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Systematic study of CVD-growth parameters in NaCl-assisted growth

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of MoSe₂ nanostructures: Nanoribbons, Dendrites and Spirals

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Abstract:

8 MoSe₂, a two-dimensional (2D) transition metal dichalcogenide (TMDC), has garnered 9 significant interest in recent years due to its semiconducting properties and tunable band gap with potential applications in optoelectronics, photocatalysis and atomically thin devices. In 10 this study, we report the controlled synthesis of $MoSe_2$ nanocrystals using a custom 12-zone 11 atmospheric pressure chemical vapour deposition (APCVD) system. NaCl is used as a seed 12 13 promoter to facilitate the growth of monolayer, bilayer, and multilayer films, often as large as 14 200 μ m. Additionally, the morphological evolution of MoSe₂ nanostructures is controlled by 15 tuning different growth parameters based on insights which we discuss in detail. The growth of dominant nanostructures, which include nanoribbons, snowflakes, monolayers and 16 multilayer domains, among others, are discussed. High-resolution optical microscopy, field 17 18 emission scanning electron microscopy (FESEM) and Atomic Force Microscopy (AFM) are used to image the as-grown crystals. Raman spectroscopy and X-ray photoelectron 19 spectroscopy (XPS) are used to verify the quality and elemental composition of our as-grown 20 21 MoSe₂ crystals. Our findings brighten the prospect of growing novel 1D and 2D TMDC 22 nanostructures with sufficient control to make them suitable for advanced optoelectronic and catalytic devices. 23

24

25 Keywords: MoSe₂, Chemical vapor deposition, NaCl, nanoribbons, dendrites

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27 1. Introduction

View Article Online Over the last decade, two-dimensional layered transition metal dichalcogenides (TMDCS), Din A00121H 28 29 general, have attracted significant attention because of their exceptional electronic and optical characteristics (1-4). Of these, MoS₂ and MoSe₂ have been particularly popular because of the 30 promise they hold for a range of applications. Within these, monolayer or few-layer MoSe₂ 31 nanostructures exhibit superior behaviour to MoS₂ due to their unique band structures (5-8). 32 Few-layer 2D TMDCs, including MoSe₂, offer enhanced mechanical and chemical stability 33 compared to their monolaver counterparts, making them more suitable for use in FETs. This 34 35 stability is crucial, as it allows these materials to withstand the harsh conditions encountered during device fabrication. An increased number of layers also provides a larger number of 36 transport channels and results in higher on-state current and carrier mobility (9). 37

Chemical vapor deposition (CVD) has been widely used to synthesize highly crystalline and large-area MoSe₂ films. The successful growth of MoSe₂ on SiO₂/Si substrates using CVD was first reported by Shaw *et al.* (10). Since then, there have been several reports of large-area MoSe₂ nanocrystals grown by CVD on many other substrates (11–14). Chang *et al.* (7) compared the optical and electronic properties of CVD-grown MoS₂ and MoSe₂ and found that the number of defects was lower in the latter. This was in part explained by Wang *et al.* (15), who initiated a discussion of the growth mechanisms involved in CVD-grown MoSe₂.

45 Two of the important growth mechanisms are worth noting. With the metal oxide 46 precursor and substrate conventionally placed in a high-temperature zone, and the chalcogen in a relatively low-temperature region (12) crystals grow in the vapor-solid-solid (VSS) mode, 47 wherein a solid crystal is deposited directly from the vapor phase onto a solid substrate. Vapor 48 49 phase precursors directly adsorb and react on the substrate surface to form nuclei, which subsequently grow into solid, typically triangular or hexagonal, domains. These shapes are 50 51 dictated primarily by the free energy of the crystal edges and the surface diffusion kinetics of 52 the precursors. However, the morphologies produced by this route are limited.

In contrast, the vapor-liquid-solid (VLS) mode, facilitated by the introduction of alkali 53 halide salts, e.g. NaCl or KCl, alters the free energy of the crystal edges (16,17) and opens/outA00121H 54 55 several new possibilities. This mechanism involves vapor-phase precursors adsorbing onto a catalytic liquid metal droplet, dissolving therein, and later precipitating at the liquid-solid 56 This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence. interface to produce a range of nanostructures such as nanowires and nanoribbons. Several van 57 der Waals layered compounds, including BN (18), NiCl₂ (19), SnS₂ (20) and Bi₂Se₂ (21), have 58 been synthesized by this method. However, control of the morphology and quality of the 59 Open Access Article. Published on 03 June 2025. Downloaded on 6/13/2025 1:47:22 PM resulting MoSe₂ nanostructures continues to be an outstanding challenge. 60 61 62 63 64 65

