Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

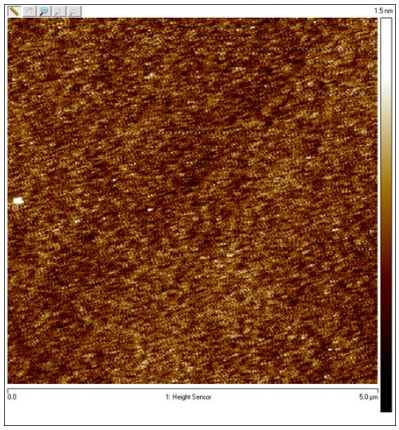

Figure S1. AFM surface image of monolayer MoS_2 grown on SiO_2/Si substrate, showing the uniformity and flatness of the 2D layer. The root mean squared (RMS) roughness is estimated to be 0.19 nm.

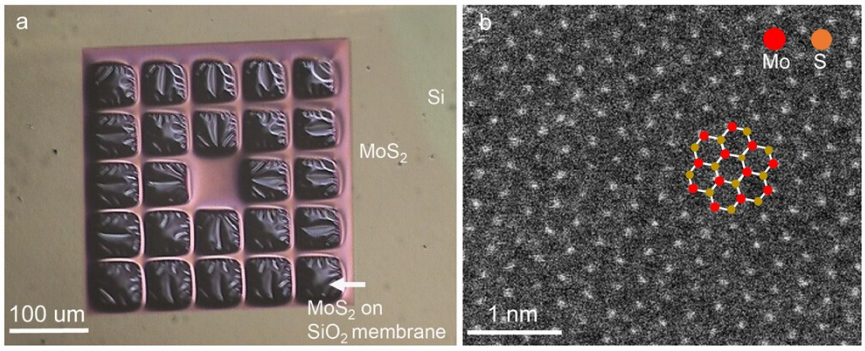

Figure S2. (a) Microscopy image of monolayer MoS_2 on the TEM grid with ultrathin support SiO_2 films for STEM, 8 nm membrane thickness. The upper right part show the bare Si for comparison. The SiO_2 support films consist of pure and amorphous thermal SiO_2 membrane with a size of 70 x 70 µm on a perfectly round 3 mm Si frame as a platform. The TEM grids offer super flatness and high-temperature tolerance. Thus, the 2D layers were directly grown on TEM grids for STEM at the same condition as on the SiO_2/Si substrates i.e. 750 ºC. (b) ADF-STEM image of monolayer MoS_2 with

alternating Mo and S columns arranging into hexagonal structure, which can be identified as the high quality 2H-MoS_2.

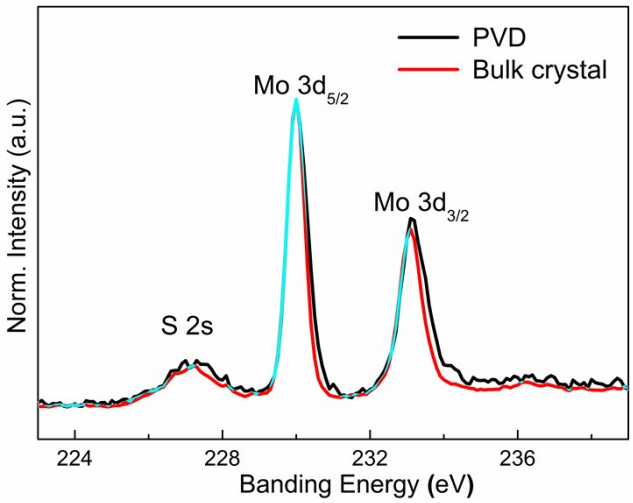

Figure S3. XPS spectra of the PVD-grown MoS_2 (black) film and bulk single crystal (red). The peaks of Mo 3d and the full width at half maximum (FWHM) are comparable.

