PCCP

Supporting Information: Role of van der Waals interaction to enhance the photon absorption capability of MoS_2/2D heterostructure†

Himanshu Saini[a], M. V. Jyothirmai[a], Umesh V. Waghmare[b*] and Ranjit Thapa[a,c*]

1 Model Structure

The heterostructures named as defined in the main publication MoS_2/GR, MoS_2/BlackP, MoS_2/InSe, & MoS_2/BlueP; were constructed using the supercell concept keeping minimal lattice mismatch (up-to 5%), which can be accessible in experimental synthesis. Heterostructures, designed by using the hexagonal lattice type were taken integer as multiples of their unit cells to make their respective supercell. In the case of MoS_2/BlackP, we considered $(1\times4\sqrt{3})/(1\times5)$, which showed the minimal lattice mismatch. The lattice mismatch, number of atoms per super-cell & other structural parameters of all the models under investigation are given in Table S1.

2 Interfacial Charge Analysis

To study the relative stability of the heterojunction formed, the interfacial binding energy (ΔE_b) was calculated by using the equation

$$\Delta E_b = E_{\text{Hetero}} - E_{MoS_2} - E_{L2} \tag{1}$$

where E_{Hetero} is total energy of heterostructure, E_{MoS_2} is total energy of MoS_2 (monolayer), & E_{L2} is total energy of respective underneath monolayers. The binding energies are negative which shows all the heterostructures are thermodynamically stable and suggests that thus can be synthesised because of their lower energy state. Table S2 shows the interface binding energies of MoS_2/2D layered interaction -14.18, -15.19, -13.29, & -15.14meV/Å^2 for GR, BlackP, InSe, & BlueP respectively. Our calculated binding energies are in agreement with the typical vdW binding energy of around 20 meV/Å^2, obtained by DFT calculations[1]. To verify the interaction and to describe the influence of charge transfer among the layers, we calculated charge density difference defined as

$$\Delta\rho = \rho_{\text{Hetero}} - \rho_{MoS_2} - \rho_{L_2} \tag{2}$$

where ρ_{Hetero} is the 3D charge density of heterostructure, ρ_{MoS_2} and ρ_{L_2} are the 3D charge density of MoS_2 and second layer under same configuration, respectively, shown in Figure- S1. In the figure, charge density lobes of the heterostructures are not overlapping, which verifies the formation of pure vdW interactions. Further, if we compare the MoS_2/2D-Semiconductor hetero-bilayer, in (Figure S1-b, c, & d) to the MoS_2/Semi-metal (Figure S1-a); the interfacial charge redistribution is greatly reinforced and one can see clearly the accumulation of charge at Mo atoms. The fortification is in agreement with the fact that interactions get strengthen with reduction in the interlayer distance. From the Table S2, interlayer distances (d) in case of MoS_2/BlackP, MoS_2/InSe, & MoS_2/BlueP are lesser than the value for MoS_2/GR. The planar averaged charge density differences normal to the MoS_2 plane were calculated to shed more light on charge distribution (Figure- S1). It confirms that the transfer of charge is taken place from underneath or second layer to MoS_2.

Quantitative analysis of charge transfer was performed by using the Lowdin charge analysis as implemented in quantum espresso, which are listed in Table S2. In case of vdW heterojunctions the values of Lowdin charges are -0.015 in MoS_2/GR, -0.067 in MoS_2/BlackP, -0.203 in MoS_2/InSe, and -0.020 in MoS_2/BlueP. Here, the negative sign shows that the charge get transferred from the second layer to MoS_2, which is in consistent with our planar averaged charge density difference (Figure- S1). These results demonstrate two aspects: these thermodynamically stable structures can be synthesised and the inter layer interaction can be engineered by using different layers to form the junction.

[a] *SRM Research Institute, SRM Institute of Science and Technology, Kattankulathur 603203, Tamil Nadu, India. *E-mail: waghmare@jncasr.ac.in, ranjit.t@srmap.edu.in*
[b] [2]*Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research Jakkur, Banglore-560064, India.*
[c] *Department of Physics, SRM University-AP, Amaravati 522502, Andhra Pradesh, India.*

Table S1 Optimised structural parameter of Heterostructures under investigation.

