Supporting Information for

Robust Interlayer Exciton in WS₂/MoSe₂ van der Waals Heterostructure under High Pressure

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**Materials and Methods**

**Sample preparation**

We constructed the WS$_2$/MoSe$_2$ vdW heterostructure on diamond directly by the dry transfer method using polydimethylsiloxane (PDMS). First, the high-quality ML-MoSe$_2$ (ML-WS$_2$) that has few impurities is directly mechanically exfoliated from bulk crystal purchased from HQ Graphene. After constructing the WS$_2$/MoSe$_2$ vdW heterostructure by the dry transfer method, it is further annealed in a vacuum at 120 °C for 2h, which can aid in minimizing surface contaminants such as adsorbed air, moisture and residual PDMS. The thickness of MoSe$_2$ is confirmed by the optical contrast and Raman spectrum. Then the ML-MoSe$_2$ is transferred on top of diamond under microscope using 10× objective. After that, the ML-WS$_2$ is prepared using the same method and transferred on top of the ML-MoSe$_2$ to construct the heterostructure. A photograph of the sample preparation process is shown in Figure S1.

**The high-pressure measurements**

The high-pressure measurements were performed in diamond anvil cells (DACs). The DAC made of BeCu alloy with two opposing anvils was used to generate high pressure. Diamond anvils with 300 μm culets were used for the measurements. In each experiment, the sample was loaded into the sample chamber (D = 200 μm hole) in a rhenium gasket pre-indent to ~25 - 40 μm in thickness. We tried to use a variety of pressure-transmitting medium, among which KBr has the least interference to the sample signal, so we finally chose KBr as the pressure-transmitting medium in our experiments. A ruby ball is loaded to serve as internal pressure standard and the pressure is determined by the R1-R2 line shift of the ruby ball \(^1\). To perform high-pressure PL and Raman measurements, a continuous-wave 514 nm laser with a spot size of ~1 μm was used to
excite the sample. The laser power was maintained at approximately 200 μw to avoid overheating during measurements. The spectra for comparison were collected under the same conditions if there were no special instructions. To perform high-pressure reflectance contrast measurements, a broadband white light spatially filtered from a tungsten halogen lamp with spot size about 5 μm was focused onto the sample. We collected the reflected light from the diamond substrate and sample using a spectrometer and calculated the reflectance contrast spectra using the formula: $\Delta R/R = (R_d - R_s)/R_d$, where $R_s$ is the reflectance of the sample on the substrate, and $R_d$ denotes the reflectance of the diamond substrate.

**Theoretical calculations**

The first-principles calculations of geometry optimization and electronic band structures were performed with a generalized gradient approximation (GGA) of density functional theory (DFT) that uses a Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional for electron exchange and correlation potentials, as implemented in the coed Vienna Ab initio Simulation Package (VASP, version 5.4.1). The Brillouin zone was sampled by a 15×15×1 Gamma k-point mesh for all of the calculations. A vacuum space of at least 15 Å was adopted to avoid adjacent interactions owing to the periodic boundary condition. All of the atomic structures were optimized fully with energy and force tolerances of $10^{-6}$ eV and 0.02 eVÅ$^{-1}$, respectively. To simulate the effects of hydrostatic pressure, we performed the geometric optimizations for bulk heterosystems and then added a vacuum layer to establish herterobilayer models in subsequent calculations. Crystal structures were fully relaxed with the inclusion of the vdW correction to the interatomic forces by means of the non-local optB86b-vdW functional.
Figure S1. A photograph of the sample preparation process. (A) Photograph of the monolayer MoSe$_2$ (ML-MoSe$_2$) transferred onto diamond substrate. (B) Photograph of the monolayer WS$_2$ (ML-WS$_2$) exfoliated onto PDMS. (C) Photograph of the WS$_2$/MoSe$_2$ heterostructure after ML-WS$_2$ is transferred on top of ML-MoSe$_2$ on diamond substrate. (D) Photograph of the WS$_2$/MoSe$_2$ heterostructure on diamond substrate under 20× objective. The diameter of diamond substrate is approximately 300 μm.
Figure S2. PL spectra of ML-MoSe$_2$, ML-WS$_2$ and WS$_2$/MoSe$_2$ heterostructure, respectively.
Table S1. PL lifetime ($\tau_1$ and $\tau_2$) and corresponding percentum of ML-MoSe$_2$, ML-WS$_2$ and WS$_2$/MoSe$_2$ heterostructure.

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$ (ps)</th>
<th>$A_1$ (%)</th>
<th>$\tau_2$ (ps)</th>
<th>$A_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML-WS$_2$</td>
<td>32±0.3</td>
<td>10.6 (99%)</td>
<td>418±26</td>
<td>0.07 (1%)</td>
</tr>
<tr>
<td>ML-MoSe$_2$</td>
<td>44±1</td>
<td>5.4 (98%)</td>
<td>604±47</td>
<td>0.1 (2%)</td>
</tr>
<tr>
<td>WS$_2$/MoSe$_2$</td>
<td>93±5</td>
<td>2.1 (87%)</td>
<td>774±81</td>
<td>0.3 (13%)</td>
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</table>
**Figure S3.** The top and side views of the WS$_2$/MoSe$_2$ heterobilayer with high-symmetry stacking structures. The interlayer distance is indicated in Type-A. The blue, yellow, green and orange balls represent W, S, Mo and Se atoms, respectively.

