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# 2D halide perovskite-based van der Waals heterostructures: contact evaluation and performance modulation

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# Abstract

Halide perovskites and van der Waals (vdW) heterostructures are both of current interest owing to their novel properties and potential applications in nano-devices. Here, we show the great potential of 2D halide perovskite sheets ( $C_4H_9NH_3$ )<sub>2</sub>PbX<sub>4</sub> (X = Cl, Br and I) that were synthesized recently (Dou *et al* 2015 *Science* **349** 1518–21) as the channel materials contacting with graphene and other 2D metallic sheets to form van der Waals heterostructures for field effect transistor (FET). Based on state-of-the-art theoretical simulations, we show that the intrinsic properties of the 2D halide perovskites are preserved in the heterojunction, which is different from the conventional contact with metal surfaces. The 2D halide perovskites form a p-type Schottky barrier ( $\Phi_h$ ) contact with graphene, where tunneling barrier exists, and a negative band bending occurs at the lateral interface. We demonstrate that the Schottky barrier can be turned from p-type to n-type by doping graphene with nitrogen atoms, and a low- $\Phi_h$  or an Ohmic contact can be realized by doping graphene with boron atoms or replacing graphene with other high-workfunction 2D metallic sheets such as *ZT*-MoS<sub>2</sub>, *ZT*-MoSe<sub>2</sub> and *H*-NbS<sub>2</sub>. This study not only predicts a 2D halide perovskite-based FETs, but also enhances the understanding of tuning Schottky barrier height in device applications.

# 1. Introduction

Halide perovskites are attracting tremendous interest from the solar cell research community because of their great potential applications in photovoltaic industry [1–3]. Very recently, their 2D counterparts have been experimentally synthesized with an atomic ratio of A<sub>2</sub>BX<sub>4</sub>, (where A = organic molecule like C<sub>4</sub>H<sub>9</sub>NH<sub>3</sub>, B = group-14 element, and X = halides) [4], which exhibit excellent properties, such as the large carrier mobility [5–10], strong light absorption, and photoluminescence [4, 10, 11], making them very promising for device applications in solar cells and field effect transistors (FET).

The rise of 2D materials motivated the design of vertically stacking different 2D sheets together forming the so-called van der Waals (vdW) heterostructures [12]. Further, 2D materials can provide interesting possibility for band-structure engineering [12, 13]. For instance, if graphene is placed on the top of the hexagonal boron nitride, the formation of the second-

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ary Dirac points can be achieved [14-18]. In addition, 2D semiconductors and 2D metals can be combined together to create tunnel junctions [19–21]. Recently, the fabrication of FETs have been experimentally realized by stacking MoS<sub>2</sub> on top of graphene, which implies that graphene can act as the electrode-like metal in devices rather than the channel [22, 23]. The advantage of such vdW junction is that unlike metal surfaces, the absence of dangling bonds in 2D materials prevents the strong bonding at the junction interface, hence preserving the intrinsic properties of semiconductors. One example is the vdW heterostructure formed by phosphorene and graphene [21], where the electronic properties of phosphorene are completely preserved upon their assembly in the heterostructure, and without any degradation that appears in the contacts with 3D metals [24, 25]. Moreover, it has been demonstrated that the Fermi level pinning is very weak in vdW metal-semiconductor contacts [26], where the Schottky–Mott rule is followed for contacts using 2D metals with different work functions as the electrode,

which solves the problem of the untunable Schottky barrier height in device applications.

Experimentally, it turns out that the performance of the organic-inorganic perovskite devices is highly sensitive to their surfaces, which suggests that hybridization of halide perovskites and various 2D materials can be effective to obtain promising device applications with tunable properties [27]. Previous work has shown that the vdW heterojunction based on 3D organohalide perovskite and 2D materials exhibits excellent FET performances [27, 28], such as a high on/off ratio and an enhanced carrier mobility. However, the instability of the 3D organohalide perovskite materials in ambient conditions limits their long-term development in device fabrication [10, 28, 29]. The 2D halide perovskites offer an excellent alternative in this regard as they possess an enhanced stability [11, 29, 30] in addition to their attractive electronic and optical properties.