System	Supercell Size	Lattice Mismatch (%)	Lattice Type	Lattice parameters	Bond Length (Å)	No. of atoms per cell
MoS_2/ GR	4×4×1/ 5×5×1	2.654	Hexagonal	a=12.6416 Å c/a=2.3731	C–C=1.42 Mo–S=2.41	98
MoS_2/ BlackP	$1\times4\sqrt{3}\times1$/ 1×5×1	4.23 in $\vec{a}$ 5.20 in $\vec{b}$	Simple Orthorhombic	a=3.2524 Å b=22.4800 Å c/a=9.2238	P–P=2.25 P–P=2.21 Mo–S=2.41	44
MoS_2/ InSe	5×5×1/ 4×4×1	2.456	Hexagonal	a=16.2000 Å c/a=1.8518	In–In=2.79 In–Se=2.66 Mo–S=2.41	139
MoS_2/ BlueP	1×1×1/ 1×1×1	3.292	Hexagonal	a=3.2680 Å c/a=9.1799	P–P=2.21 Mo–S=2.41	5

Table S2 Interlayer distance (d), Binding Energies (E_b) & Lowdin Charge Analysis (negative sign indicates charge given by layer-2 i.e. GR, BlackP, InSe & BlueP to MoS_2)

Structure	d (Å	Surface Area (Å^2)	E_b (meV/Å^2)	Lowdin Charge (e)
MoS_2/GR	3.37	138.39	-14.18	-0.015
MoS_2/BlackP	3.34	73.12	-15.19	-0.067
MoS_2/InSe	3.25	227.28	-13.29	-0.208
MoS_2/BlueP	3.16	8.64	-15.14	-0.020

Table S3 Spilling parameter values and smearing used for the calculations.

Structure	Smearing	Spilling parameter
MoS_2/GR	marzari-vanderbilt	0.0060
MoS_2/BlackP	fermi-dirac	0.0080
MoS_2/InSe	fermi-dirac	0.0039
MoS_2/BlueP	fermi-dirac	0.0079
MoS_2/h-BN	fermi-dirac	0.0059

Fig. S1 Charge Density Difference at isovalue 0.0002 e/Bohr^3 (Red-Accumulation & Green-Depletion) & Planar Averaged Charge Density Difference.

