Supplementary Material

Synthesis of WS_2 by Chemical Vapor Deposition: Role of the Alumina Crucible

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WS_2 synthesis: The tungsten precursor, WO_3 in powder form (20 mg), was positioned in the central heating zone 1 (downstream) on an alumina crucible that also supports the silicon dioxide substrate, SiO_2 (285nm)/Si (size 1 cm^2). The substrate was face down over the precursor and positioned diagonally within the alumina crucible. Another alumina crucible containing 600 mg of powdered sulphur was placed inside the furnace tube upstream (heating zone 2). Figure S1 illustrates the description made above. Substrates were cleaned using a sonication sequence in acetone and isopropanol, 15 minutes each, followed by 5 minutes of deionised water. The last step of this process was drying the substrate with N_2 gas flow. Firstly, the furnace in heating zone 1 is heated with ramping rates of 30°C/min by 20 min. Reaching a temperature of 500°C (zone 1), zone 2 reaches 250°C. Then, the oven temperature in zone 1 continues to rise to 850°C, being held for 15 min, while zone 2 was kept at 250°C. After the growth, the oven was cooled to room temperature naturally. Ultra-high purity argon gas flowed with 100 sccm during the whole growth process.

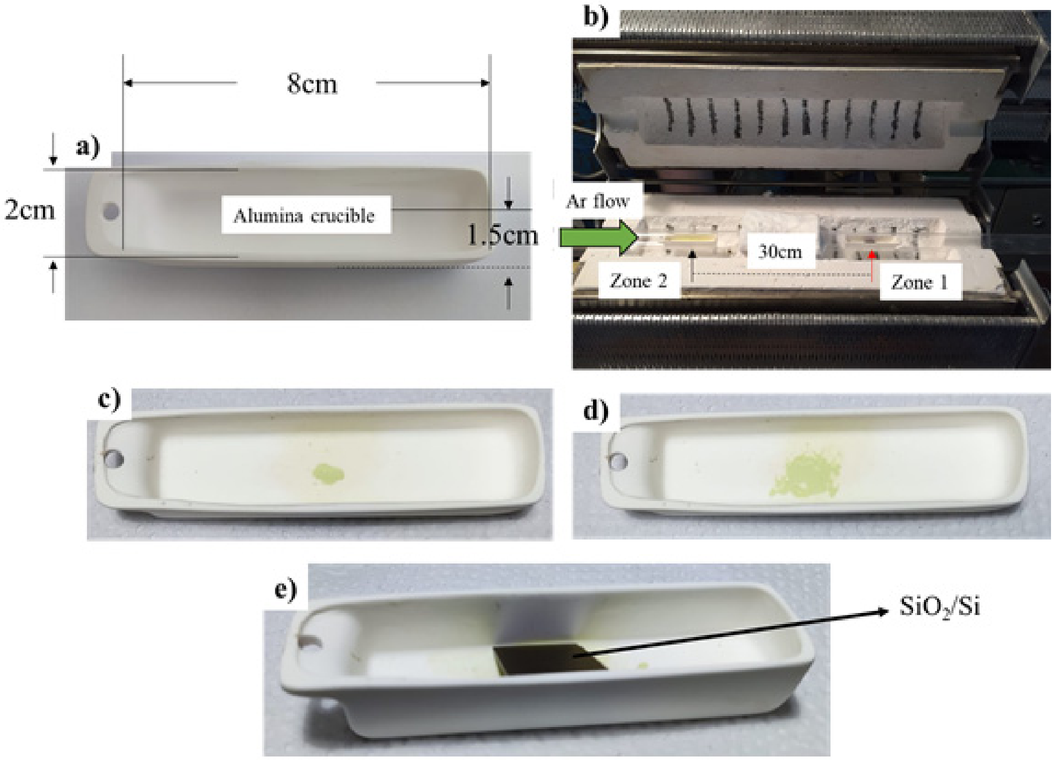

Figure S1. (a) Photo of the alumina crucible. (b) Zone 1 (downstream), where the crucible was placed with WO_3 precursor (20 mg) and the SiO_2/Si substrate. Zone 2 (upstream) shows the crucible with the sulphur precursor (600 mg). The distance between the two crucibles was 30 cm. The green arrow indicates the direction of the Ar flow. (c) shows the WO_3 agglomerated (small surface area on the crucible) (d) WO_3 spread (large surface area on the crucible). (e) position of the substrate inside the crucible face down over the WO_3 was diagonal.

