



As shown in Supplementary Figure S1c-j, with the increase of temperature beyond 890 °C, the lateral domain size of the asgrown WS₂ monolayer increases from $^{10} \mu m$ to $^{70} \mu m$, but it will start to shrink to less than $^{15} \mu m$ with the further increase in temperature. Finally, defected shape, smaller density and smaller size of $^{15} \mu m$ WS₂ monolayer crystals are obtained under growth temperature of 975 °C, as shown in Supplementary Figure S1d and h. These observations suggest that elevated temperature will destroy the growth of WS₂ and demonstrate that 950 °C would be the optimum growth temperature for the growth of monolayer WS₂ with bigger and higher crystallinity.

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2 Supplementary Figure S2. AFM images of monolayer WS₂ samples that are synthesized from FWO₃, PTWO₃, AWO₃ and PTAWO₃ powder.



Supplementary Figure S₃. Raman spectra of monolayer WS₂ samples synthesized from commercially available (FWO₃), (b) air plasma
treated (PTWO₃), (c) AWO₃ and (d) plasma treated and thermally annealed (PTAWO₃) powder, respectively. All of the WS₂ samples exhibit

6 typical Raman peaks of WS₂ monolayer with stronger E_{2g} peak at 355 cm⁻¹ compared with the A_{1g} peak at 417 cm⁻¹.



2 Supplementary Figure S4. Domain size distributions of the monolayer WS₂ crystals grown on sapphire substrate with different precursors.





2 Supplementary Figure S5: XRD patterns of WO_3 treated for different annealing durations.

3 As shown in Supplementary Figure S₅, no obvious XRD peak position change can be observed for WO₃ samples annealed

4 for 20, 30, and 40 minutes. These results suggest the WO₃ powder in our study reached a stable state upon annealing.

5 Therefore, the growth of WS_2 monolayers show no obvious dependence on the WO_3 annealing durations.



2 Supplementary Figure S6: XRD patterns of FWO₃, PTWO₃, AWO₃, PTAWO₃ and APTWO₃ powders.

3 To further explore the effect of first plasma-treated and then annealed WO₃ powder (APTWO₃) on the WO₃ stoichiometric

4 state and the growth of monolayer WS₂. From the obtained XRD results as shown in Supplementary Figure S6, APTWO₃

5 powder exhibit peak shift to a much lower diffraction angle as compared with the FWO₃ powder. Based on the previous

6 analysis and our growth results, the synthesis of WS₂ shows similar results for using APTWO₃ and FWO₃ as growth precursor.

7~ Both of APTWO_3 and FWO_3 produce defective WS_2 monolayers in small triangular shape.

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2 Supplementary Figure S7: Color of (a) FWO₃, (b) PTWO₃, (c) AWO₃ and (d) PTAWO₃ powder, respectively.





Supplementary Figure S8. Thermal gravimetric analysis (TGA) analysis of the WO₃ powders. The inset is the enlarged scale of the TGA
analysis data of the WO₃ powders.

4 The growth of the WS₂ is also extremely sensitive to the water vapor in the growth atmosphere, in order to eliminate the 5 effect of surface-absorbed water in the WO₃ powder on the growth of the WS₂, we employ thermal gravimetric 6 analysis (TGA) to investigate the water percentage contained in the WO₃ powder. The thermal behavior of the WO₃ powder 7 in TGA analysis that analyses in an air atmosphere with a heating rate of $5^{\circ}C \min^{-1}$ is shown in Supplementary Figure S8. 8 The mass loss is only less than 1% that might be assigned to the evaporation of the surface-adsorbed water for all the four 9 precursors. This imply that the surface-absorbed water in the WO₃ powder is only very little and will have negligible effects 10 on the growth process of monolayer WS₂.

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Supplementary Figure S9: X-ray photoelectron spectroscopy (XPS) spectra fitting of O_{1s} for (a) FWO₃, (b) AWO₃, (c) PTWO₃ and (d) 3 PTAWO₃ powder, respectively.

