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Salt-Assisted Vapor-Liquid-Solid Growth of 1D van der Waals Materials

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The method of salt-assisted vapor-liquid-solid (VLS) growth is introduced to synthesize 1D nanostructures of trichalcogenide van der Waals (vdW) materials, exemplified by niobium trisulfide (NbS₃). The method uses a unique catalyst consisting of an alloy of Au and an alkali metal halide (NaCl) to enable rapid and directional growth. High yields of two types of NbS₃ 1D nanostructures, nanowires and nanoribbons, each with sub-ten nanometer diameter, tens of micrometers length, and distinct 1D morphology and growth orientation are demonstrated. Strategies to control the location, size, and morphology of growth, and extend the growth method to synthesize other transition metal trichalcogenides, NbSe₃ and TiS₃, as nanowires are demonstrated. Finally, the role of the Au-NaCl alloy catalyst in guiding VLS synthesis is described and the growth mechanism based on the relationships measured between structure (growth orientation, morphology, and dimensions) and growth conditions (catalyst volume and growth time) is discussed. These results introduce opportunities to expand the library of emerging 1D vdW materials to make use of their unique properties through controlled growth at nanoscale dimensions.

1. Introduction

The discovery of graphene stimulated interested in van der Waals (vdW) bonded materials that can be mechanically or chemically exfoliated to obtain single layer sheets.^[1,2] Beyond wellknown examples, such as 2D transition metal dichalcogenides

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(TMDs), are the vdW materials based on 1D motifs. These are less-studied yet show exotic properties and promising applications resulting from their intrinsic anisotropic character.^[3-5] The prototypical family of these so-called "1D vdW" materials is the transition metal trichalcogenide (TMT) family with the formula MX_2 . Here, M is a group-IV and V transition metal such as Nb, Ta, Ti and Hf; while X is a chalcogen such as S, Se, and Te.^[4,6] These materials contain covalently bonded triagonal prismatic chains of metal (M) and chalcogens (X) that are further assembled, through weaker inter-chain covalent bonds, into bilaver sheets that are stacked as shown in Figure S1a, Supporting Information. The result is a mixture of 2D and 1D characteristics.^[7] Even in the bulk form, many of these crystals exhibit intriguing electronic, optical, and thermal properties uniquely derived from their 1D character.^[3–5] This includes charge and spin density waves,^[4] sliding charge

density waves,^[8]

superconductivity,^[4] pressure-driven superconductivity,^[9] photoinduced and photo-controlled collective excitations,^[10] thermoelectric properties,^[11] and spatially confined phonon density of states,^[3] to name just a few. Nanoscale, exfoliated forms of several TMTs have shown exotic optoelectronic^[12,13] and thermal transport characteristics,^[14] such as superdiffusive thermal transport (seen in NbSe₃ nanowires with sub-20 nm diameter^[15]), highlighting the importance of nanoscale confinement in these materials.[3,7,16,17] Many applications have been proposed for this class of materials, including back end of line interconnects for nano-electronics,^[18] photodetectors,^[19] electromagnetic shielding,^[20] and GHz switching devices.^[21]

NbS₃ is a particularly interesting TMT due to its extensive library of polymorphs and structure-dependent properties.^[22-24] Five distinct phases of NbS₃ have been observed experimentally and many more stable phases were recently predicted.^[23] Different polymorphs usually have different degrees of metal pairing (Nb-Nb distance) along the chain or different bilayer stacking order. These structural differences result in a wealth of electronic properties; for example, three distinct charge density wave instabilities in type-II NbS₃, a metallic phase with basic structure belonging to the space group $P2_1/m$.^[22,25] Despite these fascinating structures and properties, NbS3 is one of the least reported members in the family of TMTs in terms of both fundamental studies and potential applications, in part because of the lack of a synthesis method that enables precise manufacturing of the material.^[26] Successful integration of NbS₃ into nextgeneration devices that make use of its nanoscale properties would benefit from a deterministic synthesis method that allows control over the material's structural phase, chemistry, size, and placement.^[3]

Bulk TMTs are synthesized mainly by chemical vapor transport and flux growth.^[5,6] While these methods produce single crystals of high purity, they face several issues in scalable manufacturing of nanostructures.^[3,5] Long times, days to weeks, are required to grow the crystals, and additional steps such as exfoliation (mechanically or chemically) and transfer are needed to place nanoscale samples onto substrates for further characterization and applications. The need for post-growth processing often results in a lack of control of the resulting nanomaterial in terms of its size and interface quality, hindering integration with other material systems.^[5,27] A successful strategy to create 1D nanostructures with controlled size and location would therefore be valuable.

For semiconductors such as Si, Ge, and GaAs, the catalytic process of vapor-liquid-solid (VLS) growth^[28] is a promising approach for such synthesis. The working principle of VLS depends, at its most general, on the formation of a liquid eutectic between the growth material and a catalyst patterned onto the substrate at the desired location of the nanowire.^[28] For some layered materials containing low-melting metals, the VLS mechanism has been demonstrated for synthesis of nanowires: these metals include Ga (GaS,^[29] GaSe^[30]), In (In₂Se₃^[31]), Bi (Bi₂Se₃^[32]), and Ge (GeS,^[33,34] GeSe^[35]). However, to the best of our knowledge, there has not previously been a synthesis of any chalcogenide nanowire (including mono, di, and tri-chalcogenides) of group-IV and V transition metals (e.g., Nb, Ta, Ti, Hf, and Zr) by VLS. These metals have high melting points and low vapor pressure (e.g., Nb and Ti) and do not form liquid eutectic compositions with a metal such as Au in the typical CVD temperature range of 600-900 °C, as needed for successful VLS growth.