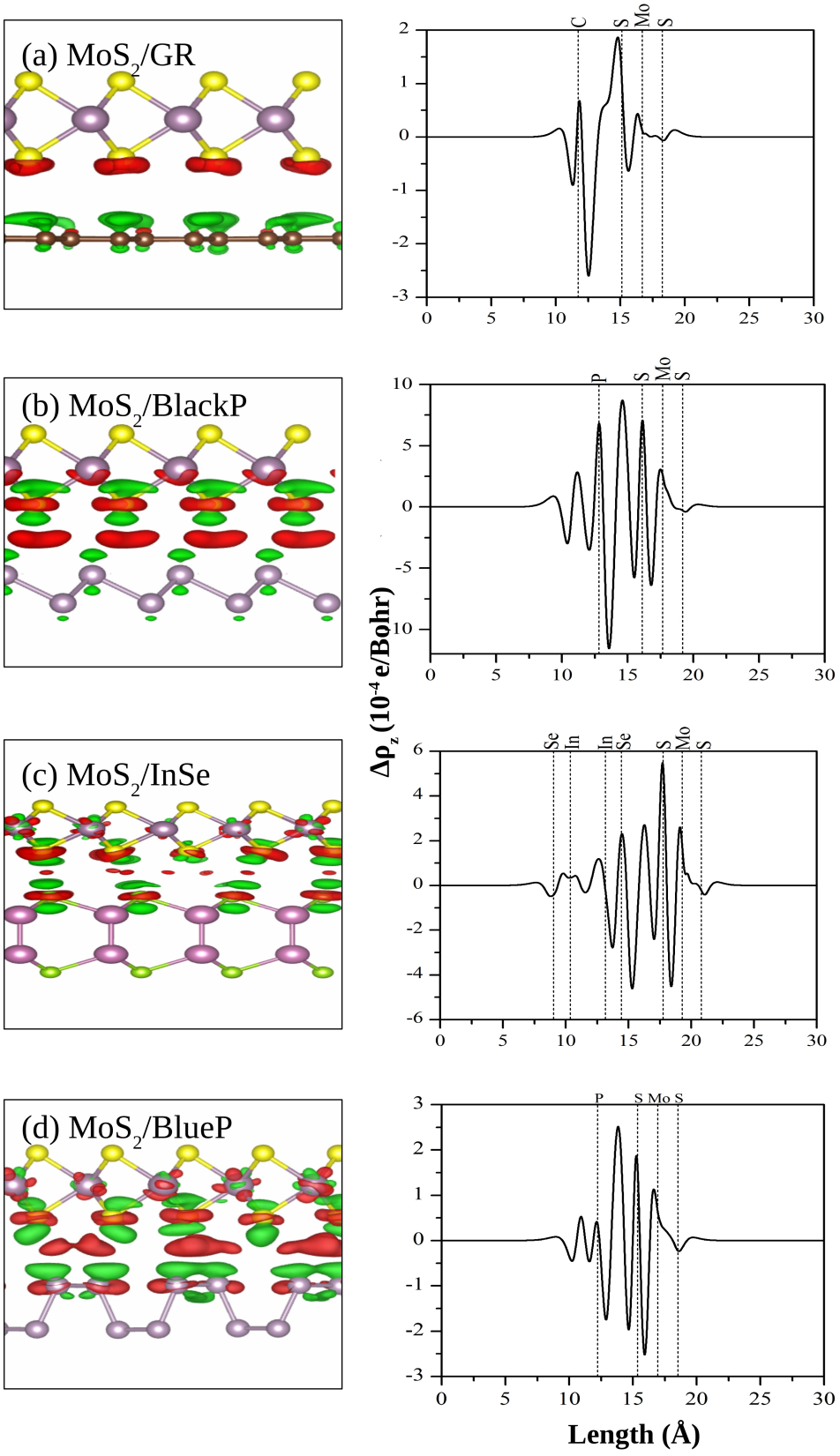


Fig. S2 Projected Density of States : Heterostructure and its constituent layers.

