Supplementary Information

MD simulations details of solid/liquid interfacial model

Molecular dynamics (MD) simulations were initially performed using the LAMMPS package to equilibrate the structure of water molecules at the interface of monolayer MoS_2.[1] The rectangular supercell of monolayer MoS_2 had a rectangular dimension of approximately 21.545×24.878 $Å^2$ in x and y direction, respectively, and a water film initially placed on the top of the surface contained a total number of 538 H_2O molecules. Periodic boundary conditions were applied in all three directions and a vacuum 5.0 nm thick was added above the water film to prevent interactions between the periodic images. We employed the flexible extended simple point charge (SPC/E) model[2] for the water solvent and maintained a fixed surface structure during the simulation. The employed force field for MoS_2 was developed by Heiranian et al.,[3] which has been demonstrated to reproduce excellent water-MoS_2 interface properties. The cutoff distance for the non-bonded interactions was set to be 10.0 Å, and the long-range electrostatic interactions were calculated using the particle-particle particle-mesh method (PPPM).[4] The canonical ensemble (NVT) was applied during the simulation, temperature was held at 300.0 K via the Nose−Hoover method, and the coupling coefficient was 0.1 ps. The entirety of the simulation was completed in 20.0 ns, where the first 10.0 ns was for equilibrium and the remaining 10.0 ns were used for data collection.

To determine the interface structure of water molecules at the interface of monolayer MoS_2, we have tried to calculate the density distribution of water molecules along the z direction, as shown in Figure 2. It is clear from this figure that there are two pronounced peaks locating at 3.2 and 6.1 Å away from the surface, indicating that the water molecules can form two well-defined solvation structures near the surface. Beyond that, the density of water molecules along the z direction keeps almost unchanged, which means that those water molecules would behave bulk-like and their

properties would seldom influence the reactions happened at the interface of monolayer Mos_2. Therefore, the water molecules are divided into parts: (a) the interface water with the distance less than 8.2 Å from the surface; (b) bulk water with the distance larger than 8.2 Å from the surface, as illustrated in Figure 2. Afterwards, the interface water molecules were first extracted from the equilibrium structure and then a hexagonal cell was cleaved from the obtained structure, which was used for the subsequent DFT calculations. Additionally, it should be mentioned that, during the cleave process, the water molecule will be maintained if its mass center is inside the hexagonal cell. The dimension of the monolayer MoS_2 is 12.44×12.44 $Å^2$and there are totally 32 water molecules on the surface.

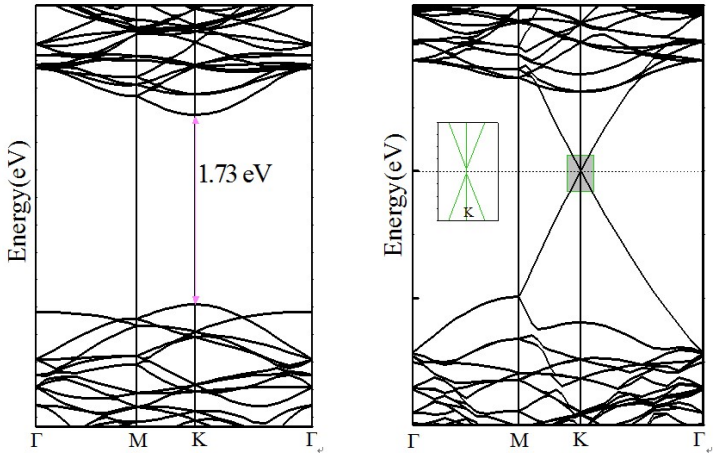

Figure 1. The band structures of monolayer MoS_2 (a) and hybrid MoS_2/graphene (b)

