

Supporting Information for

Phase Crossover in Transition Metal Dichalcogenide Nanoclusters

Wenyan Zan^{ab}, Zhili Hu^b, Zhuhua Zhang^{*b} and Boris I. Yakobson^{*bcd}

^aState Key Laboratory of Applied Organic Chemistry, Department of Chemistry, Lanzhou University, Lanzhou 730000, China

^bDepartment of Materials Science and NanoEngineering, Rice University, Houston, Texas 77005, USA

^cDepartment of Chemistry, Rice University, Houston, Texas 77005, USA

^dSmalley Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77005, United States

*Address correspondence to biy@rice.edu and zz19@rice.edu

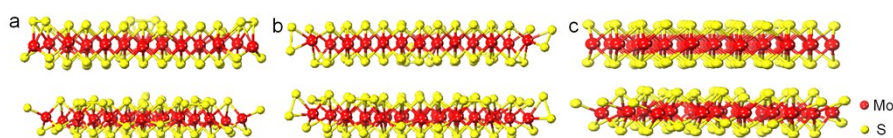


Figure S1. The side view of optimized atomic structures of (a) \triangle , (b) \blacktriangle and (c) \hexagon MoS₂ clusters. Top is H phase and bottom is T phase. Red and yellow balls stand for Mo and S atoms, respectively.

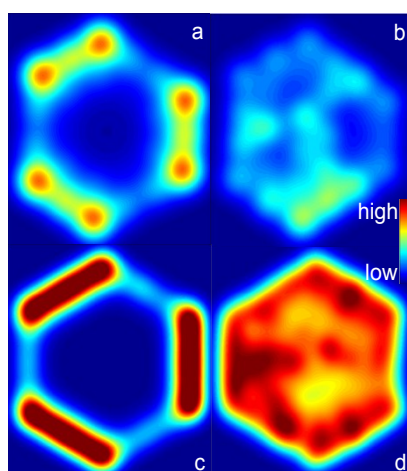


Figure S2. Mapping of high-energy electronic states on Mo atoms in MoS₂ hexagons. The high-energy electronic states are calculated by integrating the local density of states projected by Mo atoms within an energy window from -0.1 eV below E_F to 1.0 eV above E_F . The results for the (a) 3- \square_H , (b) 3- \square_T , (c) 7- \square_H (d) 7- \square_T MoS₂ clusters.