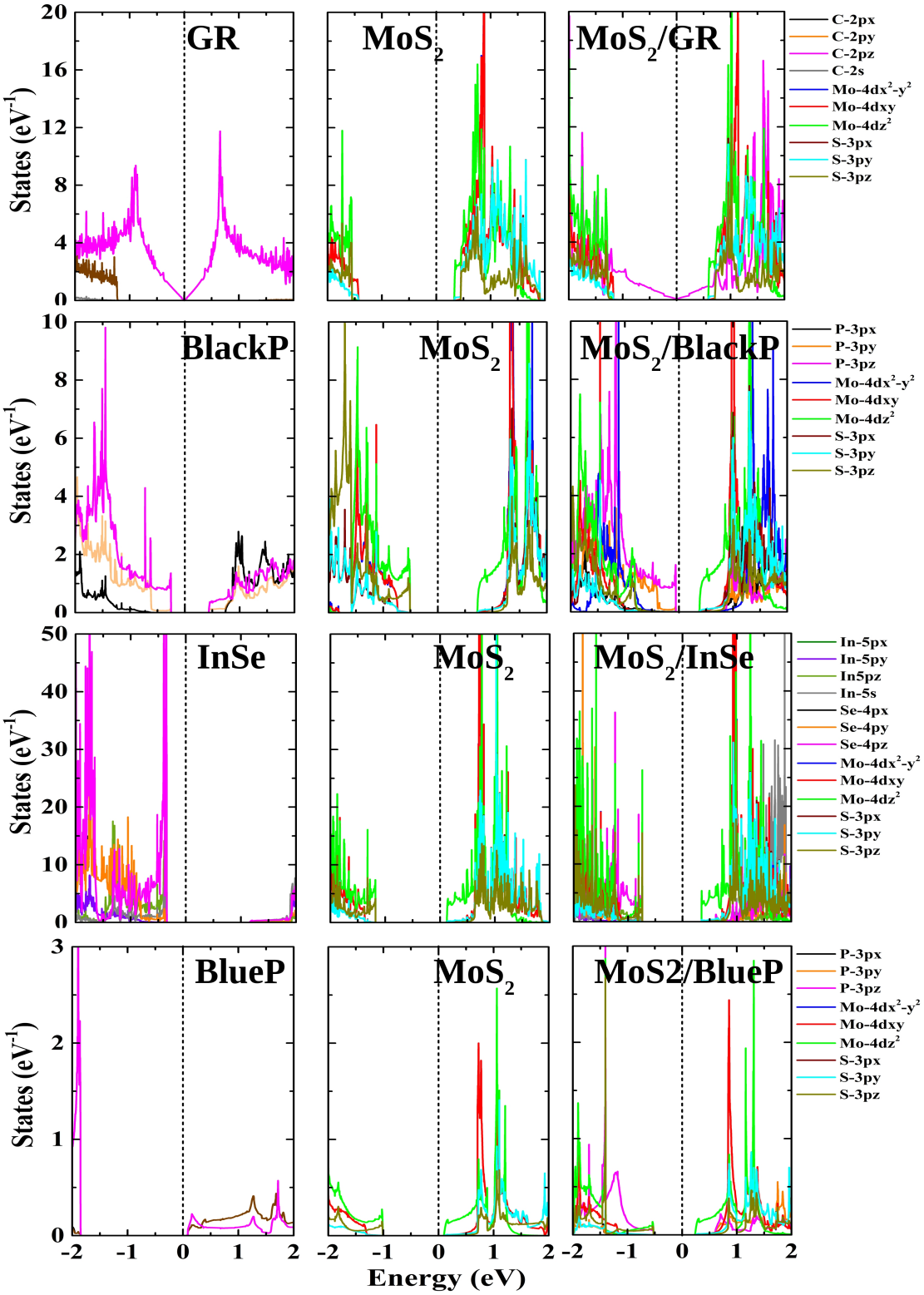


Fig. S3 VBM & CBM Electronic density and its profile of the planar average for all the heterostructures. (a)MoS_2/Graphene; (b)MoS_2/BlackP; (c)MoS_2/InSe; (d)MoS_2/BlueP. Red colour electronic density represents VBM where as green colour is used for CBM.

