Systematic study of CVD-growth parameters in NaCl-assisted growth of $MoSe_2$ nanostructures: Nanoribbons, dendrites and spirals

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S.1. CVD growth parameters

The following tables (Table S1, S2 and S3) summarise the results obtained by varying the three growth parameters, namely the amount of NaCl, the growth temperature and the selenium concentration, studied for the CVD growth of $MoSe_2$.

Table S1: CVD Growth parameters with varying NaCl concentration

S.No.	Gas Flow Ar:H_2 (sccm)	Growth Temp. (°C)	Amt of Precursor (mg)		NaCl (mg)	Avg. Domain Size (µm)
			MoO_3	Se		
1.	8:2	750	1	600	0	7
2.	8:2	750	1	600	0.5	~38
3.	8:2	750	1	600	0.8	~44
4.	8:2	750	1	600	1.0	~63
5.	8:2	750	1	600	1.3	70
6.	8:2	750	1	600	1.5	~88
7.	8:2	750	1	600	1.7	113
8.	8:2	750	1	600	2.0	~60
9.	8:2	750	1	600	2.3	~24
10.	8:2	750	1	600	2.5	~24
11.	8:2	750	1	600	2.7	25
12.	8:2	750	1	600	3.0	~26

Table S2: CVD Growth parameters with varying growth temperatures

S.No.	Gas Flow Ar:H_2 (sccm)	Amt of Precursor (mg)		NaCl (mg)	Growth Temp. (°C)	Avg. Domain Size (μm)
		MoO_3	Se			
1.	8:2	1	600	1.7	675	10.3
2.	8:2	1	600	1.7	700	13.5
3.	8:2	1	600	1.7	720	26.1
4.	8:2	1	600	1.7	750	143.3
5.	8:2	1	600	1.7	800	13.41

Table S3: CVD Growth parameters with varying Se precursor concentration:

S.No.	Gas Flow Ar:H_2 (sccm)	Growth Temp. (°C)	MoO_3 (mg)	NaCl (mg)	Se (mg)	Morphology
1.	8:2	750	1	1.7	150	Dendrite
2.	8:2	750	1	1.7	300	Triangles
3.	8:2	750	1	1.7	600	Nanoribbons

S.2. XPS data analysis for the variation in the amount of Se precursor

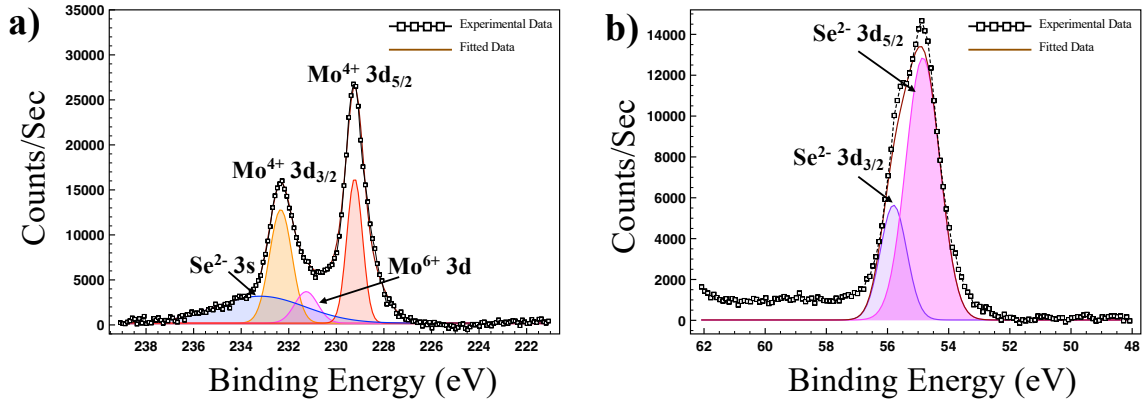

Fig. S1. High-resolution deconvoluted XPS spectra of (a) Mo 3d and (b) Se 3d of a dendritic $MoSe_2$ crystal grown with a Se precursor concentration of **150 mg.**

