Contents lists available at ScienceDirect

# **Computational Materials Science**

journal homepage: www.elsevier.com/locate/commatsci

Full Length Article

# Electrostatic gating tuned electronic, interfacial, and optical properties of an all-carbon penta-graphene/biphenylene network vdW heterostructure

Muhammad Azhar Nazir<sup>a</sup>, Yiheng Shen<sup>b</sup>, Changsheng Hou<sup>a</sup>, Chenxin Zhang<sup>a</sup>, Qian Wang<sup>a,\*</sup>, Akira Yoshikawa<sup>c</sup>, Yoshiyuki Kawazoe<sup>d,e,f</sup>

<sup>a</sup> School of Materials Science and Engineering, CAPT, Peking University, Beijing 100871, China

<sup>b</sup> Materials Genome Institute, Shanghai University, Shanghai 200444, China

<sup>c</sup> Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan

<sup>d</sup> New Industry Creation Hatchery Center, Tohoku University, Sendai, 980-8577, Japan

e Department of Physics and Nanotechnology, SRM Institute of Science and Technology, Kattankulathur, Tamil Nadu 603203, India

<sup>f</sup> Department of Physics, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

ARTICLE INFO

Keywords: All-carbon vdW heterostructure First-principles calculation Schottky barrier height Band alignment Field-effect transistor

#### ABSTRACT

The high carrier mobility of semiconducting penta-graphene (PG) discloses the possibility of realizing its van der Waals (vdW) heterostructures with improved channel performance for optoelectronic applications. Here, we rationally design an all-carbon two-dimensional vdW heterostructure by vertically stacking the semiconducting PG and the synthesized metallic biphenylene network (BPN) sheets that respectively serve as channel and electrode materials at the heterojunction interface. Based on first-principles calculations, we show that the PG/ BPN heterostructure possesses an *n*-type Schottky contact at the vertical interface with a calculated Schottky barrier height of 0.19 eV, which reduces to 0.04 eV when a vertical negative electric field of 0.6 V/Å is applied, suggesting low resistance electronic transport across the heterojunction. More interestingly, we find that the *n*-type Schottky interface can be transformed to a *p*-type contact by applying a vertical positive electric field of 0.6 V/Å, offering hole transport across the heterojunction. In addition, the PG/BPN heterostructure exhibits strong optical absorption and conductivity, ranging from infrared to ultraviolet regions, with the potential for field-effect transistors and optoelectronic devices.

#### 1. Introduction

With the shrinking size of electronic devices gradually approaching sub-nano levels, it becomes challenging for silicon-based devices to maintain Moore's law lifeline. Thus, replacing silicon with more suitable components is one of the leading motivations in device research [1,2]. To this regard, two-dimensional (2D) carbon materials can offer a helping hand as silicon substitutes in ultrathin devices because of their natural advantages, i.e., the bonding flexibility and structural stability [3]. Particularly, new optoelectronic device architectures can be realized by assembling all-carbon 2D van der Waals (vdW) heterostructures with atomically clean interfaces and unique device functionalities [4–6]. In such heterostructures, the absence of direct chemical bonds on the surface allows the formation of an artificial dangling-bond-free interface between the contacted carbon sheets, which are bounded by weak vdW forces. Notably, such an interface offers much freedom to integrate a wide range of carbon sheets into all-carbon vdW heterostructures beyond the limitations of crystal lattice matching.

In this device paradigm, penta-graphene (PG) [7] is of intensive interest due to its unique pentagonal configuration, semiconducting characteristic, auxeticity, and ultrahigh carrier mobility [8], offering a perfect structural model for the design and synthesis of other pentagonbased materials [9,10]. These intriguing properties endow PG with the potential to form heterojunctions with other 2D materials, as shown in our previous studies on the heterostructures constructed by vertical stacking PG with graphene [11], penta-BN<sub>2</sub> [12], and some transition metal surfaces [13]. Such PG-based heterojunctions exhibit enhanced auxeticity [14], robust superlubricity [15], high performance for metalion batteries [16,17], and the potential for photocatalytic watersplitting [18,19], showing the upwelling research enthusiasm in designing PG-based devices.

On the other hand, the recently synthesized ultra-flat metallic carbon

\* Corresponding author. E-mail address: qianwang2@pku.edu.cn (Q. Wang).

https://doi.org/10.1016/j.commatsci.2024.113228

Received 13 March 2024; Received in revised form 28 June 2024; Accepted 7 July 2024 Available online 12 July 2024 0927-0256/© 2024 Elsevier B V. All rights are reserved including those for text and data mining. AI trai

0927-0256/© 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.





sheet, namely, the biphenylene network (BPN) [20], has gained significant research attention due to its excellent performance in electrochemical oxygen reduction [21], magnetic and topological ordering [22], anisotropic charge transport [23], and negative thermal expansion [24]. Moreover, the metallic nature favors its potential application in metal-semiconductor heterostructure devices. This has motivated us to integrate it as a metal electrode in this study. Based on first-principles calculations, we study the electronic, interfacial, and optical properties of an all-carbon 2D vdW heterostructure composed of the semiconducting PG sheet and the metallic BPN monolayer, and evaluate its potential for field-effect transistor (FET) and optoelectronic devices.

### 2. Computational details

Our calculations are performed by using the Vienna ab initio Simulation Package (VASP) [25,26] within the framework of density functional theory (DFT) [27]. The generalized gradient approximation (GGA)-based Perdue-Burke-Ernzerhof (PBE) [28] functional is used to treat the exchange-correlation interactions of electrons for geometry relaxation, while the hybrid Hevd-Scuseria-Ernzerhof (HSE06) functional [29] is used to calculate the accurate electronic band structure. Here, it is worth mentioning that the PBE-optimized geometries may not be at the exact minima for the range-separated hybrid HSE06 functional, but the small structural differences for these two levels are generally compromised for large systems, where maintaining a good balance between computational efficiency, calculation accuracy, and costs are required [30,31]. The projector-augmented-wave (PAW) method [32] is used to describe the interactions between valence electrons and ion cores. The valence electronic configuration of  $2s^2 2p^2$  is taken for carbon, and the kinetic energy cut-off of 520 eV is used to expand the wave functions. In addition, the DFT-D3 correction [33] is considered for all the calculations to describe the vdW interactions in the PG/BPN heterostructure. A vacuum space of 25 Å along the z-axis is used to avoid interactions between the duplicate periodic images. The first Brillouin zone is sampled with a fine grid of  $14 \times 4 \times 1$  *k*-point mesh within the Monkhorst-pack scheme [34]. The atomic positions are fully relaxed with an energy and force convergence threshold of  $10^{-5}$  eV and  $10^{-2}$ eV/Å, respectively.

