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Exploring the Potential of 2D Phosphorene as a Sensor for Pharmaceutical Wastewater Pollutants: A Theoretical-Based Approach

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Abstract

Pharmaceutical wastewater, especially that containing analgesic pollutants, presents a significant environmental challenge, necessitating the development of advanced sewage treatment strategies to mitigate their persistence in municipal systems. This study explores a novel approach to this issue by employing density functional theory (DFT) to evaluate the potential of a phosphorene monolayer in removing and sensing persistent pollutants such as Carbamazepine, Metformin, and Paracetamol from the environment. To assess the monolayer's suitability for molecular sensing and capture, optimized geometries, interaction energies, and electronic band structures were analyzed. The molecular adsorption of these pollutants was found to affect the electronic band gap of pristine phosphorene, indicating its potential for detection. These findings underscore the promise of phosphorene monolayers as a smart sensing nanomaterial.

Key words: Density functional theory, blue phosphorene, biosensing, pharmaceuticals

1. Introduction

Environmental contamination arises not solely from direct disposal but also significantly through the excretion of unmetabolized parent compounds and their resultant metabolites, substances often characterized by their notable persistence within the environment [1]. Consequently, the presence of these pharmaceutical compounds has been documented across a wide spectrum of environmental matrices, including lotic ecosystems (streams and rivers), terrestrial soils, surface and groundwater resources, potable water supplies, and even agricultural crops [2].

The bio-accumulation of these substances within aquatic life presents potential risks to human health through the consumption of contaminated fish and water entering the food chain [3]. Environmental monitoring studies of aquatic systems consistently reveal a diverse array of pharmaceuticals, albeit with significant variations in detected concentrations and occurrence frequencies [4-5]. For instance, Wilkinson et al. conducted a global assessment of pharmaceutical impacts by analyzing river samples worldwide [5]. Their investigation identified Carbamazepine (CBZ), Metformin (MET), and Paracetamol (Acetaminophen, PAR) among the ten most frequently detected pharmaceuticals globally. These compounds are also frequently categorized as emerging contaminants [6].

These observations underscore the imperative for continued research focused on sensing or eliminating pharmaceutical contamination in the environment. Conventional remediation strategies encompass biological treatment, adsorption, advanced oxidation processes (AOPs), membrane

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filtration, and coagulation/flocculation [6-7]. However, each methodology presents inherent limitations, often yielding only partial degradation or engendering the formation of undesirable, potentially hazardous byproducts, such as trihalomethanes, dioxins, chlorinated phenoxyphenols, and chlorinated phenols [3]. It is evident that new methodologies are needed to reduce or eliminate existing limitations. Two-dimensional (2D) nanostructures have proven effective in detecting or retaining molecules, as demonstrated by both theoretical and experimental investigations [aa-bb]. The synthesis of graphene in 2004 spurred increased interest in 2D materials. Blue Phosphorene (BP) stands out among these materials owing to its stable 2D structure and semiconductor characteristics, making it suitable for numerous applications [8-9].
Although extensive research exists for pristine BP + molecule systems [8-10], a systematic investigation into their specific interactions with the pharmaceutical molecules CBZ, MET, and PAR appears absent from the current literature. The present study employs Density Functional Theory (DFT) calculations to address this knowledge gap, offering a comprehensive, atomistic-level analysis of these critical interactions.

2. Materials and Method

In this work, all first-principles calculations were conducted within the framework of DFT [11-12]. The exchange-correlation interactions were treated using the Generalized Gradient Approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form [13]. Geometric optimizations and electronic structure analyses were performed using version 4.1.5 of the SIESTA simulation package [14]. A double-zeta polarized (DZP) basis set was employed, with a PAO EnergyShift parameter of 100 meV. The chosen pseudopotentials were of the norm-conserving type [15].
For Brillouin zone sampling, a Monkhorst-Pack k-point grid of 3×3×1 was applied for structural relaxations, while a denser 9×9×1 grid was used for band structure calculations [16]. To model the surface and accommodate molecular adsorption, a 6×6 supercell of monolayer BP, comprising 72 atoms, was constructed. The real-space integration MeshCutoff was set to 350 Ry. Long-range dispersion interactions were accounted for using the Grimme-D2 correction scheme [17].
The system was relaxed using the Conjugate Gradient (CG) algorithm to ensure convergence to the minimum energy configuration. The interaction energy between the molecule and the substrate was evaluated according to the following expression:

$$E_{int} = E_{Total} - E_{Mol} - E_{Monolayer} \quad (1)$$

Here, E_{int} represents the interaction energy, E_{Total} is the total energy of the molecule + monolayer complex, E_{Mol} is the total energy of the isolated molecule, and $E_{Monolayer}$ refers to the total energy of the pristine monolayer.

