Near-Infrared and Visible-Range Optoelectronics in 2D Hybrid Perovskite/Transition Metal Dichalcogenide Heterostructures

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The application of ultrathin 2D perovskites in near-infrared and visible-range optoelectronics is limited owing to their inherent wide bandgaps, large excitonic binding energies, and low optical absorption at higher wavelengths. Here, it is shown that by tailoring interfacial band alignments via conjugation with low-dimensional materials like monolayer transition metal dichalcogenides (TMD), the functionalities of 2D perovskites can be extended to diverse, visible-range photophysical applications. Based on the choice of individual constituents in the 2D perovskite/TMD heterostructures, first principles calculations demonstrate widely tunable type-II bandgaps, carrier effective masses, and band offsets to enable an effective separation of photogenerated excitons for enhanced photodetection and photovoltaic applications. In addition, the possibilities of achieving a type-I band alignment for recombination-based light emitters as well as a type-III configuration for tunneling devices are shown. Further, the effect of strain on the electronic properties of the heterostructures are evaluated to show a significant strain tolerance, making them prospective candidates in flexible photosensors.

1. Introduction

2D perovskites are rapidly emerging as useful materials for optoelectronic applications because of their direct bandgaps,[1,2] high photoluminescence quantum yield,[3] broadband light emission,[1,4] and improved stability with respect to their bulk counterparts.[4,5] They are represented by the structural formula A′2AnBxX3n−x, where A′ and A are organic cations, M is transition metal (commonly Pb), and X is halogen.[1,2] In a single unit of the 2D perovskite, the 2D metal-halide octahedra is sandwiched within bulky organic spacer cations, A′, forming a hybrid organic-inorganic configuration. n determines the number of such metal halide units stacked vertically, and A represents the smaller organic cation.[3] Adjacent such units are held by weak van der Waals (vdW) interactions, rendering the possibility of micromechanical exfoliation to produce atomically thin monolayers similar to graphene-like 2D materials.[6]

In contrast to other 2D vdW systems, the dielectric confinement due to bulky organic groups gives rise to large bandgap values in monolayer (n = 1) 2D perovskites. For example, photoluminescence spectrum of the well-explored BA2PbBr4 (BA is butylammonium, C4H9NH3) yields an optical bandgap 3 eV,[3] while in BA2PbI4 and (C6H5CH2NH3)2PbCl4 the bandgaps are reported to be 2.4[2] and 3.6 eV,[7] respectively. Such wide bandgaps can limit the applications of 2D perovskites in solar cells and visible-range light emission or detection. The out-of-plane quantum well-like configuration also leads to large exciton binding energies of 200–500 meV which makes the separation of photogenerated excitons into free carriers less feasible.[8,9] However, to achieve higher photovoltaic efficiencies, an effective bandgap near the Shockley–Queisser range (1.3–1.5 eV) as well as an easy dissociation of excitons into free carriers are required.

A possible solution to overcome these limitations is to design heterostructures of 2D perovskites with suitable materials that demonstrate excellent optical properties and can lead to desired interface properties like faster exciton separation.[10] Transition metal dichalcogenides (TMDs) are well-studied van der Waals materials with exceptional electronic and optical properties, sizeable bandgaps, and high tensile strength.[11] This makes them suitable candidates to conjugate with 2D perovskites to form van der Waals heterostructures without the need of a coherent epitaxial growth and absence of dangling bonds can result in clean heterointerfaces. Such graphene/TMD/III–VI metal chalcogenide/hBN based vdW heterostructures have led to the emergence...
of unprecedented physical phenomena ranging from electrical field-effect\cite{13} and tunneling devices\cite{16} to light detectors, harvesters,\cite{15} and emitters\cite{17} to twistrionics\cite{18} based novel systems which are all governed by the heterointerface.\cite{19}

From a device aspect, most experimental reports have focused on the improved photodetection in these heterostructures, whereas photovoltaic performance and light emission are not well investigated.\cite{18,19} Recent studies of 2D perovskite/TMD heterostructures have shown interlayer exciton peaks,\cite{20} excitonic energy transfer\cite{21} as well as significant photoluminescence quenching at the interface,\cite{18} indicating a possibility of charge transfer and strong interlayer coupling between these structurally dissimilar materials. While doped-graphene and phosphorene have been proposed for forming heterojunctions with 2D perovskites, they are limited by the absence of bandgap\cite{22} and poor air stability and tunability,\cite{23} respectively. However, for specific predefined applications, the rational choice of individual TMD and 2D perovskite constituents of the heterostructure should be based on their interfacial electronic band structure.\cite{24} A possible diverse range of band alignments at the interface can enable various applications like photodetection, photovoltaic operation or light emission owing to the strong light-matter interaction in individual materials.