The thermal stability of PG/BPN heterostructure is examined by carrying out ab initio molecular dynamics (AIMD) simulations within the canonical ensemble, where the Nosé-Hoover thermostat controls the temperature fluctuation [35]. In addition, the optical properties are obtained from the frequency-dependent complex dielectric function  $\varepsilon_{ij}^{bulk}(\omega) = \operatorname{Re} [\varepsilon_{ij}^{bulk}(\omega)] + \operatorname{Im} [i\varepsilon_{ij}^{bulk}(\omega)]$ , here  $\operatorname{Re} [\varepsilon_{ij}^{bulk}(\omega)]$  and  $\operatorname{Im} [i\varepsilon_{ij}^{bulk}(\omega)]$  are the real and imaginary parts of the complex dielectric function, respectively. Im  $[i\varepsilon_{ij}^{bulk}(\omega)]$  is directly related to the electronic structure and can be evaluated by the momentum matrix relations between the occupied (unoccupied) wave functions of valence (conduction) bands using the following Eq. [36]:

$$\operatorname{Im}[i\epsilon_{ij}^{\operatorname{bulk}}(\omega)] = \frac{2e^{2}\pi}{\Omega\varepsilon_{0}} \sum_{\overrightarrow{k},\nu,c} \left| < \psi_{k}^{c} | \overrightarrow{u} \times \overrightarrow{r} | \psi_{k}^{\nu} > \right|^{2} \delta(E_{k}^{c} - E_{k}^{\nu} - E)$$
(1)

here  $\Omega$ ,  $\vec{k}$ ,  $\vec{u}$  and  $\vec{r}$  represent the volume of the supercell, wave vector, polarization direction vector of the incident electric field, and position vector. Simply, Re  $[\epsilon_{ij}^{\text{bulk}}(\omega)]$  can be evaluated from Im  $[i\epsilon_{ij}^{\text{bulk}}(\omega)]$  using the following Kramers-Kronig dispersion relation:

$$\operatorname{Re}[\varepsilon_{ij}^{\operatorname{bulk}}(\omega)] = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega'^2 \operatorname{Im}[i\varepsilon_{ij}^{\operatorname{bulk}}(\omega)]}{\omega'^2 - \omega^2} d\omega'$$
(2)

here P denotes the principal value.

Here, it is worth mentioning that  ${\rm Re}\,[\varepsilon^{\rm bulk}_{ij}(\omega)]$  and  ${\rm Im}\,[i\varepsilon^{\rm bulk}_{ij}(\omega)]$  are renormalized for 2D materials due to the thickness-dependent  $\varOmega$  in Eq.

(1), and can be written as [36,37]:

$$\operatorname{Re}[\varepsilon_{ij}^{\text{2D}}(\omega)] = 1 + \frac{L_z}{L_z^{\text{eff}}} \{\operatorname{Re}[\varepsilon_{ij}^{\text{bulk}}(\omega)] - 1\}$$
(3)

$$\operatorname{Im}[i\varepsilon_{ij}^{\text{2D}}(\omega)] = \frac{L_z}{L_z^{\text{eff}}} \operatorname{Im}[i\varepsilon_{ij}^{\text{bulk}}(\omega)]$$
(4)

here,  $L_z$  is the length of the supercell along the z-direction and  $L_z^{\rm eff}$  indicates the effective length defined as a sum of the vdW thickness and thickness of 2D material. Based on these Eqs., the absorption coefficient  $\alpha^{\rm 2D}(\omega)$  and the real part of optical conductivity Re  $[\sigma^{\rm 2D}(\omega)]$  are calculated as [37–39]:

$$\alpha^{\text{2D}}(\omega) = \sqrt{2}\omega \left[ \sqrt{\operatorname{Re}\left[\varepsilon_{ij}^{\text{2D}}(\omega)\right]^{2} + \operatorname{Im}\left[i\varepsilon_{ij}^{\text{2D}}(\omega)\right]^{2}} - \operatorname{Re}\left[\varepsilon_{ij}^{\text{2D}}(\omega)\right] \right]^{\frac{1}{2}}$$
(5)

$$\operatorname{Re}\left[\sigma^{\mathrm{2D}}(\omega)\right] = \frac{\omega}{4\pi} \operatorname{Im}\left[i\varepsilon_{ij}^{\mathrm{2D}}(\omega)\right]$$
(6)

## 3. Results and discussion

# 3.1. Structure and electronic properties of the free-standing monolayers

Before constructing a PG/BPN heterostructure, we evaluate the structural and electronic properties of the free-standing PG and BPN monolayers. The monolayer PG possesses a tetragonal P- $42_1m$  symmetry (space group no.113) with the optimized lattice constants of a = b = 3.64 Å. This structure is purely composed of pentagonal carbon rings and possesses a buckled configuration with the  $sp^3$ - and  $sp^2$ -hybridized atoms, respectively, shown by yellow and grey spheres in Fig. 1(a). Unlike PG, the monolayer BPN is composed of tetragonal, hexagonal, and octagonal carbon rings formed by purely  $sp^2$ -hybridized carbon atoms within an ultra-flat lattice (see Fig. 1b). This sheet possesses an orthorhombic *Pmma* symmetry (space group no. 47), with the optimized constants of a = 3.76 Å and b = 4.52 Å. The lattice constants of both monolayers are consistent with those in previous reports [7,40], and their dynamical, thermal, and mechanical stabilities have been well-confirmed under different conditions [7,20].