In this paper, we systematically study the structural and electronic properties of heterostructures formed from Rb<sub>2</sub>PbX<sub>4</sub> (X = Cl, Br, and I) and graphene, which combines the concepts of both vdW heterostructure and 2D halide perovskites together. Using well-chosen lattices for Rb<sub>2</sub>PbX<sub>4</sub> and graphene, we first construct a model for the heterostructure by minimizing the interfacial mismatch lattice strain. From device point of view, we then make a contact evaluation and show that it is possible to tune the position of Fermi level in the band structure of the composed system via doping graphene with different B or N concentrations or via replacing graphene with other high-work-function 2D metals. This allows the control of the Schottky barrier height, which is essential in fabricating FETs based on 2D halide perovskites.

## 2. Methods

#### 2.1. Interface modeling

To effectively build a heterostructure with minimal lattice strain between 2D halide perovskites and graphene, which have different symmetries, we implement the approach based on Zur and McGill's work [31] that can render reasonable models that are amenable to density functional theory (DFT) calculations. Figure S1 illustrates the Zur-McGill's algorithm for lattice match. The interface lattice is determined by three parameters, i.e. a, b, and  $\alpha$ , corresponding to the lengths of two vectors and the angle between them. However, not all the 2D sheets are like the primitive cells of graphene and 2D boron nitride, where the lattice mismatch between them is only 1.8%. Therefore, in most cases, we need to use a superlattice to match them together. If two different lattices are well matched, the three parameters in both of their superlattices would be close. However, it is very hard to directly search a pair of superlattices with similar  $a, b, and \alpha$ , because the symmetry of two primitive cell may be different, and the combination of two superlattices at the interface is not unique. In

our code, we look for the lattice match based on the interface area, because the area of two superlattices with close *a*, *b*, and  $\alpha$  would be also approximately the same for the two lattices. We follow Zur–McGill scheme [31] to find all superlattices for a given area, and we select those that match the most given a lattice mismatch threshold and possibly the maximum number of atoms in the heterostructure.

#### 2.2. DFT calculations

Our first-principles calculations within the framework of DFT are carried out using the Vienna ab initio simulation package (VASP) [32, 33] employing the projector augmented wave (PAW) pseudopotentials [33, 34] and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [35]. To correctly describe the effect of the vdW interactions, we employ a dispersion-corrected DFT method (optB88-vdW) [36, 37]. The plane-wave cutoff energy is 400 eV for all the calculations. Monkhorst-Pack sampling of sufficient k-points are used (details are summarized in the supplementary material (stacks.iop.org/ TDM/4/035009/mmedia)) [38]. The systems are fully relaxed until the final force on each atom is less than  $0.01\,eV\, {\rm \AA}^{-1}$  . To obtain a more accurate band gap of 2D halide perovskites, we use HSE06 functional in conjunction with spin-orbit coupling (SOC) to recalculate the band structure. Work functions are calculated by subtracting the corresponding electronic levels with respect to the vacuum level in the supercell.

### 3. Results and discussions

#### 3.1. Structure design

Figure 1(a) shows the optimized crystal structure of the 2D halide perovskites. We find that the PbX<sub>6</sub> octahedra are tilted along both the in-plane and out-of-plane directions. Here, we replace the long chain molecule  $(C_4H_9NH_3)$  with Rb atom to reduce the computational cost. It has been demonstrated that the replacement of the molecule with a large alkali metal atom does not affect the key characteristics of the 3D halide perovskites [39] even for the nature of their grain boundaries [40]. This is mainly because the band edge states are largely composed of the Pb and halide states without any contributions from the alkali metals. We have validated that this is also the case for the 2D halide perovskite  $Rb_2PbX_4$ . As seen in figures 1(b) and (c), the banddecomposed charge density of the highest valence band (HVB) and the lowest conduction band (LCB) clearly show that the Rb atoms do not appreciably contribute to these frontier bands.