We know that WO_3 initially interacts with the sulphur vapour on the crucible's surface. Two different configurations were investigated to test the effect of the precursor area exposed to the sulphur flow, keeping the WO_3 mass constant (20 mg). The first is illustrated in Figure S1c, with the precursor with a small surface exposed to flow. The second configuration is shown in Figure S1d, with the powder nearly homogeneously spread over a much larger exposed area. The results presented in the main text were obtained using WO_3 well dispersed over the surface of the crucible.

Our results are presented as a function of the number of growth cycles. Following the first growth performed using a virgin crucible, each cycle began with cleaning the tube and crucible used in the previous cycle. After correctly positioning the tube and crucibles, the carrier gas is released, starting the synthesis process described above. The cycle ends with the removal of the samples produced.

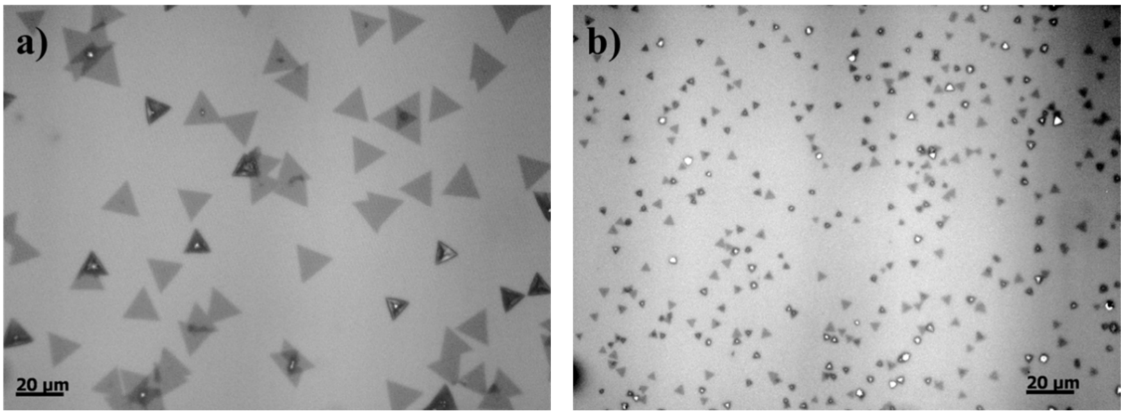

Figure S2. Optical images of specific cycles: a) the fourth growth cycle. b) the ninth growth cycle.

Table S1. Raman modes were obtained with the 473 nm wavelength.

Growth cycles	$A_{1g}(\Gamma)$		$E_{2g}(\Gamma)$		$E^2_2(M)$		2LA(M)		$2LA(M)-2E^2_{2g}(\Gamma)$	
	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	FWHM (cm^{-1})
1	418.2	4.1	357.1	2.8	336.7	7.6	350.7	19.8	295.7	6.4
2	418.2	4.1	357.1	2.9	338.8	6.9	350.7	20.3	295.7	5.2
3	418.2	4.1	357.1	3.6	333.4	6.8	349.6	21.9	295.7	4.9
4	418.2	4.1	357.1	3.0	334.5	7.9	350.7	24.0	295.7	9.2
5	418.2	4.1	357.1	3.0	332.4	7.9	350.7	21.9	295.7	5.3