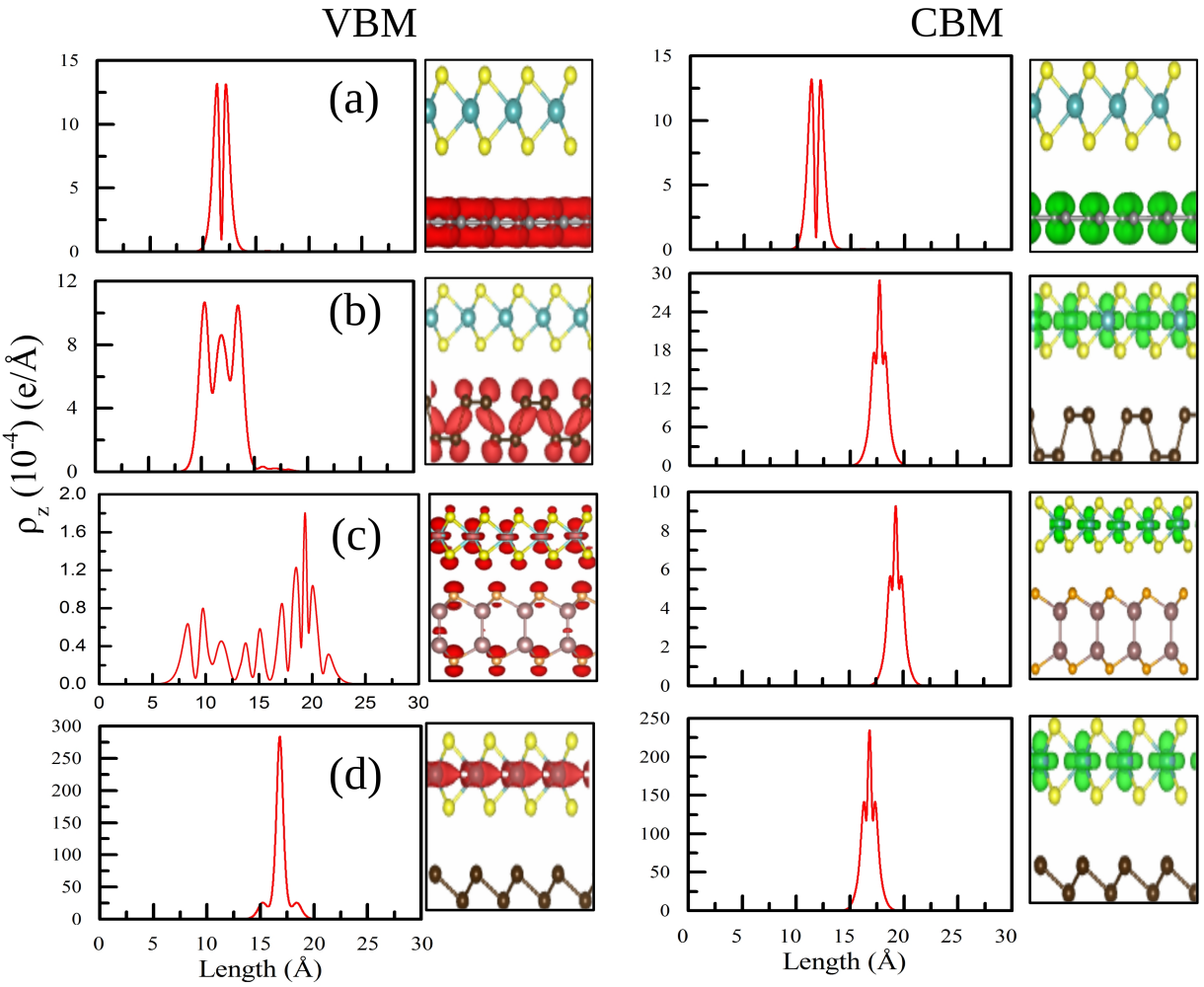


Fig. S4 Planar averaged charge density of heterostructure (Blue solid-line), layer-1 (Green solid-line), layer-2 (Gray solid-line) and sum of layer-1 & layer-2 (megenta dash-line).

