SUPPLEMENTARY INFORMATION

Phase engineering of seamless heterophase homojunctions with co-existing 3R and 2H phases in WS_2 monolayers

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Sample preparation and in-situ extension of growth condition:

Typically, we have taken as mentioned amount of WO_3 nanorod and ultra-sonicated with deionized water that sparsely deposited on SiO_2/Si substrate and placed it at center (heating zone 1) of quartz tube furnace. Before the deposition of WO_3 nanorod, SiO_2/Si substrate was cleaned by ultrasonication with Acetone, Isopropyl alcohol followed by Piranha solution (3:1 ratio of H_2SO_4 & H_2O_2) treatment for 3 hours. A boat containing ~300 mg Sulfur powder has been placed on heating zone 2 of same tube furnace such that the sulfurization of WO_3 nanorod can be achieved near growth temperature. We have adopted two different ramping rates of 20°C/min. up to 500°C and 10°C/min. to reach the final reaction temperature. Generally, heterogeneous co-existing phase of monolayer WS_2 grown in 5-10 minutes after reaching as mentioned final reaction temperature. On extending this growth duration to 30 minutes by maintaining similar growth parameters, dynamic reconstructions started between newly evolved point defects and continuous nucleation of WS_2 growth. After 30 minutes, monolayer WS_2 with large amount of clustered point defects (voids) in the region of 3R phase appeared due to high energy metastable structure.

Structure of 2H and 3R phases in WS_2:

WS_2 has mainly three allotropes in its structure which are 1T, 2H and 3R depending on coordination of S-atom with W-atoms as well as stacking order of its layers. Among the three polytypes, 2H and 3R having commonly trigonal prismatic coordination while 1T has octahedral coordination. Trigonal prismatic coordination in 2H have stacking order in form of AbA BaB AbA while in case of 3R phase, it is like AbA BcB CaC AbA. Formation of two polytypes next to each other is trivial with coexisting phase materials and stabilizing themselves resulting from the thermodynamic favored conditions as mentioned in table ST1. Strain energy minimization stabilizes co-existing phases at room temperature and has been explored here upto their decomposition states using in-situ PL measurements.

Physical and chemical properties in bulk polytype of 2H and 3R are almost equal except it's slightly changes band structure. 2H and 3R, both form of polytypes shows semiconducting in nature due to similar coordination geometry. This causes slight changes in PL position with slightly reduced intensity. While the metallic 1T phase known to show complete PL quenching, the observed 3R phase shows considerable intensity due to its semiconducting nature.

