Supplemental Materials

Band Gap Opening of Graphene by Forming Graphene/$PtSe_2$ van der Waals Heterojunction

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1. We use *CellMatch* program to investigate the stacking orders of graphene and $PtSe_2$ layers. We consider the following stacking orders: Index-1 (378 atoms, a = 81.45 Å, b = 7.49 Å), Index-2 (348 atoms, a = 74.66 Å, b = 7.49 Å), Index-3 (318 atoms, a = 68.17 Å, b = 7.49 Å), Index-4 (288 atoms, a = 61.68 Å, b = 7.49 Å), Index-5 (258 atoms, a = 55.20 Å, b = 7.49 Å) and Index-6 (30 atoms) as shown in Fig. S1, and the corresponding binding energy of very atom is -28.6, -28.2, -27.63, -27.82, -28.3 and -31.3 meV, respectively.

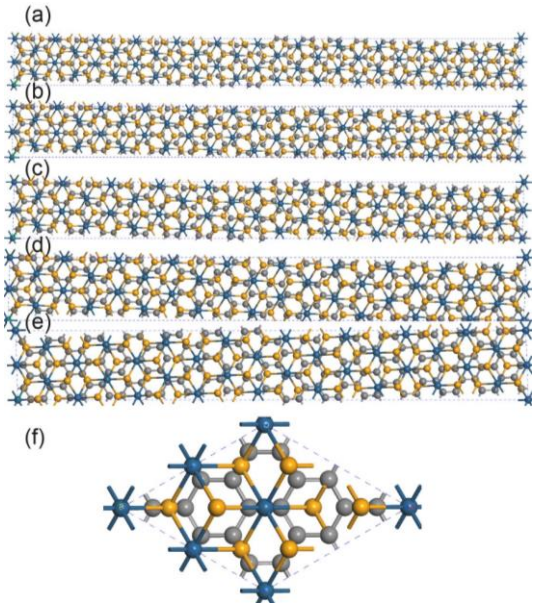

Figure. S1. The differernt stakcing orders of the graphene/$PtSe_2$ heterojunction. The top view of the optimized geometries of (a) Index-1, (b) Index-2, (c) Index-3, (d) Index-4, (e) Index-5 and (f) Index-6.

For Index-1, 2, 3, 4, 5, the value of corresponding lattice constant is larger than 55.20 Å. Considering balance between computational cost and accuracy, we choose Index-6 as the model to accomplish our computation.

2. In order to get the lattice parameter of the graphene/$PtSe_2$ heterojunction, two strategies are used:

(1) Fully relaxing all ions, with the shape and volume of the cell are relaxed. The Energy cut off is set as high as 520 eV, and the corresponding estimated lattice parameter is 7.398 Å.

(2) We also scan the lattice, and get the relationship between the energy and the lattice. The energy and lattice follows the following relationship:

$$\text{Energy} = 1458.742-456.567x+30.863x^2$$

Then we have gotten the optimized lattice is 7.397 Å. This can be understood by the high Young's modulus of the graphene. Compared with $PtSe_2$, the graphene is much "harder". The optimized lattice parameter is close to the graphene (2.460 Å).

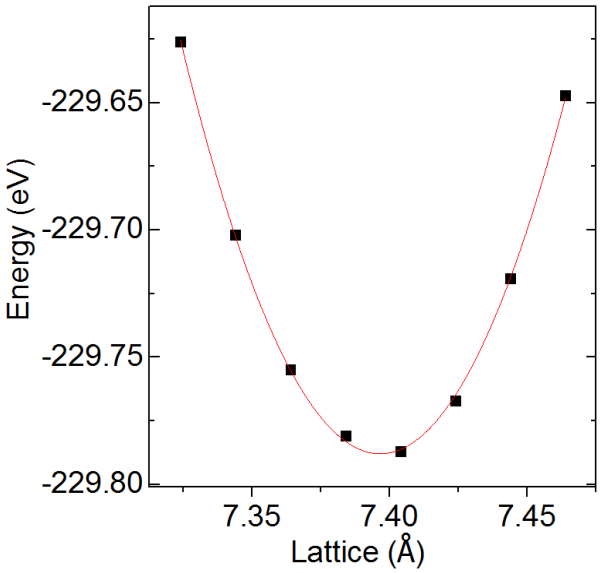

Figure S2: Variation of total energy with the lattice parameter. The red line is fitted with the quadratic function.

3. The partial density of the states $PtSe_2$ monolayer calculated by HSE06 functional. From Figure S3, we can find which atom orbitals make contribution to the VBM and CBM, respectively.