As plotted in Fig. 1(c, d), the calculated electronic band structures show that PG is a quasi-direct band gap semiconductor with a band gap of 3.26 eV at the HSE06 level, while the monolayer BPN is metallic as its partially filled energy bands across the Fermi level. Furthermore, the calculated total and partial density of states (DOS) reveal that the valence band maximum (VBM) and conduction band minimum (CBM) of the PG are mainly contributed from the  $sp^2$ -hybridized carbon atoms, whereas the *p*-orbital electrons dominantly contribute to the metallicity in the BPN sheet. The strong semiconducting and metallic natures of these monolayers allow us to integrate them into a metal–semiconductor heterostructure for promising device functionalities.

#### 3.2. Heterostructure design and stability

After confirming the electronic structure of both monolayers, we focus on rationally designing their heterostructure by controlling the lattice mismatch, and study its stability. To construct the PG/BPN heterostructure, we used *CellMatch* code [41], which is widely opted to design low-strained vdW heterostructures without any restriction to the lattice constants and symmetries of 2D sheets. Notably, in this method, one sheet is vertically placed over the other, and the most favorable stack (with a relatively low mismatch of < 2 % and a small number of atoms) is obtained by rotating one sheet along the *c*-axis with an angle ranging from 0° to 90°. Previous studies have shown that heterostructures with various rotation angles between the adjacent monolayers can be experimentally synthesized [42,43].

For the PG/BPN heterostructure, we find the best stack with a 5  $\times$  1



Fig. 1. (a, b) Top and side views of the free-standing PG and BPN monolayers. (c, d) Electronic band structures, and corresponding total and partial DOS of the PG and BPN monolayers.

supercell for PG and a 4  $\times$  1 supercell for BPN monolayer at 90° with a lattice mismatch of 1.1 %, as shown in Fig. 2(a). The optimized structure belongs to the monoclinic system of *P*2 (space group no. 3) with an interlayer distance (*d*) of 3.40 Å between the stacked PG and BPN monolayers. To examine the interface stability of this heterostructure,

we calculate the binding energy  $E_b$  using  $E_b = -[(E_H - E_{PG} - E_{BPN})/A]$ , here  $E_H$  is the total energy of the PG/BPN heterostructure,  $E_{PG}$  and  $E_{BPN}$ are the energies of the non-contacted PG and BPN monolayers, and A is the total supercell area of the heterostructure. The calculated binding energy ( $E_b = 0.04 \text{ eV/Å}^2$ ) and interlayer distance (d = 3.40 Å) are very



Fig. 2. (a) Top and side views (b) total potential energy fluctuations of the PG/BPN heterostructure at 500 K. The inset is the geometry of the PG/BPN supercell at the end of the simulation at 500 K.

close to that of vdW crystals such as graphite ( $E_b = 0.02 \text{ eV/Å}^2$  and d = 3.60 Å) [44], hexagonal BN ( $E_b = 0.04 \text{ eV/Å}^2$  and d = 3.30 Å) [45], and some recently reported pentagon-based vdW stacks such as PG/graphene ( $E_b = 0.06 \text{ eV/Å}^2$  and d = 3.14 Å) [11], PdSe<sub>2</sub>/BPN ( $E_b = 0.06 \text{ eV/}$ Å<sup>2</sup> and d = 3.40 Å) [46], and NiN<sub>2</sub>/BPN ( $E_b = 0.05 \text{ eV/Å}^2$  and d = 3.40 Å) [47], indicating the interfacial stability of the PG/BPN heterostructure bounded by weak vdW forces.

Besides the interface stability, we further investigate the thermal stability of the PG/BPN heterostructure at 500 K. After performing an AIMD simulation for 10,000 steps with a time step of 1 femtosecond (*fs*) and a simulation time of 10 picoseconds (*ps*), there is no significant geometric distortion (see Fig. 2b), and the total potential energy of the system fluctuates around a constant value, suggesting the thermal stability of the PG/BPN heterostructure at 500 K.

Since we stack two monolayers with different symmetry, it is interesting to explore how the stacking affects the in-plane mechanical properties of the heterostructure. As listed in Table 1, our calculated values for PG and BPN monolayers are well consistent with previously reported results [7,48], fully satisfying the Born-Huang stability criteria for both the monolayers and the heterostructure [49]. For comparison, we note that our calculated stiffness tensor components of this heterostructure possess larger values of the elastic constants and Young's modulus as compared to the individual components, suggesting enhanced in-plane stiffness and more resistance to deformation under applied stress. Additionally, the Poisson's ratio  $\nu$  becomes positive upon the formation of the vdW contact between PG and BPN with an intermediate value of 0.32, suggesting a moderate degree of contraction perpendicularly to the direction of applied stress. To summarize, the PG/ BPN heterostructure exhibits enhanced mechanical stiffness and resistance to deformation, showing its potential for nanoscale mechanical devices requiring high stiffness and strength.

#### 3.3. Electronic properties of the PG/BPN heterostructure

In metal–semiconductor vdW contacts, the semiconducting channel material serves as the active layer mainly responsible for carrying/ controlling the charge carriers between the electrodes. To analyze the electronic properties of the PG/BPN system, we calculate the band structure of the heterostructure, its projection on both monolayers and the corresponding DOS, as shown in Fig. 3(a-d). The PG/BPN heterostructure shows metallic behavior (see Fig. 3a), while Fig. 3(b) shows that the interlayer interactions induce downward (upward) shifting of conduction (valence) bands towards the Fermi level. In addition, Fig. 3 (c) shows that the well-preserved electronic feature of the BPN sheet mainly contributes to the DOS near the Fermi level of the PG/BPN heterostructure (see Fig. 3d).