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In this context, it is worth mentioning that the addition of alkali halides to the metal oxide enhances the growth rates and sizes of the resulting crystals (or continuous films) and reduces the growth temperature. Li et al. (22) reported that large WSe₂ and WS₂ monolayer crystals could be grown at moderate temperatures (700-850°C) using alkali metal halides as growth promoters. Li et al. (23) demonstrated a dramatic enhancement in the growth of 2D TMDCs selenides and tellurides, namely MoSe₂ and WTe₂, using mixed transition metal salts 66 and chalcogen salts. The addition of salts induced the wafer-scale growth of these TMDCs, 67 forming a continuous monolayer film and a large gain size of 100 µm-50 µm. Kim et al. (24) 68 made the same observation with regard to MoS₂. Zhou et al. (25) subsequently demonstrated 69 that molten-salt-assisted CVD can be broadly applied to produce atomically thin TMDC films. 70 71 They also showed that salt assistance increases the overall reaction rate by decreasing the 72 melting point of reactants, which in turn facilitates the formation of intermediate products. For example, metaloxyhalides, formed in reactions between halides and metal oxides, evaporate at 73 relatively low temperatures, enhancing 2D growth in the process. Chen et al. (5) reported the 74 75 controlled CVD growth of large-scale monolayer and multi-layer MoSe₂ films and nanoribbons. Li et al. (26) synthesised single-crystal, monolayer MoSe₂, with domain sizes 76 77 reaching up to 250 µm, by employing NaCl-assisted CVD. Feng et al. (27) reported that 78 increasing the growth temperature in the presence of NaCl leads to drastic changes in the

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morphology of as-grown WSe₂ samples. Singh et al. (28) similarly grew MoS₂ on different 79 substrates and demonstrated that NaCl facilitates the formation of seeding promoters, such parameters and demonstrated that NaCl facilitates the formation of seeding promoters. 80 81 a water-soluble layer of Na₂S and/or Na₂SO₄ on the substrate, which aids in the 2D planar 82 nucleation of MoS₂. Bay et al. (29) further systematised this approach by growing MoSe₂ nanocrystals, using five different water-soluble catalysts (sodium chloride (NaCl), zinc 83 chloride (ZnCl₂), potassium hydroxide (KOH), potassium chloride (KCl), potassium oxalate 84 $(K_2C_2O_4)$. These were applied as thin layers onto the SiO₂/Si substrates. Among these five salts, 85 the use of NaCl resulted in the most uniform growth of the as-synthesised flakes. 86

87 Each TMDC morphology, including nanoribbons, dendrites, fractals, and spiral formations, offers distinct advantages for various applications. For example, 1D nanoribbons 88 have shown significant promise in electronic, magnetic, and catalytic applications (30–33); 89 90 however, the controllable fabrication of MoSe₂ nanoribbons is found to be scant in the literature. Similarly, dendritic and fractal structures are particularly advantageous for catalytic 91 applications owing to the high density of the active edge sites and defects they possess. Studies 92 have shown that the rate of the hydrogen evolution reaction (HER) increases linearly with the 93 density of these features (34–37). The CVD growth of MoS₂ dendrites, as reported earlier by 94 our group (38), can be further enhanced by adding NaCl to the precursor. The formation of 95 dendrites or fractals in MoSe₂ under optimised CVD-growth conditions, as reported here, 96 97 would be suitable for HER catalytic activity. Additionally, spiral structures, which interlink the layers of MoSe₂, provide unique pathways for electrical current, enhancing the vertical 98 conductivity of the devices. This unique morphology was found to notably increase the vertical 99 conductivity in MoS₂ (39), enhancing the overall electrical conductivity and making these 100 101 structures ideal for use in nanoelectronic devices (40). Moreover, the non-inversion symmetry 102 present in these nanostructures gives rise to interesting non-linear optical (NLO) effects, 103 polarization and piezoelectricity, all of which promise to find applications in electronics and 104 optoelectronics (41-43).

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105 In this study, we systematically investigate the morphological evolution of MoSe₂ nanocrystals by varying a set of specific CVD-growth parameters. NaCl is employed as a set of specific CVD-growth parameters. 106 promoter to enhance both the growth rate and size of the crystals. By meticulously tuning these 107 108 parameters, a wide variety of nanocrystal morphologies were successfully synthesized. There are several studies on NaCl-assisted CVD growth of TMDCs available in the literature, as 109 mentioned earlier; but in addition, there are substantial research gaps. Our studies are an 110 attempt to address this gap by correlating the CVD growth of each of these different MoSe₂ 111 nanostructures, including nanoribbons, dendrites, and spiral structures, with specific regions of 112 113 parameter space. This is essential for the controlled growth of large-area crystals with desired morphologies. Initially, an optimal NaCl concentration was identified to facilitate the formation 114 115 of large flakes. Under these conditions, nanoribbons emerged as the predominant 116 nanostructure. Subsequently, by varying growth temperature and the concentration of the chalcogen precursor, a diverse array of nanostructures was obtained. This comprehensive 117 analysis defines the range of achievable morphologies and offers valuable insights into the 118 119 underlying growth mechanisms driving their formation.