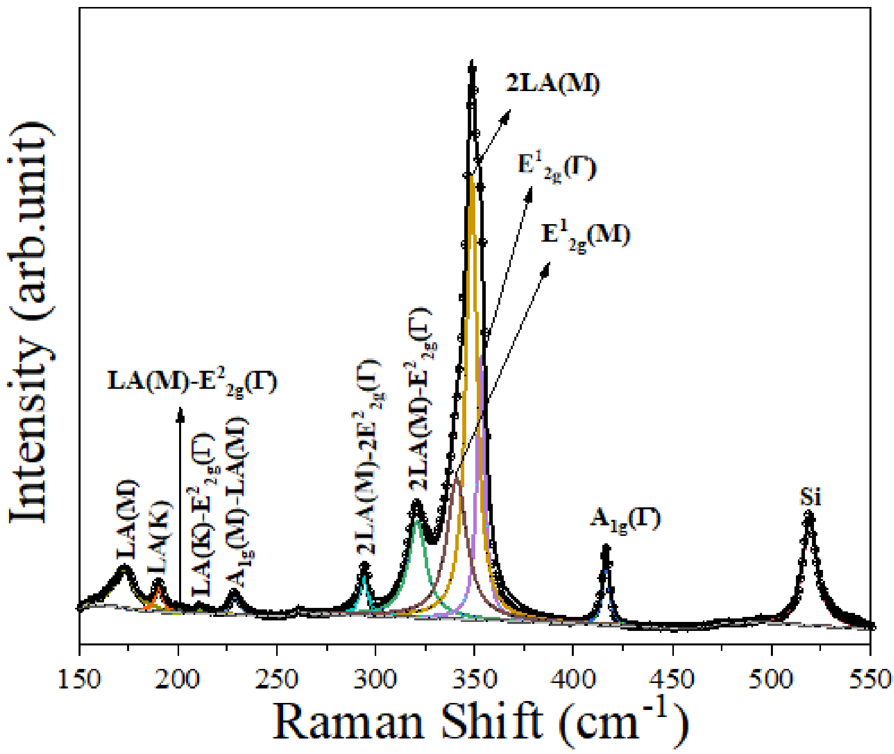

Figure S3. The full Raman spectrum of the third growth cycle using the excitation line of 532 nm. All peaks correspond to the Raman spectrum's deconvolution.

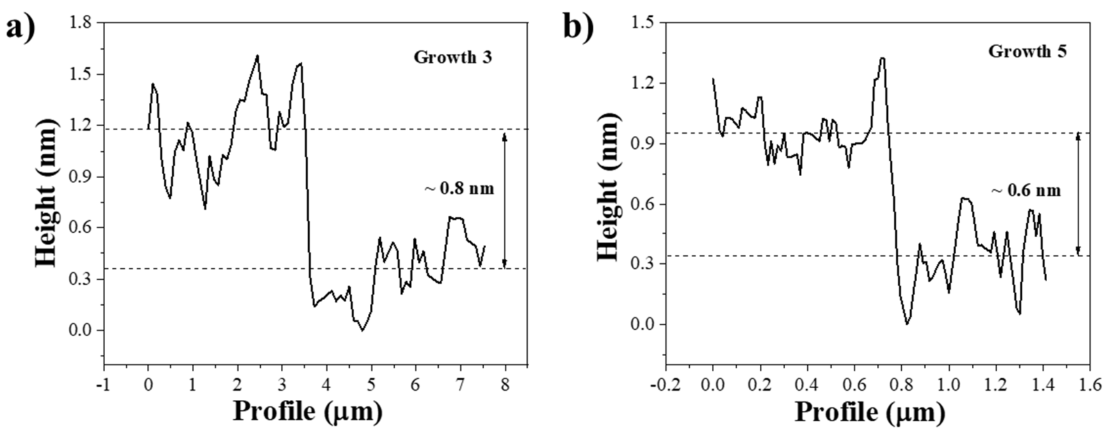

Figure S4. (a) and (b) height profiles obtained from AFM images shown in Figures 4a and 4b.