Here, we report a newly developed VLS mechanism that overcomes these challenges to enable synthesis of TMTs, as demonstrated by growth of NbS₃ 1D nanostructures. The method is based on the use of a unique alloy VLS catalyst composed of Au and an alkali metal halide, such as NaCl, in combination with solid precursors for Nb and S. We note that our growths are the first to use both NaCl and Au, for any metal chalcogenide growth based on CVD (including mono-, di-, and trichalcogenides). As we discuss below, salt is known to react with transition metals and their oxides (such as Nb/NbO_x) to form intermediate products that have high vapor pressure and lower melting points.^[36,37] Under these conditions, the addition of Au catalyst with NaCl enables VLS growth with the consequent control of 1D nanostructure dimensions, morphology, and growth locations.

We show that this newly developed growth strategy, which we refer to as salt-assisted VLS growth, results in high-density 1D materials of MX_3 with sub-ten nanometer diameter and lengths up to several tens of micrometers, the regime in which strongly correlated physics starts to emerge.^[3] In addition, using elec-

tron microscopy techniques (electron diffraction and atomicresolution scanning transmission electron microscopy), we show that the materials exhibit several distinct 1D morphologies, such as wires and ribbons and two growth orientations, namely [010] and [100] directions. We present strategies to control the growth of 1D NbS₃, varying the nanostructure size through the growth time, the 1D morphology through the catalyst size, and the growth location via catalyst patterning. We demonstrate the synthesis of other TMT nanowires, namely NbSe₃ and TiS₃, using the same approach. Finally, we propose a new growth mechanism highlighting the important role of the alloyed Au-NaCl catalyst enabling the nucleation and growth of 1D MX₃ from group-IV and V transition metals (M = Nb, Ta, Ti, Hf) via VLS. Our proposed mechanism is consistent with these findings based on the relationships we measure between the NbS₃ growth orientation, morphologies, catalyst diameter, growth time, and nanowire dimensions. Our study introduces an opportunity to expand the library of vdW materials toward emerging 1D materials, and we anticipate that the deterministic synthesis will enable the integration of 1D quantum materials into next generation quantum electronics. We also propose this as a more general approach for exploring nanowire synthesis of groups IV and V heavy metal compounds (e.g., oxides of Mo, W, Ta, Hf) based on an alloy catalyst containing both a metal and an alkali metal halide.

2. Results

2.1. Structures and Growth Orientations

We show in **Figure 1** an overview of the types of structures that we have obtained through salt-assisted VLS growth of NbS₃. Figure 1a illustrates growth over a large area, showing a high density of 1D structures with spherical particles at one end, indicative of the VLS mechanism.^[38] In this example, diameters in the range of 10–500 nm and lengths up to tens of micrometers were obtained for 30 min growth at 725 °C using 10-nm Au catalyst film. Figure S1, Supporting Information shows the selectivity of this growth, with locations controlled through patterning of Au on a SiO_x/Si substrate.

This growth and all others presented below were obtained in the deposition system shown in Figure S1b, Supporting Information, with a process that was further described in the Experimental Section. We studied growth on both bulk substrates (amorphous SiO_x/Si, SiN, sapphire, and mica) and on 2D vdW materials (single to few-layer graphene and hexagonal BN) transferred onto SiN TEM grids (Figure S1b,c, Supporting Information). Au with thickness in the range 0-50 nm was evaporated onto these substrates to provide the VLS catalyst metal; on heating, these films agglomerated into droplets from which the nanostructures grew. The solid source for Nb was mixed with NaCl. The salt was intended to react with the Nb powder precursor to form intermediate products with lower melting point, aiming to enhance the vapor pressure and increase the mass flow.^[36,39] We note that below 650 °C, the evaporation rate was very limited and the growth resulted in short and small structures. On the other hand, above 800 °C, we observed mostly NbS₂ phases (Figure S2, Supporting Information). The formation of TMTs (NbS₃) rather than TMDs (NbS₂) or other compositions depends on the source material and



Figure 1. VLS growth of NbS₃ 1D materials. a) A representative SEM image of 30-min growth on a SiO_x/Si substrate showing high density of 1D nanomaterials. Inset: High magnification SEM image displays the presence of nanoparticles residing at one end of the 1D materials. b) High-resolution TEM image with electron diffraction pattern inset. c,d) Atomic-resolution EDS chemical composition mapping of a NbS₃ nanowire showing Nb and S distribution. e–h) Typical morphologies of as-synthesized NbS₃ 1D nanostructures: nanowires having growth orientation [010] (e) and nanoribbons having growth orientation [100] (f–h).

temperature. In group IV metals, the stable phase is a TMC such as GaS or GeSe; while, in group IV and V metals such as Nb, Ti, Hf, and V, both TMTs and TMDs are stable. In these cases, temperature is important, with TMDs reported more stable at high and low temperatures.^[40] Our results are therefore in agreement with observations of the conversion of NbS₃ to NbS₂ at high temperature (1000 °C).^[40] In our experiments, an optimum temperature for TMT formation is found to be 725 °C and this is used for all the growths discussed below, unless indicated otherwise.