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121 2. Experimental Details:

Fig. 1(a) depicts a schematic diagram of the (CVD) setup for MoSe₂ growth. The CVD 122 experiments were carried out in a commercial APCVD system, ORYSTAL-CVD-1100 (44), 123 124 manufactured by Quazar Technologies (45). The furnace comprises twelve independent, 75 mm-long thermal zones, each equipped with its own heater and temperature sensor. The 125 126 temperature of each zone is individually adjustable through an intuitive graphical user 127 interface, allowing for seamless control. Adjacent zones can be integrated by synchronizing their set temperatures, enabling the formation of composite heating regions of variable lengths. 128 129 These zones maintain a temperature uniformity of $\pm 5^{\circ}$ C. This sophisticated system facilitates



131 demands of this study.

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Materials Advances Accepted Manuscript For the deposition of MoSe₂, high-purity molybdenum trioxide (MoO₃, \geq 99.5%, Sigma Aldrich), selenium (Se, \geq 99.5%, Sigma Aldrich), and sodium chloride (NaCl) powders (99.9%, CDH) were used as precursors, and 300 nm thermally oxidised SiO₂/Si wafers were used as substrates. An alumina boat containing 1mg of MoO3 and three substrates placed face down on top of it (labelled 1, 2 and 3 in Fig 1(c)) were loaded into the quartz tube. A gap of 0.5 mm was kept between wafers 1 and 2, which acts as an outlet for the precursor vapor. This ensures that some of the vapors escape the alumina boat, and uniform deposition on wafers 4 and 5 occurs, which were placed face-up adjacent to the alumina boat (Fig. 1(c)). The boat containing Se powder (600 mg) was placed upstream at a distance of 31 cm away from the MoO₃ boat (Fig. 1(a)). For the NaCl-assisted growth experiments, a mixture of the MoO₃ and NaCl powder was

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used.

Prior to deposition, the substrates (10 mm \times 10 mm) were cleaned ultrasonically in 144 acetone and isopropyl alcohol (IPA), respectively, and then dried under Ar gas. The alumination of the alumi 145 146 boat containing the mixture of MoO₃ and NaCl and the substrates was then loaded into a quartz 147 tube. The CVD furnace was configured into two heating zones: a chalcogen zone heated up to 500°C zone for Se vaporisation and the growth zone comprising MoO₃, NaCl and the 148 substrates, which was heated up to a higher temperature for MoSe₂ synthesis. The temperature 149 150 profile of these zones is shown in Fig. 1(b). The CVD system was initially evacuated and purged. This procedure was repeated five times over a total period of 30 minutes, during which 151 152 the chalcogen zone and the growth zone were maintained at room temperature and 150°C, respectively. Subsequently, the gas flow rate was set to 10 sccm, which comprised Ar(8 sccm) 153 154 and H₂(2 sccm), with H₂ acting as a reducing agent. The growth zone temperature was then 155 ramped up at a rate of 15 °C/min until it reached 750 °C. Se was rapidly evaporated at 500 °C 156 when the growth zone reached 725 °C. The system was maintained under this condition for 20 minutes. Finally, the system was cooled gradually with Ar flow at 200 sccm, stopping the H₂ 157 158 flow.

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160 **2.2 Characterization**

High-resolution optical images of the as-grown MoSe₂ flakes were captured using a Carl Zeiss
Axio Lab.A1 microscope equipped with an AxioCam ERc5s camera. Raman spectra were
recorded with a Horiba Jobin Yvon LabRAM HR spectrometer using a 532 nm excitation laser.
X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermo Fisher
Scientific K-Alpha instrument. Field emission scanning electron microscopy (FESEM) images
were acquired with an FEI Apreo LoVac microscope. Atomic force microscopy (AFM)
measurements were performed using an Agilent LS5600 system.

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169 3. Results and Discussion:

170 MoSe₂ crystals deposited using the standard recipe (without any NaCl) are triangular, with a ew Article Online maximum domain size of ~25 μ m as shown in Fig. 2(a). The crystals grown αe^{10} in Fig. 2(a). 171 172 monolayers, as confirmed by Raman spectra (Fig. 2(b)) obtained at different points on the same 173 crystal. The standard A_{1g} (out-of-plane vibrational mode) and E_{2g} (in-plane vibrational mode) peaks for monolayer MoSe₂ are observed at 239.7 cm⁻¹ and 286.2 cm⁻¹, respectively (46). The 174 175 combination modes of the longitudinal (LA(M)) and the transverse (TA(M)), originating from the vicinity of the high-symmetry M point of the MoSe₂ Brillouin zone, is observed at 247.4 176 cm⁻¹ (47,48). Fig. 2(c) and (d) show high-resolution deconvoluted XPS spectra of Mo 3d and 177 178 Se 3d core-level signals, respectively. The Mo 3d_{3/2} and 3d_{5/2} peaks are located at 232.5 eV and 229.3 eV, respectively, as depicted in Fig. 2(c). Those of Se are detected around 54 eV, as 179 shown in Fig. 2(d). These data are in agreement with the respective values of MoSe₂ found in 180 the literature (14,49). These two Mo 3d peaks represent the oxidation charge state of MoSe₂. 181 The Mo peak positions are shifted significantly from their hexavalent positions of ~235.9 eV 182 183 and 232.5 eV (Mo 3d_{3/2} and 3d_{5/2} core levels of MoO₃), indicating the reduction of Mo from Mo 6p to Mo 4p. The two comparatively weak peaks present in the Mo 3d plot are linked to 184 Mo^{6+} 3d and Se²⁻ 3s states, respectively (50). The presence of an Mo^{6+} peak indicates that a 185 186 relatively minor amount of MoO₃ is expected to be present in MoSe₂ flakes. The peak of Se around 54 eV relates to the doublet core level $3d_{5/2}$ and $3d_{3/2}$, with peak positions at 54.8 eV 187 188 and 55.5 eV, respectively.



Fig. 2 (a) FESEM image of as-grown MoSe₂ crystal on SiO₂/Si substrate using the standard recipe (without NaCl) at a growth temperature of 750 °C. (b) Raman spectrum of MoSe₂. High-resolution deconvoluted XPS spectra of (c) Mo 3d and (d) Se 3d.

3.1 Variation in growth parameters

NaCl plays a crucial role in influencing the morphology and distribution of MoSe₂ flakes. The
intermediate species formed in the reaction of NaCl with MoO₃ lowers the energy barrier and
decreases the reaction temperature, thereby facilitating the synthesis. The following chain of
chemical reactions occurs:

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$$2MoO_3 + 2NaCl \rightarrow MoO_2Cl_2\uparrow + Na_2MoO_4$$

$$3MoO_3 + 2NaCl \rightarrow MoO_2Cl_2\uparrow + Na_2Mo_2O_7$$

197 MoO₃-NaCl mixture has a large weight loss at ~550°C (51), much lower than the melting points 198 of MoO₃ and NaCl ($T_m(MoO_3) = 795°C$, $T_m(NaCl) = 801°C$). Volatile MoO₂Cl₂ is one product 199 of the reaction (52), which sublimates at a relatively low temperature of (175°C). The vapors 200 of these metal oxychlorides can travel long distances to the substrates and initiate VSS (vapor-201 solid-solid) growth, resulting in early nucleation of TMDCs. Furthermore, some reports 202 indicate that metal oxychlorides may undergo selenisation at a significantly faster rate than

203 metal oxides, which enhances the reaction rate during the growth process (25) (53). Thus, the 204 reactions of intermediate metal oxychlorides (MoO₂Cl₂), Se, and H₂ are faster and eventually A00121H 205 facilitate the nucleation and layered growth by lowering the energetic barrier. In contrast, Na 206 reacts with the transition metal oxides to form non-volatile molten salts (Na_xMoO_y) with high 207 melting points (> 600°C) on the growth substrate without vapor phase transportation (54). After 208 reaction with chalcogen vapor, MoSe₂ crystals are grown from liquid melts in the VLS (vapor-209 liquid-solid) mode. The coexistence of the VSS and VLS induced by oxychlorides and sodium 210 metal oxides results in an increased growth rate, large-area crystals and different morphological 211 nanostructures. We investigated the morphological variation of the as-grown MoSe₂ 212 nanocrystals as the CVD-growth parameters were changed in a methodical manner.

4 3.1.1 Amount of NaCl

MoSe₂ crystals were synthesised by mixing 1 mg of MoO₃ powder with different amounts of NaCl, varying it from 0.5 mg to 3 mg. With the increase in the amount of NaCl, the size of the as-grown nanocrystals increased, as shown in Fig. 3. Monolayer domains were found to be predominant upto 1.3 mg of NaCl. On further increase of the amount, a large area of multilayered MoSe₂ regions was deposited. The optimal amount of NaCl was found to be 1.7 mg, which produced multilayered-triangular crystals with large sizes $\geq 100 \ \mu m$. At higher NaCl concentrations (≥ 1.7 mg), the lateral size of the crystals decreases significantly to 5–7 μm. NaCl acts as a fluxing agent, releasing Na and Cl species that interact with MoO₃ and Se 222 precursors during the CVD process. The intermediate volatile species obtained in reactions 223 224 enhance the surface diffusion of Mo and Se adatoms, promoting anisotropic growth. The 225 decrease in size at a concentration (>1.7 mg) suggests an oversaturation effect. This is because the growth environment with NaCl-derived species favours rapid nucleation, leading to 226 227 suppressed lateral growth. The variation of domain size as a function of the amount of NaCl is 228 represented graphically in Fig. 4(b), depicting a clear trend in the variation of the size of the

- crystals. This variation is summarised in Table S1. Hence, using the optimal amount of NaCl,
- 230 it should be possible to deposit large-area, high-quality 2D TMDCs.