Unlike graphene/hBN [13] and MoS<sub>2</sub>/WS<sub>2</sub> [41] heterostructures, which can be directly stacked together because of the small lattice mismatch between their primitive lattices, the symmetry and lattice constants of the 2D halide perovskites and graphene are different from each other (see table 1). Therefore, special care is needed in construction of a stable heterostructure



**Figure 1.** (a) Crystal structure of the 2D halide perovskites ( $Rb_2PbX_4$ , X = Cl, Br and I). Band decomposed charge density of (b) the HVB and (c) the LCB. Purple, grey, and green balls represent Rb, Pb, and halide atoms, respectively. Red dashed lines show the primitive cell of the 2D halide perovskites.

**Table 1.** Lattice match between the 2D halide perovskite ( $Rb_2PbX_4$ , X = Cl, Br, and I) and graphene. *a*, *b*, and  $\alpha$  are the primitive cell parameters of the isolated 2D sheets, while *u*, *v*, and  $\gamma$  represent the superlattice parameters of the heterostructure model.

Graphene	Superlattice of 2D perovskite			Superlattice of Graphene			Mismatch between two superlattices		
$a = b = 2.46 \text{ Å}, \alpha = 120^{\circ}$	u (Å)	$\nu$ (Å)	$\gamma$ (°)	u (Å)	$\nu$ (Å)	$\gamma$ (°)	u (%)	v (%)	$\gamma$ (%)
Rb <sub>2</sub> PbCl <sub>4</sub>	8.4	42.4	90.0	8.5	41.8	90.0	1.0	1.4	0.0
$a=7.07$ Å, $b=8.44$ Å, $\alpha=90^\circ$									
Rb <sub>2</sub> PbBr <sub>4</sub>	8.8	37.9	89.5	8.9	37.2	90.0	0.9	1.6	0.6
$a=7.57$ Å, $b=8.77$ Å, $\alpha=90^\circ$									
Rb <sub>2</sub> PbI <sub>4</sub>	16.5	27.9	90.0	16.1	27.9	90.0	2.0	0.1	0.0
$a = 8.23 \text{ Å}, b = 9.30 \text{ Å}, \alpha = 90^{\circ}$									



Figure 2. Binding energy as a function of the interlayer distance between the 2D halide perovskite  $Rb_2PbX_4$  (X = Cl, Br, and I) and graphene. The inset images show the side views of the equilibrium heterostructures.

model with small lattice misfit strain. Using our inhouse code that implements the Zur–McGill scheme, we set the mismatch in u, v, and  $\gamma$  of the two superlattices all to be less than 2% to insure that the lattice strain is negligible. We also set the total number of atoms in the heterostructure to be less than 300 because DFT calculations are not computationally tractable for large systems. All the possible models that meet these requirements are presented in table S1, illustrating that there are more than one possible 2D halide perovskite/ graphene heterostructures. We choose the smallest supercell in our calculations to reduce the computational cost, as listed in table 1.

According to the lattice match of the two sheets, we choose to keep the graphene supercell fixed, while slightly stretching or compressing the 2D halide perovskites in the heterostructure (The supplementary materials provide more details on the choice of fixing graphene in the heterostructure.). Figure 2 shows the fully optimized heterostructures of Rb<sub>2</sub>PbX<sub>4</sub>/ graphene. No significant changes are observed in the geometries of both layers after optimizations, implying that their lattice strains are indeed negligible in the heterojunction models. We then characterize the bond strength of the interlayer using the binding energy defined by  $E_{\rm b} = (E_{\rm h} - E_{\rm G} - E_{\rm P})/n$ , where  $E_{\rm h}$  is the total energy of the Rb<sub>2</sub>PbX<sub>4</sub>/graphene heterostructure, E<sub>G</sub> and  $E_{\rm P}$  are the total energies of the freestanding graphene and the perovskite sheet respectively, and n represents the number of carbon atoms in the graphene layer. Figure 2 shows the binding energy as a function of the interlayer distance between the 2D perovskite and graphene. We find that the equilibrium interlayer distance for Rb<sub>2</sub>PbX<sub>4</sub>/graphene is in the range of 3.35 Å–