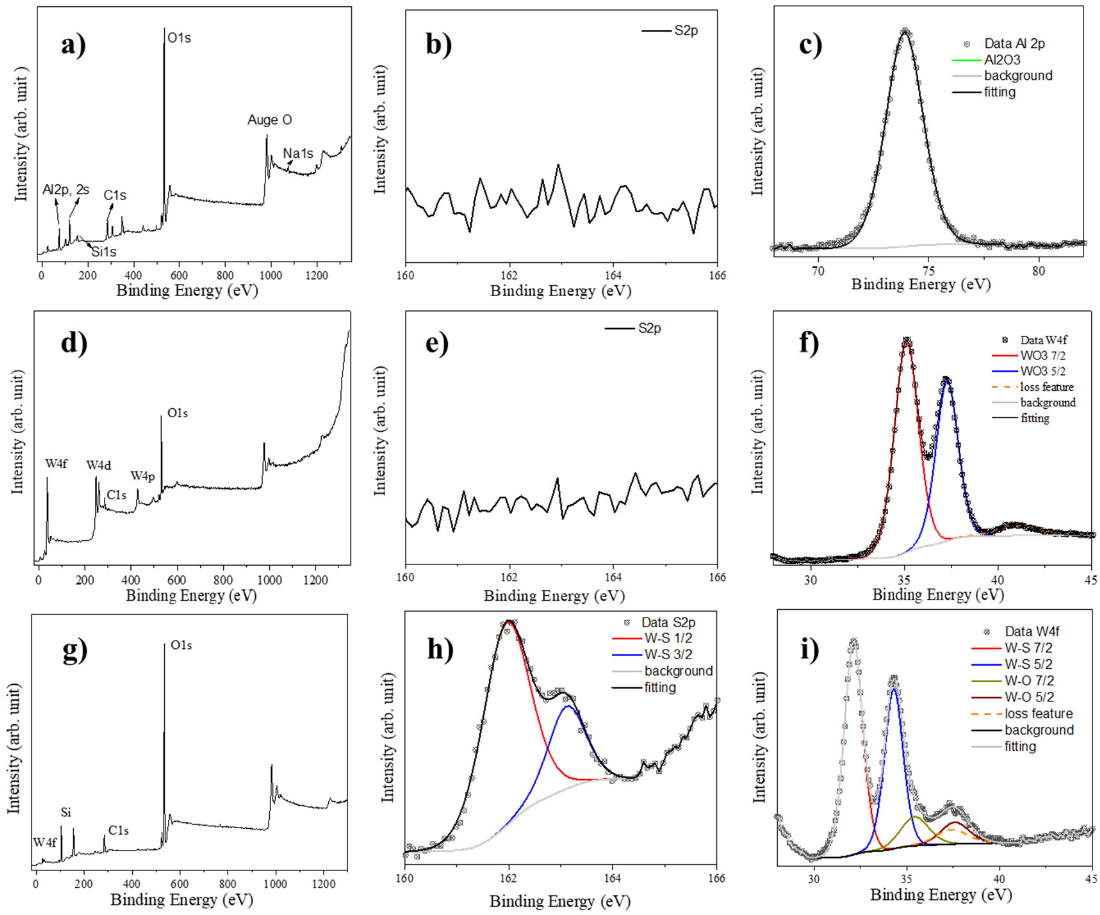

Figure S5. (a-c) XPS spectra of virgin alumina crucible's surface; (d-f) XPS spectra of WO_3. (g-i) typical APCVD-WS_2. (a),(d), and (g) are survey spectra; (b), (e), and (h) are high-resolution spectra of the S_{2p} peak. (c) the high-resolution spectrum of aluminium. (f) and (i) are high-resolution spectra of the W_{4f} peak obtained for WO_3 and APCVD-WS_2, respectively. Each contribution was associated with a duplet due to the spin-orbit presented by W_{4f} and S_{2p}.

Table S2. W/Al and Na/Al ratios were obtained from the relative atomic concentration obtained with XPS.

Crucible	Ratio	
	W/Al	Na/Al
Virgin crucible	0	0.07
Firth growth	0.03	0.10
Third growth	0.09	0.19
Ninth growth	0.30	0.22