Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Interfaces determine the nucleation and growth of large NbS_2 single crystals

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(Some figures in this article are in color only in the electronic version.)

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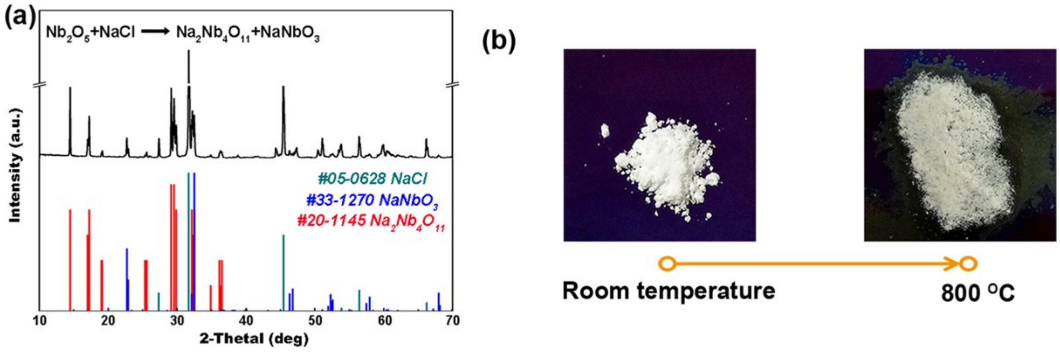


Figure S1 (a) XRD pattern of the reaction product of Nb_2O_5-NaCl mixture after a typical CVD process at 800 °C without sulfur. It contains $Na_2Nb_4O_{11}$, $NaNbO_3$ and residual NaCl. (b) Optical images of Nb_2O_5 mixed NaCl showing melting after annealing at 800 °C.

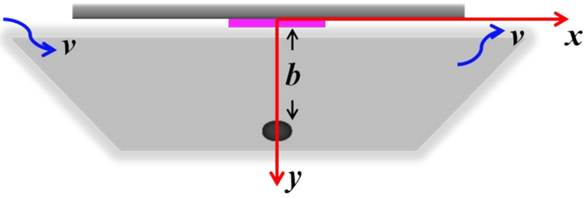


Figure S2 CVD setup and corresponding calculation model of the VS growth.

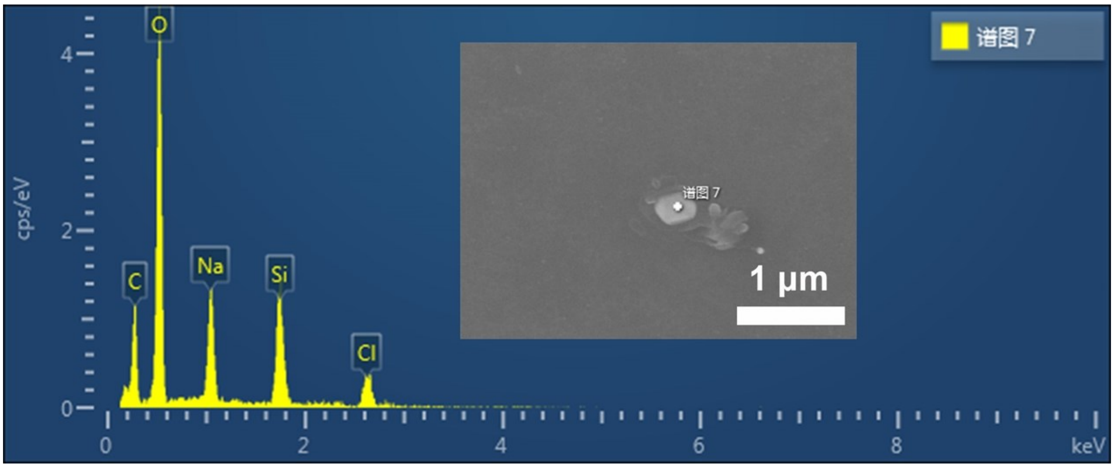
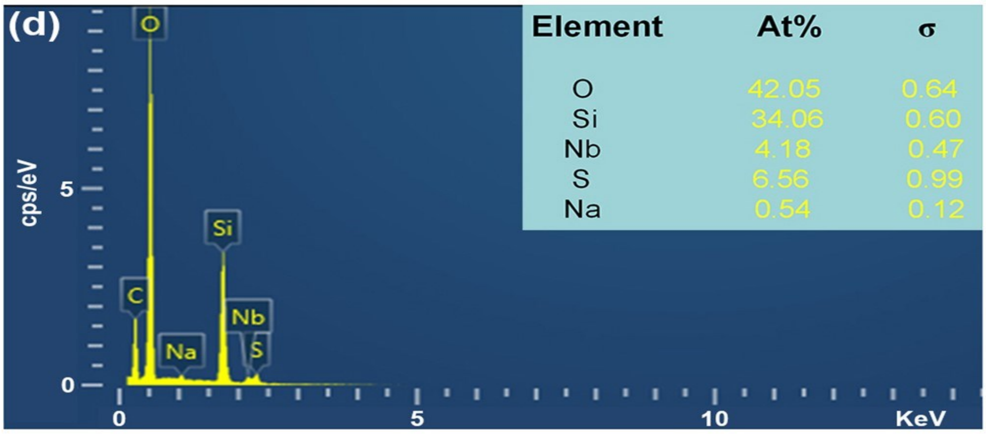


