Supporting Information:

Surface passivation induced significant
enhancement of superconductivity in layered
two-dimensional MSi$_2$N$_4$ (M = Ta, Nb) materials

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METHODS

Within the frame of the Bardeen-Cooper-Schrieffer (BCS) microscopic theory, the electron-phonon coupling (EPC) was calculated by QUANTUM ESPRESSO (QE) code using the optimized norm-conserving Vanderbilt pseudo-potentials. After convergence tests, the plane-waves kinetic-energy cutoff and the charge-density cutoff were chosen as 90 and 360 Ry, respectively. The $k$-point with a Methfessel-Paxton smearing width of 0.02 Ry and $q$-mesh for dynamic and EPC matrix elements were sampled on $36 \times 36 \times 1$ and $6 \times 6 \times 1$ grids, respectively. Meanwhile, as shown in Figure S1a, compared to the phonon spectra of $1H$-TaSi$_2$N$_4$ monolayer obtained from $4\times 4\times 1$ and $9\times 9\times 1$ $q$ mesh, the $q$ mesh of $6\times 6\times 1$ is large enough in our calculations. Furthermore, the convergence of $\lambda$ against Gaussian broadening was tested and confirmed the variations $\lambda$ to be smaller than 0.01 (Figure S1b), verifying the calculated $\lambda$ and $T_c$ in this work. Based on the Migdal-Eliashberg equations, the magnitude of the EPC $\lambda_{q\nu}$, which determines the contribution to $\lambda$ from individual phonon modes, can be evaluated as

$$
\lambda_{q\nu} = \frac{\gamma_{q\nu}}{\pi \hbar N(E_F) \omega_{q\nu}^2},
$$

(1)

where $\gamma_{q\nu}$, $\omega_{q\nu}$ and $N(E_F)$ are the phonon linewidths, the frequency of a lattice vibration with crystal momentum $q$ in the branch $\nu$ and the density of states at the Fermi level, respectively. Here, the phonon linewidths $\gamma_{q\nu}$ scale as

$$
\gamma_{q\nu} = \frac{2\pi \omega_{q\nu}}{\Omega_{BZ}} \sum_{k,n,m} |g_{kn,k+qm}^{\nu}|^2 \delta(\epsilon_{kn} - \epsilon_F) \delta(\epsilon_{k+qm} - \epsilon_F),
$$

(2)

where $\Omega_{BZ}$ is the volume of Brillouin zone (BZ), $\epsilon_{kn}$ and $\epsilon_{k+qm}$ are the Kohn-Sham energy, $\epsilon_F$ is the Fermi energy and $g_{kn,k+qm}^{\nu}$ is the EPC matrix element. According to the linear response theory, the $g_{kn,k+qm}^{\nu}$ can be determined self-consistently. Subsequently, the Eliashberg electron-phonon spectral function $\alpha^2 F(\omega)$ and the cumulative frequency-dependent EPC
function $\lambda(\omega)$ are given by

$$\alpha^2 F(\omega) = \frac{1}{2\pi N(E_F)} \sum_{q\nu} \gamma_{q\nu} \frac{\omega}{\omega_{q\nu}} \delta(\omega - \omega_{q\nu})$$

(3)

and

$$\lambda(\omega) = 2 \int_0^\omega \frac{\alpha^2 F(\omega)}{\omega} d\omega,$$

(4)

respectively. Then, the logarithmic average frequency $\omega_{\log}$ and the superconducting transition temperature $T_c$ can be obtained as follows:

$$\omega_{\log} = \exp \left[ \frac{2}{\lambda} \int_0^\infty \frac{d\omega}{\omega} \alpha^2 F(\omega) \log \omega \right]$$

(5)

and

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right],$$

(6)

where $\mu^*$ is the effective screened Coulomb repulsion constant with a typical value of 0.1.

**Stabilities for TaN$_2$**

Here, the mechanical, thermal and kinetical stability are evaluated firstly. The elastic constants $C_{ij}$ are calculated using energy-strain method, which is corresponding to the second partial derivative of strain energy with respect to the applied strains (Figures S4a,b). As for hexagonal crystal, two elastic constants: $C_{11}$ and $C_{12}$ are independent, and $C_{66}$ can be obtained by $0.5*(C_{11}-C_{12})$. The 2D elastic modulus $E^{2D}$ (N/m) and Poisson’s ratio $\nu$ were derived via $(C_{11}^2-C_{12}^2)/C_{11}$ and $C_{12}/C_{11}$, respectively. Furthermore, in-plane Young’s modulus $(Y)$ could be calculated by $E^{2D}/h$ ($h$ represents the theoretical thickness of crystals and...
were adopted to be 10.3 Å to compare with following experimental value of SL 1H-MoSi$_2$N$_4$).