In this work using first principles calculations, we illustrate a number of heterostructures of 2D perovskites with transition metal dichalcogenides that can result in new device functionalities and extend the optical bandwidth of the 2D perovskites for improved optoelectronic performance. In particular, the emergence of a type-II band alignment at the interface of BA$_2$PbBr$_4$/MoS$_2$, heterojunction with a lower effective bandgap in the near-infrared region along with the possibility of enhanced interlayer separation of photogenerated charge carriers can result in improved photodetection and photovoltaic performance. In a heterostructure of BA$_2$PbBr$_4$ with WS$_2$, the possibility of a type-I band alignment could enable carrier recombination for light-emitting devices. We discuss the chalcogen-dependent properties of various TMD heterojunctions with the homologous series of 2D perovskites BA$_2$PbBr$_4$, BA$_2$PbI$_4$ and BA$_2$PbCl$_4$ and show that tunneling-based (type-III) devices are also possible by the apt choice of constituents. Finally, we show that 2D perovskite/TMD heterostructures can withstand considerable tensile strains without significant degradation of the electronic properties potentially enabling their applications on stretchable substrates for flexible devices.

2. Results and Discussion

2.1. Structure Analysis

We explore the interface of various Group-6 TMDs (MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$) with 2D perovskites, BA$_2$PbCl$_4$, BA$_2$PbBr$_4$, and BA$_2$PbI$_4$, through first-principles-based density functional theory (DFT) calculations. BA$_2$PbX$_n$ (X = Cl/Br/I) is a n = 1 2D perovskite made up of the inorganic [PbX$_4$]$^{2-}$ octahedra incorporated between the large Ba cations as shown in the schematic in Figure 1a. The hybrid 2D perovskites and group-6 TMDs discussed in this work have orthorhombic and hexagonal unit cells, respectively. The optimized lattice parameters for all perovskites and monolayer TMDs are provided in Section S1 (Supporting Information). Additionally, we also compare the lattice parameters and bandgap values using different van der Waals corrected methods (DFT-D3, DFT-D2, and optB86vdW) in Section S1 (Supporting Information).

2.2. Electronic Properties

Figure 1b shows the band structure of single layer BA$_2$PbBr$_4$ as a representative of the 2D perovskites considered here. As also illustrated in Figure S2 (Supporting Information), the band structures of all 2D perovskites depict direct bandgaps with the conduction band minimum (CBM) and valence band maximum (VBM) occurring at Γ of the orthorhombic Brillouin zones (BZ). The direct bandgap values calculated using both generalised gradient approximation (GGA) as well as Heyd–Scuseria–Ernzerhof (HSE06) formalism are found to be in the near-ultraviolet region and even higher. As an example, incorporating the van der Waals corrected DFT-D3, the DFT-GGA and HSE06 bandgaps of BA$_2$PbBr$_4$ are 2.50 and 3.37 eV, respectively, while the experimental value is reported to be around 3 eV.\cite{18,25} For the case of TMDs, our calculations show the DFT-GGA bandgap in monolayer MoS$_2$ to be 1.72 eV (HSE06 yields 2.23 eV, Figure S3, Supporting Information) and the experimentally obtained optical bandgap using photoluminescence (PL) is $\approx$1.9 eV.\cite{26} Further, the pre-contact band alignments of the TMDs- MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$, as well as the 2D perovskites used in this study, calculated using the respective work functions, are shown in Figure 1c. In general, the bandgap values obtained by using HSE06 formalism are closer to the experimental values, consistent with several reports.\cite{24,27}

We model 2D perovskite/TMD heterostructures using an orthorhombic supercell to ensure a good lattice matching between the 2D perovskite and TMD layers. Each supercell consists of a 2 × 2 unit cell of the perovskite and 5 × 3 rectangular unit cell of the TMD layer, aligned in such a way to ensure a minimum possible strain due to lattice mismatch and to enable a uniform comparison of electronic properties across different heterostructures. The details of the lattice mismatch for all heterostructures considered are provided in Section S4 (Supporting Information). Both 2D perovskites and TMDs demonstrate significant strain tolerance, hence in the resulting heterostructure supercell the strain is split equally between the two layers.\cite{28,29} In most configurations (see Section S4, Supporting Information), the in-plane strain values are low, which is not expected to significantly impact the electronic characteristics.