Atomic structure and chemistry of the as-synthesized materials are measured by electron microscopy. Atomic-resolution TEM images and electron diffraction (Figure 1b) reveal the Nb-Nb repeat distance along the chain direction is $b = 3.36 \pm 0.12$ Å; while, the other lattice parameters are $a = 9.63 \pm 0.21$ Å and $c = 19.62 \pm 0.29$ Å. These parameters indicate that the deposited material is monoclinic NbS₃ (NbS₃-II phase), a stable and metallic phase of NbS₃ that has previously been synthesized in the bulk.^[24,25] Atomic-resolution energy dispersive spectroscopy (EDS) shows that the 1D structures are composed of S and Nb with atomic ratio $S/Nb = 3.23 \pm 0.20$, matching closely with the stoichiometry expected for NbS₃ (Figure 1c,d; Figures S3 and S4, Supporting Information). Examples of quantitative measurements, including lattice parameters, EDS spectra, and EDS quantification are shown in Figure S3, Supporting Information. We note that there is \approx 1–5at% of Na and Cl in our samples as impurities. This EDS characterization also reveals that, post-growth, the particle contains Au, Nb, S, and notably, Na and Cl (Figure S5, Supporting Information). This observation suggests a second role of NaCl due to its presence in the VLS catalyst, in addition to its use as an evaporation promoter, as reported in the literature.^[41,42] We note that our growth is the first to use both NaCl and Au for any metal chalcogenide (including mono-, di-, and tri-chalcogenide) growth by CVD. We discuss below the critical role of NaCl in forming a unique alloyed VLS catalyst that guides the growth of MX_3 1D structures.

Figure 1e,f highlights the two morphologies of 1D materials that we typically see in our synthesis: one type is straight with an approximately square cross-section (referred to as nanowires [NWs], Figure 1e); while, the other has a ribbon morphology and rectangular cross section (referred to as nanoribbons [NRs], Figure 1f-h). We note that Figure 1e, f is representative of our synthesized materials regardless of the substrate; either SiO_x/Si or few-layer graphene suspended on a SiN TEM grid (Figure S1c, Supporting Information). The growth is reproducible: in a typical 30 min-growth using 10 nm Au; more than 90% of the Au droplets have nucleated a nanostructure. The cross-sectional area of NbS₃ nanowires does not change greatly along the nanowire. In contrast, NbS₃ nanoribbons are more variable. Their cross section is rectangular (Figure 1f-h), with non-planar sidewalls and growth direction varying along the length. A typical nanoribbon has a uniform width throughout its length (Figure 1f); while, we also observe other nanoribbons that show tapering (Figure 1g,h) or a non-uniform cross-section (Figure 1h). Moreover, many nanoribbons are thin and do not remain attached to the substrate. Some curl up toward the free-end tip, resembling a spiral structure (Figure 1f). Similar "topological crystals"^[43,44] have been

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Figure 2. Atomic structure of VLS NbS₃ 1D structures. a,b) Atomic-resolution HAADF–STEM images of a typical b-nanowire (b-NW) (a) and ananoribbon (a-NR), showing the catalyst (bright region). The growth orientations are indicated by the white arrows (b). c) Bilayer stacking disorder in a-NR. Rotation and rigid body shift between adjacent bilayer domains, indicated by the red and blue arrows, respectively, result in boundaries, some of which are displayed as the white dashed lines within the structure. (Inset): Higher magnification image of NbS₃ chains showing ordered regions and stacking disorder. Further examples of stacking disorder are shown in Figure S7, Supporting Information.

observed in bulk NbSe₃ and TaSe₃ synthesized by chemical vapor transport.^[43] Measurements of the cross-section areas, lengths, and diameters of different NbS₃ morphologies can be found in Figure S6, Supporting Information.

Atomic-resolution imaging provides more insight into nanowire and nanoribbon morphology. In **Figure 2**, high-angle annular dark-field (HAADF) STEM images show two distinct growth orientations, [100] (interchain) in Figure 2a and [010] (intrachain) in Figure 2b, in which the chain direction is parallel or perpendicular to the material growth direction, respectively (see atomic models in Figure S1a, Supporting Information). We will therefore refer to the nanostructures as b-nanowires (b-NW) and a-nanoribbons (a-NR), respectively, following the crystallographic convention that b is the chain direction in the crystal structure. Viewing the structure along the b direction, as in Figure 2c, visualizes the bonding of neighbor chains into bilayers, a signature of TMT materials.^[3,23]

