Supporting Information (SI)

Highly sensitive band alignment of graphene/MoSi$_2$N$_4$ heterojunction via external electric field

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1. The geometry structure and lattice parameters of monolayer MoSi$_2$N$_4$

![Geometry Structure](image)

**Figure S1.** Top (a) and side (b) views of the optimized geometry structure for monolayer MoSi$_2$N$_4$.

**Table S1.** The structural parameters of monolayer MoSi$_2$N$_4$

<table>
<thead>
<tr>
<th>Lattice constants</th>
<th>Angles</th>
<th>Space group</th>
<th>$E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a=b=2.902$ Å</td>
<td>$\alpha=\beta=90^\circ\gamma=120^\circ$</td>
<td>$P\bar{6}m2$</td>
<td>1.79 eV</td>
</tr>
</tbody>
</table>

2. Energy band structures
Figure S2. Energy band structures of 2×2 graphene layer and √3×√3 MoSi$_2$N$_4$ sheets without (a, b) and with strain (c, d). Here, the Fermi level is set to zero and marked by horizontal red dotted lines.

Figure S3. Energy band structure of monolayer MoSi$_2$N$_4$ using hybrid functional HSE06.
The state-of-the-art hybrid DFT approach based on the Heyd-Scuseria-Ernzerhof functional (HSE06) was used to calculate the electronic structure of monolayer MoSi2N4 after geometric optimization. In the default hybrid functional HSE06, the norm-conserving pseudopotentials were used for all-electron calculations. The calculated band gap of monolayer MoSi2N4 is 2.34 eV, which is larger than the experimental band gap of about 1.94 eV.


3. Highest occupied molecular orbital (HOMO) and Lowest unoccupied molecular orbital (LUMO)

![Figure S4](image)

**Figure S4.** Side views of the (a) HOMO and (b) LUMO for graphene/MoSi2N4 heterojunction.

4. Work functions

The work function is defined as follows

\[
W = E_{\text{vac}} - E_F
\]  

where \(E_{\text{vac}}\) is the energy of a stationary electron in the vacuum nearby the surface; \(E_F\) is the energy of the Fermi level, which is used to determine the ground-state electronic structure.
Figure S5. The electrostatic potentials of (a) monolayer MoSi$_2$N$_4$, (b) graphene, (c) graphene/MoSi$_2$N$_4$ heterojunction.

5. Changing the interlayer spacing

Figure S6. The relation between the cohesive energies and interlayer spacing $d$ for model II after geometric optimization.
Figure S7. The calculated work functions of graphene/MoSi$_2$N$_4$ heterojunction with different interlayer spacings.

The charge density difference is defined as

\[ \Delta \rho = \rho_{\text{graphene/MoSi}_2N_4} - \rho_{\text{graphene}} - \rho_{\text{MoSi}_2N_4} \]  

(S2)

where \( \rho_{\text{graphene/MoSi}_2N_4} \), \( \rho_{\text{graphene}} \) and \( \rho_{\text{MoSi}_2N_4} \) are the charge densities of graphene/MoSi$_2$N$_4$ heterojunction, graphene and MoSi$_2$N$_4$ sheets, respectively. Namely, the charge density differences could be obtained by subtracting the electronic charge density of graphene/MoSi$_2$N$_4$ heterojunction from those of the corresponding isolated graphene and MoSi$_2$N$_4$ layers, respectively.

Figure S8. 3D charge density difference of graphene/MoSi$_2$N$_4$ heterojunction with different interlayer spacing, (a) 2.8 Å, (b) 3.2 Å, (c) 3.6 Å and (d) 4.0 Å.

6. Applying an external electric field
Figure S9. The shifts of Fermi level, interfacial charge transfer process and 3D charge density difference under the different external electric fields, (a) from -0.05 to -0.50 V·Å⁻¹, (b) from +0.05 to +0.50 V·Å⁻¹.