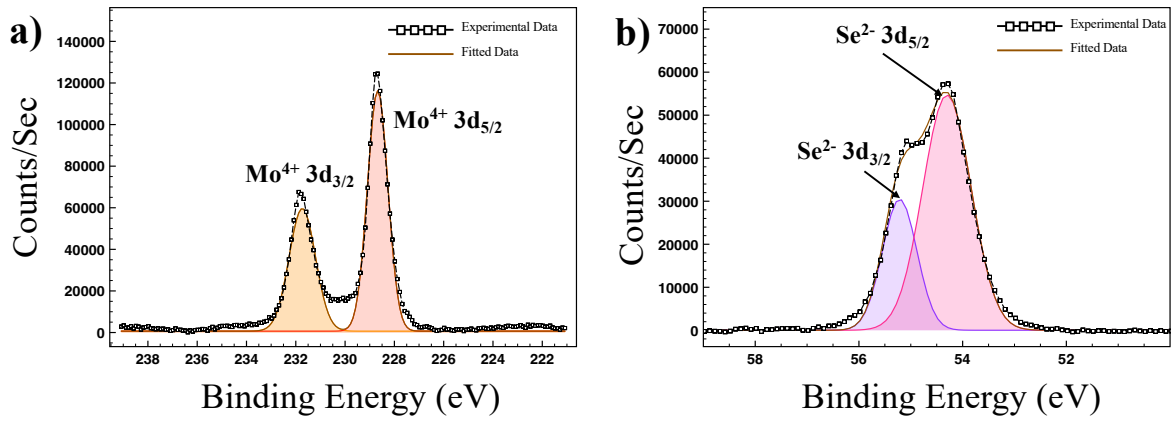

Fig. S2. High-resolution deconvoluted XPS spectra of (a) Mo 3d and (b) Se 3d of a triangular $MoSe_2$ crystal grown with a Se precursor concentration of **300 mg.**

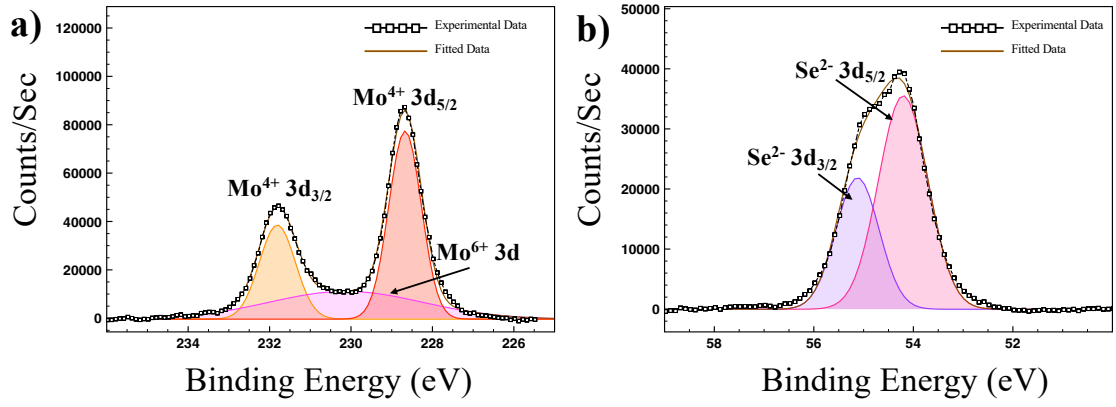

Fig. S3. High-resolution deconvoluted XPS spectra of (a) Mo 3d and (b) Se 3d of a nanoribbon grown with a Se precursor concentration of **600 mg.**

The stoichiometric ratio for the $MoSe_2$ triangular crystals should be ideally Mo:Se = 1:2. The changes in this ratio indicate a Se-deficient or Se-rich environment. To calculate this ratio, the following steps were followed:

$$\text{Correlated Intensity } (I_{corr,Mo}) = \left(\frac{I}{RSF}\right)Mo_{3d}$$

where I = Integrated area under the Mo 3d
RSF = Relative sensitivity factor

Similarly for Se_{3d},

$$\text{Correlated Intensity } (I_{corr,Se}) = \left(\frac{I}{RSF}\right)Se_{3d}$$