A prominent feature of both types of nanostructures is the variation in the stacking sequence and orientation of the bilayers. The stacking defects are clearly displayed in a-NRs oriented so that the prismatic chains point in the beam direction (Figure 2b,c; Figure S7, Supporting Information). This end-on view provides a unique perspective of how the bilayers stack and arrange. In few-nm domains, the bilayers stack in the same orientation with a rotation or rigid body shift between neighboring domains. In b-NWs, the disorder is visible in the variable spacing between the vertical lines (dark in TEM imaging, bright in STEM) in Figures 1b and 2a and in the streaking in electron diffraction shown in the inset of Figure 1b. The different crystal phases of NbS₃ are known to form depending on the growth conditions.^[24,26] The structure of the self-assembled NRs suggests that this may in part be attributed to the fact that the bilayer arrangement appears prone to stacking defects such as rotations and rigid body shifts, especially if new material is being added along the side of a series of chains. Changes in stacking order introduced during growth may eventually result in the different polymorphs reported in the literature.^[24,26]

2.2. Size Control of 1D NbS₃ Structures

We find that the nanostructure length can be controlled through the growth time. **Figure 3**a–c shows growths using 10-nm Au films on SiO_x/Si substrates for different periods of time with post-growth SEM showing the length of the nanostructures (Figure 3d). The catalyst sizes for the three growth times are comparable (250 ± 120 nm) and are similar to droplet sizes after heating in the absence of the growth flux (Figure S6a, Supporting Information). This is consistent with dewetting kinetics of a uniform film where rapid initial dewetting is followed by a slowerchanging configuration.^[45] After 5 min, we see short nanowires (90 ± 30 nm) emerging from several catalyst particles. At this stage, it is hard to distinguish between a-NRs and b-NWs based on our SEM resolution. After 15 min, almost all catalysts form a nanostructure; the average length is 420 ± 140 nm and one can start visually differentiating between a-NRs and b-NWs. For





Figure 3. Size control of 1D NbS₃ materials. a–c) SEM images of NbS₃ growth using 10-nm Au catalyst film for growth times of 5, 15, and 30 min. d) a-NR and b-NW length as a function of growth time. For each growth, 50–150 nanostructures are measured, exclusive of droplets without visible growth. The dash purple line indicates a linear fit to extract the growth rate. e) Diameter of a-NR and b-NW as a function of Au diameter for 10 and 15-nm-thick Au (the thicknesses that produced the highest nanostructure yield). For a-NRs with a rectangular cross section, the longer side is used, as defined in Figure S6a, Supporting Information schematics of a-NR and b-NW that indicate length, diameter, and thickness. The purple line represents a 1:1 ratio of catalyst/nanowire diameters.

30-min growth (a typical growth time for data presented in this study), a-NRs are longer with an average length of 1300 ± 480 nm and b-NW are shorter at 650 ± 360 nm. A linear fit to length data (Figure 3d) suggests an incubation time before growth begins of ≈ 2.5 min. After that period, the nanostructures elongate linearly with a rate of 29.0 ± 8 nm min for a-NRs and 25.0 ± 12 nm min⁻¹ for b-NWs. We note that the deviation in the measurement might partially come from the tilt of the structures, with respect to the imaging direction.

The diameter of the 1D NbS₃ materials can also be controlled with catalyst droplet size. Figure 3e shows the diameter of individual a-NRs and b-NWs as a function of their catalyst diameter for two growths that used 10-nm and 15-nm Au films. These films dewet to produce droplets with different but overlapping size distributions.^[45] Other growth conditions such as precursor mass, growth temperature, and growth time are kept the same. It appears that for both growths, the a-NRs have diameters comparable to their droplet diameter. This relationship is typical amongst VLS nanowires grown from other materials.^[46] On the other hand, the diameter of b-NWs is smaller than their catalyst diameter; the ratio of catalyst/nanowire diameters for b-NW in both cases is \approx 1.8. It is worth noting that the a-NRs observed here are distinctive compared to what has been reported in nano-ribbon structures of oxides,^[47] such as ZnO and SnO₂, and layered materials;^[48] for example, Bi₂Se₂ and GaSe. In these materials, the catalyst diameter is often much smaller than the width of the ribbons and the droplets reside at one corner of the ribbon's top surface (somewhat like the structure in Figure 1h). The growth mechanisms of these ribbon structures are therefore often attributed to a mixture of both VLS and vapor-solid (VS) mechanisms^[47,48] with VS dominating and creating highly tapered structures. We will compare the growth mechanism of our NbS₂ a-NRs with these reports in the subsequent discussion. We note that the smallest diameter observed in our 1D NbS₃ nanostructures is ≈ 10 nm, which is defined by the catalyst droplet size. According to the curvature-induced Gibbs–Thomson effect^[49] in the droplet and the nanowire, small nanowires will not grow stably. This sets a lower limit for the catalyst size in VLS growth, which is \approx 3–5 nm for many semiconductors (e.g., Ge^[50]). In addition, many TMTs are reported to be sensitive to the environment: at the nanoscale, such effects could be intensified due to a high volume of surface atoms. Both factors contribute to a lower limit for NbS₃ nanowire diameters that we expect can be synthesized, yet stable. We note that there are several studies in which these challenges were overcome by growing single atomic chains of TMTs within the cavity of nanotubes.^[7,17]

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0 nm Au film





Figure 4. Relationship between Au thickness and NbS₃ morphology. a–e) SEM images of NbS₃ structures synthesized using Au thin films with different thickness (0, 1, 5, 10, and 15 nm) for the same growth time of 30 min and growth temperature of 725 $^{\circ}$ C. For 50-nm Au, refer to the patterned growth in Figure S1d, Supporting Information. f) Population percentage of 1D structures without Au catalyst particle, a-NR and b-NW observed in the growths using different Au film thicknesses.