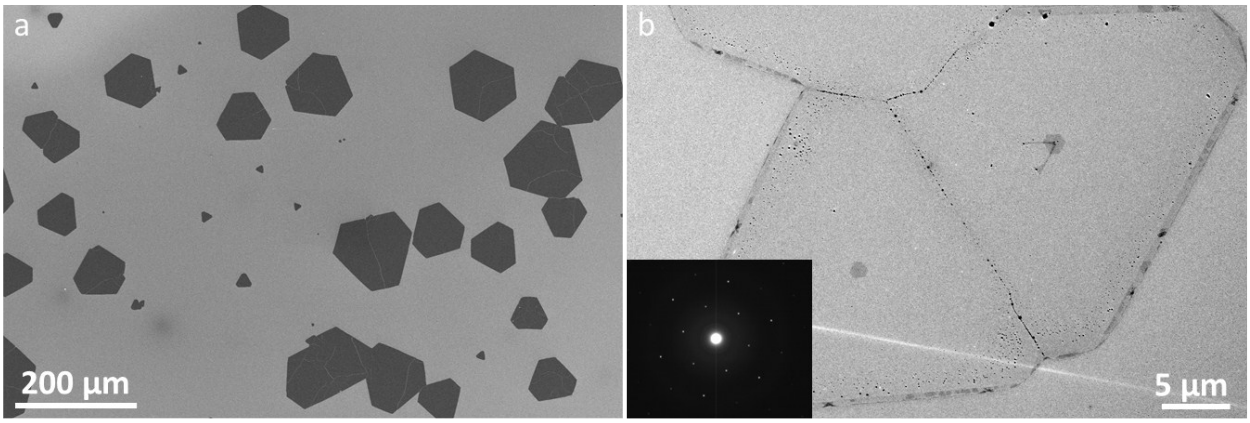

Figure S0: Electron microscopic view of monolayer WS_2; (a) FESEM image of large size CVD grown monolayer WS_2 having no contaminants and corresponded similar (b) TEM image for as-grown monolayer WS_2 directly on Si_3N_4 grid along with attached (inset) SAED pattern reflecting crystalline monolayer formation.

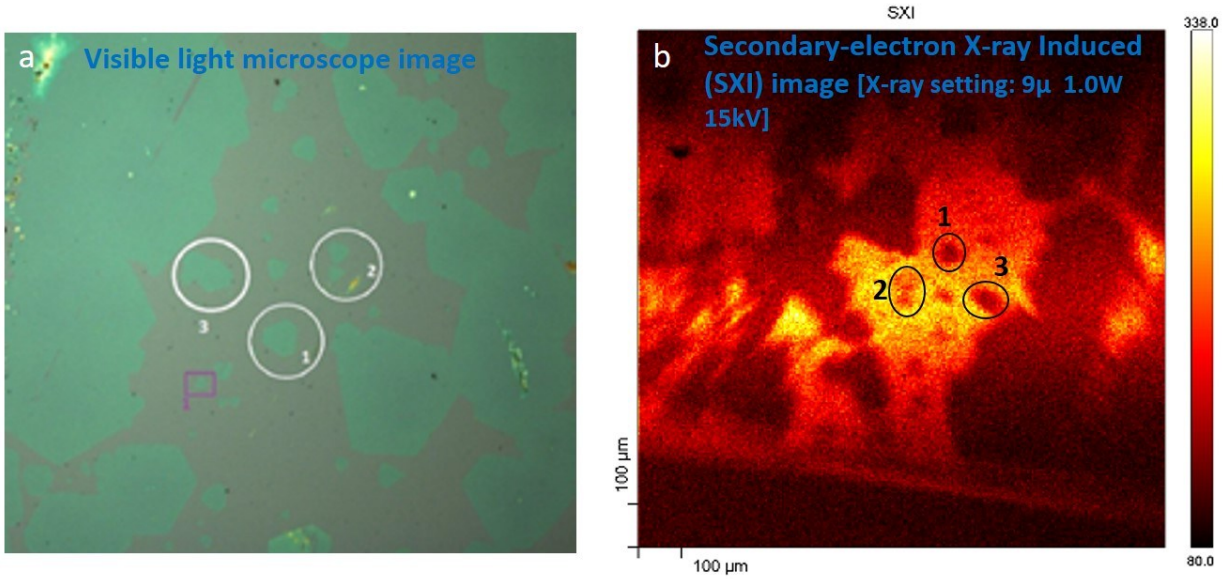

Figure S1: (a) Visible light microscope image as shown is used to locate individual flake for further XPS measurement, (b) SXI imaging has been performed to locate exact position of corresponding flakes for XPS measurement.