#### 3.4. Interfacial properties of the PG/BPN heterostructure

We further evaluate the potential of PG/BPN heterostructure as a metal–semiconductor FET device by calculating three types of energy barriers, namely, the tunneling barrier ( $\Phi_{\text{TB}}$ ), Schottky barrier ( $\Phi_{\text{SB}}$ ), and lateral barrier ( $\Phi_{\text{LB}}$ ).

Firstly, we discuss the  $\Phi_{TB}$  that exists at the vertical interface due to a potential energy mismatch between the stacked monolayers, where the

#### Table 1

Summary of the elastic constants ( $C_{ij}$  in GPa·nm), Young's modulus (E in GPa·nm), and Poisson's ratio ( $\nu$ ) of PG, BPN, and PG/BPN heterostructure.

| System   | <i>C</i> <sub>11</sub> | C <sub>22</sub> | C <sub>12</sub> | C <sub>66</sub> | Ε      | ν      |
|----------|------------------------|-----------------|-----------------|-----------------|--------|--------|
| PG       | 268.63                 | 268.63          | -21.63          | 149.74          | 270.37 | - 0.08 |
| PG [7]   | 265.00                 | 265.00          | -18.00          | 152.00          | 263.80 | -0.07  |
| BPN      | 264.13                 | 241.04          | 98.35           | 82.12           | 227.51 | 0.37   |
| BPN [48] | 294.00                 | 240.00          | 91.00           | 83.00           | 259.70 | 0.38   |
| PG/BPN   | 416.47                 | 362.68          | 133.86          | 163.86          | 373.45 | 0.32   |

tunneling probability (TP) of charge carriers can be determined by the height ( $h_{\text{TB}}$ ) and width ( $w_{\text{TB}}$ ) of the tunneling barrier potential. For the PG/BPN heterostructure, the TP is calculated with the Wentzel–Kramer–Brillouin (WKB) approximation [46]:

$$TP = \exp\left(-2\frac{\sqrt{2mh_{TB}}}{\hbar} \times w_{TB}\right)$$
(7)

here *m* is the electron mass, and  $\hbar$  is the reduced Planck's constant. From the electrostatic potential profile in Fig. 4(a), we calculate the  $h_{\text{TB}}$  and w<sub>TB</sub> as 2.42 eV and 1.97 Å, respectively, which lead to a TP of 4.39 % in the PG/BPN heterostructure (see Fig. 4b), higher than recently reported TP values for 2D metal-semiconductor vdW heterostructures such as MoSi<sub>2</sub>N<sub>4</sub>/NbS<sub>2</sub> (1.3 %), WSi<sub>2</sub>N<sub>4</sub>/NbS<sub>2</sub> (1.5 %), MoSi<sub>2</sub>N<sub>4</sub>/graphene (1.5 %), WSi<sub>2</sub>N<sub>4</sub>/graphene (1.7 %) [50], In<sub>2</sub>Se<sub>3</sub>/TaS<sub>2</sub> (3.45 %) [51], NbS<sub>2</sub>/ MoSe<sub>2</sub> (2.74 %) [52], graphene/α-Ga<sub>2</sub>O<sub>3</sub> (0.77–1.86 %) [53], MoSH@MoS2 (3.39 %), MoHS@MoS2 (4.10 %) [54], NbS2/MoSSe (3.23 %) [55], etc. Here, it is worth mentioning that a small d may induce strong interactions at the interface and lead to a smaller  $h_{\text{TB}}$  and the larger corresponding TP (up to 100 %) in bulk metal/semiconductor systems such as in PG/bulk metal (Al, Cr, and Ti) contacts [13], which is not the case for PG/BPN heterostructure. In addition, our calculated TP mainly depends on the weak vdW interactions. From these two factors, it is easy to understand why  $h_{\text{TB}}$  is larger, and the TP is lower in the PG/ BPN heterostructure as compared to those of PG/metal contacts.

Next, we focus on the  $\Phi_{SB}$ , which refers to the energy barrier formed at the vertical interface due to the difference in the work functions, resulting in the contact resistance to carrier injection/extraction between the metal and semiconductor materials. For the PG/BPN heterostructure, we follow the Schottky-Mott model [46], in which the  $\Phi_{SB}$ height for electrons ( $\Phi_e$ ) and holes ( $\Phi_h$ ) can be determined by the energy difference between the Fermi level and the respective energy band edges of the semiconductor in the heterojunction,

$$\Phi_e = E_{CBM} - E_F, \Phi_h = E_F - E_{VBM} \tag{8}$$

here  $E_{\rm F}$  represents the Fermi level energy,  $E_{\rm CBM}$  and  $E_{\rm VBM}$  are the band edge positions of PG identified from the projected band structure in Fig. 3(b). Notably, the calculated  $\Phi_{\rm SB}$  values of 0.19 eV for  $\Phi_{\rm e}$  and 1.07 eV for  $\Phi_{\rm h}$  are significantly lower than the reported values for PG/graphene [11] and PG/penta-BN<sub>2</sub> [12] contacts (see Table 2), implying the lower Schottky contact barrier in this heterostructure. In addition, as  $\Phi_{\rm e}$ is much smaller than  $\Phi_{\rm h}$ , an *n*-type Schottky contact is naturally formed at the vertical interface of the PG/BPN heterojunction, suggesting that electrons as the major transporting carriers flow across the interface.

Further, the  $\Phi_{LB}$  occurs at the lateral interface between the heterostructure and the channel material. It can be obtained by aligning the energy levels of the heterostructure and the channel material, and calculating the resulting band bending ( $\Delta E_{\rm F}$ ) between them. For the PG/ BPN heterostructure, the band alignment is plotted in Fig. 4(c) under the scheme of the current-in-plane (CIP) model [11], which is mainly divided into three parts: the left side for the PG/BPN heterostructure, the interface between the heterostructure and the non-contacted PG as marked with the red dashed line in the middle, and the right side for the non-contacted monolayer PG. The energy levels of the heterostructure and the non-contacted PG sheet are well aligned to the vacuum energy  $E_{\rm vac}$ . The difference between vacuum energy and Fermi energy is calculated as the work functions  $W_{\rm H} = 4.62$  eV and  $W_{\rm PG} = 6.00$  eV for the heterostructure and the non-contacted PG, respectively. As listed in Table 2, the calculated  $\Delta E_{\rm F} = W_{\rm H} - W_{\rm PG} = -1.38$  eV with the negative value ( $\Delta E_F < 0$ ) confirms that an *n*-type channel is naturally formed between the PG/BPN heterostructure and non-contacted PG at the lateral interface, similar to the reported situations for PG/graphene (-1.63 eV) [11], and PG/BN<sub>2</sub> (-1.00 eV) [12] heterojunctions.

