and both match perfectly (ESI<sup>†</sup>). Fast Fourier transforms taken from these atomic resolution HAADF images of individual flakes demonstrate that the sheets are comprised of single crystals of ReS<sub>2</sub>. Energy dispersive X-ray (EDX) elemental mapping of the Re L<sub>α</sub> (8.6 keV) (Fig. 3b) and S K<sub>α</sub> (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 ReS<sub>2</sub> 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 ReS<sub>2</sub> sheets from ReS<sub>2</sub> thin films grown by AACVD. Our ReS<sub>2</sub> nanosheets are identical in phase to those reported previously by Chen and co-workers and have similar thickness,<sup>35</sup> 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 ReS<sub>2</sub> by AACVD with top-down LPE to produce ultrathin ReS<sub>2</sub>,

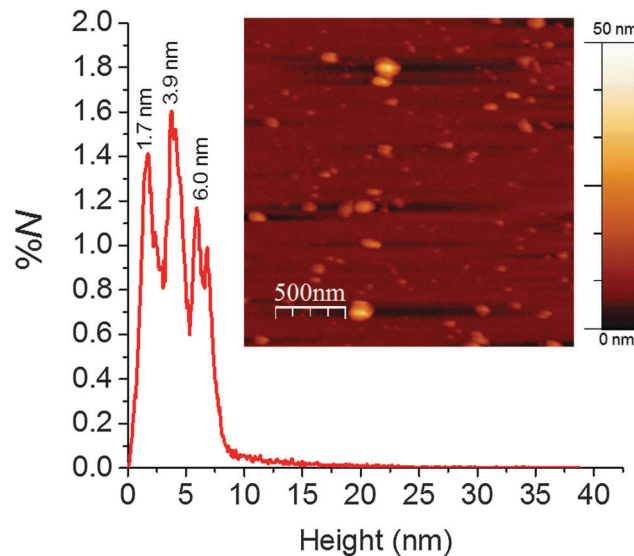


Fig. 4 Particle size distribution of ReS<sub>2</sub> nanosheets exfoliated from thin films of ReS<sub>2</sub> grown by AACVD at 550 °C as-measured by AFM showing significant peaks at 1.7, 3.9 and 6.0 nm. Inset: Representative height profile AFM image of exfoliated ReS<sub>2</sub> nanosheets spin coated from NMP suspension onto a Si@SiO<sub>2</sub> substrate.

nanosheets. In the case of ReS<sub>2</sub>, 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,<sup>18</sup> there may also be scope to produce doped 2D materials in the future which are interesting for a range of applications.<sup>19</sup>

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