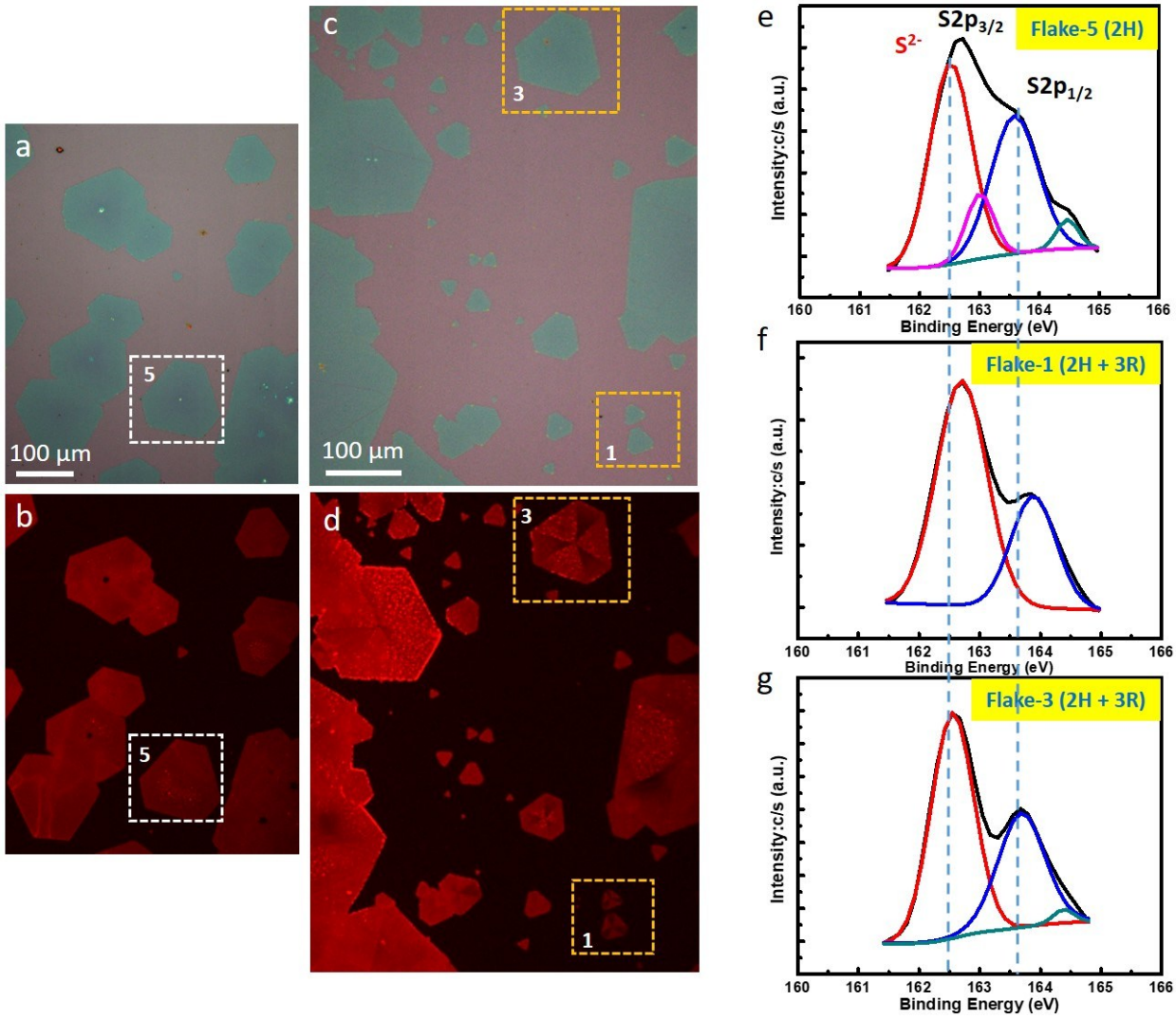

Figure S2: XPS measurement across the planar and hetero-phase formation in monolayer for corresponding three different flakes showing S2p orbital binding energy.