**Figure 3.** Band structure of Rb<sub>2</sub>PbI<sub>4</sub>/graphene heterojunction projected at (a) the Rb<sub>2</sub>PbI<sub>4</sub> layer and (b) the graphene layer. (c) Average electrostatic potential in the plane normal to the interface of Rb<sub>2</sub>PbI<sub>4</sub>/graphene heterojunction. (d) Schematic plot of a CIP device where the Rb<sub>2</sub>PbI<sub>4</sub>/graphene heterostructure is connected to a freestanding Rb<sub>2</sub>PbI<sub>4</sub> channel. *W*<sub>H</sub> and *W*<sub>P</sub> are the work functions of the Rb<sub>2</sub>PbI<sub>4</sub>/graphene heterostructure and the single-layer Rb<sub>2</sub>PbI<sub>4</sub>, respectively. Purple cross stands for the Dirac point of graphene. *E*<sub>vac</sub> represents the vacuum level, with respect to which all the values in the figure are aligned. Note that the Fermi level and the VBM of pristine Rb<sub>2</sub>PbI<sub>4</sub> are at the same position.

3.46 Å (see figure 2). The binding energy is 40, 36, and 34 meV per carbon atom for Cl, Br and I heterostructures, respectively. The downtrend in  $E_b$  is attributed to variation of the electronegativity of halogen atoms, where Cl has the largest electronegativity, leading to a larger binding energy. Compared with other vdW crystals [42], such as graphite (d = 3.33 Å,  $E_b = 52$  meV), hexagonal boron nitride (d = 3.33 Å,  $E_{\rm b} = 65$  meV), and phosphorene on graphene (d = 3.45 Å,  $E_b = 60$ meV), both the interlayer distance and binding energy are of the same order of magnitude with these systems, indicating that the 2D halide perovskites/graphene can indeed be classified as a vdW heterostructure. Note that the binding energy in the Rb<sub>2</sub>PbX<sub>4</sub>/graphene heterojunction is slightly smaller than that of other typical vdW crystals. We argue that this is because the 2D halide perovskite has three atomic layers, and the bottom layer that is directly in contact with graphene is not as dense as the middle one, overall leading to a weaker vdW interaction with graphene as vdW interactions are additive.

#### 3.2. Contact evaluation

We first study the electronic properties of the Rb<sub>2</sub>PbX<sub>4</sub>/graphene heterojunction. Here, we take Rb<sub>2</sub>PbI<sub>4</sub>/graphene as an example. Figures 3(a) and (b)

show the calculated projected band structure of the Rb<sub>2</sub>PbI<sub>4</sub>/graphene heterojunction at the GGA/PBE level, which clearly demonstrate that the electronic structures of both the 2D halide perovskite and graphene are well preserved after stacking together. This further confirms that the Rb<sub>2</sub>PbX<sub>4</sub>/graphene heterojunction possesses the a key of a vdW crystal, namely, keeping the intrinsic properties of the isolated parts intact. It is well known that the PBE functional usually leads to an underestimated band gap. However, several studies have pointed out that the PBE functional is able to reproduce the band gap close to the experimental value because of the fortuitous error cancellation [10, 39, 43, 44]. We recalculated the band structure of Rb<sub>2</sub>PbI<sub>4</sub> by using the HSE06 hybrid functional with spin-orbit coupling (SOC), which was demonstrated to give more accurate band gaps in halide perovskite systems [44]. We find that the band gap calculated using PBE and HSE + SOC has the same value of 2.21 eV (see figure S2 for details), which is in good agreement with previous calculations [10, 43], implying that the PBE functional is acceptable in predicting electronic properties. Given the favorable computational cost of PBE compared to HSE, we use PBE to carry out the remaining electronic structure calculations in our study.

