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Chemical Vapor Deposition of 2D Transition Metal Dichalcogenides – Just Add Salts

Chemical vapor deposition (CVD) of 2D transition-metal dichalcogenides (TMDCs) usually involves the conversion of vapor precursors into solid products via a vapor-solid-solid (VSS) mode ($\text{WO}_3 + \text{S/Se} + \text{H}_2 \rightarrow \text{WS}_2/\text{WSe}_2$). It always requires an extremely high temperature and low pressure to sublime the transition metal oxides. In 2015, we published a pioneering work on halide-assisted atmospheric-pressure CVD of WSe_2 and WS_2 monolayers at lower temperature due to the formation of low-melting-point volatile tungsten oxychlorides ($\text{WO}_3 + \text{NaCl} \rightarrow \text{WO}_x\text{Cl}_y$, $\text{WO}_x\text{Cl}_y + \text{S/Se} + \text{H}_2 \rightarrow \text{WS}_2/\text{WSe}_2$, Figure.1a).^[1,2] This method has been widely used for growing ~ 50 types of 2D TMDCs in the last five years.^[3]

Vapor transportation as the core process in CVD of 2D TMDCs, one inevitable problem is the spatial inhomogeneity of the vapors. The non-stoichiometric supply of transition-metal precursors and chalcogen leads to poor control in products' location, morphology, crystallinity, uniformity and batch to batch reproducibility. In 2018, we revealed the important vapor-liquid-solid (VLS) growth of TMDCs which is triggered by the alkali metals in salt-assisted CVD ($\text{MoO}_3 + \text{NaCl} \rightarrow \text{Na}_2\text{Mo}_x\text{O}_y$, $\text{Na}_2\text{Mo}_x\text{O}_y + \text{S} \rightarrow \text{MoS}_2$). The in-situ generated non-volatile Na-Mo-O droplets mediate the growth of 1D MoS_2 nanoribbons on NaCl crystal and 2D MoS_2 film (Figure 1b).^[4] The VLS growth involves non-volatile molten precursors (e.g., Na_2MoO_4 , Na_2WO_4) shows great advantages in wafer-scale growth of 2D TMDC film and patterned (site-controlled) growth of 2D TMDC monolayers (Figure 1c).^[5] Taking advantage of the VLS growth, we recently achieved two important achievements: (i) 2-inch-wafer-scale growth of continuous MoS_2 film with a grain size exceeding 100 μm on sapphire substrates, and (ii) pattern (site-controlled) growth of MoS_2 flakes. We clarified that the VLS growth thus pave the new way for the high-efficient, scalable synthesis of two-dimensional TMDC monolayers. It opens a new research direction for the 2D community.

References

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Figures

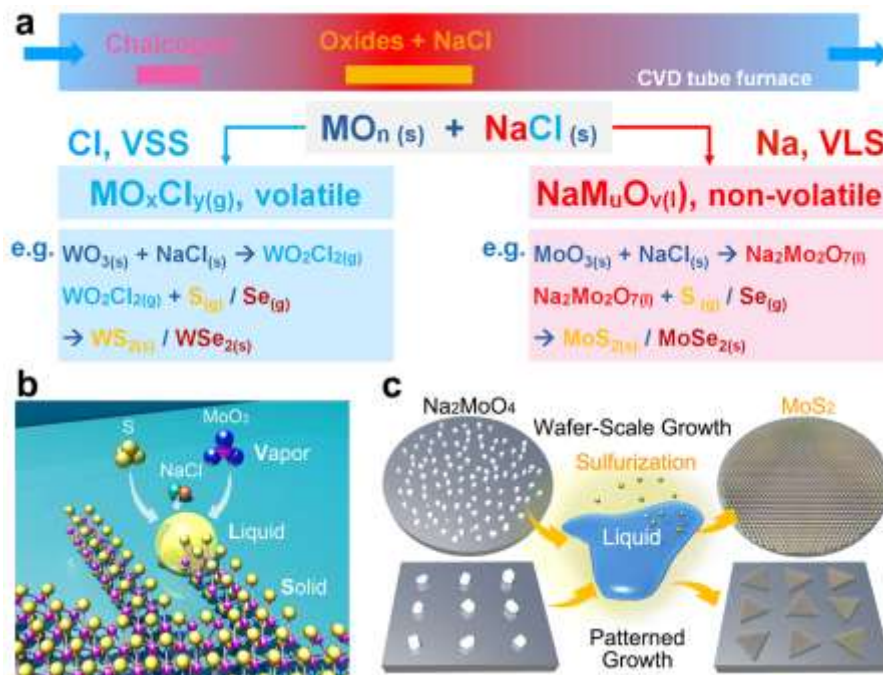


Figure 1: (a) Schematic of the VSS and VLS growths of 2D TMDs in salt-assisted CVD. (b) Schematic of VLS growth of 1D MoS₂ nanoribbons. (c) Schematic of wafer-scale and patterned VLS growth of 2D MoS₂ monolayers by sulfurization of non-volatile Na₂MoO₄ liquid.