To minimize the contact resistance and improve the FET device performance, a Schottky contact with small or tunable  $\Phi_{SB}$  is preferred. To tune the  $\Phi_{SB}$  values, the most common and practical approach is to



Fig. 3. (a) Band structure of the PG/BPN heterostructure and its projection on (b) PG and (c) BPN. (d) Total DOS of the PG/BPN heterostructure, and partial DOS contributed from PG and BPN.



Fig. 4. (a) Schematic model of the PG/BPN-based transistor. (b) calculated electrostatic potential of PG/BPN heterostructure. (c) Schematic of CIP model and band alignment in the PG/BPN heterostructure.

| Table 2                                                                                                                                                 |
|---------------------------------------------------------------------------------------------------------------------------------------------------------|
| Calculated structural and interfacial parameters of PG/BPN heterostructure                                                                              |
| including $d$ (in Å), $E_{\rm b}$ (in eV/Å <sup>2</sup> ), $h_{\rm TB}$ (in eV), $w_{\rm TB}$ (in Å), TP (in %), $\Phi_{\rm e}$ (in eV), $\Phi_{\rm h}$ |
| (in eV) and $\Delta E_{\rm F}$ (in eV).                                                                                                                 |

| Structure               | đ    | Eb   | h <sub>TB</sub> | w <sub>TB</sub> | TP   | $\Phi_{\rm e}$ | ${\pmb \Phi}_{\rm h}$ | $\Delta E_{\rm F}$ |
|-------------------------|------|------|-----------------|-----------------|------|----------------|-----------------------|--------------------|
| PG/BPN                  | 3.40 | 0.04 | 2.42            | 1.97            | 4.39 | 0.19           | 1.07                  | -1.38              |
| PG/graphene<br>[11]     | 3.14 | 0.06 |                 |                 |      | 0.42           | 1.69                  | -1.63              |
| PG/BN <sub>2</sub> [12] | 2.48 |      |                 |                 |      | 1.06           | 1.16                  | -1.00              |
| PG/Al [13]              | 2.13 | 0.45 | 0               | 0               | 100  | 1.20           | 2.07                  |                    |
| PG/Cr [13]              | 2.07 | 1.63 | 0               | 0               | 100  | 1.90           | 1.37                  |                    |
| PG/Ti [13]              | 2.37 | 0.66 | 0               | 0               | 100  | 1.60           | 1.67                  |                    |

apply an external electric field (E<sub>ext</sub>), which can tune the electronic structure of the vdW heterostructures for improving device functionality [5,11]. We note that an electric field strength of  $\pm$  0.1 V/Å was used to

tune the electronic band structures of the layered material as well as its performance in an experiment [56]. While in many reported computational studies, an electric field with the strength in the range of  $\pm$  0.1–1.5 V/Å is applied to study its effect on the behavior and properties of junction interfaces [55,57–61].

In the PG/BPN heterostructure, we apply an  $E_{ext}$  in the vertical direction with its strength varying from -0.6 to + 0.6 V/Å, and the resulting electronic band structures are shown in Fig. 5. For  $E_{ext} < 0$ , the applied electric field induces the downward shift of the CBM of PG, leading to a reduction in  $\Phi_{e}$ . At -0.6 V/Å,  $\Phi_{e}$  is reduced to 0.04 eV from 0.19 eV, implying the formation of an *n*-type Schottky contact with negligible  $\Phi_{SB}$  (see Fig. 5a). On the contrary, for  $E_{ext} > 0$ , the applied electric field leads to an increase in  $\Phi_{e}$  and a reduction in  $\Phi_{h}$ . At + 0.6 V/Å,  $\Phi_{h}$  is reduced to 0.72 eV from 0.19 eV, implying the induced transition from *n*-type to a *p*-type interface by an electric field (see Fig. 5d).

In addition, it is worth mentioning that the *d* remains unaffected in



Fig. 5. Projected electronic band structures of PG in the PG/BPN heterostructure under external (a, b) negative and (c, d) positive electric fields.

the PG/BPN heterostructure under the application of  $E_{ext}$ , while the shifting of energy levels strongly depends on the  $E_{ext}$ . Based on the above analysis, the reduced  $\Phi_{SB}$  at -0.6 V/Å can promote the low-resistance transport of electrons across the interface, further improving the tunneling efficiency of this system.

# 3.5. Optical properties of the PG/BPN heterostructure

The enhanced optical response of a metal-semiconductor vdW heterostructure is desired for optoelectronic devices such as solar cells and photodetectors. Although the total electronic band structure of the PG/ BPN heterostructure shows metallic behavior, it can still exhibit considerable optical efficiency due to the existence of semiconducting PG. In this regard, we calculate the  $\alpha^{2D}(\omega)$  and Re  $[\sigma^{2D}(\omega)]$  of BPN, PG and the PG/BPN heterostructure. As shown in Fig. 6(a, b), the absorption and conductivity spectra of the heterostructure not only preserve the combined intrinsic features of both individual monolayers but also offer an enhanced absorption of up to 8 %. This phenomenon can be attributed to the coupled contributions of both monolayers after stacking in vdW assembly, suggesting that photons can make electronic excitations from the valence to the conduction band, depending on the specific bandgap energy between the transition k-paths. To verify, one can observe that absorption and conductivity peaks ranging from 0 eV to 2.9 eV are dominated by the BPN sheet, as PG is a poor absorber in this range. At the same time, the increasing peaks above 2.9 eV are induced by the PG sheet, where BPN shows reducing optical efficiency. In addition, we note that both the  $\alpha^{2D}(\omega)$  and  $\operatorname{Re}[\sigma^{2D}(\omega)]$  are mainly dominated by Im  $[i\epsilon_{ii}^{2D}(\omega)]$ , which is directly related to the electronic transitions, optical absorption and conductivity based on Eqs. (5) and

(6).