3. Results

Initial computational efforts focused on determining the optimized geometric structure of the pristine BP monolayer, as depicted in Figure 1-a. To ensure an accurate representation of the molecule-surface interactions, 6x6 BP supercell was constructed. Computational analysis yielded a P-P bond length of 2.28 Å. Furthermore, the electronic band structure of the pristine BP

monolayer was calculated. The minimum equilibrium distance between the adsorbate and the surface in this configuration was determined to be 2.97 Å, occurring between a hydrogen atom of PAR and a surface P atom. Similarly, the shortest molecule-surface distance for CBZ was found between a hydrogen atom and a surface P atom, measuring 2.96 Å. For MET, the closest approach distance was calculated to be 2.57 Å, which is closer to the surface than others.

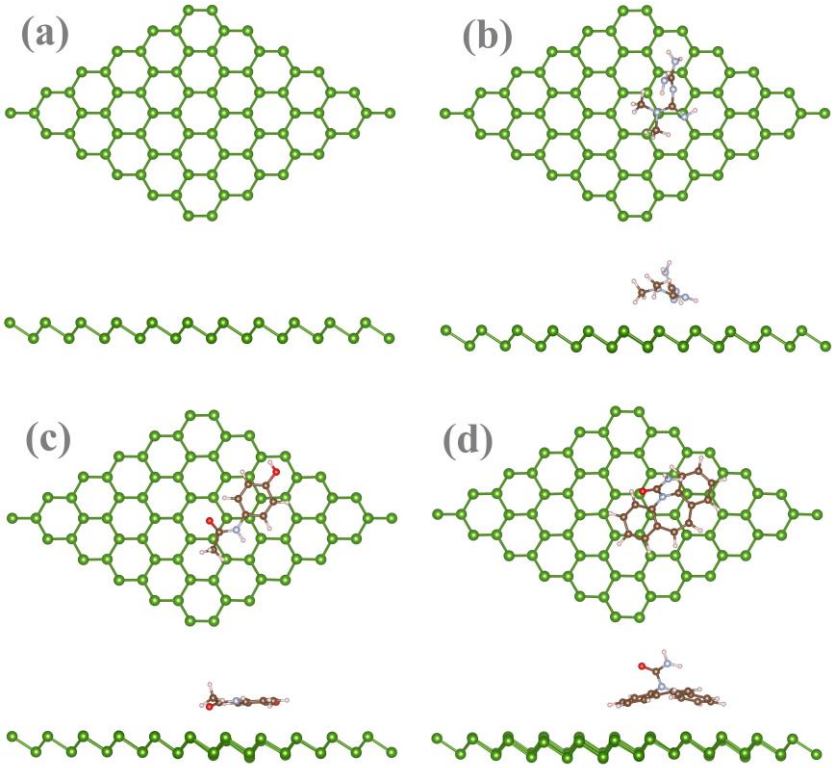

Figure 1 The minimum energy configurations of a) pristine BP, b) MET+ BP, c) PAR+ BP, d) CBZ+ BP. Green, brown, blue, red and pink indicate as P, C, N, O and H atom, respectively.

Interaction energy represents a paramount metric for characterizing the adsorption process. The negative values obtained for the interaction energies confirm that the adsorption of all three pharmaceuticals onto BP is an exothermic process, implying thermodynamic favorability or spontaneity [18]. Furthermore, the magnitude of this negative energy quantifies the strength of the interaction, with more negative values signifying stronger binding [18]. As detailed in Table 1, the calculated interaction energies for CBZ and PAR were identical at -1.44 eV and -1.48 eV, respectively, whereas the corresponding value for MET was -1.22 eV.