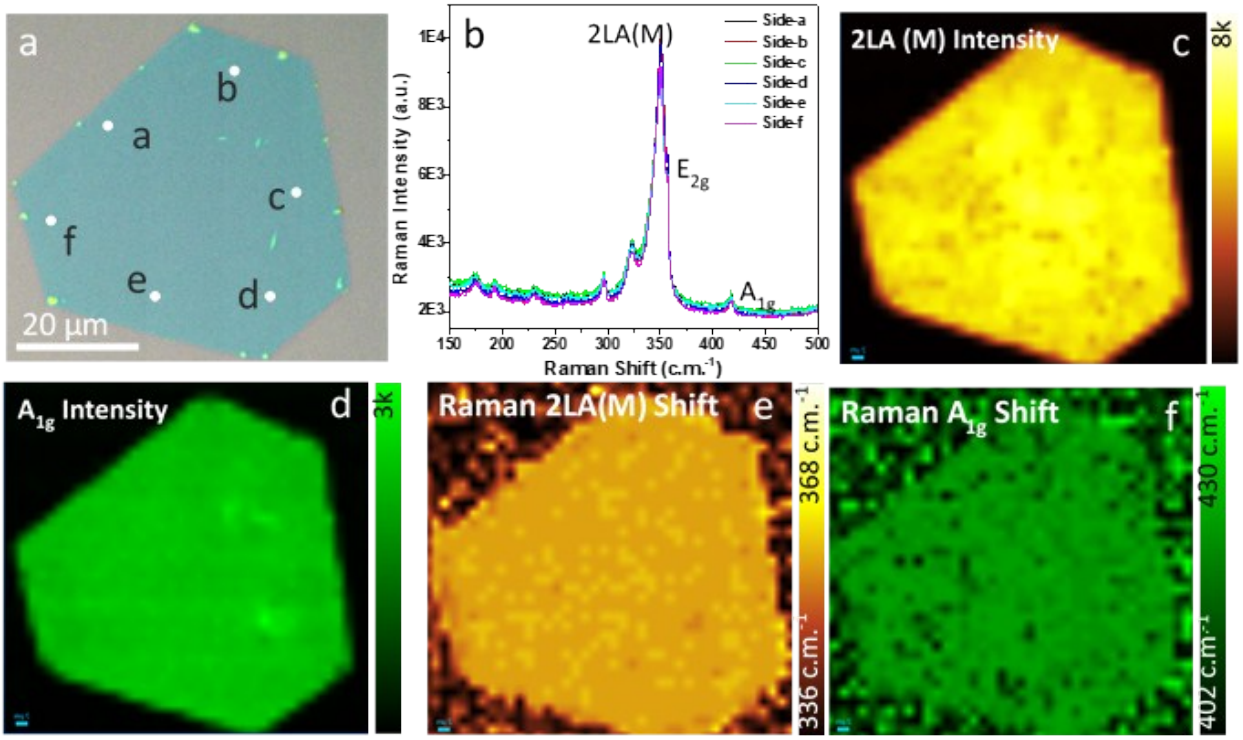

Figure S3: Structural phase heterogeneity (2H and 3R) in monolayer WS_2 (flake 2) forming alternate seamless homojunction; (a) VLM image of monodomain single layer WS_2 which shows no optically visible phase contrast. (b) Raman point spectrum for each alternate phase forming seamless homojunction along with Raman intensity mapped images for both dominant vibrational modes, (c) 2LA and (d) A_{1g} and Raman position mapped images (e) 2LA(M) (f) A_{1g} respectively having no any distinguished contrast within truncated hexagonal monolayer WS_2 confirming very small defect concentration leading to formation of heterophase (scale bar is same for all).