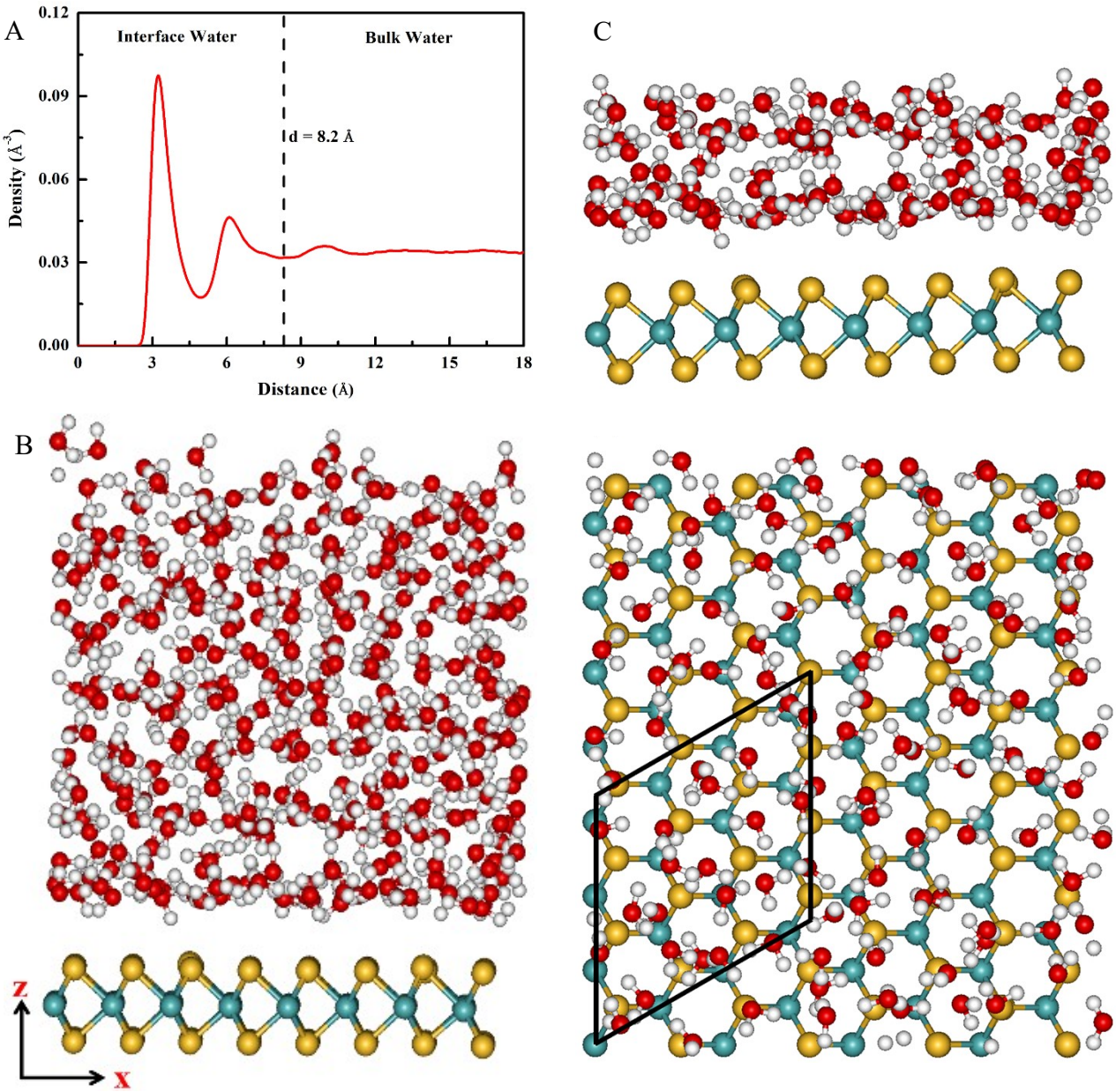

Figure 2. (A) Density distribution of water molecules at MoS_2surface along the z-direction. (B) Equilibrium snapshot of the water molecules at the interface of monolayer MoS_2 surface. The surface is placed at d = 0.0 Å. **(C)** Side and Top views of interfacial water molecules at the interface of monolayer MoS_2 surface. The super cell labeled by the black box in C is used for DFT calculations, which includes 16 MoS_2 units and 32 water molecules.

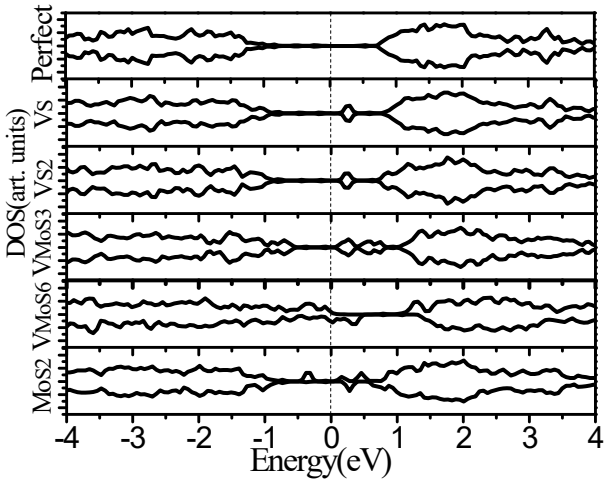

Figure 3. Total density of states (TDOS) for MoS_2/graphene system with different intrinsic defects: V_S, V_{S2}, V_{MoS3}, V_{MoS6} and Mo_{S2}, respectively. The vertical black dashed line indicates the position of the Fermi level, taken as zero energy.