Table 1. Interaction energy and work function (φ) for pristine BP and molecule systems.

Molecules	Interaction Energy (eV)	$\boldsymbol{\varphi}$ (eV)
CBZ	-1.44	4.08
MET	-1.22	4.35
PAR	-1.48	4.47

The calculated band gap for the BP+MET composite system is 1.38 eV. Notably, interaction with either CBZ or PAR leads to a very similar reduction in the band gap, yielding a value of 1.43 eV and 1.46 eV for BP+CBZ and BP+PAR systems, respectively. These represent an approximate 29% decrease compared to the pristine BP band gap (2.00 eV).

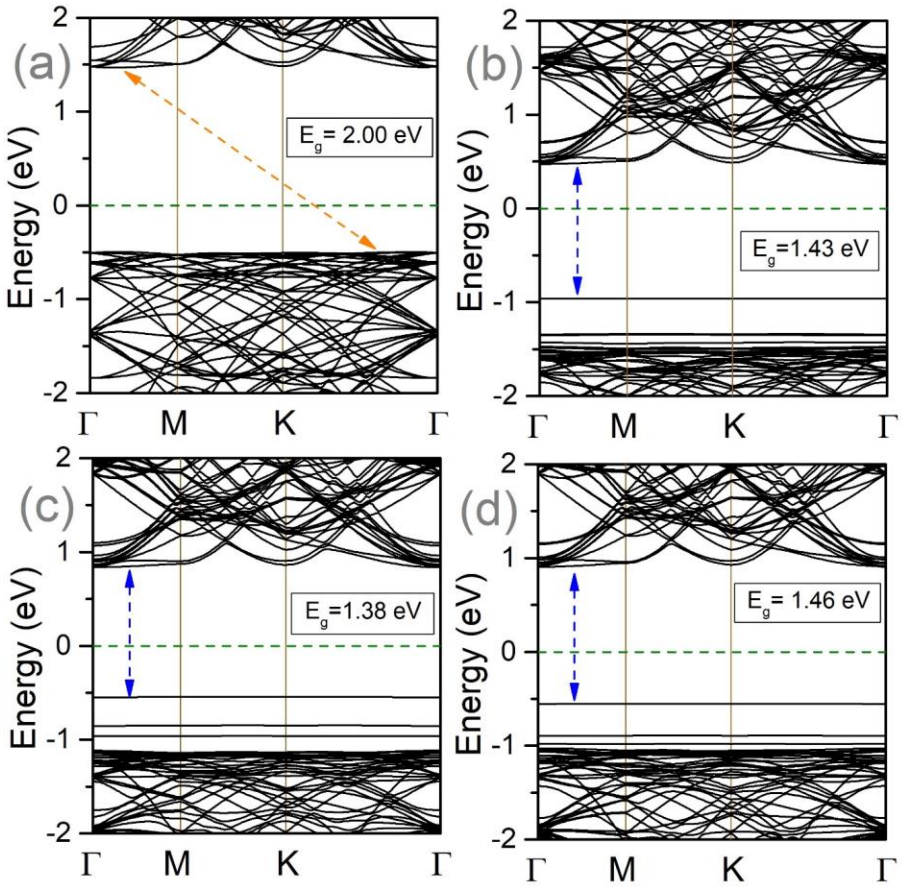

Figure 2 The band structure of a) pristine BP, b) BP+CBZ, c) BP+MET and d) BP+PAR systems. The Fermi level is set to zero. Eg indicates band gap.

The work function (φ) is a surface-sensitive property frequently employed to gauge the suitability and sensitivity of materials for work-function-based chemical sensors. These devices typically operate by quantifying the change in the sensing material's work function (Δφ) upon exposure to an analyte, often measured using techniques like the Kelvin probe method [19]. The magnitude of Δφ directly correlates with the sensor's response intensity. The work function is formally defined as;

$$\varphi = |V_\infty - E_f| \quad (2)$$

where E_f represents the Fermi level of the material and V_∞ is the vacuum potential energy level. Our calculations determined the work function of the pristine BP monolayer to be 5.05 eV. As presented in Table 1, the adsorption of CBZ, MET and PAR molecules onto the pristine BP surface induces significant changes in its work function.