Finally, to calculate the stoichiometric ratio:

$$\textbf{Ratio (Mo/Se)} = \left(\frac{I}{RSF}\right)\mathbf{Mo3d} \Big/ \left(\frac{I}{RSF}\right)\mathbf{Se3d}$$

RSF values for Mo3d and Se3d were taken to be:
$RSF_{Mo3d} = 3.321$ and $RSF_{Se3d} = 0.853$ (3)

Table S4: The Mo: Se ratio calculated from integrated Mo3d and Se3d peaks, obtained from XPS data for different Se precursor concentrations: 150 mg, 300 mg and 600 mg.

S.No.	Se(mg)	Mo_{3d} Peak (eV)		Integrated Area Mo (I_{Mo3d})× 10^3	Se_{3d} Peak (eV)		Integrated Area Se (I_{Se3d})× 10^3	Mo:Se	Morphology	Remarks
		$3d_{3/2}$	$3d_{5/2}$		$3d_{3/2}$	$3d_{5/2}$				
1.	150	232.3	229.2	893.25	55.7	54.8	498.77	0.46	Dendrite	Se deficient
2.	300	231.7	228.6	51.08	55.1	54.2	23.02	0.52	Triangular	Optimal Se
3.	600	231.7	228.6	2034.41	55.1	54.1	778.68	0.67	Nanoribbons	Se Rich

S.3. XPS data analysis of Na1s peak with the variation in the growth temperature

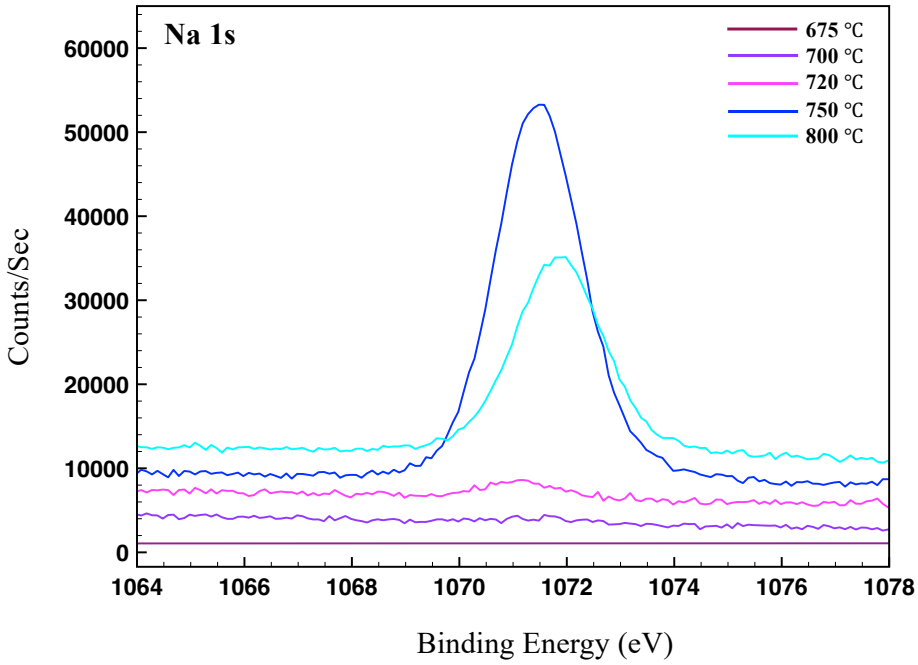

Fig. S4. XPS spectra showing variation in the intensity of Na1s peak with increase in growth temperature. The Na1s peak observed at 1071.69 eV represents Na_2MoO_x (1)(2). At the low growth temperature measured (675°C and 700°C), no signal of Na was detected in XPS. The onset of Na peak was first found at 720°C. The peak intensity increased considerably at higher temperatures 750°C and 800°C. The growth of nanoribbons were initiated at 720°C with the maximum length obtained at 750°C. The growth of nanoribbons, as discussed in section 3.2.1 with the VLS mechanism, is due to the formation of intermediate Na-Mo compounds. Thus, the high intensity of Na peaks on the surface, as depicted by these XPS data, indirectly confirms the VLS growth mechanism as discussed in section 3.2.1.

