Supporting information for

Microscopic Mechanism of van der Waals Heteroepitaxy in the Formation of MoS$_2$/hBN Vertical Heterostructures

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Figure S1. a): typical AFM image of MoS$_2$ grown on hBN; b): corresponding averaged height profile along the blue line shown in Fig. S1a.
**Figure S2.** An optical image of MoS$_2$/hBN used for calculating the distribution of MoS$_2$ grain orientation (Table 1).
Figure S3. Stacking-angle dependent total energy of the MoS$_2$ cluster using the LJ potential. The calculation procedure (optimizing interlayer distance at 0° and calculating energy at each stacking angle with fixed interlayer distance) is the same as that used in the DFT calculation (shown in Fig. 2a).
Figure S4. A schematic representation of the method for calculating interaction energies
Table S1. List of $n$, number of Mo atoms and edge length of each MoS$_2$ clusters, and the most stable center position of the MoS$_2$ cluster at a stacking angle of 0°.

| $n$ | Chemical formula | Edge length (nm) | Center       |
|-----|------------------|-----------------|--------------|
| 1   | Mo$_3$S$_6$      | 0.3             | on B atom    |
| 2   | Mo$_{12}$S$_{24}$| 0.6             | on B atom    |
| 3   | Mo$_{27}$S$_{54}$| 0.9             | on N atom    |
| 4   | Mo$_{48}$S$_{96}$| 1.3             | on B atom    |
| 5   | Mo$_{75}$S$_{150}$| 1.6         | on B atom    |
| 6   | Mo$_{108}$S$_{216}$| 1.9      | on N atom    |
| 7   | Mo$_{147}$S$_{294}$| 2.2         | on N atom    |
| 8   | Mo$_{192}$S$_{384}$| 2.5         | on B atom    |
| 9   | Mo$_{243}$S$_{486}$| 2.8         | on B atom    |
| 10  | Mo$_{300}$S$_{600}$| 3.2         | on N atom    |
| 11  | Mo$_{363}$S$_{726}$| 3.5         | on N atom    |
| 12  | Mo$_{332}$S$_{664}$| 3.8         | on B atom    |
| 13  | Mo$_{507}$S$_{1014}$| 4.1        | on B atom    |
| 14  | Mo$_{588}$S$_{1176}$| 4.4         | on N atom    |
| 15  | Mo$_{675}$S$_{1300}$| 4.7         | on N atom    |
| 16  | Mo$_{768}$S$_{1536}$| 5.1         | on B atom    |
| 17  | Mo$_{867}$S$_{1734}$| 5.4         | on B atom    |
| 18  | Mo$_{972}$S$_{1944}$| 5.7         | on N atom    |
Figure S5. Schematic images of stable MoS$_2$/hBN structure at a stacking angle of 0°. Upper images show the whole view of MoS$_2$ cluster and lower images correspond to magnified images of each cluster's center position. A list of stable center positions can be seen in Table S1. a) to r) show result of a): Mo$_3$S$_6$, b): Mo$_{12}$S$_{24}$, c): Mo$_{27}$S$_{54}$, d): Mo$_{48}$S$_{96}$, e): Mo$_{75}$S$_{150}$, f): Mo$_{108}$S$_{216}$, g): Mo$_{147}$S$_{294}$, h): Mo$_{192}$S$_{384}$, i): Mo$_{243}$S$_{486}$, j): Mo$_{300}$S$_{600}$, k): Mo$_{363}$S$_{726}$, l): Mo$_{432}$S$_{864}$, m): Mo$_{508}$S$_{1016}$, n): Mo$_{588}$S$_{1176}$, o): Mo$_{675}$S$_{1350}$, p): Mo$_{768}$S$_{1536}$, q): Mo$_{867}$S$_{1734}$, and r): Mo$_{972}$S$_{1944}$ cluster. Purple, yellow, green, and grey sphere correspond to Mo, S, B, and N atom, respectively.
Figure S6. Element-decomposed interlayer energy mapping of a Mo$_{48}$S$_{96}$ (an edge length of 1.3 nm) cluster with a stacking angle of 0°. S$_2$ pairs are marked as yellow circles. Magenta dotted lines correspond to the moiré superlattice period of the structure.
Figure S7. An in-plane interaction-energy map of a Mo$_{768}$S$_{1536}$ cluster (an edge length of 5.1 nm) with the stacking angle of 0°. To make this map, we calculated interaction energies at various lateral positions with the stacking angle fixed. Grey and green spheres correspond to typical positions of N and B atoms, respectively.
Additional discussion: effect of MoS$_2$ cluster shape

We have used hexagonal-shape MoS$_2$ clusters to calculate interaction energies because the obtained MoS$_2$ crystals are truncated triangles (Fig. 1a). However, in most cases, the shape of MoS$_2$ crystals is triangular.$^1$ We, therefore, have checked the effect of MoS$_2$ crystal shape onto interaction energies. Figure S8 shows a stacking-angle dependence on the total energy of triangular-shape MoS clusters (Mo$_3$S$_{14}$ and Mo$_{351}$S$_{750}$: an edge length of 0.6 and 7.9 nm, respectively). The obtained energy evolution (Fig. S8a) is similar to the results obtained from hexagonal-shape one: 1): 0 or 60° stacking can be local or global energy minimum with crystal size evolution; and 2): there are energy minimums around 10–20 and 40–50° in the result of Mo$_{351}$S$_{750}$ cluster. Therefore, we have concluded that MoS cluster shape does not significantly affect the energy landscape obtained with the LJ potential; the lateral position and stacking angle are expected to change at the early stage of the growth even in the triangular MoS clusters.

Figure S8. a): cluster size and relative stacking angle evolution of total energy using a triangular-shaped MoS cluster; b) and c): schematics of stable (b): Mo$_6$S$_{14}$ and c): Mo$_{351}$S$_{750}$/hBN structure at the stacking angle of 0°. The upper and lower image shows the whole view and magnified image at the center of gravity of the clusters. Purple, yellow, green, and grey sphere correspond to Mo, S, B, and N atom, respectively.
References

1. van der Zande, A. M.; Huang, P. Y.; Chenet, D. A.; Berkelbach, T. C.; You, Y.; Lee, G.-H.; Heinz, T. F.; Reichman, D. R.; Muller, D. A.; Hone, J. C., Grains and Grain Boundaries in Highly Crystalline Monolayer Molybdenum Disulphide. *Nat. Mater.* **2013**, *12* (6), 554-561.