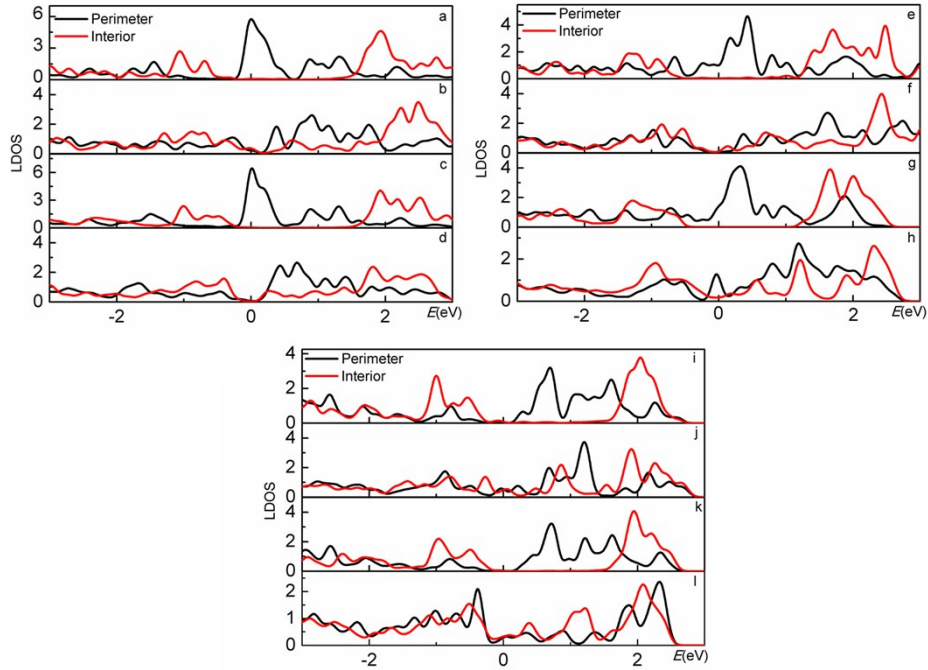


Figure S3. Local density of states of Mo 3d orbitals at the perimeters and interiors of (a) 5- \triangle_H , (b) 5- \triangle_T , (c) 8- \triangle_H , (d) 8- \triangle_T , (e) 3- \square_H , (f) 3- \square_T , (g) 7- \square_H (h) 7- \square_T , (i) 5- \blacktriangle_H , (j) 5- \blacktriangle_T , (k) 8- \blacktriangle_H and (l) 8- \blacktriangle_T MoS₂ clusters.

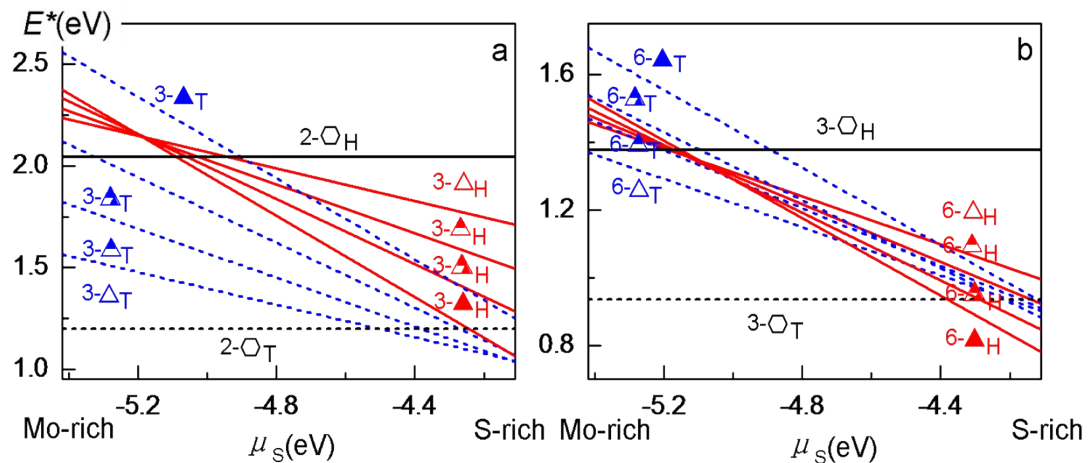


Figure S4. Formation energies per Mo atom of (a) 3- $\triangle/\blacktriangle/\blacktriangle$ and 2- \square MoS₂

clusters, (b) 6- $\triangle/\triangle/\triangle/\triangle$ and 3- \square clusters, as a function of S chemical potential, plotted in the range $-5.42 \text{ eV} < \mu_{\text{S}} < -4.11 \text{ eV}$.

