**Molybdenum Sulfide Clusters Immobilized on Defective Graphene:**

**A Stable Catalyst for Hydrogen Evolution Reaction**

Yixin Ouyang¹, Qiang Li¹, Li Shi¹, Chongyi Ling¹, and Jinlan Wang*¹,²

¹School of Physics, Southeast University, Nanjing 211189, China

²Synergetic Innovation Center for Quantum Effects and Applications (SICQEA), Hunan Normal University, Changsha 410081, China

**Supporting Information**

Fig. S1 Relaxed adsorption structures with energy difference for different configurations of the Mo₃ and Mo₂ on defect-free graphene. The total energy of the lowest energy configuration is used as the reference.
**Fig. S2** Relaxed adsorption structures with energy difference for different configurations of the Mo2 on mono-vacancy graphene. The total energy of the lowest energy configuration is used as the reference.

**Fig. S3** Relaxed adsorption structures with energy difference for different configurations of the Mo3 on mono-vacancy graphene. The total energy of the lowest energy configuration is used as the reference.
Fig. S4 Relaxed adsorption structures with energy difference for different configurations of the Mo2 on di-vacancy graphene. The total energy of the lowest energy configuration is used as the reference. The di-vacancy tends to form two pentagons and one octagon \( \text{V}_2(5-8-5) \) defect rather than forming S-C bonds with Mo2.

Fig. S5 Relaxed adsorption structures with energy difference for different configurations of the Mo3 on di-vacancy graphene. The total energy of the lowest energy configuration is used as the reference. The di-vacancy tends to form two pentagons and one octagon \( \text{V}_2(5-8-5) \) defect rather than forming S-C bonds with Mo3.
Fig. S6 Ab initio molecular dynamics simulations of structure evolution of the most stable chemisorption configurations of Mo2@graphene at (a)100K, (b)200K and (c)300K in 5 picoseconds.
**Fig. S7** Ab initio molecular dynamics simulations of structure evolution of the most stable chemisorption configurations of Mo3@graphene at (a) 100K, (b) 200K and (c) 300K in 5 picoseconds.
**Fig. S8** Favorable H adsorption configurations on Mo2 and Mo3 and $\Delta G$ of Mo2 and Mo3 on graphene support.

**Fig. S9** Charge density difference of (a) Mo2 and (b) Mo3 on defect-free graphene, (c) Mo2 and (d) Mo3 on graphene with mono-vacancy. Depletion and accumulation spaces are revealed in green and blue, respectively.
Fig. S10 Four most favorable 2H adsorption configurations on Mo3@Graphene. Their associated $\Delta G$ values are listed below each structure.