Fig. 3. High-resolution OM images showing variation in the size of MoSe₂ crystal on SiO₂/Si substrate with different amounts of NaCl. (a–l) ranging from 0 to 3 mg at a growth temperature of 750°C.

As the size of the crystals increased with the amount of NaCl, it was observed that the 231 large area crystals were surrounded by solidified liquid droplets along the edges. This is 232 depicted in the OM image of Fig. 4(a). These droplets attach themselves to the energy 233 favourable sites along the edges of as-grown crystals, serving as catalysts, enhancing the mass 234 235 transport along the edges, thereby increasing the lateral size of the crystals (17,55). In Fig. 4(c), the domain size of the crystals was plotted as a function of the distance between the metal 236 237 precursor (MoO₃ + NaCl) and the position of the as-grown crystals on the substrate. Zero 238 denotes the position of the metal oxide precursor. It is evident from the graphs that the addition of NaCl increases the size of the crystals considerably. The reduction in the size of the crystal 239 as the distance from the source precursor increases is evident in Fig. 4(c). This is due to a 240 241 concentration gradient of the Mo vapors across the substrate. The presence of such a concentration gradient is due to the fact that the local Mo: Se ratio varies along the length of 242

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a)

c)²⁰⁰

150 ШШ

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Domain Size (100 Growth with NaCl

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the growth substrate. The crystal quality of NaCl-assisted MoSe₂ crystal was determined by

Raman spectroscopy (Fig. 4(d)). A_{1g} and E_{2g} peaks for monolayer MoSe₂ are observed at 23959A00121H cm⁻¹ and 28 cm⁻¹, respectively. The separation, Δ , between the A_{1g} and E¹_{2g} peaks is 45.1 cm⁻¹, further confirming the monolayer nature of the crystals (56). Solidified liquid Growth without NaC 10 ó Distance (mm)

XPS experiments were carried out to study the chemical composition of the MoSe₂

b) 150

Size (µm) 100

Domain

d)

intensity (a.u.)

droplet

50 µm

20

50

0.0

0.5

Monolayer MoSe₂

1.0

1.5

2.0

T(AM)+L(AM)

 E^{1}_{22} 285 cm

Amount of NaCl (mg)

 A_{1g}

240.1 cm

2.5



grown using NaCl. Peaks of Mo, Se, and O elements can be clearly seen in the XPS survey 248 spectrum (Fig. 5a). Fig. 5b shows the binding energy of Na 1s located at 1072.7 eV, indicating 249 that Na from NaCl combines with the precursor, forming intermediates such as Na₂MoO₄(57). 250 Figure 5c displays energy core-level peaks located at 229.4 eV and 232.6 eV, which are 251 attributed to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ of Mo⁴⁺, respectively. Mo⁶⁺ 3d peak is not observed in the 252 spectrum, indicating that the films are high-quality MoSe₂ and the addition of NaCl does not 253 compromise the quality of the crystal. The peaks located at 54.9 eV and 55.8 eV correspond to 254 the binding energies for Se $3d_{5/2}$ and Se $3d_{3/2}$, representing the Se²⁻ oxidation state (Fig. 5d). 255

3.5

3.0

 $\lambda = 532 \text{ nm}$



Fig. 5. XPS spectra of MoSe₂ monolayer grown on SiO₂/Si. (a) XPS survey spectrum. (b–d) Core-level spectra of Na 1s, Mo 3d, Se 3d, respectively.

257 3.1.2 Growth Temperature

After fixing the optimal concentration of NaCl at 1.7 mg and keeping all the other parameters 258 constant, the variation in growth temperature was studied. Fig. 6 depicts the morphological 259 evolution of MoSe₂ flakes deposited at different growth temperatures. Monolayer MoSe₂ 260 crystals were predominant at growth temperatures of 675°C and 700°C, along with the 261 formation of some multilayered islands. At a higher temperature of 750°C, large-area 262 multilayered crystals with lateral sizes of ~200 µm were observed. The nucleation density was 263 found to increase progressively with the rise in temperature. On further increasing the 264 265 temperature to 800°C, the size of the crystals reduced drastically, and a continuous multilayered film was deposited. 266

The morphological evolution in MoSe₂ domains on temperature can be explained by the diffusion rates of Mo, Se, and NaCl at elevated temperatures. The diffusion rate and the This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence

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Fig. 6. High-resolution OM images showing variation in the morphology of $MoSe_2$ on SiO_2/Si at different growth temperatures using 1.7 mg of NaCl (a)-(e) ranging from 675°C-800°C. (f) The domain size of $MoSe_2$ as a function of growth temperature.