**Table 2.** Contact evaluation of the Rb<sub>2</sub>PbX<sub>4</sub>/graphene (X = Cl, Br, and I) heterostructure.  $\Delta V$ ,  $w_B$ , and  $T_B$  are the tunneling barrier height, tunneling barrier width, and tunneling probability, respectively.  $\Delta E_F$  represents the value of band bending.  $\Phi_e$  and  $\Phi_h$ are the n-type and p-type Schottky barrier height, respectively.

	Rb <sub>2</sub> PbCl <sub>4</sub> / graphene	Rb <sub>2</sub> PbBr <sub>4</sub> / graphene	Rb <sub>2</sub> PbI <sub>4</sub> / graphene
$\Delta V(\text{eV})$	0.60	0.72	0.81
$w_{\rm B}$ (Å)	1.03	1.15	1.17
$T_{\rm B}~(\%)$	43.84	36.48	33.68
$\Delta E_{\rm F} ({\rm eV})$	0.56	0.63	0.43
$\Phi_{\rm e}  ({\rm eV})$	2.16	1.82	1.70
$\Phi_{\rm h}\left({\rm eV}\right)$	0.80	0.72	0.51

There are three major criteria to evaluate the carrier injection efficiency in semiconductor-metal contact, including tunneling barrier, band bending, and Schottky barrier. Tunneling barrier is characterized by its width ( $w_B$ ) and height ( $\Delta V$ ), which is formed when electrons cross the vdW gap between two contact layers, and measured by the electrostatic potentials. The calculated average electrostatic potential of the Rb<sub>2</sub>PbI<sub>4</sub>/ graphene heterojunction is given in figure 3(c). One can see that there is a  $\Delta V = 0.81$  eV tunneling barrier at the Rb<sub>2</sub>PbI<sub>4</sub>/graphene interface. We estimate the tunneling probability  $T_B$  using the WKB formula [25, 45] employing square potential approximation with equivalent depth to  $\Delta V$  (indicated by rectangle box in figure 3(c)),

$$T_{\rm B} = \exp\left(-2\frac{\sqrt{2m\Delta V}}{\hbar} \times w_{\rm B}\right),$$

where m and  $\hbar$  are the free electron mass and Planck's constant, respectively. The tunneling probability  $T_{\rm B}$  of the Rb<sub>2</sub>PbX<sub>4</sub>/graphene (X = Cl, Br, and I) heterostructures are listed in table 2 along with  $\Delta V$  and  $w_{\rm B}$ . We note that  $\Delta V$  is in the range of 0.60 eV-0.81 eV, which is comparable to that of Au-based contacts, like phosphorene/Au [25] and transition metal dichalchogenides (TMD)/Au [46]. Generally, a small physical separation at the interface may lead to a small  $\Delta V$  [46]. However, the interlayer distance is usually larger than 3 Å in vdW crystals. In addition, the metallization of semiconductors from the strong bonding with 3D metal surfaces can decrease  $\Delta V$ [25, 47], which is absent in the present systems. From these two factors, it is easy to understand why  $\Delta V$  is slightly larger in the Rb<sub>2</sub>PbX<sub>4</sub>/graphene (X = Cl, Br, and I) heterostructures, as compared to that in phosphorene/3D metal contacts [25]. The corresponding tunneling probability is calculated to be 43.84%, 36.48% and 33.68% for the Rb<sub>2</sub>PbX<sub>4</sub>/graphene heterostructure with X = Cl, Br, and I, respectively. From the results given in table 2, we can conclude that the smaller tunneling barrier height and width lead to a larger tunneling probability. The existence of tunneling barrier in  $Rb_2PbX_4$ /graphene (X = Cl, Br, and I) heterojunction makes it a type-1 contact, as is the case of Au- and In-TMD contacts [46].