2.3. Morphology Control of 1D NbS₃ Structures: Nanowires Versus Nanoribbons

We now investigate the role of Au in determining the growth morphology, particularly whether VLS growth takes place at all and whether the structure is an a-NR or b-NW. We find that the deposited Au thickness, or equivalently, the catalyst size,^[45] does affect the nanostructure type (Figure 4). Figure 4a shows growth on SiO_x/Si substrates without Au catalyst (0 nm Au film), resulting in mostly b-NWs. This non-catalyzed growth mode is shown in more detail in Figure S8, Supporting Information. 1-nm and 5-nm Au films similarly result in no VLS nanowires (Figure 4b,c). NbS₃ nanostructures are visible but are broad and flat, similar to what we observe in growth without Au (Figure 4a) and are decorated by several small droplets around their edges instead of having a single particle at one end, as in the typical VLS nanowires in Figures 1 and 2. This suggests that for thin Au (1 and 5 nm), the NbS₃ 1D structures nucleate spontaneously and Au particles attach to them. With thicker Au (10, 15, 50 nm), the grown materials show the telltale signatures of VLS growth described above. Further, the nanostructure type is correlated with the Au film thickness. The fraction of the population that consists of a-NR, b-NW, and uncatalyzed growth in experiments using different Au film thicknesses is shown in Figure 4f. As the film thickness increases, a-NRs become dominant. This trend is most striking at 50-nm Au, where a-NRs make up 70% of the grown nanowires.

In Figure 4e, we show that on a single substrate, a-NRs and b-NWs grow from an overlapping distribution of Au droplets, but there is a trend for the larger droplets to produce more a-NRs. The increasing proportion of a-NRs in thicker Au films is consistent with this observation because thicker films dewet into droplets that are larger on average. Overall, we suggest that the possibility exists for controlling the 1D morphologies of NbS₃ by choice of the Au film thickness or by using catalysts of well-defined initial size.

Au film thickness (nm)

2.4. Materials Control: Salt-Assisted VLS Synthesis of Other 1D Transition Metal Trichalcogenides

We extend our salt-assisted VLS method to synthesize nanostructures in two other vdW chain materials, NbSe₃ and TiS₃, to explore the generality of the approach to a variety of transition metals (Nb, Ti) and chalcogens (S, Se). **Figure 5** shows representative SEM images of NbSe₃ and TiS₃ 1D structures with SEM-EDS elemental mapping shown in Figure S9, Supporting Information. We note that for NbSe₃, the yield of 1D materials at the optimum NbS₃ growth temperature of 700–750 °C is lower than in the growth of NbS₃. To increase the density of NbSe₃ nanostructures, the substrate temperature is raised to the 800–850 °C range. The result is NbSe₃ with nanowire morphology (Figure 5b) with [010] growth orientations, similar to NbS₃ and consistent with the



Figure 5. Salt-assisted VLS growth of various TMTs. SEM images showing 1D nanomaterials observed in the salt-assisted VLS growth of a-c) NbSe₃ and d-f) TiS₃.

similarity of the NbSe₃ and NbS₃ crystal structures. However, we also observe plate-like half-hexagon structures stemming from a single Au catalyst (Figure 5c). We attribute this 2D-like structure to the presence of the layered hexagonal material NbSe₂ because at the high growth temperature, NbSe₂ is known^[51,52] to be more stable than NbSe₃. This is analogous to the presence of NbS₂ at high growth temperatures discussed above and in Figure S2, Supporting Information. TiS₃ synthesized under the same condition as NbS₃ (Figures 5d-f) displays a mix of 1D wire and truncated trapezoid morphology. By analogy, we suggest that at 700–750 °C, there exists a mix of 1D TiS3 and 2D TiS2, $^{[12,53]}$ which results in structures having mixed features of wire-like (1D) and plate-like (2D) morphologies. Optimization of the synthesis parameters, mostly the interplay between the temperature of the substrate and precursors and even the choice of alkaline metal halides,^[54] should offer prospects for improving the density of NbSe₃ nanowires and increasing the proportion of the 1D phase of TiS₃.