deposition of the MoO₃, Se, and NaCl vapors on the substrate surface vary with the change in 269 270 temperature. At lower temperatures, the MoO₃ clusters deposited on the substrate's surface have 271 a lower concentration and are small in size. At the onset of deposition, monolayers are formed 272 on the substrate surface by reducing the MoO₃ vapors. Further deposition results in an increase 273 in the domain size, and the MoSe₂ domains are thus formed with both monolayer and bilayer 274 structures. In the case of growth at high temperatures, the high diffusion rate of the precursors results in the transport of a high concentration of nanoparticles on the surface of the substrate. 275 This results in rapid selenisation and growth of the MoSe₂ crystals with the deposition of 276 multilayer nuclei of the $MoO_{3-x}Se_y$ nanoparticles. This results in higher vapor pressure of the 277 metal precursors and enhanced reaction rate. The further growth of these nanoparticles induces 278 the growth of larger crystals. As the temperature is increased beyond 750°C, the flake size 279 280 decreases along with predominant multilayer deposition. The domain sizes decrease due to enhanced desorption, favouring vertical growth. Thus, 750°C was the optimal temperature for 281 282 the growth of large-area MoSe₂ crystals.



Fig. 7. (a) Temperature-dependent Raman spectra of the $MoSe_2$ crystal depicting evolution of the Raman peak; different colors represent different temperatures. (b) Frequency peaks of A_{1g} mode plotted w.r.t growth temperature.

283 The Raman spectrum in Fig. 7(a) further confirms the dependence of growth temperature on the thickness of MoSe₂ films. At a growth temperature of 675°C, the A_{1g} 284 vibrational mode appears at 239.2 cm⁻¹, characteristic of monolayer MoSe₂. At 700°C, a further 285 shift to 240 cm⁻¹ is observed. Consequently, with the increasing growth temperature, a blue 286 287 shift in the A_{1g} peak is observed (as plotted in Fig. 7(b)), indicating an increase in the film thickness (58,59). At 800°C, a maximum shift of 3 cm⁻¹ is measured. This is consistent with 288 the formation of multilayer MoSe₂. The low-intensity E_{1g} peak at ~283.4 cm⁻¹ diminishes 289 290 considerably with increasing thickness. The effects of the growth temperature on the morphology of the MoSe₂ crystals are summarised in Table S2. 291

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3.1.3 Amount of Se precursor

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Besides growth temperature, the Mo: Se ratio is the primary criterion affecting the growth of TMDCs. Here, we investigated the effect of Se concentration on the growth of MoSe²⁰ Heres^{A00121H} while keeping the NaCl amount and growth temperatures fixed at 1.7 mg and 750°C, respectively. By controlling the Se vapor pressure, the as-grown atomic crystals undergo a three-stage shape transformation from fractals and dendrite deposition to 2D compact nanocrystals and eventually to nanoribbons, as illustrated by the flowchart in Fig. 8.



Fig. 8. Flowchart illustrating the change in morphology of MoSe₂ crystals with varied amounts of Se precursor.

300 At lower Se concentration (150 mg), fractal and dendritic crystals with thick branches were 301 observed. The size of these crystals varies, with a maximum length of \sim 100 µm. At higher Se 302 concentrations (300 mg), the gaseous atmosphere becomes enriched with Se and Mo. More Se 303 atoms reach the substrate, resulting in compact triangular crystal structures. When the

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304 concentration of Se is further increased to 600 mg, nanoribbons with lengths $\geq 100 \ \mu m$ were

observed. Preferential growth of the nanoribbons along the edges of the triang@laip.MoSegA00121H
domains was predominant. The variation in morphology with Se concentration is summarised
in Table S3.

The analysis of XPS data to study the stoichiometry of these crystals is reported in the 308 309 supplementary information (section S.2). The high-resolution deconvoluted XPS spectra of Mo3d and Se3d peaks of crystals grown at 150 mg, 300 mg and 600 mg Se concentrations are 310 shown in Fig. S1, S2 and S3, respectively. The Mo:Se ratio for dendritic crystals was 311 312 determined to be ~ 0.47, corresponding to a Se-deficient condition. This sub-stoichiometric composition can also be ascribed to Se vacancies (56). This ratio for the triangular crystals was 313 found to be 0.5, which is congruent with the literature. Whereas, for the nanoribbons, the value 314 of the Mo:Se ratio was ~0.67, corresponding to a Se-rich environment. The details of these 315 316 calculations are reported in Table S4.

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318 **3.2 Morphological Evolution**

319 On systematic variation of growth parameters, diverse nanostructures were deposited. Among 320 them, nanoribbons were dominant. The transition from fractals to snowflakes and dendrites 321 was also prevalent. In addition, spiral growth on MoSe₂ triangular domains was found. The 322 growth mechanism of these nanostructures is discussed in the following sub-sections.