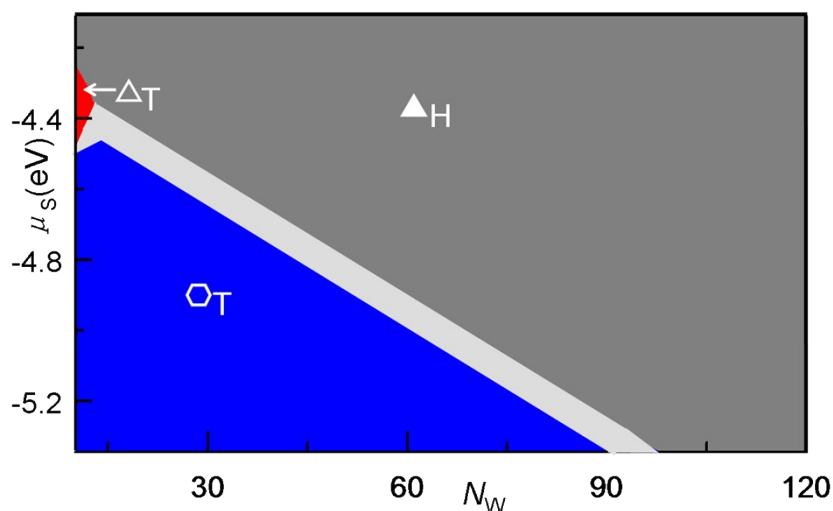


Figure S5. Phase diagram of WS_2 clusters based on comparing the formation energies per W atom as functions of N_{W} atoms and chemical potential of S. The thick boundary in light grey represents gradual transition through truncated triangles which appear as intermediate shapes between standard hexagons and triangles.

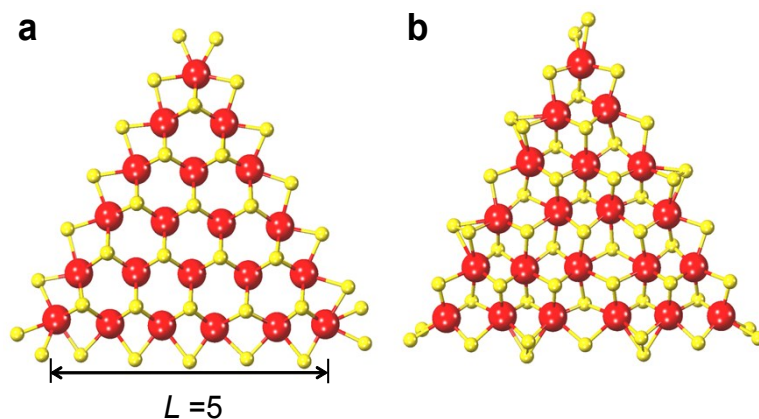


Figure S6. Optimized atomic structures of Mo-terminated (a) \triangle_{H} and (b) \triangle_{T} MoS_2 clusters. Red and yellow balls stand for Mo and S atoms, respectively.

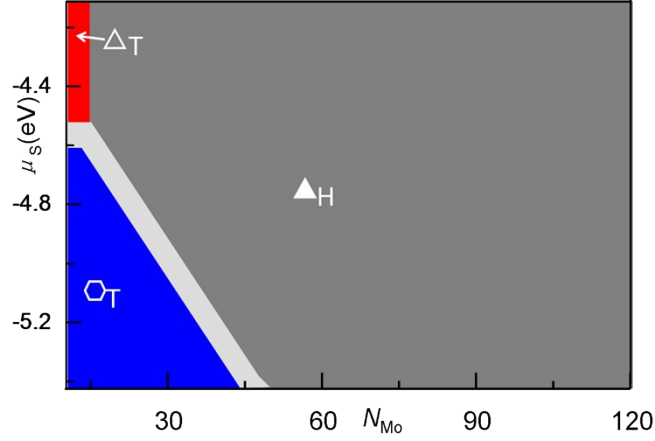


Figure S7. Phase diagram of MoS₂ clusters with Mo-oriented edges based on comparing the formation energies per Mo atom as functions of N_{Mo} atoms and chemical potential of S. The thick boundary in light grey represents gradual transition through truncated triangles which appear as intermediate shapes between standard hexagons and triangles.

Local density of states of Mo 3d orbitals of MoS₂ clusters

In the $L_{2\text{H}}\text{-}\blacktriangle$, S-passivation of the corners shifts the LDOS peaks of the Mo 3d states around the perimeter to higher energy levels above the Fermi level, suggesting that the stability of the cluster is enhanced upon the passivation. In contrast, no remarkable change is found in the Mo 3d states for the $L_{1\text{T}}\text{-}\blacktriangle$ family with the same chemical modification. This difference in the change of electronic structures is in line with the higher stability of the $L_{2\text{H}}\text{-}\blacktriangle$ than the $L_{1\text{T}}\text{-}\blacktriangle$.