Even without appreciable charge transfer between the 2D halide perovskite and graphene, if we consider a current-in-plane (CIP) structure, an important issue is the band bending because charge carriers move from the stacked junction to the freestanding layers. A schematic diagram of a CIP model is given in figure 3(d). The CIP system is composed of three parts with the left part of the Rb<sub>2</sub>PbI<sub>4</sub>/graphene heterostructure, the right part of the single-layer Rb<sub>2</sub>PbI<sub>4</sub> sheet, and the interface in the middle. We estimate the band bending by calculating the Fermi level difference of the heterostructure and freestanding Rb<sub>2</sub>PbI<sub>4</sub>, which is defined by:  $\Delta E_{\rm F} = W_{\rm H} - W_{\rm P}$ , where  $W_{\rm H}$  and  $W_{\rm P}$  are the work functions of the stacked system and the pristine Rb<sub>2</sub>PbI<sub>4</sub> perovskite, respectively. From the calculated values 4.74 and 5.17 eV for W<sub>H</sub> and W<sub>P</sub> we obtain a value of -0.43 eV for the band bending ( $\Delta E_{\rm F}$ ). Because  $\Delta E_{\rm F} < 0$ , the electrons move from the Rb<sub>2</sub>PbI<sub>4</sub>/graphene heterostructure to the single-layer halide perovskite, leading to an n-type channel. For the Rb<sub>2</sub>PbCl<sub>4</sub> and Rb<sub>2</sub>PbBr<sub>4</sub> contacts, the calculated values of band bending are also negative (see table 2), hence these contacts tend to generate n-type CIP devices without further doping. From the CIP device point of view, the smaller is the band bending, the better is the contact. The calculated values of band bending  $(\Delta E_{\rm F})$  in such 2D halide perovskite/graphene heterojunction is comparable to or even smaller than that of some metal/phosphorene (TMDs) contacts [24, 46], which shows the potential of the Rb<sub>2</sub>PbX<sub>4</sub>/graphene heterostructures for nanoscale electronic devices.

Next we discuss the Schottky barrier in the  $Rb_2PbX_4/$ graphene (X = Cl, Br, and I) heterojunction, which is the most important parameter that determines the contact resistance in a FET device. Schottky barrier height (SBH) is defined as the energy difference between the Fermi level and the band edge of the semiconductor in a heterostructure:

$$\Phi_{\rm e} = E_{\rm CBM} - E_{\rm F}, \ \Phi_{\rm h} = E_{\rm F} - E_{\rm VBM}$$

where  $\Phi_e$  and  $\Phi_h$  are the SBHs for electrons and holes,  $E_{\rm F}$  represents the Fermi level, while  $E_{\rm CBM}$  and  $E_{\rm VBM}$ denote the energy of the conduction band minimum (CBM) and the valence band maximum (VBM) of the semiconductor in the heterostructure, respectively, which are identified from atom projected density of states (see figures 3(a) and (b)). From figures 3(a) and (d), we obtain a SBH of 0.51 eV for holes and 1.70 eV for electrons in the Rb<sub>2</sub>PbI<sub>4</sub>/graphene heterostructure. The Fermi level is closer to the edge of the valence band of Rb<sub>2</sub>PbI<sub>4</sub>, indicating a p-type Schottky barrier with holes as the major transport carriers. Both Rb<sub>2</sub>PbCl<sub>4</sub> and Rb<sub>2</sub>PbBr<sub>4</sub> contacts also show p-type Schottky barriers, but with larger SBHs as compared to Rb<sub>2</sub>PbI<sub>4</sub> (see table 2). As mentioned before, the band edges are mainly contributed by Pb and halide atoms in these systems, thus the chemical trend of SBH from Cl to I can be understood by the fact that the higher 5p orbital of I<sup>-</sup> anion with more electrons can promote the



**Figure 4.** Variation of Schottky barrier height of  $Rb_2PbI_4$  on the top of (a) B atoms doped graphene, (b) N atoms doped graphene, and (c) different 2D metallic TMDs with various work functions. In (a) and (b), the top ticks denote the doping concentration. For example, 1/20 means that the atomic ratio of B or N to C is 1 to 20. The straight lines are linear fits to assess the applicability of Schottky–Mott rule. If the slope is close to 1, the effect of Fermi level pinning is weaker.