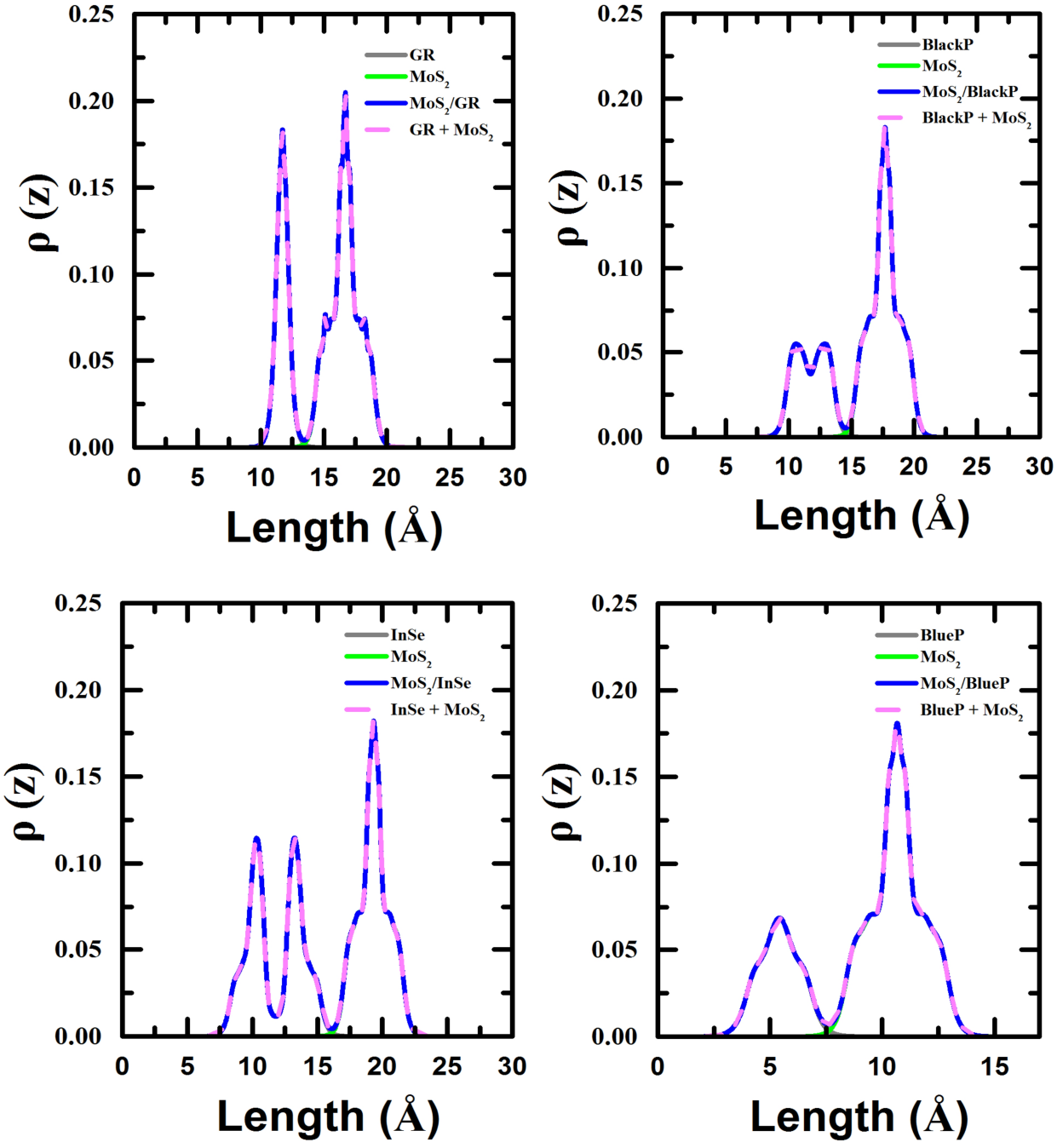


Fig. S5 Planar averaged DFT potential of MoS_2/h-BN. The red curve represents MoS_2 (V_{tot}^{L1}), blue curve shows the total potential (V_{tot}^{L2}) of h-BN, the sum of V_{tot}^{L1} & V_{tot}^{L2} is shown by light magenta colour and the black curve illustrate the potential profile of heterostructure (V_{tot}^{HET}). $\Delta V_{Int.}$ represent the potential difference between the vacuum level (V_vacc) and V_{tot}^{HET}; ΔV_{xc} shows the exchange and correlation potential which is calculated using $V_{tot}^{HET} - (V_{tot}^{L1} + V_{tot}^{L2})$.

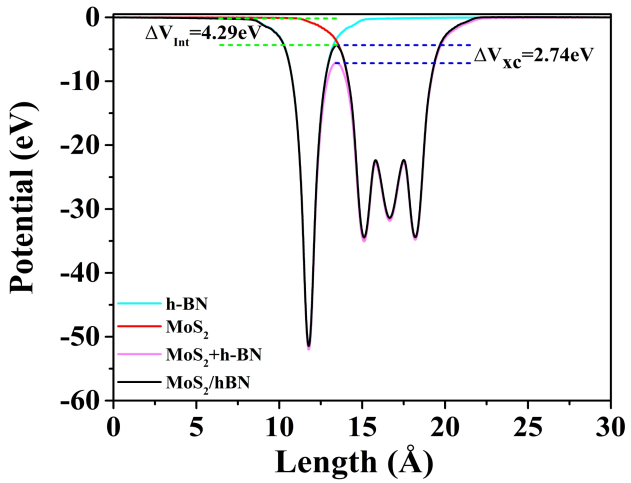


Fig. S6 Absorption coefficient and Reflectivity are shown with respect to photon energy and wavelength.