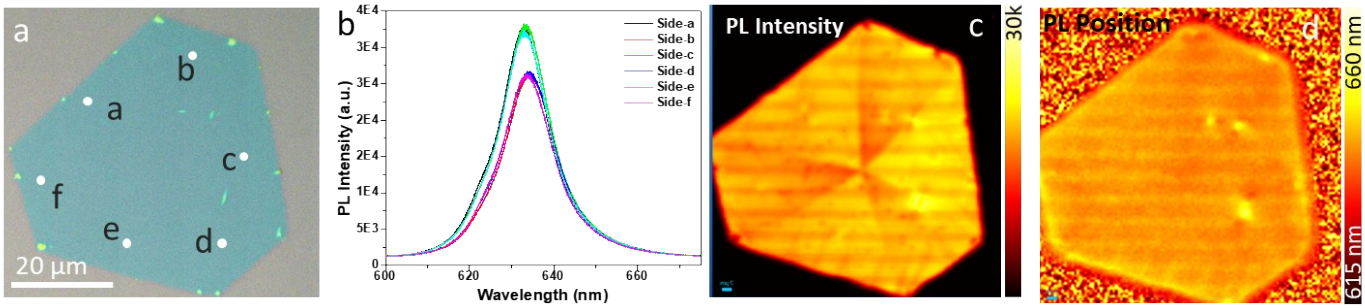

Figure S4: Structural phase heterogeneity "2H and 3R" in monolayer WS_2 (flake 2) forming alternate seamless homojunction; (a) VLM image of monodomain single layer WS_2 which shows no optically visible phase contrast and corresponding (b) PL point spectrum for each alternate phase forming seamless homojunction in between with different luminescence behavior, (c) PL intensity mapping as well as (d) PL position mapping corresponded to as shown VLM image as in figure a (scale bar is same for all).