A closer look at the electronic density of states of BA$_2$PbX$_4$ in Section S2 (Supporting Information) shows that the conduction and valence band edges of the hybrid 2D perovskites are constituted by the p-orbitals of Pb and halogen, respectively, and the states contributed by the organic species (C, H, N) are far away from the Fermi level.\cite{21,30} Therefore, we test the feasibility of an all-inorganic 2D perovskite structure by substituting the organic BA groups in the hybrid system by a single large inorganic monopositive cation like Rb (shown as pink spheres in Figure 1a) and retaining the lattice parameters of the corresponding hybrid 2D perovskite.\cite{30,31} The calculated band structure of the all-inorganic Rb$_2$PbBr$_4$ shows a good resemblance to that of the hybrid perovskite, depicted using red dashed lines in Figure 1b. Furthermore, our results show that substituting the organic layers on one side of the PbX octahedra (Figure 1a)
results in a mixed organic–Rb structure (BARbPbBr₄) which also demonstrates an excellent resemblance to the band structure characteristics in Figure 1c (Section S5, Supporting Information). Such substitutions can significantly reduce the computational cost involved in investigating the 2D perovskite/TMD supercells. Further studies are required to explore the experimental feasibility and stability of such Ruddlesden–Popper or Dion–Jacobson based all-inorganic 2D perovskites.

Next, to study the interaction between the 2D perovskite and TMD in the heterostructure, we first use the hybrid organic–inorganic structure for the 2D perovskite (HS1). We also consider a second heterostructure made up of the all-inorganic Rb-substituted 2D perovskite structure (HS2). We compare the nature of bands and bandgap values for both configurations by using the illustrative example of MoS₂ as the TMD layer.

The band structure of the hybrid organic–inorganic BA₂PbBr₄/MoS₂ heterostructure (HS1) is shown in Figure 2a, where the DFT-GGA calculated interface bandgap of 0.78 eV is significantly lower than the gaps of the individual 2D constituents of the heterostructure (1.9 eV for MoS₂, 3.0 eV for BA₂PbBr₄). From the band structure of the all-inorganic Rb₂PbBr₄/MoS₂ (HS2) shown in Section S6 (Supporting Information), the nature of the bands is identical to that in Figure 2a and the calculated gap value of 0.73 eV is in good agreement with HS1. Further, to elucidate the nature of interaction between the two materials we also examine a mixed organic–Rb substituted structure (HS3, Section S5, Supporting Information) in which the organic groups away from the heterointerface are substituted by Rb. The similarity in band features in the three cases proves that the interactions between the lead halide core of the 2D perovskite and TMD is not significantly affected by the presence of nonpolar organic species or Rb at the heterointerface. Therefore, for accurate calculations at a reasonable computational cost, the properties of various 2D perovskite/TMD heterojunctions can be analyzed using the corresponding Rb-substituted inorganic structures. For a more accurate description of the bandgap in HS2, the hybrid HSE06 functional was employed which resulted in 1.12 eV. Interestingly, the heterostructure comprising MoS₂ layer rotated by 90° and stacked on top of the 2D perovskite shows comparable electronic properties as demonstrated in Section S6 (Supporting Information).

As illustrated in Section S7 (Supporting Information), these
heterostructures considered here are thermodynamically stable with negative formation enthalpies. Based on the experimental demonstration of a few stable TMD/2D perovskite heterostructures, we also anticipate such heterostructures to be dynamically stable. Further confirmation of this can be obtained via calculations of phonon spectra. Given the large size of heterostructure supercells (402 atoms in HS1 and 146 atoms in HS2), such calculations can possibly be performed using empirical force-fields, subject to their availability.

Next, we look at the band structure at the heterointerface of BA\textsubscript{2}PbBr\textsubscript{4} with WS\textsubscript{2} (Section S8, Supporting Information) which demonstrates a nature comparable to the above-described MoS\textsubscript{2} based system. For the all-inorganic Rb\textsubscript{2}PbBr\textsubscript{4}/WS\textsubscript{2} structure, DFT-GGA calculated bandgap is 1.04 eV and that obtained via HSE06 is 1.44 eV, close to the desirable value predicted by Shockley-Queisser theory for optimum photovoltaic efficiency.

The sizeable bandgaps at the 2D heterointerface of BA\textsubscript{2}PbBr\textsubscript{4} with monolayer MoS\textsubscript{2} or WS\textsubscript{2} allows the possibility of photogeneration across a broad range of the electromagnetic spectrum including: i) visible (intralayer in MoS\textsubscript{2} or WS\textsubscript{2}), ii) near-UV (intralayer in BA\textsubscript{2}PbBr\textsubscript{4}), and iii) near-IR (heterointerface) as shown in Figure 2b. Moreover, the spatially separated interlayer excitons (shown in gray color in Figure 2b) could be possible in these heterostructures in addition to intralayer excitons (black) localized in the same material. Sub-bandgap photodetection enabled by such interlayer excitons across the interfacial

