Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Band Structure Engineering of Monolayer MoS_2 by Surface Ligand Modification for Enhanced Photoelectrochemical Hydrogen production Activity

The calculation of the average electrostatic potential

The plane average potential can be defined as $\overline{V}(z) = \frac{1}{A}\iint_{cell} V(x, y, z)dxdy$, where A is the area of the surface unit cell, $V(x, y, z)$ is the electrostatic potential on a grid in real space. Plotting $\overline{V}(z)$ as the function of z, we can easily obtain the value $V(\infty)$, which is the electrostatic potential of the vacuum level.

The vacuum level is set to be zero as the reference state. The band edge energies, that is, CBM and VBM can be obtained by aligning the eigenvalues to the vacuum level.

The favorable configurations of ligand modified MoS_2

To determine the favorable adsorption configuration, three adsorption sites, including the top site of S (TS) and Mo atom (TM), and the hollow site of the hexagonal lattice (H site), are considered. The initial ligand orientations are set to be perpendicular or parallel to the surface. As shown in Fig. S1, for O_2 and H_2O adsorption, the mass center locates at TM site and H site for the most favorable configuration, respectively. For COOH adsorption, the adsorption at the C side is found to be the energetically most favorable configuration. For C_6H_5CN and $C_6H_5CH_2NH_2$ adsorption, there is a tilt angle between the ligand and the surface for the most favorable configuration.

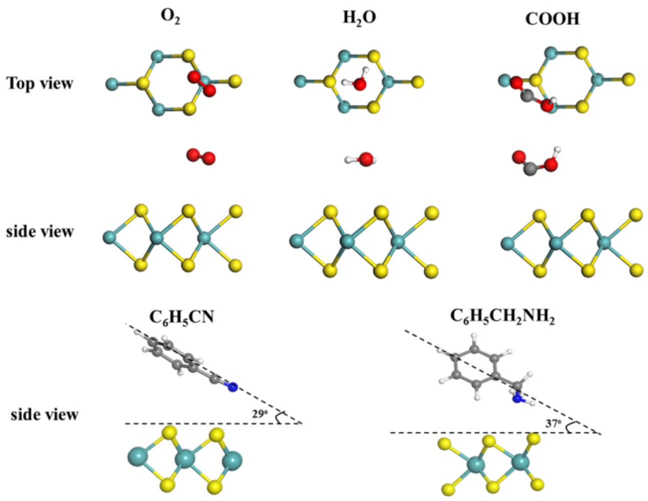

Fig. S1 Top and side views of the most favorable configurations for O_2, H_2O and COOH on ML-MoS_2 and side view of C_6H_5CN and $C_6H_5CH_2NH_2$ on ML-MoS_2.

The average electrostatic potential of C_6H_5CN modified MoS_2

The work function, that is, $W = V(\infty) - E_F$, where, $V(\infty)$, E_F is the electrostatic potential of the vacuum level and Fermi level, respectively. We defined the work function change caused by ligand with respect to the pure MoS_2 surface as $\Delta W = W_{ligand/MoS2} - W_{MoS2}$. As shown in Fig. S2, for C_6H_5CN modified MoS_2, the work function reduced by 1.534 eV compared to pure MoS_2, leading the band edge up-shift by 1.534 eV.

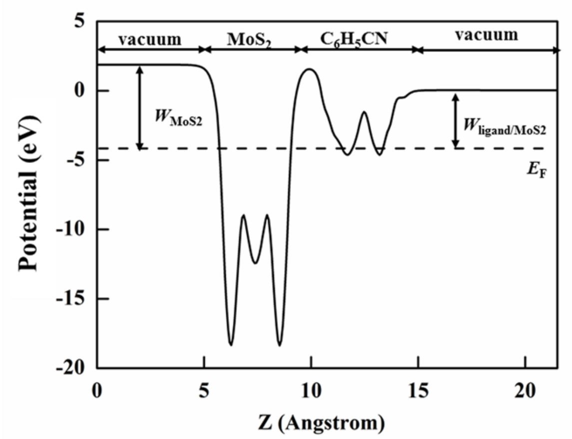

Fig. S2. The average electrostatic potential of C_6H_5CN modified MoS_2, where MoS_2 is a 2×2 supercell.

The average electrostatic potential of MoS_2/graphene

The band edge upshifts by ~ 0.06 eV for MoS_2/G compared to free-standing MoS_2 as shown in Fig. S3(a). This shift comes from the induced dipole moment of MoS_2 because the presence of graphene breaks the symmetry of MoS_2, and induced interface dipole moment between MoS_2/graphene.

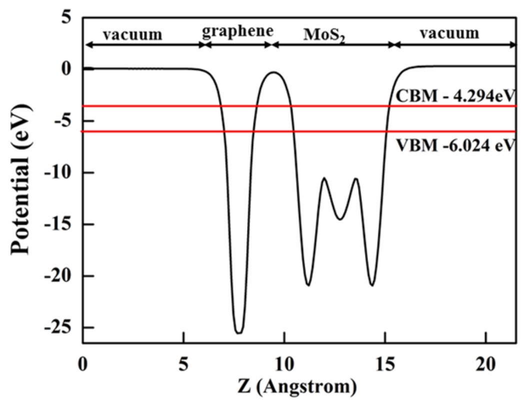

Fig. S3. (a) Average electrostatic potential of MoS_2/graphene (black solid line), the red solid lines denote the CBM and VBM of the hybrid nanostructure.