2.5. The Mechanisms at Work During Salt-Assisted VLS Growth of MX_3 1D Nanostructures

To understand potential growth mechanisms that could describe the above results, we consider the relationships among the source materials, growth parameters, and morphologies of NbS₃ 1D nanostructures. We first discuss the possible role of NaCl in VLS growth. We note that our growth is the first to use both NaCl and Au for any metal chalcogenide (including mono-, di-, and tri-chalcogenide) growth by CVD. NaCl alone has been shown as an effective growth promoter in the synthesis of 2D vdW materials such as MoS_2 , WSe_2 , and $NbSe_2$.^[41,42] In these cases, it was suggested that NaCl reacts with transition metal precursors, for instance the metal and its oxide (e.g., MoO_3 , W, Nb_2O_5), to create volatile intermediate compounds (metal oxychlorides) with much lower melting points, and thus, higher vapor pressures at a given growth temperature compared to the metal or metal oxide precursors alone.^[36,37] For example, the possible reaction route for the case of WSe₂ is:^[42]

$$3WO_3(s) + 2NaCl(s) \rightarrow Na_2W_2O_7(l) + WO_2Cl_2(g)$$
(1)

The nucleation and growth of WSe₂ take place by a dissociation/formation reaction to replace W—O and W—Cl bonds at the step edges of the material by W—Se bonds, as suggested recently in Ref.[54]:

$$WO_{2}Cl_{2}(g) + 2Se(g) + 3H_{2} \rightarrow WSe_{2}(s) + 2HCl(g) + 2H_{2}O(g)$$
(2)

In our growth of NbS₃, we postulate that similar reactions between the NaCl and Nb (presumably with an oxide shell, Nb₂O₅, because the source was prepared and growth carried out at ambient pressure^[55]) generate metal oxychloride products, such as NbOCl₃, which has a moderately low melting point of 200 °C.^[56] These volatile species are then transported to the growth substrate simultaneously with the S vapor (see the growth setup in Figure S1, Supporting Information) to initiate the formation of the final structure. A control experiment using only Nb or S results in little or no NbS₃ formation, suggesting that virtually no evaporation of the Nb precursor takes place at 600–850 °C. This supports the role of NaCl as an evaporation promoter.

However, our EDS results mentioned earlier and shown in Figure S5, Supporting Information indicate a second potential role of NaCl in our VLS growth of NbS₃ nanowires. We find that post-growth catalyst particles contain not only Au, Nb, and S but also Na and Cl. The Na and Cl concentrations are comparable to those of the growth species, suggesting that this is not merely a small contamination of NaCl arising from its role as

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a growth precursor. This observation may help explain why, to the best of our knowledge, there has not previously been a synthesis of any chalcogenide nanowire (including mono, di, and tri-chalcogenides) of group-IV and V transition metals by VLS. VLS growth generally requires the formation of a eutectic between the catalyst and the nanowire materials. However, Au does not form eutectic droplets with Nb or S (based on the individual binary phase diagrams) below 1064 °C, the melting point of Au. The lack of a reactive Au compound to act as a VLS catalyst has been demonstrated in the literature for some growths of transition metal dichalcogenide materials, for example MoS₂ and WS₂, where Au only serves as a growth substrate^[57] or nucleation point^[58] rather than directly participating in the growth process. Moreover, Au foil and deposited Au triangles in the presence of transition metals (Mo, W) and chalcogen (S) vapors in these studies (at a similar temperature range of 650-750 °C to that used in our synthesis) do not react, instead, remaining in their original morphologies^[58] rather than transforming into spherical particles, as we observed (post-growth) in our NbS₃ experiments. In this regard, we hypothesize that the catalyst droplet forms as a eutectic composition of Au and Na/Cl-containing intermediates at our growth temperature of \approx 725 °C. We suggest that NaCl vapor (abundant at the growth temperature of 725-750 °C) is mobile under the growth conditions and is able to be incorporated into the Au nanostructures. We note that the post-growth spherical shape of the catalyst particles and observations we have made of adjacent particles that have merged could imply a liquid eutectic state during the growth.

We therefore propose that NaCl in our growth plays two roles. It serves as an evaporation promoter that reacts with Nb precursors to create volatile metal oxychloride intermediates (one possibility being NbClO₃), which enhance the mass flux of precursors to enable or accelerate growth at low temperatures (650–750 °C). We also suggest that NaCl vapor may adsorb on Au and form a eutectic alloy, creating a reactive liquid surface at which Nb vapor compound(s), such as NbClO₃ and S, are incorporated after arriving from the vapor phase to result in NbS₃ nanowires via the VLS mechanism.

We now consider the morphologies produced as growth proceeds. In VLS, the growth species have two pathways^[59] by which adatoms incorporate into the growth front of a nanowire. The first pathway, which is unique to VLS growth, is adatom absorption through the catalyst droplet, assumed due to a higher sticking coefficient on the droplet surface compared to the substrate; this drives supersaturation of the growth species in the droplet, and therefore, subsequent nucleation and growth of atomic layers at the catalyst-nanowire interface.^[38] To validate that this VLS pathway is indeed active in the formation of our nanostructures, we perform an interrupted growth in which a TEM-compatible substrate (Figure S10a, Supporting Information) is imaged directly after growth and then returned to the furnace for a second growth under the same conditions (Figure S10b, Supporting Information). Comparison of the images for one NbS₃ b-NW (marked by the red rectangle) show that growth takes place at the catalystnanowire interface (Figure S10c, Supporting Information), as expected for the VLS mechanism, rather than, for example, at the non-Au tip of the nanowire.