The results of elastic constants, $E^{2D}$, $Y$ and Poisson’s ratio ($\nu$) were listed in Table S1. Obviously, SL 1T- and 1H-TaN$_2$ meet the Born criteria of hexagonal crystal, namely, $C_{11} > |C_{12}|$ and $C_{66} > 0$. Their $Y$ are larger than those of phosphorene (24−103 N/m), silicene (62.31 N/m) and comparable to that of MoS$_2$ (123 N/m). Besides, the equal $\nu$ along $x$ and $y$ directions shows their isotropic nature. To evaluate the thermal stability, 4 × 4 × 1 supercell of 2D TaN$_2$ were adopted to perform ab initio molecular dynamics (AIMD) simulations within Nosé-Hoover thermostat. The variations of free energy within 5 ps, along with the last frame of the photographs are exhibited in Figure S5. The average value of the free energy and structural framework of 1T-TaN$_2$ monolayer are well maintained uppon 600 K (Figure S5a), while the structural disruption appears after 3-ps simulation at 900 K (Figure S5b). As for SL 1H-TaN$_2$, it only retains integrity about 300 K without fluctuations of free energy during the entire simulation period ((Figures S5c,d). All in all, SL 1T- and 1H-TaN$_2$ satisfy the thermal stability at room temperature. The later dynamical analyses with lacking imaginary frequencies in first Brillouin zone (BZ) (Figures 4a,g), also confirmed their dynamical stabilities. The cohesive energies $E_{coh}$ of 1T- and 1H-TaN$_2$ monolayers are 7.13 and 6.94 eV/atom, respectively, and their corresponding formation energies $E_f$ are −0.27 and −0.08 eV/atom, indicating its potentially experimental synthesis with exothermic feature.

Table S1. Calculated elastic constant $C_{ij}$ (N/m), 2D elastic modulus $E^{2D}$ (N/m), Young’s modulus $Y$ (N/m) and Poisson’s ratio $\nu$ for SL 1T-TaN$_2$, 1H-TaN$_2$, 1H-MoSi$_2$N$_4$, 1H-TaSi$_2$N$_4$ and 1H-NbSi$_2$N$_4$.

<table>
<thead>
<tr>
<th>configuration</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{66}$</th>
<th>$E^{2D}$</th>
<th>$Y_{x/y}$</th>
<th>$\nu_{x/y}$</th>
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<tr>
<td>1T-TaN$_2$</td>
<td>184.17</td>
<td>55.80</td>
<td>64.18</td>
<td>167.26</td>
<td>162.39</td>
<td>0.30</td>
</tr>
<tr>
<td>1H-TaN$_2$</td>
<td>161.00</td>
<td>90.76</td>
<td>35.12</td>
<td>109.84</td>
<td>106.64</td>
<td>0.56</td>
</tr>
<tr>
<td>1H-MoSi$_2$N$_4$</td>
<td>539.33</td>
<td>153.00</td>
<td>193.17</td>
<td>495.83</td>
<td>481.39</td>
<td>0.28</td>
</tr>
<tr>
<td>1H-TaSi$_2$N$_4$</td>
<td>508.71</td>
<td>154.98</td>
<td>176.87</td>
<td>461.49</td>
<td>448.04</td>
<td>0.30</td>
</tr>
<tr>
<td>1H-NbSi$_2$N$_4$</td>
<td>488.66</td>
<td>156.97</td>
<td>165.85</td>
<td>109.84</td>
<td>438.23</td>
<td>0.32</td>
</tr>
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</table>
Figure S1. (a) The phonon spectra of 1H-TaSi$_2$N$_4$ monolayer calculated on 4×4×1, 6×6×1 and 9×9×1 q meshes, respectively. (b) The evolutions of \( \lambda \) on different Gaussian broadening. The color-marked value is adopted in this work.
Figure S2. Possible magnetic configurations of (a-d) 1T- and (e-f) 1H-TaN\textsubscript{2} monolayers. The spin-up and spin-down orientations are indicated by red plus and blue minus sign, respectively.

Figure S3. The ELF for (a-b) SL 1T- and (c-d) 1H-TaN\textsubscript{2} from top (left plane) and side (right plane) views. The difference charge density plots from top (left plane) and side (right plane) views of (e-f) 1T- and (g-h) 1H-TaN\textsubscript{2} monolayer. The isovalues of ELF and difference charge density are selected to be 0.4 and 0.01 a.u, respectively.
Figure S4. The elastic energy via strains from -0.02% to 0.02% for (a) SL 1T- and (b) 1H-TaN$_2$.