To gain further insight into the optical performance of the PG/BPN heterostructure, we calculate its  $\alpha^{\text{2D}}(\omega)$  and Re [ $\sigma^{\text{2D}}(\omega)$ ] with an external electric field  $\text{E}_{\text{ext}}$  ranging from –0.6 to + 0.6 V/Å. Distinct from the cases with  $\text{E}_{\text{ext}} < 0$  (see Fig. 7a, b), we observe the switching of absorption and conductivity peaks for varying positive  $\text{E}_{\text{ext}}$  ranges, as shown in Fig. 7(c, d). As mentioned above, the electric field with  $\text{E}_{\text{ext}} > 0$  significantly shifts the VBM (CBM) of PG in the PG/BPN heterostructure upwards (away) from the Fermi level, in turn changing the corresponding wave function and transition matrix, and altering the overall absorption and conductivity spectra. Consequently, the *p*-type contact formation endows excellent potential in the PG/BPN heterostructure, providing more channels for electronic excitations and transport.

# 4. Conclusion

In this work, we report the electronic, interfacial, and optical properties of an all-carbon vdW heterostructure composed of the 2D PG and BPN monolayers, respectively, acting as channel and source materials because of their intrinsic electronic features. The PG/BPN heterostructure possesses an *n*-type Schottky contact at the vertical interface of the heterojunction with a barrier height of 0.19 eV, which is reduced to 0.04 eV under an external electric field of -0.60 V/Å. Besides, the PG/BPN heterostructure also exhibits an *n*-type to *p*-type contact transition as electric field strength reaches + 0.60 V/Å. In addition, as compared to the free-standing monolayers, the PG/BPN heterostructure can harvest a wide range of the solar spectrum (from infrared to ultraviolet regions) with strong optical absorption and conductivity, implying its potential in optoelectronic devices.



Fig. 6. (a) Calculated optical absorption (in %) and (b) optical conductivity spectra of PG, BPN, and the PG/BPN heterostructure in units of  $\sigma_0 = e^2/4\hbar$ .



Fig. 7. Calculated optical absorption and conductivity of the PG/BPN heterostructure for (a, b) negative and (c, d) positive electric fields.

# CRediT authorship contribution statement

Muhammad Azhar Nazir: Writing – review & editing, Writing – original draft, Visualization, Methodology, Data curation, Conceptualization. Yiheng Shen: Writing – review & editing, Visualization, Data curation. Changsheng Hou: Writing – review & editing, Methodology. Chenxin Zhang: Writing – review & editing, Methodology, Data curation. Qian Wang: Writing – review & editing, Visualization, Supervision, Resources, Project administration, Funding acquisition, Data curation. Akira Yoshikawa: Discussions, Resources. Yoshiyuki Kawazoe: Discussions, Resources, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

# Acknowledgments

This work is partially supported by grants from the National Natural Science Foundation of China (Grant Nos. NSFC-12274007 and NSFC-11974028). This work is also supported by the high-performance computing platform of Peking University, China. Y. Kawazoe acknowledges the partial support by Suranaree University of Technology (SUT), Thailand Science Research and Innovation (TSRI), and National Science Research and Innovation Fund (NSRF) (NRIIS Project Number 90465). The authors also thank the crew of the Center for Computational Materials Science, the Institute for Materials Research, Tohoku University (Japan) for their continuous support of the MASAMUNE-IMR supercomputing facility.

# References

- [1] R.K. Cavin, P. Lugli, V.V. Zhirnov, Science and engineering beyond Moore's law, Proc. IEEE 100 (2012) 1720–1749.
- [2] H. Ilatikhameneh, T. Ameen, B. Novakovic, Y. Tan, G. Klimeck, R. Rahman, Saving Moore's law down to 1 nm channels with anisotropic effective mass, Sci. Rep. 6 (2016) 31501.
- [3] M.A. Nazir, Y. Shen, C. Zhang, Q. Wang, A stable trigon-based 3D carbon allotrope with ultralow lattice thermal conductivity, J. Mater. Chem. C 11 (2023) 10722–10729.
- [4] M. Woszczyna, A. Winter, M. Grothe, A. Willunat, S. Wundrack, R. Stosch, T. Weimann, F. Ahlers, A. Turchanin, All-carbon vertical van der Waals heterostructures: non-destructive functionalization of graphene for electronic applications, Adv. Mater. 26 (2014) 4831–4837.
- [5] J. Huang, J. Kang, Two-dimensional graphyne–graphene heterostructure for allcarbon transistors, J. Phys. Condens. Matter 34 (2022) 165301.
- [6] B. Cai, H. Yin, T. Huo, J. Ma, Z. Di, M. Li, N. Hu, Z. Yang, Y. Zhang, Y. Su, Semiconducting single-walled carbon nanotube/graphene van der Waals junctions for highly sensitive all-carbon hybrid humidity sensors, J. Mater. Chem. C 8 (2020) 3386–3394.
- [7] S. Zhang, J. Zhou, Q. Wang, X. Chen, Y. Kawazoe, P. Jena, Penta-graphene: a new carbon allotrope, PNAS 112 (2015) 2372–2377.
- [8] J. Deb, N. Seriani, U. Sarkar, Ultrahigh carrier mobility of penta-graphene: a firstprinciple study, Phys. E: Low-Dimens. Syst. Nanostruct. 127 (2021) 114507.
- [9] M.A. Nazir, A. Hassan, Y. Shen, Q. Wang, Research progress on penta-graphene and its related materials: properties and applications, Nano Today 44 (2022) 101501.
- [10] Y. Shen, Q. Wang, Pentagon-based 2D materials: classification, properties and applications, Phys. Rep. 964 (2022) 1–42.