In order to compare the band structures of monolayer and bilayer WS$_2$/MoSe$_2$ vdW heterobilayers, we first examined the lattice constants and band structures of monolayer WS$_2$/MoSe$_2$ vdW heterobilayers. The optimized values of lattice constants of MoSe$_2$ and WS$_2$ are found to be 3.317 Å and 3.191 Å respectively, well consistent with previously reported results $^5$-$^6$. To obtain the most stable stacking structure, we consider various highly symmetric stacking structures. Six stacking structures configurations from bilayer WS$_2$/MoSe$_2$ heterobilayers are considered (Figure. S2). In order to confirm the stability of these systems, we calculated the binding energies ($E_b$) of bilayer WS$_2$/MoSe$_2$ heterobilayers, which is defined as $E_b = E_{WS2/MoSe2} - E_{MoSe2} - E_{WS2}$. $E_{WS2/MoSe2}$, $E_{MoSe2}$ and $E_{WS2}$ are the total energies of the WS$_2$/MoSe$_2$ vdW heterobilayer, free ML-MoSe$_2$, and free ML-WS$_2$ respectively (Table S2). The binding energies of the most stable stacking structures (Type-D) are shown in Figure S2.
Table S2. The binding energy $E_b$ of bilayer WS$_2$/MoSe$_2$ heterobilayers with different stacking configurations.

<table>
<thead>
<tr>
<th>stacking structures</th>
<th>Type-A</th>
<th>Type-B</th>
<th>Type-C</th>
<th>Type-D</th>
<th>Type-E</th>
<th>Type-F</th>
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<tbody>
<tr>
<td>$E_b$ (binding energy, eV)</td>
<td>-0.18966</td>
<td>-0.2627</td>
<td>-0.26684</td>
<td>-0.26747</td>
<td>-0.21554</td>
<td>-0.19333</td>
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</table>
Figure S4. The reflectance contrast spectra of the WS$_2$/MoSe$_2$ heterostructure under different pressures.

Here, $\Delta R/R = (R_d - R_s)/R_d$, where $R_s$ is the reflectance of the sample on the substrate, and $R_d$ denotes the reflectance of the diamond substrate. In the limit of weak reflectance contrast (for the relevant case of a transparent substrate), the reflectance contrast is proportional to the absorption of the sample $^7$-$^8$. 
**Table S3.** The intensity ratio of the IX peak and the A exciton peak ($P_{IX}/P_{XWS2}$) with different pressures.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>0</th>
<th>2.09</th>
<th>2.92</th>
<th>3.83</th>
<th>8.91</th>
</tr>
</thead>
<tbody>
<tr>
<td>R ($P_{IX}/P_{XWS2}$)</td>
<td>1: 2.71</td>
<td>1: 1.68</td>
<td>1: 1.74</td>
<td>1: 0.22</td>
<td>1: 0</td>
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</tbody>
</table>
Figure S5. (A) The optical photograph of the constructed WS₂/MoSe₂ heterostructure for PL, Raman and reflectance contrast measurements in the supporting information. (B) Pressure-dependent PL spectra of the WS₂/MoSe₂ heterostructure. The intensity of interlayer exciton peaks is normalized to compare peak energy at varying pressures.
Figure S6. The Raman spectra of the WS$_2$/MoSe$_2$ heterostructure under different pressures. (A) The out-of-plane $A_{1g}$ mode (at 240 cm$^{-1}$). (B) The in-plane $E^{1}_{2g}$ mode (at 353 cm$^{-1}$). (C) The out-of-plane $A_{1g}$ mode (at 417 cm$^{-1}$).
**Figure S7.** The calculated partial charge density of the WS₂/MoSe₂ heterobilayer. The left column shows the top (top) and side (bottom) views of the WS₂/MoSe₂ heterobilayer. The right two columns show the partial charge density plot of the WS₂/MoSe₂ heterobilayer at K, Y, and Γ point. CB (VB) stands for the conduction (valence) bands.
Figure S8. The pressure dependent band structures of the WS$_2$/MoSe$_2$ heterobilayer including spin-orbit coupling. (A) The band structures of the WS$_2$/MoSe$_2$ heterobilayer at 0 GPa. (B) The band structures of the WS$_2$/MoSe$_2$ heterobilayer at 0.67 GPa. Under small pressure, the WS$_2$/MoSe$_2$ heterobilayer takes place band gap transition from direct-to-indirect band gap.

According to the functional relationship between $d$ (metal atom distance between the layer) and pressure, it can be concluded that with the increase of pressure, $d$ decreases and the interaction between layers becomes stronger.
References

(1) Mao, H. K.; Xu, J.; Bell, P. M., Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. *J. Geophys. Res.* 1986, 91 (B5), 4673.