Figure 2. Band structure of 2D perovskite/TMD heterojunction. a) Band structure of BA\textsubscript{2}PbBr\textsubscript{4}/MoS\textsubscript{2} heterostructure showing an indirect bandgap. The contributions from MoS\textsubscript{2} and BA\textsubscript{2}PbBr\textsubscript{4} are marked using red and blue circles, respectively. b) Schematic showing the various photogeneration possibilities in the heterostructure of BA\textsubscript{2}PbBr\textsubscript{4} with sulfide based TMDs (MoS\textsubscript{2} and WS\textsubscript{2}). c) Band structure of BA\textsubscript{2}PbBr\textsubscript{4}/WSe\textsubscript{2} showing a nearly direct bandgap (difference between direct and indirect gaps is very low) along Γ – X. Here too, the contribution from WSe\textsubscript{2} is in red and that of the perovskite is in blue. d) Hexagonal and rectangular Brillouin zones of the respective unit cells of the TMD and 2D perovskite (with high symmetry points marked). \( b_{o1}, b_{o2} \) represent the orthogonal axes of the orthorhombic cell and \( b_{h1}, b_{h2} \) represent those of the hexagonal cell. Due to the folding of the hexagonal Brillouin zone of TMDs onto the rectangular Brillouin zone of 2D perovskites, the high symmetry point K of the TMDs appears along Γ – X direction of the rectangular Brillouin zone of 2D perovskites.
gap has been shown for the case of MoS₂/WSe₂[33] and WSe₂/ReS₂[34] based TMD heterostructures. Further, near-IR interlayer exciton emission involving electrons/holes at K valleys of both materials has also been reported for MoS₂/WSe₂ heterojunctions.[35] These observations suggest that BA₂PbBr₄/MS₂ heterostructures considered here can enhance the versatility of 2D perovskites by enabling interlayer emission or optical absorption in the visible and near-infrared energies, below the bandgap of the 2D perovskite.

Considering the bandgap character, for both MS₂-based heterostructures, the bandgap is indirect in nature, with the VBM at Γ and CBM located along the high symmetry line Γ–X. The k point at which CBM occurs is related with the folding of the hexagonal BZ of the TMD onto the orthorhombic BZ of the heterostructure. By unfolding the electronic states of the heterostructure into the hexagonal irreducible Brillouin zone (IBZ) of TMD, the point at CBM (K′ along Γ–X) in the rectangular supercell BZ corresponds to the K point of the hexagonal IBZ of TMDs (Figure 2d).[35] Further, the band structures unfolded onto the hexagonal IBZ of TMD as well as the orthorhombic IBZ of BA₂PbBr₄ can be found in Section S9 (Supporting Information) and show good resemblance with the pristine materials as can be seen from the overlaid picture. Therefore, the weak van der Waals interaction preserves these intrinsic characteristics of the constituents in the band structure of the heteromaterial system. Moreover, the heterostructure comprising MoSe₂ and BA₂PbBr₄ (Section S8, Supporting Information) exhibits features like the sulfide-based structures owing to similar band alignments.

In contrast to the heterostructures discussed above, the band structure of selenide-based heterostructure BA₂PbBr₄/WSe₂ in Figure 2c demonstrates a direct bandgap at K′ along Γ – X of the BZ and the DFT-GGA calculated gap is around 1.55 eV, close to that of pristine WSe₂. The energy difference between the direct (K′) and indirect (S – Y) gaps is low (<25 meV), hence the optical transitions across the direct bandgap will be more favorable. The bands of the all-inorganic Rb₂PbBr₄/WSe₂ heterojunction (shown in Section S6, Supporting Information) depict similar characteristics in terms of the nature and gap value, thereby reinforcing our methodology on Rb-substitution of the BA group. The HSE06 formalism yields a higher bandgap of 2.02 eV. Further, from Section S9 (Supporting Information), the unfolded bands of Rb₂PbBr₄/WSe₂ also show good correlation with that of the pristine WSe₂ and Rb₂PbBr₄. The band structures of Rb-substituted perovskites with MoS₂ and WSe₂ in presence of spin–orbit coupling (SOC) are shown in Section S10 (Supporting Information). In presence of SOC, the bandgap values show a slight reduction, however, the nature of bands remains unchanged.

To understand the atom-wise contributions in the electronic band structure of 2D perovskite/TMD heterostructure, we examine the projected density of states calculated using Gaussian smearing with a low smearing width of 0.05 eV. For the BA₂PbBr₄/MoS₂ heterostructure, the electronic states at the conduction band edge are made up of Mo and S (Figure 3a) gaps is low (0.09 eV), such systems can show a transition from type-II to type-I with external factors like strain. For all the Rb-substituted structures, the states from Rb are located deeper in the valence and conduction bands, away from the Fermi level. Therefore, we can conclude

Figure 3. Atom projected density of states of a) BA₂PbBr₄/MoS₂ (type-II, indirect) and b) BA₂PbBr₄/WSe₂ (type-I, direct) heterostructures showing the contributions to energy states around the Fermi level. In both cases, the contribution of Rb from the corresponding all-inorganic structures is also included. The partial charge densities corresponding to valence band maximum and conduction band minimum states show c) type-II band alignment in BA₂PbBr₄/MoS₂ and d) type-I alignment in BA₂PbBr₄/WSe₂.
that a type-II band alignment is obtained for heterostructures of MoS₂, WS₂, and MoSe₂ with 2D A₂PbBr₄ (where A = butylammonium, BA or Rb) perovskite in which the valence and conduction band edges are contributed by the 2D perovskite and TMD, respectively. The band decomposed partial charge densities corresponding to valence band maximum and conduction band minimum of MoS₂ (Figure 2b) and WSe₂ (2d)-based heterostructures agree with the band alignments discussed above. Partial charge plots of other heterostructures are available in Section S11 (Supporting Information).