energy level of the VBM as compared to the 3p (4p) orbital of Cl<sup>-</sup> (Br<sup>-</sup>) anion [10, 44]. If we neglect the interaction between the metal and semiconductor, the SBH can be defined as the energy difference between band edge and metal work function ( $\Phi_e = W - E_{ea}$ ,  $\Phi_h = E_{ip} - W$ ) [20]. Since Rb<sub>2</sub>PbI<sub>4</sub> has the highest level of VBM, the band offset is consequently smaller in the Rb<sub>2</sub>PbI<sub>4</sub>/graphene heterojunction.

#### 3.3. Performance modulation

For device applications, it is better to get a smaller Schottky barrier height or even induce an Ohmic contact to reduce the contact resistance. It has been demonstrated that Schottky barriers can be tuned by applying a perpendicular external electric field [21, 48, 49]. Here, we propose two different approaches to tune the position of the Fermi level in the band structures of the 2D halide perovskites via doping graphene or replacing the electrode. We choose Rb<sub>2</sub>PbI<sub>4</sub>/graphene heterojunction for these explorations because it has the smallest SBH (see table 2).

According to the Schottky–Mott rule ( $\Phi_e = W - E_{ea}, \Phi_h = E_{ip} - W$ ), SBH is related to the metal work function. We first show that boron (B) or nitrogen (N) doping of graphene can be used to tune the SBH. The Fermi level is the total chemical potential for electrons at zero K. If we ignore band structure rearrangements, then the Fermi level can be modified by changing the total number of electrons in the system. Thus, by increasing or decreasing electrons in graphene, the work function will be changed accordingly due to changes in the Fermi energy. Boron and nitrogen are respectively located to the left and right of carbon in the periodic table, thus if a C atom is replaced by B (or N) atom, the system will lose (or gain) an electron.

First, we dope graphene with B atoms with various doping concentrations. In the Rb<sub>2</sub>PbI<sub>4</sub>/graphene contact, the supercell of graphene contains 172 carbon atoms. We respectively substitute C atoms with 2, 4, 8, and 16 B atoms (structures can be seen in figure S3). We optimize the geometries of the heterostructures and calculate the Fermi level  $(E_{\rm F})$  of these doped graphene layers. We note that the Fermi level decreases with the increasing doping concentration, implying that boron doping can effectively change the work functions. We then use the B-doped graphene layer as the electrode, and calculate the SBHs of these systems, as plotted in figure 4(a), which shows that boron doping significantly reduces the  $\Phi_h$ , and leads to a very small SBH of  $0.06 \,\mathrm{eV}$  when the doping concentration reaches 1/10. The Schottky-Mott rule also suggests that the linear dependence between SBH and metal work function has a slope of  $\pm 1$  [26]. We linearly fit these points in figure 4(a), obtaining a slope of -0.43, which implies that Fermi level pinning exists in these heterojunctions. According to the trends that appears in figure 4(a), we predict that a Schottky-barrier-free junction can be even achieved, making it an Ohmic contact at ~1/8 B-doping concentration.

We then use nitrogen atoms to substitute the carbon atoms by following the same procedure as described before. Because N has one more electron than C, N doping up shifts the Fermi level, thus leading to a smaller work function. The calculated work functions and SBHs for the Rb<sub>2</sub>PbI<sub>4</sub>/N-doped graphene heterojunctions with the different N-doping concentrations are given in figure 4(b). We note that  $\Phi_h$  increases from 0.51 eV to 1.10 eV, while  $\Phi_e$  decreases from 1.70 eV to 1.11 eV at the N-doping concentration of 1/85 (see figure 4(b)). If the doping concentration is further increased, the Schottky barrier transforms from p-type to n-type, because the Fermi level is closer to the CBM of Rb<sub>2</sub>PbI<sub>4</sub>. Based on our results, when the N-doping concentration is larger than 1/85, an n-type contact is formed, at which electrons move from the N-doped graphene layer to the Rb<sub>2</sub>PbI<sub>4</sub> layer. The Fermi level pinning is very weak in the N-doped heterostructures as the slope of the linear fitting is  $\pm 1.04$ , suggesting it is

an effective way to tune the Schottky barrier height by doping N atoms into graphene.