- [11] Y. Guo, F.Q. Wang, Q. Wang, An all-carbon vdW heterojunction composed of penta-graphene and graphene: tuning the Schottky barrier by electrostatic gating or nitrogen doping, Appl. Phys. Lett. 111 (2017) 073503.
- [12] K. Zhao, Y. Guo, Q. Wang, Contact properties of a vdW heterostructure composed of penta-graphene and penta-BN2 sheets, J. Appl. Phys. 124 (2018) 165103.
- [13] A. Hassan, Y. Guo, Q. Wang, Y. Kawazoe, P. Jena, Interfacial properties of pentagraphene-metal contacts, J. Appl. Phys. 125 (2019) 065308.
- [14] V.H. Ho, D.T. Ho, W.H. Shin, S.Y. Kim, Auxeticity of monolayer, few-layer, vdW heterostructure and ribbon penta-graphene, PCCP 25 (2023) 4528–4541.
- [15] S. Sun, G. Ru, W. Qi, W. Liu, Molecular dynamics study of the robust superlubricity in penta-graphene van der Waals layered structures, Tribol. Int. 177 (2023) 107988.
- [16] L. Chen, M. Yang, F. Kong, J. Guo, H. Shu, J. Dai, Metallic penta-graphene/penta-BN<sub>2</sub> heterostructure with high specific capacity: a novel application platform for Li/Na-ion batteries, J. Alloy. Compd. 901 (2022) 163538.
- [17] T. Wang, Y. Qi, M. Li, X. Zhao, C. Xia, Y. An, S. Wei, First-principles study of pentagraphene/MoS<sub>2</sub> vdW heterostructure as anode material for lithium-ion batteries, Diam. Relat. Mater. 136 (2023) 109928.
- [18] W. Zhang, S. Xi, Y. Liang, C. He, Construction of novel PG/GeP<sub>2</sub> and PG/SiP<sub>2</sub> vdW heterostructures for high-efficiency photocatalytic water splitting, Appl. Surf. Sci. 608 (2023) 155106.
- [19] W. Zhang, J. Hou, M. Bai, C. He, J. Wen, Spontaneously enhanced visible-lightdriven photocatalytic water splitting of type II PG/AlAs<sub>5</sub> van der Waal heterostructure: a first-principles study, Chin. Chem. Lett. 108270 (2023).
- [20] Q. Fan, L. Yan, M.W. Tripp, O. Krejčí, S. Dimosthenous, S.R. Kachel, M. Chen, A. S. Foster, U. Koert, P. Liljeroth, Biphenylene network: a nonbenzenoid carbon allotrope, Science 372 (2021) 852–856.
- [21] T. Liu, Y. Jing, Y. Li, Two-dimensional biphenylene: a graphene allotrope with superior activity toward electrochemical oxygen reduction reaction, J. Phys. Chem. Lett. 12 (2021) 12230–12234.
- [22] Y.-W. Son, H. Jin, S. Kim, Magnetic ordering, anomalous Lifshitz transition, and topological grain boundaries in two-dimensional biphenylene network, Nano Lett. 22 (2022) 3112–3117.
- [23] I. Alcón, G. Calogero, N. Papior, A. Antidormi, K. Song, A.W. Cummings, M. Brandbyge, S. Roche, Unveiling the multiradical character of the biphenylene network and its anisotropic charge transport, J. Am. Chem. Soc. 144 (2022) 8278–8285.
- [24] Q. Li, J. Zhou, G. Liu, X. Wan, Extraordinary negative thermal expansion of monolayer biphenylene, Carbon 187 (2022) 349–353.
- [25] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169.
- [26] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmentedwave method, Phys. Rev. B 59 (1999) 1758.
- [27] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140 (1965) A1133.
- [28] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865.
- [29] J. Heyd, G.E. Scuseria, M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, J. Chem. Phys. 118 (2003) 8207–8215.
- [30] L. Yao, J. Yun, P. Kang, H. Zhao, J. Yan, W. Zhao, Z. Zhang, Electronic properties, interface contact and transport properties of strain-modulated MS2/ borophosphene and MSeS/borophosphene (M= Cr, Mo, W) heterostructure: Insights from first-principles, Appl. Surf. Sci. 652 (2024) 159363.
- [31] G. Li, H. Bao, Y. Peng, X. Fu, W. Liao, C. Xiang, Strain controllable band alignment, interfacial and optical properties in tellurene/GaAs van der Waals heterostructures, PCCP 26 (2024) 16327.
- [32] P.E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953.
- [33] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys. 132 (2010) 154104.
- [34] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13 (1976) 5188.
- [35] S. Nosé, A unified formulation of the constant temperature molecular dynamics methods, J. Chem. Phys. 81 (1984) 511–519.
- [36] C. Hou, Y. Shen, Q. Wang, Y. Kawazoe, P. Jena, Large second harmonic generation in a penta-CdO<sub>2</sub> sheet exfoliated from its bulk phase, J. Mater. Chem. A 11 (2023) 167–177.
- [37] G. Yang, S.-P. Gao, A method to restore the intrinsic dielectric functions of 2D materials in periodic calculations, Nanoscale 13 (2021) 17057–17067.