The large exciton binding energies, around 300 meV for BA₂PbBr₄ is a major limitation for photovoltaics using few-layer 2D perovskites since it can lead to a fast recombination of photogenerated charge carriers that could otherwise drive a photocurrent in the circuit. This has led to low power conversion efficiency values for the 2D perovskite solar cells as well as poor light detection. However, the type-II band alignment of the heterostructures of MoS₂, WS₂ and MoSe₂ with 2D A₂PbBr₄ perovskite allows the formation of spatially separated interlayer excitons. The photogenerated electrons could reside in the sulfide-based TMD while holes move to BA₂PbBr₄ in the case of interlayer excitons. For example, the sizeable conduction band offset (CBO) in BA₂PbBr₄/MoS₂ heterostructure of 1.86 eV and valence band offset (VBO) of 0.97 eV are larger than the intralayer exciton binding energy, which could promote the separation of these photocarriers across the heterojunction at low electric fields to generate large photocurrents. The dissociation rate of interlayer excitons has been shown to be significantly higher than intralayer excitons for TMD based type-II heterostructures due to their reduced binding energies. Hence, heterostructures of MoS₂, WS₂ and MoSe₂ with 2D A₂PbBr₄ perovskite can enable an improved excitonic solar cell performance as well as enhanced photodetection.

In contrast, for the BA₂PbBr₄/WSe₂ heterojunction, the conduction and valence band edges are both made up of the 5dₓ²₋₃ᵧ², 5dₓᵧ orbitals of W and 4pₓ, 4pᵧ orbitals of Se (Figure 3b). As both band edges are from the same material, the electronic structure demonstrates a type-I band alignment, and the band offsets (CBO = 0.79 eV and VBO = 0.34 eV) are small as shown in Figure 3b. This type-I configuration drives a unidirectional transport of the photoexcited electrons and holes in BA₂PbBr₄ to the WSe₂ layer. The accumulation of electrons and holes in WSe₂ could promote enhanced radiative recombination of these electron-hole pairs leading to light emission. A recent experimental study on n = 4 2D perovskite/TMD heterostructure shows a 150-fold enhancement of PL emission and 25-times increase in optical absorption owing to the type-I band alignment at the hetero-interface. Therefore, in our case, the direct bandgap values could enable carrier recombination-based devices in the near-infrared/visible, similar to that observed in monolayer ReS₂/MoS₂ type-I heterojunction.

We have also calculated the optical absorption spectra using time-dependent HSE06 (TD-HSE06) method for different all-inorganic heterostructures are shown in Section S12 (Supporting Information). The TD-HSE06 method enables BSE-level accuracy at a reasonable computational cost for estimation of excitonic features which are absent in the random phase approximation (DFT-RPA) calculations. However, it should be mentioned that our obtained optical absorption spectra presented in Section S12 (Supporting Information) are only of qualitative nature, due to the coarse k points grid used to ensure the calculation of absorption spectra for heterostructures with large number of atoms remains computationally feasible. The direction-dependent optical features in the absorption spectra are owing to anisotropic nature of the heterostructures.

The electrical transport in 2D perovskite/TMD heterostructure will be strongly influenced by the effective mass (m*) of charge carriers at the interface which can be obtained from the band structures in Figure 2 using m* = h² / 2E₂k², where h is reduced Planck's constant, E is energy, and k is wave vector. For BA₂PbBr₄/MoS₂ heterostructure, the effective mass of holes (m₃) is found to be 0.29m₀ (m₀ is static mass of free electron) by using the parabolic approximation at the VBM edge. For electrons, m₁ is found to be 0.52m₀ at the conduction band minimum. For comparison, the effective masses of electrons and holes in the monolayer BA₂PbBr₄ are 0.22m₀ and 0.30m₀, respectively. For monolayer MoS₂, the effective mass of electrons is 0.51m₀ and for holes is 0.60m₀. The effective masses of charge carriers in all 2D perovskite/TMD heterostructure are comparable to the individual materials, indicating that the carrier transport will not be significantly degraded upon the formation of vdW heterostructures.