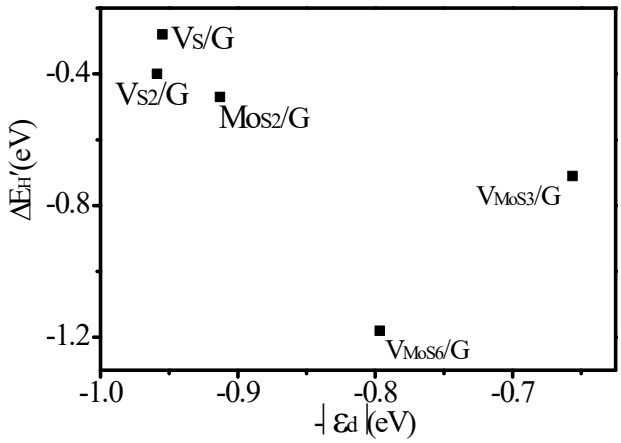

Figure 4. Relationship between $\Delta E_H'$ and $-|\varepsilon_d|$ for MoS_2/graphene system with different intrinsic defects: V_S, V_{S2}, V_{MoS3}, V_{MoS6} and Mo_{S2}, respectively.

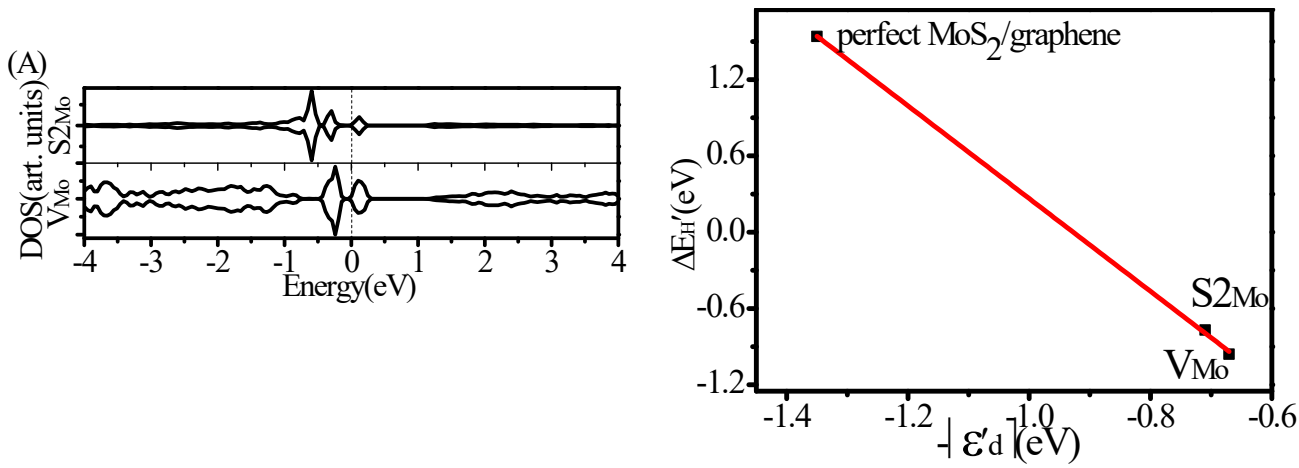

Figure 5. (A) Projected p-orbital DOS of S atoms for MoS_2/graphene system with V_{Mo} and $S2_{Mo}$ defects. (B) Relationship between $\Delta E_H'$ and $-|\varepsilon'_p|$ for perfect MoS_2/graphene and defective MoS_2/graphene with V_{Mo} and $S2_{Mo}$ cases.

Reference:

(1) LAMMPS; http://lammps.sandia.gov

(2) Yuet, P. K.; Blankschtein, D. Molecular Dynamics Simulation Study of Water Surfaces: Comparison of Flexible Water Models. J. Phys. Chem. B 2010, 114, 13786−13795.

(3) Heiranian, M.; Wu, Y. B.; Alurub, N. R. Molybdenum disulfide and water interaction parameters. J. Chem. Phys. 2017, 147, 104706.

(4) Hockney, R. W.; Eastwood, J. W. Computer Simulation Using Particles, 2nd ed.; IOP: Bristol, U.K., 1988.