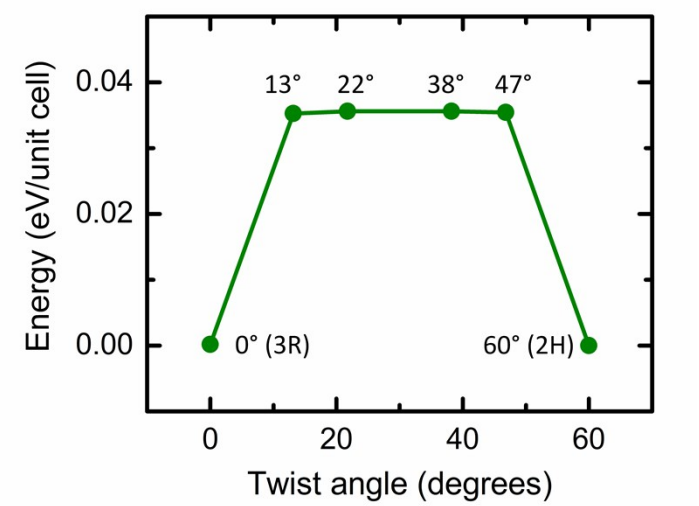

Figure S4. Calculated structure energy of heterostructures with different twist angles, relative to the most stable 2H structure with the lowest energy (set at zero). The stability of 3R is comparable to that of 2H, whereas the structures with $0° < \theta < 60°$ twist angles are less stable by about 0.035 eV.

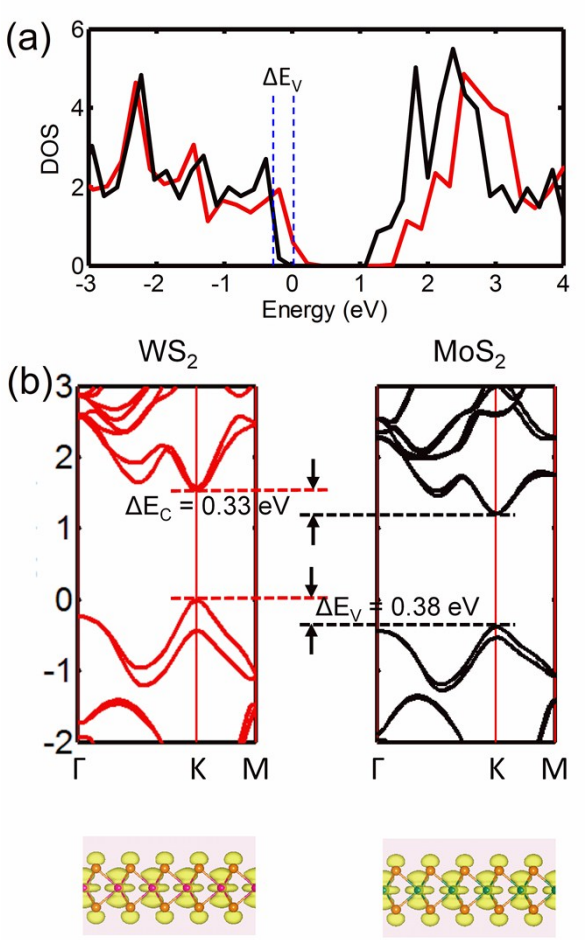

Figure S5. (a) Density of states (DOS) for WS_2 monolayer (red curve) and MoS_2 monolayer (black curve). (b) The band structures and the partial charge densities (at Γ point in VBM) of WS_2 and MoS_2 monolayers by DFT calculations. The VBO and CBO of the WS_2/MoS_2 heterostructure are estimated to be 0.38 eV and 0.33 eV, respectively.

Table S1. Calculated interlayer distance (d), total energy (ΔE), and band gap of the heterostructures with different configurations.

Twisted angle	Interlayer distance (Å)	Total energy (meV/unit cell)	Γ-K (eV)	K-K (eV)
0° (3R)	6.20	0.20	1.10	1.29
13°	6.44	35.27	1.16	1.23
22°	6.43	35.62	1.16	1.23
38°	6.44	35.62	1.16	1.23
47°	6.44	35.41	1.16	1.23
60° (2H)	6.20	0.00	1.08	1.24
60° (2H)	6.20 + 0.24	-	1.19	1.23
60° (2H)	6.20 + 0.5	-	1.26	1.22
60° (2H)	6.20 + 1.0	-	1.35	1.21
60° (2H)	6.20 + 1.5	-	1.40	1.20
60° (2H)	6.20 + 2.0	-	1.42	1.20