Figure S5. During the AIMD simulations, the variations of the free energy of SL 1T-TaN$_2$ at (a) 600, (b) 900 K and SL 1H-TaN$_2$ at (c) 300, (d) 600 K. The insets are the top and side views of the last structural snapshots at their corresponding temperature.
Figure S6. Orbital projected band structures of (a-c) 1T- and (e-g) 1H-TaN$_2$ weighted by major states near the Fermi level. The Fermi levels are selected to be 0 eV.
Figure S7. Phonon dispersions according to in-plane mode of (a/d) N-xy, (b/e) out-of-plane modes of N-z, (c/f) in-plane modes of Ta-xy and (d/g) out-of-plane modes of Ta-z for 1T/1H-TaN2 monolayer.
Figure S8. (a) Top and (b) side views for SL 1T-TaSi$_2$N$_4$ or 1T-NbSi$_2$N$_4$. The phonon spectrum of (c) 1T-TaSi$_2$N$_4$ and (d) 1T-bSi$_2$N$_4$ monolayers. (e) Barrier energy of SL 1T-TaSi$_2$N$_4$ transferring to 1H-TaSi$_2$N$_4$.

Figure S9. (a/c) Top and (b/d) side view of ELF/difference charge density plots for 1H-TaSi$_2$N$_4$ monolayer. The isovalue of ELF and difference charge density are set to be 0.5 and 0.018 a.u, respectively.
Figure S10. Variations of the free energy in the AIMD simulations during the time scale of 5 ps along with the last frame of photographs for (a,b) SL 1H-TaSi$_2$N$_4$ and (d,e) 1H-NbSi$_2$N$_4$. The elastic energy as a function of strains from $-2\%$ to $2\%$ for (c) 1H-TaSi$_2$N$_4$ and (f) 1H-NbSi$_2$N$_4$ monolayer.
Figure S11. Orbital projected band structures of (a-d) 1H-TaSi$_2$N$_4$ and (g-j) NbSi$_2$N$_4$ weighted by major states near the Fermi level. The Fermi levels are taken as zero.
Figure S12. Phonon spectra of (a-d) SL 1H-TaSi$_2$N$_4$ and (e-h) 1H-NbSi$_2$N$_4$ resolved in terms of the vibration directions of in-plane mode and out-plane modes of Si, N1, N2, Ta and Nb atoms.

Figure S13. (a) Orbital projected band structures of 1H-NbSi$_2$N$_4$. (b) The phonon spectrum magnituded by $\lambda_{q\nu}$. (c) PhDOS, (d) $\alpha^2F(\omega)$ and $\lambda(\omega)$, (e) $T_c(\omega)$ along with its derivate of 1H-NbSi$_2$N$_4$. (f) Integrated EPC distributions in the BZ.
Figure S14. Phonon spectra subjected to external biaxial strains from $-4\%$ to $4\%$ and doped by electron and hole from $0.3$ e/cell to $0.3$ h/cell for (a-e) 1H-TaSi$_2$N$_4$ and (f-i) 1H-NbSi$_2$N$_4$, respectively.

Figure S15. The band structures calculated within SOC level and compared with without (w/o) SOC for (e) 1H-TaSi$_2$N$_4$ and (k) 1H-NbSi$_2$N$_4$ monolayer.
Figure S16. Phonon spectra of (a) SL 1T- and (e) 1H-TaN\textsubscript{2} with SOC. The magnitude of the EPC $\lambda$ in individual phonon modes within SOC level for (b) 1T- and (f) 1H-TaN\textsubscript{2} monolayer. (c/d) Eliashberg spectral function $\alpha^2 F(\omega)$ along with cumulative frequency dependent EPC function [$\lambda(\omega)$], (g/h) $T_c(\omega)$ and its derivative within SOC for 1T/1H-TaN\textsubscript{2} monolayer.
Figure S17. When subjected to the SOC effects, the (a/e) phonon spectra, distributions of (b/f) $\lambda_{qv}$, (c/g) $\alpha^2 F(\omega)$ with $\lambda(\omega)$, (d/h) $T_c(\omega)$ along with its derivate for SL 1H-TaSi$_2$N$_4$/NbSi$_2$N$_4$. 
Figure S18. The calculated $T_c$ as a function of $\mu^*$ for SL 1H-TaSi$_2$N$_4$/NbSi$_2$N$_4$ monolayer.
References


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