The second pathway involves either direct impingement onto the sidewall or adatom diffusion from the substrate to some part of the nanowire, followed by diffusion along the nanowire sidewalls and incorporation at any part of the nanowire surface, resulting in growth via the vapor-solid (VS) mechanism.^[46] This type of surface diffusion pathway is similar to the growth mechanism suggested in salt-assisted synthesis of 2D transition metal dichalcogenide materials,^[36,54] in which MoS₂ grows quickly by reaction and attachment of adatoms preferentially at the step edges. As the overall geometry and nature of the surface are important parameters in the VS process, we might expect the VS pathway to have a different overall effect on a-NRs and b-NWs. These nanostructures exhibit surfaces with different attachment sites and diffusion parameters due to the relationship between the anisotropic crystal structure and the growth direction. For b-NW, with growth orientation [010] or intrachain orientation, the available surface for transporting adatoms is along the chains. For a-NRs, with growth orientation [100] or interchain orientation, the surfaces present are either parallel to the chains or composed of a perpendicular plane that cuts through chains. b-NWs generally show flat step-free surfaces, suggesting that diffusion along these planes is fast and attachment is difficult unless steps are present. a-NRs show rougher surfaces implying that attachment is more favorable. This may therefore imply that a-NRs could be growing with a proportionally larger contribution from VS compared to VLS growth. This is consistent with the greater variety in shape and frequent tapering visible in a-NRs, as shown in Figure 1f-h. Indeed, a general observation, when considering the contribution of VS to a VLS process, is that each nanostructure may be affected differently due to the variable geometry of the sidewalls present. Here, some a-NRs crawl along the surface while others grow off the surface (Figure 1). This may account for the scatter in data for dimension and growth rates in Figure 3d; Figure S6, Supporting Information, even for similar catalyst diameters, and hence, VLS growth rates.

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We finally discuss the factors that determine whether growth will produce a-NR or b-NW morphologies. In VLS growth (in the most general case, say where droplets are present on an amorphous substrate), the initial nucleation event is the formation of a small crystallite either at the triple phase line or at the droplet surface.^[60,61] The shape of this nucleus depends on the energies of the interfaces between the growth material and droplet material, growth material and substrate, and growth material and vapor phase. These parameters are generally unknown, but in growths without Au catalysts (Figure 4a), we observe structures that appear more like b-NWs (Figure S8, Supporting Information). This suggests that in NbS₃, the planes that are parallel to the chain directions may have lower energies. If the initial nucleus follows these energetic considerations, it is likely to be elongated in the b direction. Needle-shaped nuclei lying at the droplet surface will create a-NR structures as material is added to the planes parallel to the chain directions. However, if the nucleus rotates^[60] at all, then elongation along the b direction becomes impossible and a b-NW is more likely to result. Geometrically, we might therefore conclude that a larger droplet with lower surface curvature favors the orientation of needle shaped nuclei parallel to the droplet surface, and hence, the growth of a-NRs. This is consistent with our finding that thicker Au films produce more a-NRs compared to the number of b-NWs. This simple argument neglects the complexities of the energetics and kinetics; further

experiments with well-defined catalyst geometry would help to explore these possibilities.

Based on these discussions, we propose that the salt-assisted VLS synthesis of NbS₃ 1D nanostructures operates simultaneously with a VS mechanism that appears to contribute relatively more to the growth of a-NRs. We suggest that the morphology that is produced depends on the geometry present at the nucleation event, and this may depend on the anisotropy in surface energies and growth rates for the nucleus. Further studies with size-selected Au nanoparticles, rather than the dewetted films used here, will enable exploration of the specifics of how the catalyst-related VLS and attachment/diffusion-related VS pathways favor the formation of a-NR versus b-NW morphologies.

3. Conclusion

We present a growth strategy that uses an alloy from Au and NaCl as a catalyst to synthesize a variety of 1D vdW materials, NbS₃, NbSe₃, and TiS₃ on bulk substrates (SiO_x/Si, SiN, sapphire, mica), as well as on van der Waals surfaces (graphene, hexagonal BN). The method we describe, salt-assisted VLS growth, combines key benefits of both vapor-liquid-solid and salt-assisted growth processes. We show that the thickness of the Au film that dewets to form the catalytic droplets and the positions at which it is patterned onto the substrate offer the ability to control the size and location of the structures, as is the case in a conventional VLS process. The presence of salt offers advantages of fast growth at moderate temperatures (650-750 °C), producing a high yield of NbS3 nanostructures with sub-ten nanometer diameter and lengths up to several tens of micrometers within a relatively short time (15-45 min), compared to growth in the absence of salt. For NbS₃, we describe two distinct morphologies that result from this growth mechanism: b-NWs, straight nanowires in which the growth direction is along the chain direction ([010]) and a-NRs, where dimensions are more variable and growth is perpendicular to the chain direction ([100]). We outline the key synthesis parameters, particularly the growth time and the thickness of the initial Au film, that influence the dimensions and morphologies of these different NbS₃ 1D structures. We show in particular, that thicker Au (50 nm) results in more a-NRs; while, thinner initial Au (10 nm) favors the growth of b-NWs. The diameter of b-NWs can be constrained within a small range (80-100 nm) by controlling the Au layer thickness, and hence, the droplet size after Au dewetting. We demonstrate the generality of salt-assisted VLS growth by creating nanowire morphologies in other 1D transition metal trichalcogenides, NbSe₃, and TiS₃. We explore the details of the salt-assisted growth mechanism through the relationship between morphology and growth parameters. We propose the coexistence of two pathways, catalyst limited growth and surface diffusion limited growth (VLS and VS), to account for the difference in the growth rates, geometry, and relative frequency of NbS₂ a-NRs and b-NWs.