- [38] L. Matthes, O. Pulci, F. Bechstedt, Optical properties of two-dimensional honeycomb crystals graphene, silicene, germanene, and tinene from first principles, New J. Phys. 16 (2014) 105007.
- [39] V. Wang, N. Xu, J.-C. Liu, G. Tang, W.-T. Geng, VASPKIT: A user-friendly interface facilitating high-throughput computing and analysis using VASP code, Comput. Phys. Commun. 267 (2021) 108033.
- [40] A. Bafekry, M. Faraji, M. Fadlallah, H. Jappor, S. Karbasizadeh, M. Ghergherehchi, D. Gogova, Biphenylene monolayer as a two-dimensional nonbenzenoid carbon allotrope: a first-principles study, J. Phys. Condens. Matter 34 (2021) 015001.
- [41] P. Lazić, Cell Match: Combining two unit cells into a common supercell with minimal strain, Comput. Phys. Commun. 197 (2015) 324–334.
  [42] J.M. Fitzgerald, J.J. Thompson, E. Malic, Twist angle tuning of moiré exciton
- polaritons in van der Waals heterostructures, Nano Lett. 22 (2022) 4468–4474.
   [43] Y. Yang, J. Li, J. Yin, S. Xu, C. Mullan, T. Taniguchi, K. Watanabe, A.K. Geim, F.
- [43] Y. Yang, J. Li, J. Yin, S. Xu, C. Mullan, T. Taniguchi, K. Watanabe, A.K. Geim, K. S. Novoselov, A. Mishchenko, In situ manipulation of van der Waals heterostructures for twistronics, Sci. Adv. 6 (2020) eabd3655.
- [44] S.D. Chakarova-Käck, E. Schröder, B.I. Lundqvist, D.C. Langreth, Application of van der Waals density functional to an extended system: adsorption of benzene and naphthalene on graphite, Phys. Rev. Lett. 96 (2006) 146107.
- [45] H.K. Neupane, N.P. Adhikari, Effect of vacancy defects in 2D vdW graphene/h-BN heterostructure: first-principles study, AIP Adv. 11 (2021) 085218.
- [46] M.A. Nazir, Y. Shen, A. Hassan, Q. Wang, The electronic and interfacial properties of a vdW heterostructure composed of penta-PdSe<sub>2</sub> and biphenylene monolayers, Mater. Adv. 4 (2023) 1566–1571.
- [47] M.A. Nazir, Y. Shen, C. Zhang, Q. Wang, Schottky-barrier-free vdW contact in a 2D penta-NiN<sub>2</sub>/biphenylene network heterostructure, J. Phys. Chem. C 127 (2023) 24452–24457.
- [48] Y. Luo, C. Ren, Y. Xu, J. Yu, S. Wang, M. Sun, A first principles investigation on the structural, mechanical, electronic, and catalytic properties of biphenylene, Sci. Rep. 11 (2021) 19008.
- [49] M. Born, K. Huang, Dynamical theory of crystal lattices, Clarendon Press, 1954.
- [50] Q. Wang, L. Cao, S.-J. Liang, W. Wu, G. Wang, C.H. Lee, W.L. Ong, H.Y. Yang, L.K. Ang, S.A. Yang, Designing efficient metal contacts to two-dimensional semiconductors MoSi<sub>2</sub>N<sub>4</sub> and WSi<sub>2</sub>N<sub>4</sub> monolayers, arXiv preprint arXiv: 2012.07465, (2020).
- [51] H. Su, T. Hu, F. Wu, E. Kan, Controllable vdW contacts between the ferroelectric In<sub>2</sub>Se<sub>3</sub> monolayer and two-dimensional metals, J. Phys. Chem. C 125 (2021) 10738–10746.
- [52] N.D. Khang, C.Q. Nguyen, C.V. Nguyen, Achieving Ohmic contacts in NbS<sub>2</sub>/MoSe<sub>2</sub> van der Waals heterostructure: a first-principles study, Adv. Theory Simul. (2023) 2300757.
- [53] X. Wu, Z. Xie, Y. Zhang, X. Liu, J. Bi, W. Wang, Z. Zhang, R. Cao, Electric field and strain engineering tuning of 2D Gr/α-Ga<sub>2</sub>O<sub>3</sub> van der Waals heterostructures, J. Mater. Chem. C 11 (2023) 13924–13934.
- [54] S.-T. Nguyen, C.Q. Nguyen, N.N. Hieu, H.V. Phuc, C.V. Nguyen, First-principles investigations of metal-semiconductor MoSH@MoS<sub>2</sub> van der Waals heterostructures, Nanoscale Adv. 5 (2023) 4979–4985.
- [55] P. Nha, C.V. Nguyen, N.N. Hieu, H.V. Phuc, C.Q. Nguyen, Theoretical prediction of electronic properties and contact barriers in a metal/semiconductor NbS<sub>2</sub>/Janus MoSSe van der Waals heterostructure, Nanoscale Adv. (2024) 1193–1201.
- [56] B. Deng, V. Tran, Y. Xie, H. Jiang, C. Li, Q. Guo, X. Wang, H. Tian, S.J. Koester, H. Wang, Efficient electrical control of thin-film black phosphorus bandgap, Nat. Commun. 8 (2017) 14474.
- [57] S. Kaur, A. Kumar, S. Srivastava, K. Tankeshwar, Van der Waals heterostructures based on allotropes of phosphorene and MoSe<sub>2</sub>, PCCP 19 (2017) 22023–22032.
- [58] L.H. Li, T. Tian, Q. Cai, C.-J. Shih, E.J. Santos, Asymmetric electric field screening in van der Waals heterostructures, Nat. Commun. 9 (2018) 1271.
- [59] Y. Jia, Y. Zhang, X. Wei, T. Guo, J. Fan, L. Ni, Y. Weng, Z. Zha, J. Liu, Y. Tian, GaTe/CdS heterostructure with tunable electronic properties via external electric field and biaxial strain, J. Alloy. Compd. 832 (2020) 154965.
- [60] X. Lu, L. Li, X. Guo, J. Ren, H. Xue, F. Tang, Effects of vertical strain and electric field on the electronic properties and interface contact of graphene/InP vdW heterostructure, Comput. Mater. Sci 198 (2021) 110677.
- [61] K. Iordanidou, R. Mitra, N. Shetty, S. Lara-Avila, S. Dash, S. Kubatkin, J. Wiktor, Electric field and strain tuning of 2D semiconductor van der Waals heterostructures for tunnel field-effect transistors, ACS Appl. Mater. Interfaces 15 (2022) 1762–1771.