4. Discussion

Obtained structural parameters are in good agreement with previously reported data [8-9]. Illustrated in Figure 2-a, our analysis reveals that pristine BP possesses an indirect band gap of approximately 2.00 eV. This result exhibits close correspondence with established theoretical (2.00 eV) values documented in the literature [8-9]. Moreover, the calculated band structure confirms the intrinsic nonmagnetic character of pristine BP.

The molecular architecture of PAR incorporates a hydroxyl group (OH), an amide moiety (HN-CO-R), and an aromatic benzene ring. Upon interaction with the pristine BP surface, the energetically most favourable configuration for PAR was identified when its aromatic benzene ring aligned parallel to the BP plane (Figure 2-c). This parallel orientation maximizes the van der Waals contact area between the molecule and the surface, thereby promoting a lower energy state indicative of a more stable interaction.

Conversely, the most stable adsorption geometry for CBZ interacting with pristine BP is presented in Figure 2-d. As illustrated, CBZ features an amide group and a nitrogen atom situated within a cyclic azepane ring; these functional groups play a significant role in mediating its interaction with the BP surface, analogous to the interaction observed for PAR.

Unlike CBZ and PAR, MET lacks an aromatic ring structure that could facilitate extensive planar interaction with the BP surface. This structural distinction is reflected in the calculated interaction energetics. Consequently, the structural differences inherent to the MET molecule manifest as variations in both its binding energy and its equilibrium proximity to the surface compared to the other pharmaceuticals. However, it did not strength the interaction energy compared to CBZ+BP or PAR+BP systems. This is mainly due to the lack of the ring for MET.

Obtained interaction energies are notably robust when compared against values reported for similar physisorption systems in the existing literature [20-21].

Alterations in the electronic band structure upon molecular adsorption are fundamental to the transduction mechanism in many semiconductor-based sensors. Modifications induced by adsorbates can serve as detectable electronic signatures for molecular identification. Our calculations reveal that interaction with the pharmaceutical molecules introduces discernible changes to the BP band structure relative to its pristine state (Figure 2-a). This band gap narrowing arises from the introduction of new electronic states, associated with the molecular orbitals of the adsorbates, within the original band gap region (visible as relatively flat bands in the band structure diagrams). These substantial modifications underscore the potential utility of BP for the electronic detection of these specific pharmaceuticals.

The most substantial work function modulation is observed upon CBZ adsorption, resulting in a variation of approximately 24% relative to the pristine value. Adsorption of MET and PAR molecules induces work function changes of 16% and 13%, respectively. The considerable magnitudes of these work function variations provide compelling theoretical evidence for the high sensitivity of the pristine BP monolayer towards all four investigated molecules, with a particularly pronounced response predicted for CBZ detection.

Conclusions

In this study, we conducted a comprehensive computational investigation into the adsorption

behaviour of three pharmaceutical molecules - PAR, CBZ, and MET - on a pristine BP monolayer. Prior to evaluating molecule-surface interactions, the structural and electronic properties of the constituent components were thoroughly characterized. The adsorption configurations revealed that both PAR and CBZ preferentially adopt planar orientations on the BP surface, facilitating enhanced van der Waals interactions through their aromatic ring structures. In contrast, MET, lacking such a structural motif, exhibited a closer approach distance yet weaker interaction energy, highlighting the significance of molecular architecture in modulating adsorption characteristics. Importantly, the adsorption of these molecules induced notable changes in the electronic structure of BP, particularly a substantial narrowing of the band gap-up to approximately 29% for the BP+MET system. These modifications stem from the introduction of molecular orbital-derived states within the band gap, which are evident in the band structure as flat bands. Such alterations suggest that BP's electronic properties are highly sensitive to molecular adsorption, underscoring its potential as a selective and responsive platform for pharmaceutical detection. Moreover, the calculated work function changes upon adsorption, particularly the substantial 24% increase observed with CBZ, offer compelling evidence of BP's potential for use in work-function-based sensor platforms. Overall, our findings provide valuable insights into the interfacial behaviour of drug molecules on 2D materials and support the viability of BP-based sensors in biomedical and environmental monitoring applications.

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