Figure S3 EDX spectrum of the particles distributed on the NbS_2 surface, which are identified as NaCl.



Element	At%	σ
O	42.05	0.64
Si	34.06	0.60
Nb	4.18	0.47
S	6.56	0.99
Na	0.54	0.12

Figure S4 EDX spectrum of particles shown in Figure 2(h), which contains elements of Nb, S, Na, O.

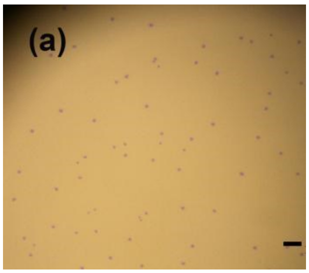
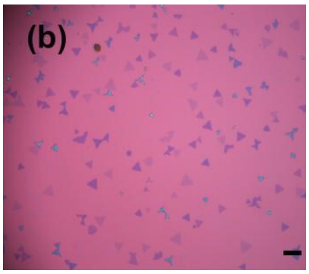
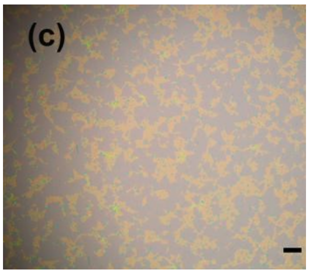
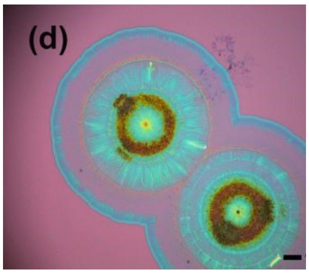
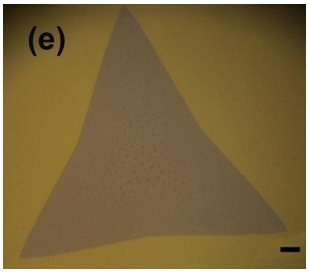
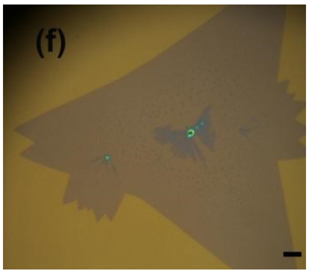
Temperature Growth Methods	**750℃**	**800℃**	**850℃**
VS			
VLS			

Figure S5 The effect of temperature on the growth of NbS_2 in VS and VLS modes. (a−c) Optical images of NbS_2 grown in VS mode with growth temperature from 750 to 850 °C. (d-e) Optical images of NbS_2 grown in VLS mode with growth temperature from 750 to 850 °C. Scale bars: 25 µm.

The temperature in a CVD system may strongly affect the evaporation, transport, and diffusion rates of precursors, resulting in the difference of nucleation density and growth rate. For the VS growth of NbS_2, with the increase of growth temperature, more $NbOCl_3$ vapors can be evaporated and transported to the growth interface. Therefore, the nucleation density of NbS_2 crystals increased with the increase of crystal size (Figure S5(a-b)). Furthermore, as the growth temperature further increases during VS growth, more vaporized precursors would be adsorbed on the NbS_2 basal plane, which would result in the formation of secondary nucleation (Figure S5(c)). In contrast, with increasing growth temperature during VLS growth, the side length of the triangular domains increases but the probability of new NbS_2 nuclei is very small on the substrate surface (Figure S5(d-f)). On the one hand, although more NbS_x monomers are synthesized at the vapor-liquid interface with increasing growth temperature, the monomers at the growth interface maintain the moderate concentration due to the concentration gradient in droplet, which is beneficial to the growth of large-sized single crystals. On the other hand, the thermal ionic motion in molten droplets is more intense at high growth temperature, thus greatly decreasing the diffusion barrier of NbS_x monomers.