We also explore the heterostructures based on BA₂PbI₄ and BA₂PbCl₄ which are members of the homologous series of n = 1 2D perovskites. For monolayer BA₂PbI₄, our calculations yield a HSE06 bandgap of 2.91 eV similar to other reports, whereas absorption measurements show 2.38 eV. The HSE06 gap of BA₂PbCl₄ is 3.92 eV while experimentally it has been found to be around 3.6 eV. The heterostructure of BA₂PbI₄ with WSe₂ shows a type-II band alignment with an interlayer bandgap of 1.16 eV, different from the BA₂PbBr₄/WSe₂ structure. The CBO and VBO of BA₂PbI₄/WSe₂ are lower than the BA₂PbBr₄/MoS₂ heterostructure described earlier. A recent experimental study on (iso-BA₂)PbI₄/WSe₂ heterojunction shows the presence of interlayer excitons at around 1.6 eV, which is lower than the bandgaps of monolayer WSe₂ and (iso-BA₂)PbI₄. This confirms the type-II nature at the interface, thereby independently validating these results.

For the BA₂PbI₄/MoS₂ heterojunction, the conduction and valence bands in DFT-GGA results nearly overlap along Γ – X of the BZ, leading to a transition from type-II to type-III alignment. On the other hand, HSE predicts a low bandgap value of 0.18 eV. This crossovers of the bands could be due to the larger inherent strain (~4.1%) inevitable for good lattice matching in the supercell. However, such a broken band alignment could be useful for tunneling-based devices and the energy overlap for tunneling could be tuned via a transverse electric field (gate) or external strain. In the above-mentioned experimental report also, no interlayer excitons are seen for the case of (iso-BA₂)PbI₄/MoS₂. Further, the heterostructure of BA₂PbCl₄ with MoS₂ also depicts a type-II band alignment with sizeable band offsets and a gap of 1.29 eV. In both these heterostructures, the CBM and VBM are composed of MoS₂ and the 2D perovskite, respectively. The band structures and projected density of states plots for these heterostructures are provided in Section S13 (Supporting Information). In conjunction with our calculations, recent experimental evidence of interlayer excitons
in 2D perovskite/monolayer TMD hetero systems indicate the strong interlayer electronic coupling mediated by charge transfer across the interface of these materials.

To understand the extent of charge transfer through the van der Waals gap, we next examine the planar-averaged charge density difference along the direction perpendicular to the interface (z). Figure 4a shows a clear separation of charges across the interface in $\text{BA}_2\text{PbBr}_4/\text{MoS}_2$ structure as expected from the type-II alignment. The positive charge difference indicates electron accumulation at the MoS$_2$ edge and holes at BA$_2$PbBr$_4$ edge. While the BA$_2$PbBr$_4$/$\text{WSe}_2$ in Figure 4b shows a build-up of charges at the junction owing to the straddling gap. The average potential profiles along the z-axis for both structures are shown in Figure 4c. The peaks corresponding to the atoms of the TMD and 2D perovskite are seen.

From the analysis of the electronic structure, band alignments and interfacial charge transfer of various 2D perovskite/TMD heterostructures, different types of band alignments (type I, II, and III) are feasible (Table 1). This highlights the need for a first principles-based selection of individual constituents of the heterostack to guide specific experimental realizations. $\text{BA}_2\text{PbBr}_4/\text{WSe}_2$ heterostructure demonstrates a type-I alignment while $\text{BA}_2\text{PbI}_4/\text{MoS}_2$ is of type-III. The multiple possibilities of obtaining type-II alignment are provided by combining BA$_2$PbBr with MoS$_2$, WS$_2$, and MoSe$_2$ as well as BA$_2$PbI$_4$/WSe$_2$ and BA$_2$PbCl$_4$/MoS$_2$ structures, wherein the tunability in interface bandgaps is an important feature. Section S14 (Supporting Information) lists the calculated carrier effective masses at band edges and the conduction and valence band offsets which are key properties that govern optoelectronic applications. The trends in bandgaps, band offsets and alignments for different heterostructures calculated using HSE06 functional are comparable to the DFT-GGA results and are also included in Section S14 (Supporting Information).

2.3. Effect of Strain

Next-generation applications in flexible solar cells and wearable (photo)sensors require materials which exhibit stable optoelectronic attributes under repeated strain and relaxation cycles. In this context, 2D perovskites have been shown to accommodate lattice strain without drastic structural deformation due to the bulky organic layers that provide enhanced stability to the layered 2D phase which is not present in the 3D bulk perovskites.[42] For 2D perovskites strained via tensile lattice expansion or laser-induced thermal stress, a monotonic decrease in bandgap has been experimentally observed[29,42] which is restored upon withdrawal of the external stress. Moreover, monolayer TMDs can also withstand considerable lattice strain owing to their high effective Young’s modulus.[28]