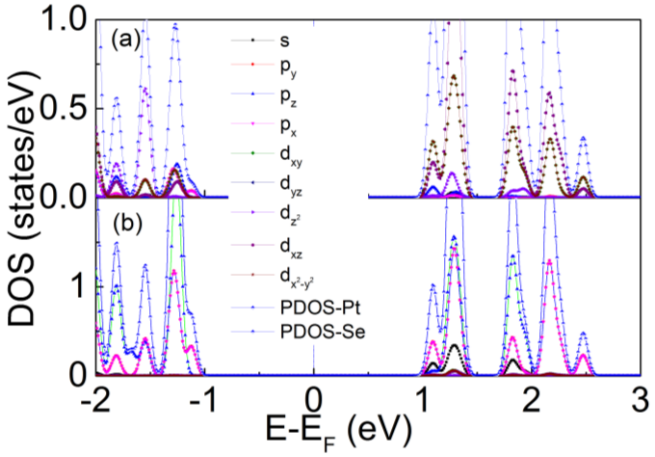

Figure S3: PDOS of the $PtSe_2$ monolayer calculated by HSE06, PDOS of (a) the Pt atoms, and (b) the Se atoms, respectively. The Fermi level (E_F) was set to 0 eV.

4. The accuracy of the HSE06 is concerned, so we have added the band structure of the free standing graphene under HSE06 functional. The adopted supercell is hexangular cell. So the Dirac cone locates at K point.

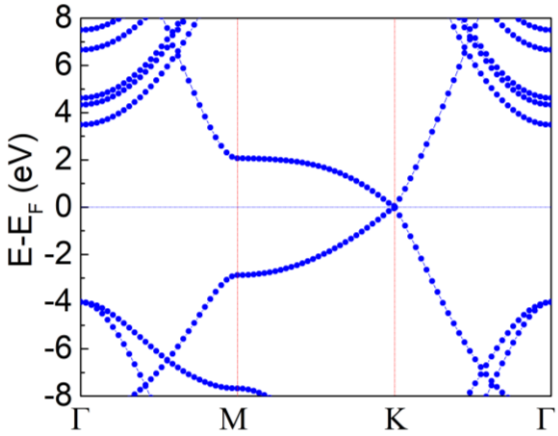

Figure S4: The band structure of the graphene supercell is calculated under HSE06 functional. The Γ, M, K points are (0, 0, 0), (0, 1/2, 0), and (1/3, 1/3, 0), respectively.

5. The band structure of the graphene/$PtSe_2$ heterojunction is also calculated by DFT-D3 method of Grimme and self-consistent vdW. The optimized distance between graphene and $PtSe_2$ is about 3.31, and 3.30 Å, respectively. And the band structure of graphene/$PtSe_2$ heterojunction calculated by DFT-D3 is shown in Figure S5, and the corresponding band gap is 0.036 eV.

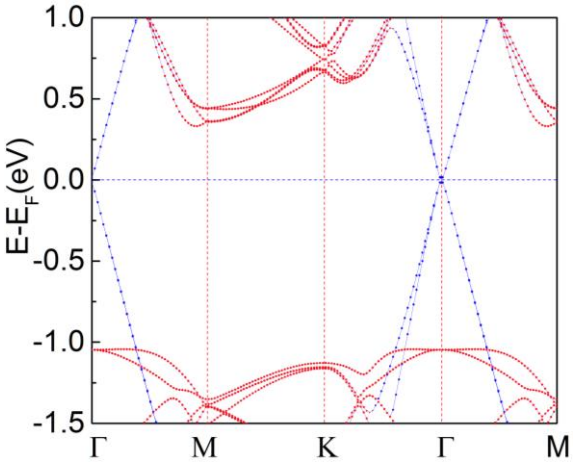

Figure S5: The band structure of the graphene/$PtSe_2$ heterojunction is calculated by DFT-D3. The size of the red and blue dots represent the weights of $PtSe_2$ and graphene, respectively. The Γ, M, K presents (0, 0, 0), (0, 1/2, 0), and (1/3, 1/3, 0), respectively.

6. We also calculate the charge transfer by integrating the differential charge density to get the total charge transfer, and there is about 0.07 *e* charge transferring from $PtSe_2$ to graphene layer.

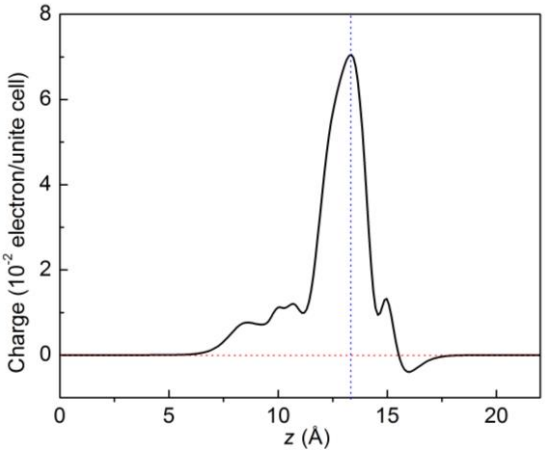

Figure S6: Integrated differential electron density of the graphene/$PtSe_2$ heterojunction.