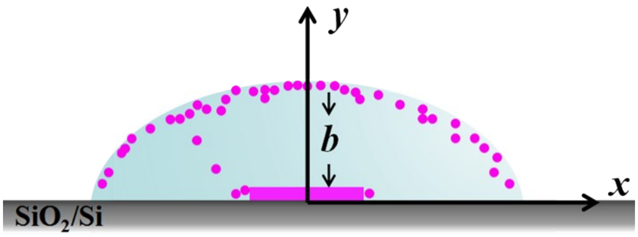


Figure S6 The model of the VLS growth in the calculation.

Kinetics of VLS growth: The steady-state concentrations of NbS_2 monomers in melting Na-Nb-O droplets was calculated by using the two-dimensional steady-state diffusion model,[1]

$$\frac{\partial c(x,y)}{\partial t} = D\left[\frac{\partial^2 c(x,y)}{\partial x^2} + \frac{\partial^2 c(x,y)}{\partial y^2}\right] - \upsilon \frac{\partial c(x,y)}{\partial x} \tag{s1}$$

where D is the diffusion coefficient of the NbS_2 monomers, c is the concentration, υ is the average spreading rate of droplets. D is expressed as

$$D = D_\infty \exp(-{E_{diff}}/{kT}) \tag{s2}$$

where D_∞ is a constant coefficient, E_{diff} is the diffusion barrier. Although the NbS_2 monomers diffuse widely from the vapour-liquid interface to the growth interface, we only consider the concentration gradient along the Y-axis for simplification in this model. The boundary conditions for the region with $x>0$, $0<y<b$ (b is taken as a constant for simplicity) will apply

$$\text{At } (x, 0),\ c=0 \tag{s3}$$

$$\text{At } (x, b),\ \partial c/\partial y = 0 \tag{s4}$$

$$\text{At } (0, y),\ c=c_0 \tag{s5}$$

The solution of $c(x,y)$ can be obtained as:

$$c(x,y)=\frac{4c_0}{\pi}\sin(\frac{\pi y}{2b})\exp(-\frac{\pi^2 Dx}{4\upsilon b^2}) \tag{s6}$$

The flux of NbS_2 monomers to the growth interface can be written as

$$J(x)=-D\frac{\partial c(x,y)}{\partial y}\Big|_{y=0} \tag{s7}$$

The resultant deposit growth rate R is related to $J(x)$ through simple material constants by

$$R=\frac{M_{NbS2}}{\rho_{NbS2}M_{NbS2monomer}}J(x)=\frac{2c_0 M_{NbS2}}{b\rho_{NbS2}M_{NbS2monomer}}D\exp(-\frac{\pi^2 Dx}{4\upsilon b^2}) \tag{s8}$$

where M_{NbS2} and $M_{NbS2monomer}$ are the molecular weight of NbS_2 and monomers, which are numerically equivalent here. ρ_{MoS2} is the density of NbS_2 in this model. For our setup, giving the the saturated concentration of metal precursor at the growth interface, around 10 μg of Nb_2O_5 are consumed during a period of 10 min (out of a total of 10 mg of Nb_2O_5 and 2 mg of NaCl).[2] Therefore, we can calculate that about M=7.8 μg of NbS_2 monomer is generated in droplet for the VLS growth. The droplet volume can be expressed as

$$V=[\pi b(3r^2+b^2)]/6 \tag{s9}$$

where r is the radius of the droplet on the substrate, b is the height of the droplet. The experimental results show that as-synthesized samples are distributed at 2×2 cm^2 region on the substrate. Therefore, r can be estimated to be 1 cm and b~0.1 cm. The concentration constant c_0 can be estimated to be c_0=M/V=4.84×10^{-5} g/cm^3. The spreading rate of droplets υ~1.2 cm/s can be estimated by experimental observation shown in Figure 2. Although the calculated values of gas diffusivity for the growth of MoS_2 were very large (~ 8.7 cm^2/s),[1] the actual D is smaller than the calculated values according the report of Rajan group.[2] We therefore used an average value (~ 0.7 cm^2/s) to describe the gas diffusivity.

Kinetics of VS growth: From the model of VS growth shown in Figure S2, we can demonstrate that the VS growth process is similar to that of VLS growth, where the precursor in aluminium oxide boat diffuses to the substrate surface at a certain concentration gradient. Therefore, the same diffusion model and boundary conditions can be used to calculate the growth rate of NbS_2 in VS mode. The concentration constant (c_0) can be estimated to be 4.84×10^{-5} g/cm^3, the drift velocity v~0.13 cm/s can be estimated by the flow rate of the carrier gas (500 sccm) and the inside diameter (O.D.) of the quartz tube, b ~0.1 cm. The gas diffusivity can be estimated to be 0.1 cm^2/s.