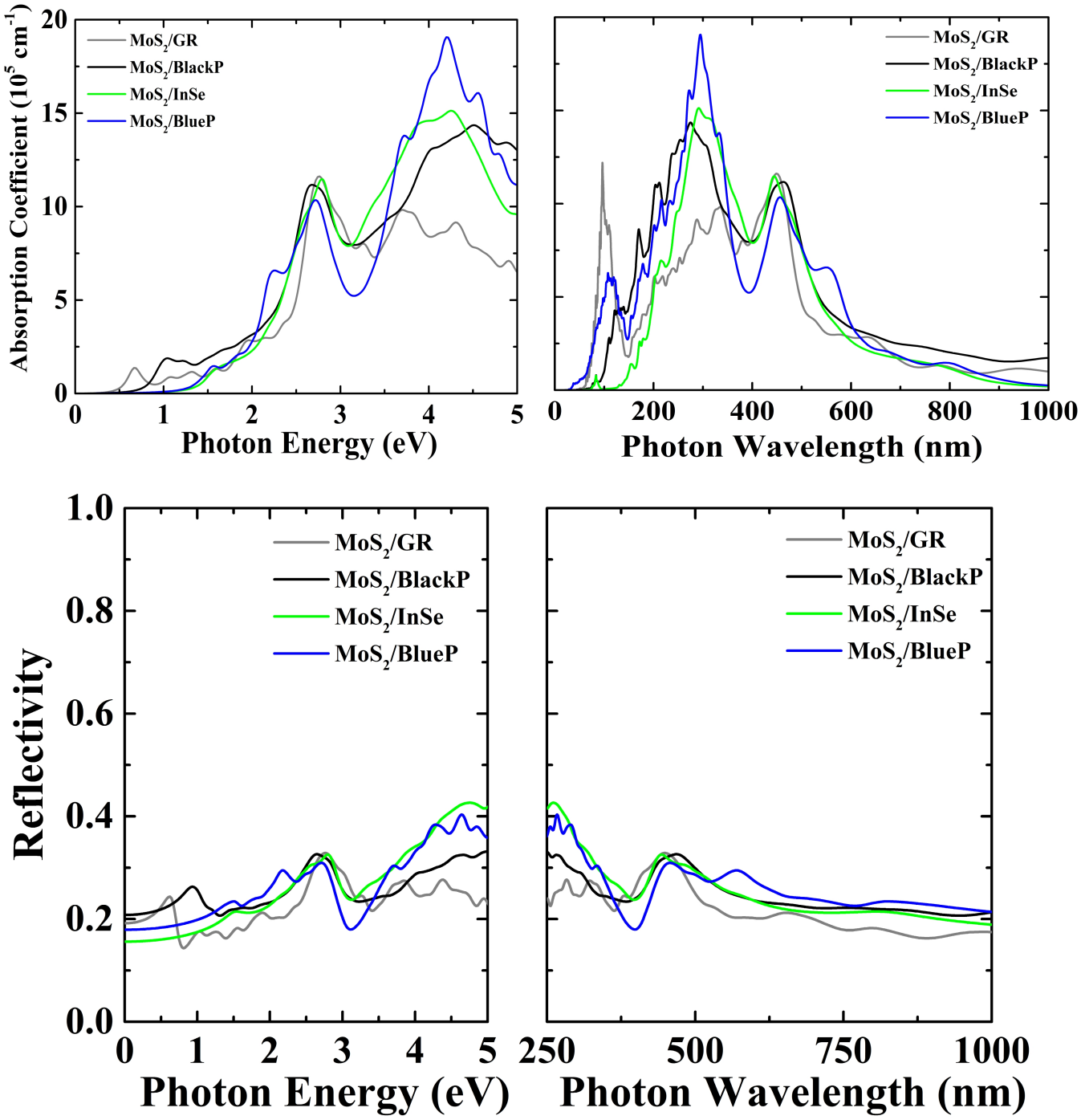
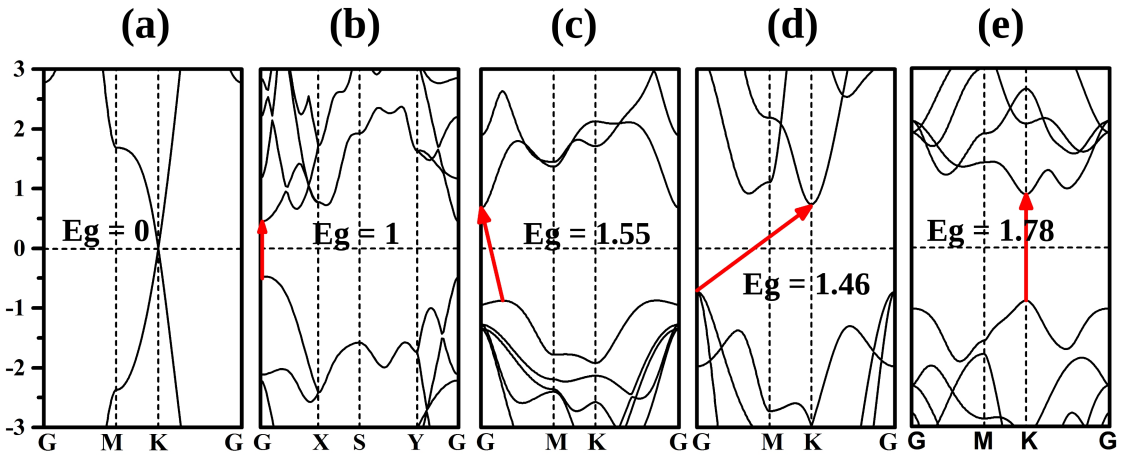


Fig. S7 DFT-PBE Electronic band structure of all the monolayers under consideration and band gap E_g is mentioned in eV unit with Fermi energy at 0 eV. (a)Graphene, (b)BlackP, (c) InSe & (d)BlueP.



.

References

1 T. Björkman, A. Gulans, A. V. Krasheninnikov and R. M. Nieminen, *Phys. Rev. Lett.*, 2012, **108**, 235502.