Edge energy fitting and the expressions of A, B, and C in total energy equations:

The edge energy of $L\text{-}\triangle$ and $L\text{-}\blacktriangle$ can be expressed as:

$$(E_{\text{cls}} - N_{\text{MoS}_2}\mu_{\text{MoS}_2} - 2L\mu_{\text{S}} - E_{\text{cor}})/3L = \gamma(\mu) = \gamma^0 - \mu/3 \quad (\text{S1})$$

and that of $L\text{-}\square$ is expressed as

$$(E_{\text{cls}} - N_{\text{MoS}_2}\mu_{\text{MoS}_2} - E_{\text{cor}})/6L = \gamma \quad (\text{S2})$$

For $L\text{-}\triangle$, direct counting yields the number of constituent MoS₂-pairs: $N_{\text{MoS}_2} = 0.5L(L+3)$; one extra Mo atom at a corner is omitted due to the insignificant contribution from the corners; there are $2L$ extra S atoms along the perimeter. For $L\text{-}\blacktriangle$, the corresponding expression is $N_{\text{MoS}_2} = 0.5(L+1)(L+2)$, with four extra S atoms at two corners being omitted and $2L$ extra S atoms distributed along the perimeter. For $L\text{-}\square$, it is $N_{\text{MoS}_2} = 3L^2$ and no extra S atom.

The total energy of $L\text{-}\triangle_{\text{H}}$, $L\text{-}\triangle_{\text{T}}$, $L\text{-}\blacktriangle_{\text{H}}$ and $L\text{-}\blacktriangle_{\text{T}}$ can be expressed as:

$$E_{\text{cls}} = 0.5\mu_{\text{MoS}_2}^{\text{H}}L^2 + (1.5\mu_{\text{MoS}_2}^{\text{H}} - 4.54)L + E_{\text{cor}} \quad (\text{S3})$$

$$E_{\text{cls}} = 0.5\mu_{\text{MoS}_2}^{\text{T}}L^2 + (1.5\mu_{\text{MoS}_2}^{\text{T}} - 6.36)L + E_{\text{cor}} \quad (\text{S4})$$

$$E_{\text{cls}} = 0.5\mu_{\text{MoS}_2}^{\text{H}}L^2 + (1.5\mu_{\text{MoS}_2}^{\text{H}} - 4.52)L + \mu_{\text{MoS}_2}^{\text{H}} + E_{\text{cor}} \quad (\text{S5})$$

$$E_{\text{cls}} = 0.5\mu^{\text{T}}_{\text{MoS}_2}L^2 + (1.5\mu^{\text{T}}_{\text{MoS}_2} - 6.68)L + \mu^{\text{T}}_{\text{MoS}_2} + E_{\text{cor}} \quad (\text{S6})$$

and that of $L-\triangle_{\text{H}}$ and $L-\triangle_{\text{T}}$ is expressed as

$$E_{\text{cls}} = 3\mu^{\text{H}}_{\text{MoS}_2}L^2 + 12.96L + E_{\text{cor}} \quad (\text{S7})$$

$$E_{\text{cls}} = 3\mu^{\text{T}}_{\text{MoS}_2}L^2 + 3.15L + E_{\text{cor}} \quad (\text{S8})$$

Total energy expression of Mo-oriented clusters

The total energy of MoS₂ clusters with Mo-oriented edges: $E = AL^2 + BL + C$. For \triangle_{H} , $A = -10.89$, $B = -34.17$ and $C = -64.86 + 2\mu$. For \triangle_{T} , $A = -10.61$, $B = -34.94$ and $C = -65.24 + 2\mu$. This analysis agrees well with our DFT results by setting $\mu = 14.56$ for the \triangle_{H} , and $\mu = 14.16$ for the \triangle_{T} .