Next, we investigated another approach to tune the SBH by replacing graphene with some other experimentally synthesized metallic transition metal dichalchogenide (TMD) sheets, like ZT-MoSe<sub>2</sub>, ZT-MoS<sub>2</sub>, and H-NbS<sub>2</sub>. The motivation is that graphene has a relatively smaller work function than these 2D materials [26], hence electrode replacement may result in a low- $\Phi_{\rm h}$  contact. Figure 4(c) shows the variation of p-type SBH ( $\Phi_h$ ) of the 2D Rb<sub>2</sub>PbI<sub>4</sub> sheet on top of these 2D metals. As expected, we find that the Fermi level of the composed system shifts down becoming closer to the VBM of Rb<sub>2</sub>PbI<sub>4</sub>, thus leading to a smaller  $\Phi_h$ . For instance, if we use ZT-MoS<sub>2</sub> as the electrode, the  $\Phi_h$  is reduced to only 0.09 eV, consequently a lower contact resistance can be achieved. Interestingly, it is worth noting that the Fermi level is below the VBM of Rb<sub>2</sub>PbI<sub>4</sub> due to the very large work function of H-NbS<sub>2</sub> [26], turning this contact into an Ohmic one, which facilitates a spontaneous hole injection from metal to semiconductor. The slope of the linear fitting is smaller than that of in figure 4(a), indicating a stronger Fermi level pinning in these systems. We argue that the Fermi level pinning is due to the interface dipole induced by the charge density redistribution [26], which will shift the electronic energy levels. In figure S4, we plot the averaged charge density difference ( $\Delta \rho = \rho$ (heterojunction) –  $\rho(\text{metal}) - \rho(\text{semiconductor}))$  of the Rb<sub>2</sub>PbI<sub>4</sub>/ graphene heterojunction. As clearly seen, the charge redistribution is not symmetric between two layers, leading to the formation of the interface dipole.

# 4. Conclusions

In summary, we have studied the heterojunctions composed of 2D halide perovskites and graphene, and other 2D metallic sheets including ZT-MoSe<sub>2</sub>, ZT-MoS<sub>2</sub> and H-NbS<sub>2</sub>. To minimize supercell size and lattice mismatch, we apply the Zur-McGill scheme to obtain heterostructures with a lattice mismatch less than 2%. Our DFT calculations show that: (1) the intrinsic properties of 2D halide perovskites are totally conserved in the heterostructures because of the weak van der Waals interaction at the interface, which is different from the metallization in conventional contact with 3D metal surfaces; (2) tunneling barriers exist in  $Rb_2PbX_4$ /graphene (X = Cl, Br, and I) heterojunctions due to the large van der Waals gap, making them type-1 contacts; (3) a negative value of band bending appears at the lateral interface of the CIP system, implying that the electrons move from graphene to the halide perovskite layer; (4) a p-type Schottky barrier ( $\Phi_h$ ) is formed between  $Rb_2PbX_4$  (X = Cl, Br, and I) and graphene, and a low- $\Phi_h$  contact can be achieved by doping graphene with B atoms or replacing graphene with other highwork-function metallic TMD sheets. Interestingly, a spontaneous hole injection can be realized by using

*H*-NbS<sub>2</sub> as the electrode; (5) the Schottky barrier can change from p-type to n-type via N-doping graphene. Our work on perovskite-based heterojunctions not only provides an efficient method for structure design of van der Waals heterostructures, but also broadens the applications of 2D halide perovskites.

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# Author contributions

QW conceived the initial idea of this research; YG performed the calculations; all authors analyzed the data and wrote the paper.

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