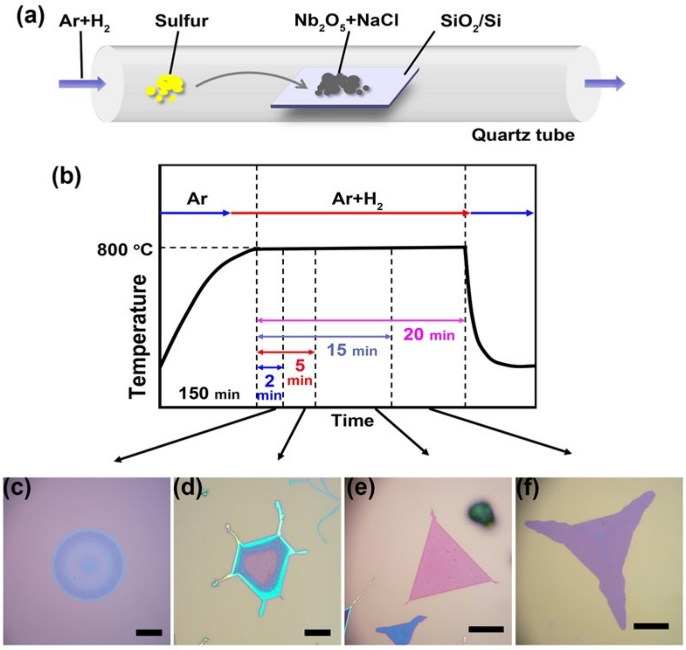


Figure S7 The growth of single crystal NbS_2 by the NaCl-assisted CVD method. (a) Setup for synthesizing NbS_2 single crystals. (b) Schematic diagrams of the NbS_2 growth procedure. (c)-(f) The crystal morphology of NbS_2 at each growth step. The scale bars are 20 μm in (c)-(d) and 50 μm in (e)-(f).

Figures S7(c)-(f) show optical microscopy images of NbS_2 growing with the assistance of NaCl for 2 to 20 mins. At the beginning, we can clearly see that the as-grown NbS_2 shows morphology of “coffee-ring”, indicating that the precursors were in a liquid state during the growth (Figure S7 (c)). With the growth time increased to 5 mins, large size hexagonal NbS_2 was achieved (Figure S7(d)). It is noteworthy that there were special ribbon-like nanostructures at the corners of the hexagonal domain, which was similar to the morphology of droplets crawling from six corners of the hexagon to the substrate surface. Moreover, according to the color change of the sample under the optical microscope, we can conclude that the thickness of NbS_2 domain increases gradually from center to the edge. These are characteristic features of nanostructures formed by "2D spreading mode" of droplets on the substrate during growth.[3,4] It is well known that when a drop is put in contact with a solid surface, it will in general be far from its equilibrium state. Hence the droplet surface stretches until the equilibrium contact angle is reached. This phenomenon, known as droplet spreading,[5] is ubiquitous in nature and technology. Here, we suppose that the liquid precursor is in a non-equilibrium state during growth. It spreads on the SiO_2/Si surface, thus mediating 2D growth of NbS_2 films.

When the growth time increased to 15 mins, the side length of triangular domain with characteristic corner structures can be as large as ~140 μm (Figure S7(e)). In particular, with further increasing the growth duration to 20 mins, the two elongated edges of corners became curved rather than straight, developing kinks at the positions with negative curvature (Figure S7(f)).

References

(1) J. Zhou, et al., A library of atomically thin metal chalcogenides, Nature 556 (2018) 355−359.

(2) A. Govind Rajan, J. H. Warner, D. Blankschtein, M. Strano, Generalized mechanistic model for the chemical vapor deposition of 2D transition metal

dichalcogenide monolayers, ACS Nano 10 (2016) 4330-4344.

(3) Y. L. Jiao, X. J. Liu, M.H. Pang, K. Liu, Analyses of droplet spreading and the movement of wetting line on a solid surface, Acta Phys. Sin. 65 (2016) 016801.

(4) J. Becker, G. Grun, The thin-film equation: recent advances and some new perspectives, J. Phys.: Condens. Matter 17 (2005) 291-307.

(5) D. Bonn, Wetting and spreading, Rev. Mod. Phys. 81 (2009) 739-804.