323

324 3.2.1 Nanoribbons

The growth of nanoribbons can be explained by the vapour-liquid-solid (VLS) mechanism. In the synthesis process, the precursors evaporate and undergo a chemical reaction between the vapors of MoO₃ and NaCl, forming intermediate species like Na₂MoO₄ /Na₂MoO₇ (33). A mixture of gas-liquid droplets is formed when these intermediate species diffuse and melt on the substrate. Vaporised Se dissolves into the droplet continuously and results in the formation This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

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of MoSe₂ seeds. As the droplet crawls on the surface, Se continues to dissolve into the droplet,
inducing further growth and yielding ribbon-like structures (60). In the XPS data (Fig. S⁴) and A00121H
Fig. S5), the Na1s peak is observed at 1071.69 eV corresponding to Na₂MoO_x (61), which
confirms the presence of intermediate Na-Mo compounds on the surface. This peak intensifies
at higher growth temperatures, namely 750°C. This was also the optimal temperature for the
CVD growth of long MoSe₂ nanoribbons in our studies. This further gives evidence of the role
of intermediate species in the growth of nanoribbons.



Fig. 9. (a), (b) and (c) are high-resolution OM images of MoSe₂ nanoribbons. (d) Raman data of the nanoribbons. (e) Plot showing variation in the length of nanoribbons w.r.t the amount of NaCl used. FESEM images showing (f) nanoribbons grown along the edges of the MoSe₂ crystals, indicated by yellow arrows; (g) zoomed-in image with encircled nanoparticle; (h) AFM image and height profile (along the line AB) of the as-grown MoSe₂ nanoribbons.

338 \sim 120 µm. The lengths vary with the amount of NaCl mixed with the MoO₃ precursor. It was

³³⁷ The average length of the nanoribbons was measured to be \sim 70 µm, with a maximum length of

found that the growth of nanoribbons was initiated with NaCl concentration greater than 1.3 mg. The length increases with increases in NaCl concentration, reaching a saturation point Addition of MaCl. This Beyond this, there is no effect on the length of the nanoribbons with the addition of NaCl. This observation is congruent with the variation in the size of the crystals with NaCl concentration. The variation in the average nanoribbon length as a function of NaCl amount is shown in Fig. 9(e). The growth of nanoribbons observed in this study is predominantly along the edges of the underlying domain, as evident from Fig. 9(a) and 9(f).

The alignment of these ribbons is primarily determined by the orientation of the underlying 346 347 crystal. Additionally, a few-layered nanoribbons extending from the nucleation site on the MoSe₂ domain are observed as shown in the high resolution OM images of Fig. 9(b) and 9(c). 348 349 These ribbons are locally aligned but exhibit occasional regular kinks, suggesting that the 350 growth is guided either by the substrate or the crystal facets of the underlying MoSe₂ domain. It is observed that some of the nanoribbons are terminated with a nanoparticle. Fig. 9(g) shows 351 a zoomed-in FESEM image of such nanoparticles. The size of these particles is measured to 352 match with that of the width of the ribbons (~0.14 μ m). As mentioned earlier, these 353 354 characteristic features of nanostructures result from the crawling mode of VLS growth. For a 355 few nanoribbons, there were no nanoparticles at their ends. In some cases, the absence of the nanoparticle can be explained by the fact that the liquid droplet precursor might have been 356 consumed during the growth of the ribbon. Fig. 9(d) shows the Raman measurement of the 357 nanoribbons grown on triangular MoSe₂ domains. The difference between A_{1g} and E_{2g} (Δ = 42 358 cm⁻¹) in the data confirms that the multilayer nanoribbons are grown on a few-layer MoSe₂ 359 360 domains. AFM measurements were acquired to study the surface morphology and the thickness of the MoSe₂ nanoribbons. Fig. 9(h) depicts the AFM image and the height profile of a 361 nanoribbon scanned in the non-contact mode, respectively. The contrast in the image indicates 362 the difference in the heights of the structure. A height profile along the line AB denotes a 363 thickness of ~6 nm, corresponding to a thickness of around 10 layers. 364

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366 3.2.2 Fractals- Snowflakes-Dendrites

367 A transition from compact triangles to fractal to dendritic deposition was observed under 368 certain growth conditions. We observed the growth of fractals and snowflakes at a 1 mg 369 concentration of NaCl (Mo: Se = 1 mg: 600 mg), but thick-branched dendrite structures were 370 observed at a low Se concentration (Mo: Se = 1 mg: 150 mg). In Fig. 10(a) and 10(b), a clear 371 transition from the compact island to fractals at the edges is observed.