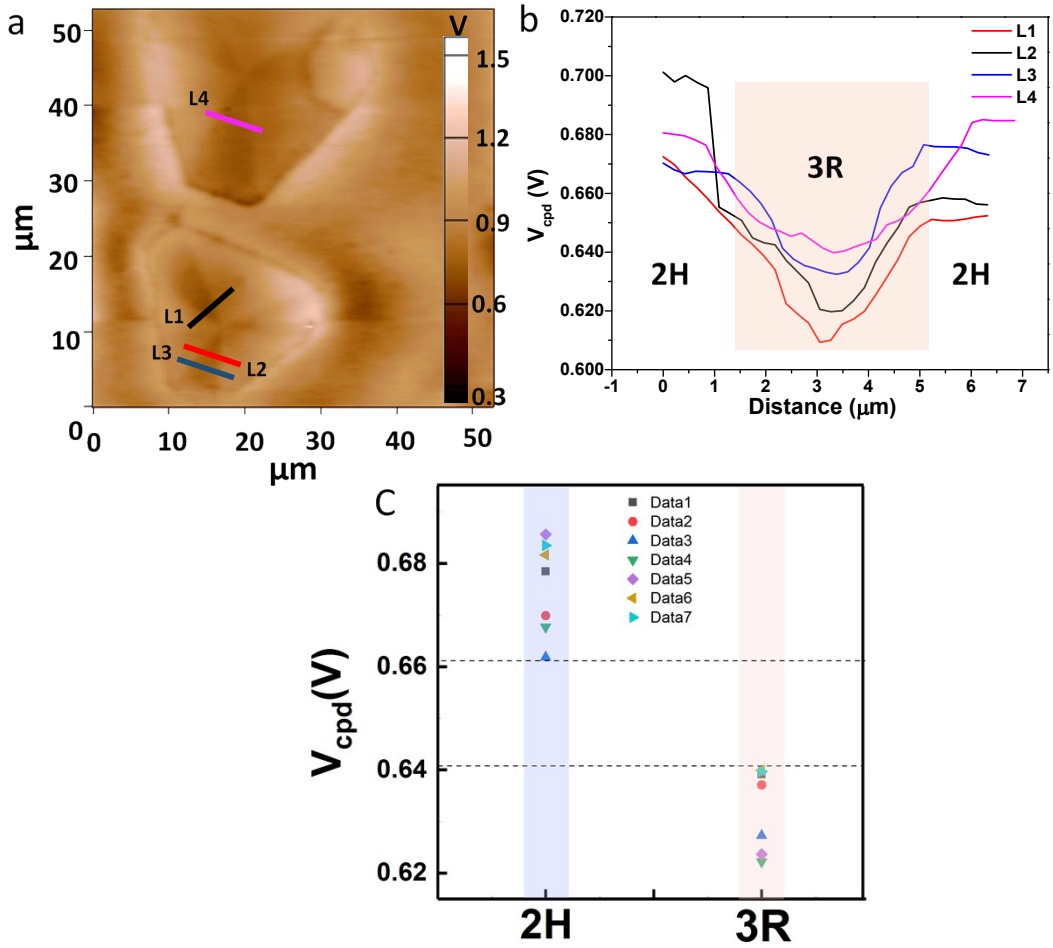

Figure S5: (a-b) Different line profile analysis to confirm the energy differences across interface of homojunction formed by 2H-3R WS_2. (c) Plots showing varying Contact potential difference (V_{cpd}) values for several data points on the 2H and 3R phases of WS_2 flake for as measurements done. The V_{cpd} value difference of ~40 mV is constantly present between the two phases.

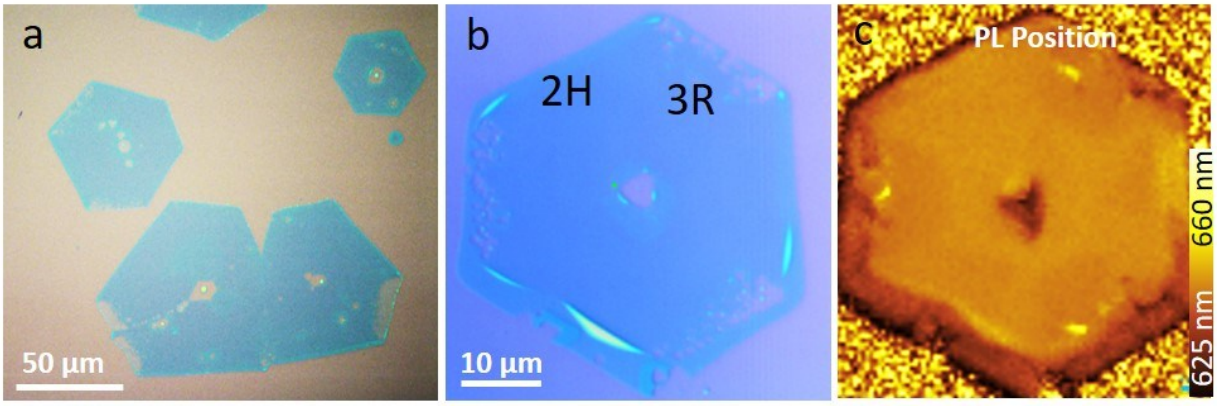

Figure S6: Defect formation and favorable enriched defects nucleated facet region shown in atomically thin heterophase 2D monolayer WS_2.

Reaction Parameters				Concentration		Resultant Product		
Temp. : Zone 1 (WO_3) ~ 850°C	Temp. : Zone 2 (S) ~ 200-250°C * S inserted when zone1 temp. reached to 700°C	Gaseous environment : Ar+H_2 (95+5%) ~ 50 sccm.	Growth duration : ~ 5-10 min.	Sulfur (S)	WO_3 Nanorod (1µg/ml)	Monolayer Domain Size	Monolayer Heterogeneity	
							Growth Temp. ~ 850°C	Growth Temp. ~ 900°C
							Homogeneous	Heterogeneous
				200 mg	1-4 µl	Nothing formed	NA	
					6 µl	Very small domain (<5 µm)	Could not analyzed	
					8 µl	Medium domain (~5-10 µm)	Yes	Yes
					10-12 µl	Large domain (~50-150 µm)	Yes	Yes
					15-20 µl	Bilayer domain (~100 µm)	Yes	Yes

Table ST1: Optimized parameters for controlled growth of heterogeneous structure of monolayer WS_2 forming in single domain with large lateral dimension.