7. In order to study the character of the states near the fermi-level, we calculate the projected band of the graphene/$PtSe_2$ heterojunction. The states near the fermi-level are mainly consist of p_z orbital of the graphene.

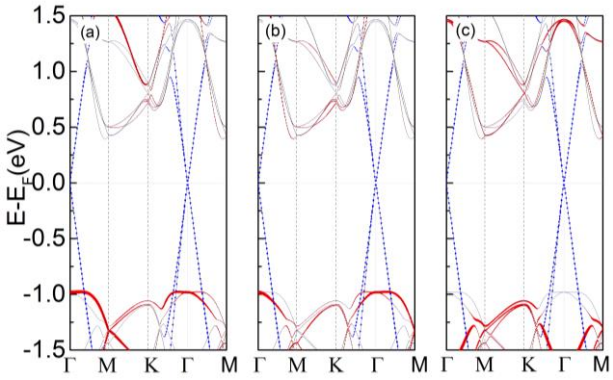

Figure S7: The projected band of the Graphene/$PtSe_2$ heterojunction, p_z orbital of the graphene and (a) p_x orbital of the $PtSe_2$, (b) p_y orbital of the $PtSe_2$, and (c) p_z orbital of the $PtSe_2$. The blue and red line presents contribution of the p_z orbital of the graphene and each p orbital of the $PtSe_2$, respectively.

8. We also calculate the band structure of the graphene/$PtSe_2$ heterojunction by DFT-D3 method of Grimme changing with the vertical strains. The E_{gap} under PBE as a function of strain is found to follow an exponential relationship:

$$E_g = -0.002 + 0.033 \times \exp(2.146\varepsilon) \text{ (PBE)}$$

$$E_g = 0.176 + 0.073 \times \exp(1.630\varepsilon) \text{ (HSE06)}$$

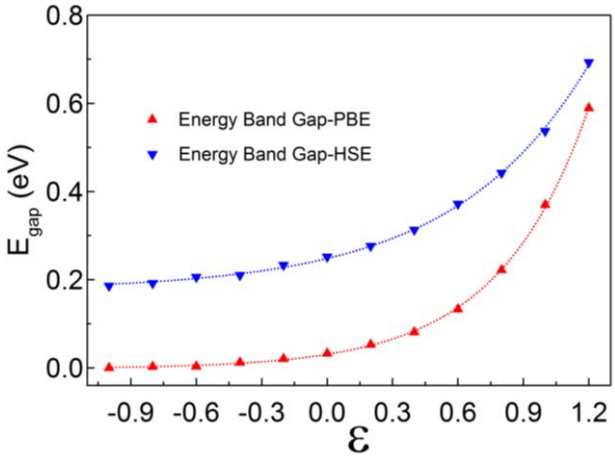

Figure S8: The energy gap of the graphene/$PtSe_2$ heterojunction calculated by DFT-D3 method of Grimme is as function of the vertical strains. The red and blue dots present the fitted exponential curves calculated by PBE and HSE06, respectively.

9. For the bigger compressive vertical strains, the effect of spin-orbit coupling (SOC) on the energy band gap becomes important. Especially at quite large strain, such as Ɛ= 1.0, 1.2 Å, both CBMs of the heterojunctions lie at Γ point, while the VBM transfers from the Γ point to the K point, for the strong mutual interaction between $PtSe_2$ and graphene and enhancement of the SOC. So we calculate the band structure with HSE06 including SOC effect. For Ɛ = 0.8, 1.0, and 1.2 Å, the corresponding E_{gap} at Γ point is 0.449, 0.617 and 0.850 eV, respectively.

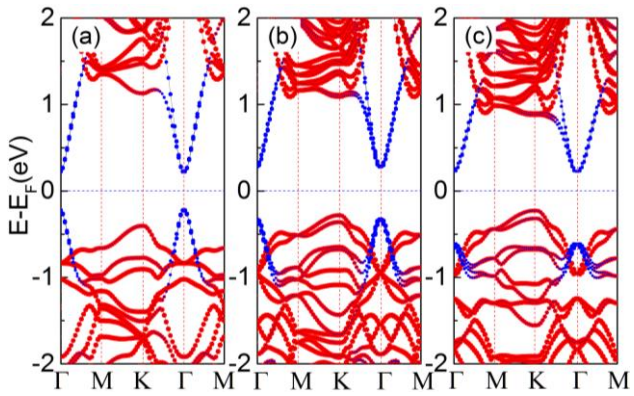

Figure S9: The band structure of the graphene/$PtSe_2$ heterojunction with HSE06 plus SOC. The band structure with vertical Ɛ (a) 0.8, (b) 1.0, and (c) 1.2 Å, respectively.