We believe that our demonstration of this new growth mechanism for nanowires and nanoribbons of transition metal trichalcogenides (NbS₃, NbSe₃, and TiS₃) will expand the ability to grow emerging 1D vdW materials, including their heterostructures, and make use of their properties. We propose that our method will also create opportunities to explore nanowire synthesis and nanowire heterostructures in group IV and V heavy-metal www.advmat.de compounds (e.g., oxides of Mo, W, Ta, and Hf). The synthesis of oxide nanowires of Mo, W, Ta, and Hf based on vapor-phase synthesis, including VLS, is challenging, mainly because of the difficulty of creating and supplying sufficient vapor pressure of the metal precursors. The results obtained for NbS₃ show this challenge can be overcome with the presence of salt under appropriate conditions; in this way, the reactants can be incorporated into a catalyst particle, as in the case of conventional VLS, to direct the growth of nanowires. Further measurements are required to explore the range of applicability of the salt-assisted VLS process, including the effect of catalyst diameter^[50] and combinations of different salts and metals^[54] on the growth kinetics of TMTs, and the role of salts as dopants^[62] introduced during the growth to manipulate the materials' electronic properties.

Going forward, it is important to measure the properties of the grown nanostructures to establish any effects of the catalytic elements present. It will then be possible to understand how the native anisotropy of these synthesized TMT materials governs properties such as conductivity and linear dichroism and how the defects we see within the selfassembled nanostructures affect their electrical and thermal transport properties. The capability we have demonstrated, to create TMT nanostructures with some control of diameter and growth location, opens opportunities for such studies. We anticipate a greater understanding of the basic science of this versatile class of materials and technological advances as components of quantum devices where precise placement of individual identical nanowires is required,^[63] for example, in nano-thermoelectrics, fault-tolerant quantum circuits, high current-density interconnects for nanoscale electronics,[14,18,27] or a new generation of neuromorphic devices exploiting the collective excitation (charge density wave) nature of TMT materials.^[21]

4. Experimental Section

Substrate Preparation: SiO_x/Si , SiN, a-sapphire and mica bulk substrates were cleaned with isopropanol and deionized water, followed by oxygen plasma (150 mTorr, 5 min). To create 2D substrates, few-layer graphene and hexagonal boron nitride were first mechanically exfoliated by a Scotch-tape method; then, transferred onto holey SiN TEM grids. Au films were then e-beam evaporated onto the substrates with different thickness (1, 3, 5, 10, 15, 30, and 50 nm).

CVD Growth: 50 mg of Nb powder was mixed with 25 mg of NaCl (Sigma-Aldrich), and, the mixture was loaded into an alumina boat. A growth substrate was placed upside down right on top of the precursor mixture and the Nb/NaCl/substrate boat was set to a temperature of 650-800 °C. 150-200 mg of S (Sigma-Aldrich) was put upstream and far away from the hot zone. The S boat was kept at room temperature in the beginning of each growth and it was pushed into a hot zone (130-150 °C) only after the Nb/NaCl/substrate boat reached the target temperature. 100-150 sccm of high purity Ar (Airgas) was used as the carrier gas. The growth time varied from 5 to 45 min. At the end of the growth, the carrier gas was turned up to 200 sccm and the tube furnace's cap was open to cool down the furnace quickly. For growths on 2D materials on SiN TEM grid, a boron nitride holder was machined, which allowed to load a TEM grid upside down to maintain the same growth setup as in the growths using a bulk substrate. For the growths of NbSe₃ and TiS₃, the same growth parameters were used, except $T_{\text{growth}} = 800 \,^{\circ}\text{C}$ for NbSe₃ and 50 mg of TiO₂ for TiS₃ synthesis.

Material Characterization: SEM imaging was carried out at 5–20 kV on an FEI Helios Nanolab 600. S/TEM characterization was carried out

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in a Themo Fisher Scientific Themis Z STEM operated at 200 kV. Typical aberration-corrected STEM imaging conditions were 19 mrad semiconvergent angle (resulting in an estimated sub-angstrom probe size) and 80 pA probe current. Energy dispersive spectroscopy (EDS) was collected at a higher probe current of 120–200 pA. Electron energy loss spectroscopy (EELS) was collected using a JEOL ARM200 equipped with a K2 pixelated camera. Quantitative measurements, including lattice parameters and chemical composition by EDS, were carried out using GMS (Gatan Inc.) and Velox (ThermoFisher) software. Examples of the procedure used are shown in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

T.P. and F.M.R. conceived the project. T.P. developed the synthesis and acquired electron microscopy data. K.R., J.D.T., B.W., and N.D. contributed to the growth process. T.P., M.A.F., and F.M.R performed analysis. T.P. and F.M.R. wrote the manuscript with input from all authors. M.A.F and F.M.R. supervised the project and acquired funding.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

1D van der Waals material, nanowires, niobium trisulfide, salt-assisted growth, vapor-liquid-solid

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