As an illustrative example, here we employ uniaxial and biaxial tensile strain on the all inorganic, $\text{Rb}_2\text{PbBr}_4/\text{MoS}_2$ heterojunction to understand its effects on the electronic structure and associated properties. We apply uniaxial tensile strain from 0 to 10% applied along the y-direction and the ions are allowed to relax in the x-direction which is expected to redistribute the effect of strain on the structure. In the $\text{Rb}_2\text{PbBr}_4/\text{MoS}_2$ heterostructure, with increasing uniaxial strain, the bandgap shows a slight increase up to 5% strain and thereafter, it decreases at a rate of 34 meV%$^{-1}$ strain. The experimentally observed variation of bandgap is 13.3 meV%$^{-1}$ in n = 5 2D perovskite (strain up to 1.18%)[43] which is smaller than the 45 meV%$^{-1}$ seen in single layer MoS$_2$.[44] The change in bandgap values and evolution of band structures with uniaxial tensile strain are shown in Figure 4a and Section S15 (Supporting Information), respectively. In terms of electronic properties, the effective masses of electrons show a slightly decreasing trend at higher uniaxial

![Figure 4](https://www.advancedsciencenews.com/)

**Figure 4.** Planar averaged charge density difference profile along the direction normal to the interface (z) for a) $\text{BA}_2\text{PbBr}_4/\text{MoS}_2$ and b) $\text{BA}_2\text{PbBr}_4/\text{WSe}_2$ heterostructures. c) Electrostatic potential profile along z-direction for both structures where the average potential difference across the interface for both systems ($\Delta V_{\text{w}}$, $\Delta V_{\text{m}}$) are marked.

| Material       | $\text{BA}_2\text{PbBr}_4$ | $\text{Rb}_2\text{PbBr}_4$ | $\text{BA}_2\text{PbI}_4$ | $\text{BA}_2\text{PbCl}_4$ | $\text{Rb}_2\text{PbCl}_4$ |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| MoS$_2$       | 0.77            | 0.73 (1.12)     | 0.03            | 0.0 (0.18)      | 1.29            | 1.21 (1.72)     |
| WSe$_2$       | 1.55, direct    | 1.52 (2.02), direct | 1.19            | 1.09 (1.49)     |                 |                 |
| WS$_2$        | 1.12            |                 | 1.04 (1.44)     |                 |                 |                 |
| MoSe$_2$      | 1.40            |                 | 1.27 (1.67)     |                 |                 |                 |
|               | Type-I          | Type-II         | Type-III        |                 |                 |                 |
tensile strain and that of holes shows an increase (Figure 5b),
but are comparable to the unstrained structure, confirming that
the carrier transport properties remain mostly unchanged. For
uniaxial strains, the CBM contributed by MoS2 shows a shift
away from the K' point of the BZ toward X while the VBM
remains at Γ. The tensile stretching of the supercell increases
the average equatorial (Pb-Br-Pb) bond angles and elongates the
average Pb-Br bonds, leading to distortions in the lead-halide
octahedra which affects the electronic band structure.

In comparison to 1D lattice stretching, the lowering of the
interface bandgap is more pronounced when biaxial strain is
applied by stretching the unit cell along both x and y directions.
Particularly, at a large biaxial strain of 10% the conduction and
valence bands cross-over, resulting in a semiconductor-to-metal
transition (type-II to -III) in Rb2PbBr4/MoS2 heterostructure.

In monolayer MoS2, with the application of tensile strains, the
valence band maximum at Γ shifts upward relative to that at K
and at large biaxial stretching a significant decrease in bandgap
leading to semiconductor-to-metal transition is predicted by
first-principles calculations.\cite{45} In the heterostructure, the sharp
decrease in bandgap and ultimately the crossing-over can be
attributed to MoS2 from the projected density of states of the
strained structures as shown in Figure 5c. Further, the orbital
contributions reveal that the d_z^2 orbitals of Mo from valence
and conduction bands overlap at 10% biaxial strain. The band
structures of the biaxially strained structures are shown in
Section S15 (Supporting Information). From the above analysis,
we can conclude that under externally applied strains,
dynamic reorientation of the lead-halide octahedra as well as
the linked organic chains could take place in the 2D perovskite
lattice.\cite{46} Furthermore, the variation in electronic properties
with strain is seen to be consistent for various TMDs,\cite{47} hence
the response of the various other 2D perovskite/TMD hetero-
structures toward tensile strain is expected to be fairly similar
to the trends described here.