372 At increased flux of metal precursor, the dominant morphology is fractal due to surface 373 diffusion prevailing over edge diffusion (62). The adatoms reaching the edge of growing 374 triangular domains do not contribute to the lateral growth. They diffuse randomly, which leads 375 to the formation of fractals. The edge diffusion is highly suppressed, but the incoming adatoms 376 attach themselves to the domain edges predominantly via diffusion-limited aggregation (DLA) (63). Adding NaCl as a seed promoter, there is an obvious increase in the metal flux because 377 of the increase in volatile metal oxychlorides (MoO_xCl_y). Thus, the formation of fractals along 378 379 the edges of a compact triangular domain and that of isolated fractals are promoted.



Fig. 10. (a) FESEM image of a MoSe₂ crystal with fractal edges. (b) zoomed-in image of the area enclosed in a red square showing the fractals near the edges in Fig. 9(a). (c) AFM image showing the fractal edge of a triangular crystal. (d) FESEM images of snowflakes, inset contains a high-resolution OM image of the same. (e) and (f) High-resolution OM images of as-grown MoSe₂ dendrite structures.

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380 The transition from the triangular to truncated, further to fractal and dendritic MoSe₂ flakes, is attributed (64,65) to accelerated directional growth of either a Moa 189/Sevanou21H 381 382 terminated edge under a Se-deficient or Mo-rich growth environment, respectively. Thus, inducing different dendritic shapes, including snowflakes. Dendritic structures are observed at 383 384 a low Se concentration, mainly at the substrate-boat contact interface, which creates a confined 385 space leading to a high flux of metal precursors (61,66). The abundance of MoO_{3-x} vapour in the confined reaction space also leads to fractal edges surrounding the compact triangular 386 flakes, as shown in the AFM image of Fig. 10(c). The fractal edges observed in our experiment 387 388 could be understood to be driven by kinetics rather than thermodynamics. This is congruent with our earlier work on MoS_2 dendrites (38). These dendrites develop as atoms diffuse 389 390 preferentially along specific directions, forming the characteristic "branches" of the structure. 391 From Fig. 10(d), it can be observed that most of the dendrites align with the three crystallographic directions typical of snowflakes. The larger dendrites have a greater number 392 of branches, as shown in Fig. 10(e) and 10(f). The anisotropic influence of neighbouring atoms, 393 394 combined with the tendency of dendrites to grow only along lower-energy directions, causes their preferential growth along specific directions. 395

397 3.2.3 Spiral growth

In addition to different morphologies, the growth of spiral MoSe₂ pyramids was observed. The optical contrast change of spiral MoSe₂ in Fig. 11 indicates that the thickness increases from the edge to the centre of spiral MoSe₂. The size of these domains ranges from 50 μ m to 80 μ m.

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The formation of the spiral growth depends on the MoSe₂ flux. At low MoSe₂ flux, monolayer
MoSe₂ is formed, whereas, as the flux increases, both monolayer and spiral^DMoSe₂^{View Article Online}
obtained. At a high flux of MoSe₂, thick spiral MoSe₂ with screw dislocation are formed. A
diffusion-limited growth mechanism causes the formation of a domain when it is growing.



Fig. 11. (a) - (c) High-resolution OM images showing spiral MoSe₂ pyramid.

405 During this growth, one grain boundary can elevate over another when two edges encounter a 406 lattice mismatch within the same domain (42). A line of unsaturated chalcogen dangling bonds 407 is formed on the lifted edge. A screw dislocation appears at the end of this line, which favours the growth of spirals. The generation of screw dislocations is thus increased if the probability 408 409 of a misaligned meeting of two exposed edges is increased. These accidental overgrowths occur frequently when the 2D growth rate increases. The rapid growth of certain edges is thus 410 favoured over slower ones when the growth rate is high. The spiral growth is observed in the 411 412 as-grown MoSe₂ crystals on adding NaCl with amounts ≥ 1.3 mg at a growth temperature of

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413 750°C. The considerable increase in growth rate when adding salt promotes the formation of

414 edge dislocations. As growth advances around the screw dislocation, the exposed edges arace A00121H

415 the corners of the underlying layer edges. This leads to the formation of the spirals.

416

417 4. Conclusions:

The controlled growth of diverse MoSe₂ nanostructures synthesised using an APCVD was 418 systematically investigated, with NaCl serving as a seed promoter. Key CVD growth 419 parameters, including the optimal NaCl concentration, growth temperature, and chalcogen 420 421 precursor amount, were optimised to grow unique morphologies such as nanoribbons, 422 dendrites, snowflakes, and spirals. A morphological mapping of a clearly defined parameter 423 space is proposed to grow the desired nanostructures. This study not only establishes precise 424 conditions for the reproducible synthesis of these unique structures but also provides insights 425 into their growth mechanisms. This comprehensive study can be extended to the controlled CVD growth of various other TMDC nanostructures to be used in various next-generation 426 427 applications.

428

429 Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personalrelationships that could have appeared to influence the work reported in this paper.

432

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