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	FWO ₃			PTWO ₃			AWO ₃			PTAWO ₃		
	Position	FWHM	Area	Position	FWHM	Area	Position	FWHM	Area	Position	FWHM	Area
	(eV)	(eV)	(%)	(eV)	(eV)	(%)	(eV)	(eV)	(%)	(eV)	(eV)	(%)
W ^(IV) 4f _{7/2}	32.8	3.09	0.21	32.8	2.50	0.26	32.8	7.82	0.40	32.8	3.10	15.40
$W^{(IV)} 4f_{5/2}$	34.9	3.09	0.27	34.9	2.50	0.35	34.9	7.82	0.53	34.9	3.10	20.49
W ^(V) 4f _{7/2}	35.5	1.03	3.27	35.5	1.35	37.35	35.5	1.22	6.40	35.5	1.03	3.27
W ^(V) 4f _{5/2}	37.6	1.03	4.35	37.6	1.35	28.10	37.6	1.22	8.52	37.6	1.03	4.35
W ^(VI) 4f _{7/2}	36.0	1.69	16.48	36.0	1.98	15.11	36.0	1.76	14.03	35.9	1.69	29.92
W ^(VI) 4f _{5/2}	38.1	1.69	21.92	38.1	1.98	20.10	38.1	1.76	18.66	38.0	1.69	22.50
W ^(VI) 5p _{1/2}	41.2	4.72	53.50	41.2	4.55	52.81	41.2	4.54	51.46	41.2	5.00	56.00
$O^{(IV)}1s_{1/2}$	530.8	0.20	0.02	530.8	-	-	530.8	3.60	2.95	530.8	1.85	6.63
O ^(V) 1s _{1/2}	531.5	2.43	30.45	531.5	2.87	33.46	531.5	3.09	23.15	531.5	2.64	30.12
$O^{(VI)} 1s_{2/2}$	530.5	1.64	69.53	530.5	1.72	66.54	530.5	1.71	73.90	530.5	1.62	63.25

3 Supplementary Table 1: XPS spectra fitting results of binding energy for W4f and O 1s in FWO₃, PTWO₃, AWO₃, and PTAWO₃ powder.





5 Supplementary Figure S10. Raman spectra of untreated and pretreated WO₃ powders.



2 Supplementary Figure S11. Peak deconvolution of the low temperature photoluminescence (PL) spectra of face light emitting (FLE) WS_2

3 monolayer sample (a), inner region (b) and edge region (c) of the edge light emitting (ELE) WS₂ monolayer sample measured at ⁷⁷ K.

		FLE		E	LE Inner		ELE Edge		
Types of charges	Position	FWHM	Area	Position	FWHM	Area	Position	FWHM	Area
	(eV)	(meV)	(%)	(eV)	(meV)	(%)	(eV)	(meV)	(%)
Exciton	2.09	14.60	45.40	2.09	28.40	4.49	2.09	20.40	4.16
Trion	2.06	20.90	13.97	2.05	14.40	0.19	2.05	15.90	20.01
Biexciton/ Bound defect Exciton	-	-	-	-	-	-	2.03	13.10	9.70

5 Supplementary Table 2. Low temperature PL intensity spectra fitting results of electron energy measured at ⁷⁷ K for FLE, ELE inner region







and ELE edge region monolayer WS₂.



2 Supplementary Figure S13. Optical characterization of FLE WS2 monolayer sample being exposed to ambient condition for more than

- 3 one month. (a) Optical image of FLE WS2 monolayer. (b) Raman spectra and Raman intensity mapping (inset) of the FLE WS2 monolayer.
- 4 (c) PL spectra and PL intensity mapping (inset) of the FLE WS2 monolayer.



6 Supplementary Figure S14. XPS spectra of the FLE WS₂ monolayer on a sapphire substrate. (a, b) XPS spectra corresponding to the 7 W 4f and S 2P orbital, respectively.

8 "As shown in Supplementary Figure S14, the XPS analysis confirms the presence of the WS₂ in the sample and shows that

9 the monolayer FLE WS₂ sample also consists of tungsten trioxide (W $4f^{(v)}$ and W $4f^{(v)}$). For CVD grown monolayer WS₂, the

10 substrate will consist of unreacted WO₃ sources during growth and this will contribute to the XPS environmental result.

11 Therefore, XPS analysis is insufficient to confirm the presence of WO₃ in the as-grown monolayer WS₂. Besides, from the

12 optical images, AFM images, optical characterization as well as the STEM analysis, there is no any stacking effects in the

13 $\,$ monolayer WS_{_2} sample, indicating that the sample is purely WS_{_2}."

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- 2 Supplementary Figure S15. Comparison of PL intensity for FLE and ELE WS $_2$ monolayers.



2 Supplementary Figure S16. Defect mapping of scanning transmission electron microscope annular dark field (STEMADF) image for FLE

- 3 WS₂ monolayer, including monosulfur vacancy (V_s), and antisite defects where a W atom substituting a S₂ (W_{S2}) or a S₂ column substituting
- 4 a W atom (S_{2w}).