2.4. Device and Growth Aspects

TMDs have been used as selective charge carrier transport
layers to improve the efficiencies of bulk perovskite solar cells,
specifically as electron transport layer (ETL) in solar cells with
MAPbI3 absorber layer.\cite{48} In the type II A2PbX/MZ2 heterojunctions considered here, the TMD can enable the transport of
photogenerated electrons away from the 2D perovskite and at the same time block the transport of holes owing to the significant band offsets thereby reducing charge recombination. Therefore, the protective layer of TMDs on top of the 2D perovskite can be an effective ETL for improved power conversion efficiencies. To illustrate this, we have also calculated the power conversion efficiencies of all heterostructures considered in our study using the methodology proposed by Scharber et al. (see Section S16, Supporting Information for details). Depending on the choice of both the 2D perovskite and the TMD, we find that the power conversion efficiency varies in the range of 1%–15%. The highest calculated power conversion efficiency of ≈15% for BA2PbI4/MoS2 is higher than the efficiency values reported in single phase Ruddlesden–Popper 2D perovskites.[51]

In bare, freestanding 2D perovskite layers, external strain could result in the loss of organic species and greater reactivity toward moisture which can impair the hybrid 2D framework and cause structural damage as in the case of 3D perovskites.[29] Therefore, in our heterostructures, the TMD as a capping layer also functions as an impermeable protection against oxygen and moisture which has been shown to degrade the properties of strained 2D perovskites at a faster rate.[52] Hence, the 2D TMD in heterojunction with 2D perovskite can impart better stability to the latter for flexible device applications.

A commonly encountered experimental challenge while fabricating heterostructures with 3D perovskites like MAPbI3 is the possibility of multiple edge terminations at the interface—either Pb or MAI. DFT calculations have shown that in comparison to the PbI-terminated surfaces, the MAI terminations can have CBM and VBM up to 1 eV lower in energy, thereby resulting in experimental inconsistencies.[53] However, in case of 2D perovskites, the van der Waals interaction holding the adjacent layers and absence of dangling bonds could envisage better interfacial properties. Recently, vapor phase growth of 2D perovskite layers on TMDs has demonstrated a good promise for photodetection because of the strong interlayer coupling.[54] Chemical vapor deposition (CVD) based growth of TMDs has been successful in yielding large area films with excellent electrical and optoelectronic properties. Along with that, CVD and vapor phase deposition methods have been used for lateral and vertical TMD heterostructures. Therefore, other solution- and/or CVD-based processes at moderate temperatures need to be developed to enable the large area growth of 2D perovskite layers on TMD templates for photovoltaic applications.

3. Conclusions

To summarize, we have systematically explored the properties of the heterojunctions comprising 2D perovskite and TMDs for optoelectronic applications using first principles calculations. The presence of an interlayer bandgap at the interface of heterostructures of BA2PbBr4 with MoS2, MoSe2 and WS2 enables optical absorption at energies much lower than its intrinsic bandgap of ≈3 eV. The type-II band alignment in these heterostructures could lead to interlayer separation of photogenerated carriers with TMD as an efficient electron transport layer and help to overcome the large intralayer exciton binding energy. The heterostructure also shows a good tolerance toward externally applied tensile strain with low modulation of the bandgap with unidirectional strain, essential for flexible technologies. Additionally, the presence of a type-I bandgap at the BA2PbBr4/WSe2 heterojunction makes it ideal for light emission applications in the visible range. Further, the type-III alignment in BA2PbI4/ MoS2 structure could open up applications for 2D perovskites for tunneling devices. The capping of 2D perovskite with TMD monolayer can render enhanced air stability and device longevity. Understanding the carrier transport properties across the different heterostructures could shed more light on the device-level application of these heterostructures.

4. Experimental Section

In all the atomistic simulations implemented using Vienna Ab initio Simulation Package (VASP), the generalized gradient approximation of Perdew–Burke–Ernzerhof form was used to describe the exchange correlation[55,56] and projector augmented wave (PAW) pseudopotentials were used to account for the frozen core-valence electron interactions. To introduce van der Waals interaction between the two materials, the dispersion corrected DFT-D3 method was used.[57] For structural optimization, a plane wave cut-off of 400 eV and Γ-centered k-points grid of 5 × 5 × 1 were used. The self-consistent calculations used a higher energy cut-off of 500 eV and denser k-points grid of 9 × 9 × 1. The optimizations were performed until the energy convergence limit of 0.1 meV was reached and the Hellman–Feynman forces on the structures were less than 0.01 eV Å−1. Sufficient vacuum of at least 25 Å was incorporated in all supercells along the transverse direction to avoid spurious interactions between adjacent periodic images. As the bandgaps are typically underestimated by the GGA-PBE formalism, hybrid calculations using HSE06 scheme were also used for accurate prediction of bandgaps.[58] Maximal localized Wannier wavefunctions using Wannier90 were employed for HSE band structure calculations.[59] The electronic properties calculated using van der Waals corrected GGA-PBE and HSE06 methods provide a realistic range for the properties predicted in our study. VASPKit tool was used for post-processing of the calculated data.[60] VESTA was used to visualize the crystal structures.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

A.V., Y.Y., and N.V.M. designed the study. A.V. carried out the computations with help from Y.Y. and M.W. A.V., Y.Y., and N.V.M. wrote the manuscript with inputs from S.L. All authors have approved of the manuscript.
Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2D perovskite, density functional theory, heterostructures, optoelectronics, transition metal dichalcogenides

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