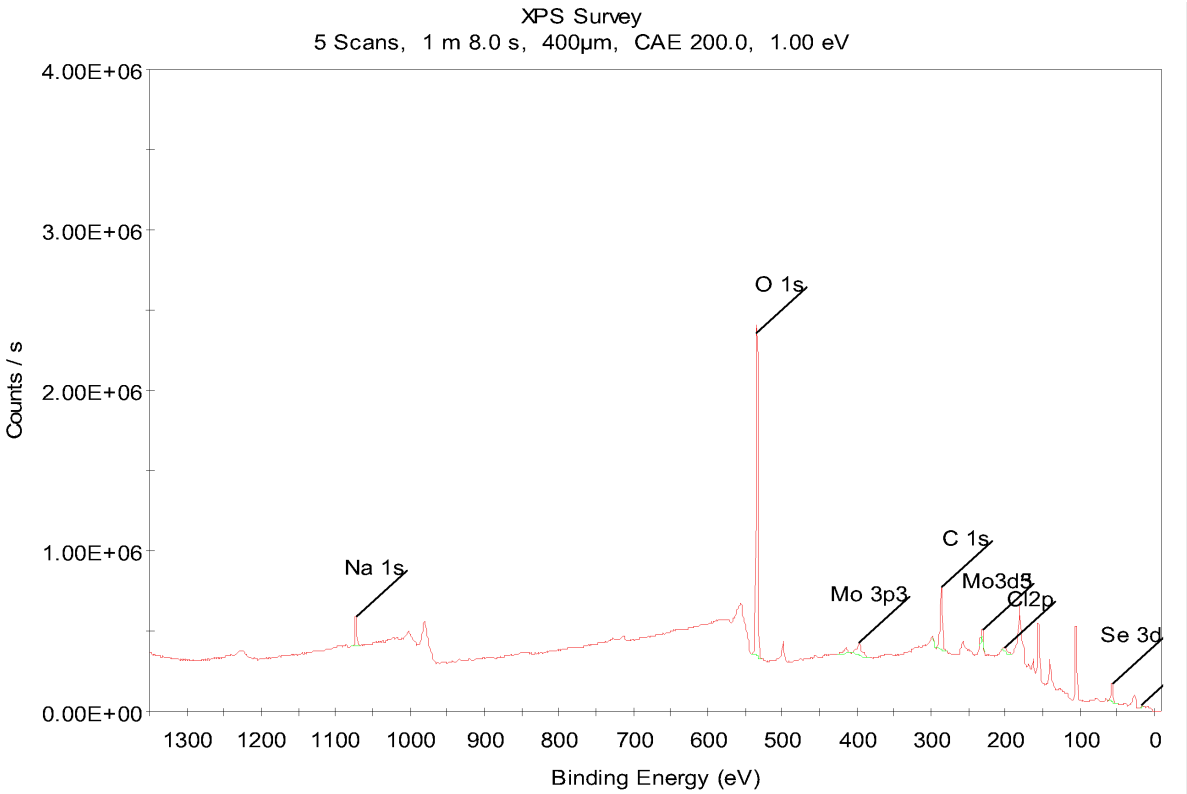

Fig. S5. XPS survey scan at 750°C showing a prominent Na1s peak.

References:

1. Suleman M, Lee S, Kim M, Nguyen VH, Riaz M, Nasir N, Kumar S, Park HM, Jung J, Seo Y. NaCl-Assisted temperature-dependent controllable growth of large-area MoS_2 crystals using confined-space CVD, *ACS Omega*, 2022 Aug 21;7(34):30074–86.
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