Supplementary Information (SI)

A Promising Strategy to Tune the Schottky Barrier of MoS$_2$(1-x)Se$_2x$/graphene Heterostructure by Asymmetric Se Doping

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1. MoS$_2$/Gr heterostructure

![Figure S1. The stereo matching strategy of monolayer MoS$_2$ and graphene. Top views of (a) monolayer MoS$_2$ with 4×4×1 lateral periodicity and (b) graphene with 5×5×1 lateral periodicity; (c) Side view of MoS$_2$/Gr heterostructure.](image)

**2. Definition of vacancy formation energy**

The vacancy formation energy required to remove a sulfur atom from the surface of monolayer MoS$_2$ is represented as:

$$E_V = E_d^o(MoS_{2n-1}) + \mu_6 - E_d^o(MoS_{2n})$$

where $E(MoS_{2n-1})$ and $E(MoS_{2n})$ are the total energies of the defective and stoichiometric slabs, respectively. The vacancy formation energy depends on growth conditions, which may be varied from S-rich to S-poor condition. For S-rich condition, cycle S$_6$ molecular is used to determine the chemical potential $\mu_6 = \mu(S_6)/6$. However, for S-poor condition, the chemical potential of S element can be
expressed by $\mu = E(\text{MoS}_2) - \mu_{\text{bulk}}$, where $\mu_{\text{bulk}} = E(\text{Mo}_{\text{bulk,cell}})/n$ and $n$ is the number of Mo atom in bulk metal Mo. The formation energy of single S-vacancy is -2.928 eV for S-poor condition.

Figure S2. Top view of S-vacancy (red dashed line) pattern. The 4x4x1 supercell of monolayer MoS$_2$ is used to avoid the periodic interactions between the neighboring defects.

3. Energy band structures

The state-of-the-art hybrid DFT approach based on the Heyd-Scuseria-Ernzerhof functional (HSE06) was used to calculate the electronic structures of MoS$_2$ after geometric optimization. In the default hybrid functional HSE06, the screening parameter $\mu$ and the mixing parameter $\alpha$ are set as 0.21 Å$^{-1}$ and 0.25, respectively. And norm-conserving pseudopotentials were used for all-electron HSE06 calculations. The calculated band gap of monolayer MoS$_2$ is 2.23 eV at the high symmetry K point, which is slightly larger than the experimental band gap of about 1.80 eV.

Figure S3. Energy band structures of monolayer MoS$_2$ using hybrid functional HSE06.
References


4. TDOS and PDOS of MoS$_{2(1-x)}$Se$_{2x}$/Gr heterostructure

Figure S4. Calculated TDOS of MoS$_{2(1-x)}$Se$_{2x}$/Gr heterostructure with different Se doping concentration (a) inside and (b) outside the interface. The calculated PDOS of (c) C, (e) S, (g) Se atoms in MoS$_{2(1-x)}$Se$_{2x}$/Gr heterostructure with different Se dopant concentration inside the interface. The calculated PDOS of (d) C, (f) S, (h) Se atoms in MoS$_{2(1-x)}$Se$_{2x}$/Gr heterostructure with different Se dopant concentration outside the interface. The vertical line is Fermi level.
5. Interface distance

Table S1. Interface distance at different Se concentrations of MoS$_{2(1-x)}$Se$_{2x}$/Gr heterostructure.

<table>
<thead>
<tr>
<th>MoS$_2$/Gr</th>
<th>MoS$<em>{1.75}$Se$</em>{0.25}$/Gr-in</th>
<th>MoS$<em>{1.50}$Se$</em>{0.50}$/Gr-in</th>
<th>MoS$<em>{1.25}$Se$</em>{0.75}$/Gr-in</th>
<th>MoS$<em>{1.00}$Se$</em>{1.00}$/Gr-in</th>
</tr>
</thead>
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<tr>
<td>2.388 Å</td>
<td>2.390 Å</td>
<td>2.389 Å</td>
<td>2.388 Å</td>
<td>2.387 Å</td>
</tr>
<tr>
<td>2.364 Å</td>
<td>2.365 Å</td>
<td>2.367 Å</td>
<td>2.366 Å</td>
<td>2.367 Å</td>
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6. Se dopant atoms on both side of Mo

Figure S5. The MoS$_{1.25}$Se$_{0.75}$/Gr heterostructure with different Se distributions inside or outside interface. Side views of (a) Se inside (x=0.125) and outside (x=0.625) interface, (b) Se inside (x=0.625) and outside (x=0.125) interface. The aquamarine, yellow, grey, and red balls denote Mo, S, C, and Se atoms, respectively.
Figure S6. Energy band structures of MoS$_{1.25}$Se$_{0.75}$/Gr heterostructures with different Se distributions inside or outside interface. (a) Se inside ($x=0.125$) interface and outside ($x=0.625$) interface, (b) Se inside ($x=0.625$) interface and outside ($x=0.125$) interface, (c) Se outside ($x=0.75$) interface, (d) Se inside ($x=0.75$) interface for MoS$_{1.25}$Se$_{0.75}$/Gr heterostructure, in which green areas and red areas represent n-SBH and p-SBH, respectively. The Fermi level is set to zero and marked by red dotted lines.

7. Electrostatic potentials

Figure S7. Calculated electrostatic potentials for (a) graphene, (b) monolayer MoS$_2$, (c) MoS$_2$/Gr heterostructure.
Figure S8. Calculated electrostatic potentials for (a) MoS$_{1.75}$Se$_{0.25}$/Gr-in, (b) MoS$_{1.50}$Se$_{0.50}$/Gr-in, (c) MoS$_{1.25}$Se$_{0.50}$/Gr-in, (d) MoS$_{1.00}$Se$_{1.00}$/Gr-in; and (e) MoS$_{1.75}$Se$_{0.25}$/Gr-out, (f) MoS$_{1.50}$Se$_{0.50}$/Gr-out, (g) MoS$_{1.25}$Se$_{0.50}$/Gr-out, (h) MoS$_{1.00}$Se$_{1.00}$/Gr-out. The blue and red dashed lines denote the vacuum energy level and Fermi level, respectively.

8. Three-dimensional (3D) charge density difference
Figure S9. Side and top views of the charge density difference (0.001 e·Å$^{-3}$) for (a) MoS$_{1.75}$Se$_{0.25}$/Gr-in, (b) MoS$_{1.50}$Se$_{0.50}$/Gr-in, (c) MoS$_{1.25}$Se$_{0.50}$/Gr-in, (d) MoS$_{1.00}$Se$_{1.00}$/Gr-in, (e) MoS$_{1.75}$Se$_{0.25}$/Gr-out, (f) MoS$_{1.50}$Se$_{0.50}$/Gr-out, (g) MoS$_{1.25}$Se$_{0.50}$/Gr-out and (h) MoS$_{1.00}$Se$_{1.00}$/Gr-out.