Remarkable enhancement in catechol sensing by the decoration of selective transition metals in biphenylene sheet: A systematic first-principles study

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Abstract
Motivated by the recent successful synthesis of biphenylene structure (Fan et al 2021 Science 372 852), we have explored the sensing properties of this material towards the catechol biomolecule by performing the first-principles density functional theory and molecular dynamics simulations. Pristine biphenylene sheet adsorbs catechol molecule with a binding energy of −0.35 eV, which can be systematically improved by decorating the transition metals (Ag, Au, Pd, and Ti) at various possible sites of biphenylene. It is observed that the catechol molecule is adsorbed on Pd and Ti-decorated biphenylene sheets with strong adsorption energies of −1.00 eV and −2.54 eV, respectively. The interaction of the catechol molecule with biphenylene and metal-decorated biphenylene is due to the charge transfer from the O-2p orbitals of the catechol molecule to the C-2p orbitals of biphenylene and d-orbitals of metals in metal-decorated biphenylene, respectively. From the Bader charge calculation, we found that 0.05e amount of charge is transferred from the catechol molecule to pristine biphenylene, which gets almost double (∼0.1e) for the Ti-decorated biphenylene sheet. The diffusion energy barrier for the clustering of the Pd and Ti atoms comes out to be 2.39 eV and 4.29 eV, computed by performing the climbing-image nudged elastic band calculations. We found that the catechol molecule gets desorbed from the pristine biphenylene sheet at 100 K but remains attached to metal (Pd, Ti) decorated biphenylene sheets at room temperature by performing the ab-initio molecular dynamics simulations. The Ti-decorated biphenylene sheet has more sensitivity toward catechol adsorption while the Pd-decorated biphenylene sheet has a suitable recovery time at 500 K. The results suggest that the Pd and Ti-decorated biphenylene sheets are promising materials for catechol detection.

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(Some figures may appear in colour only in the online journal)

1. Introduction

The combustion of fossil fuels through industrial and transport activities produces many toxic species harmful to the environment and human health. The gas molecules such as NO₂ [1], NO [2], NH₃ [3], CO [4], etc, are toxic and cause detrimental environmental effects. The detection of toxic materials is essential for medical diagnosis, detecting ecological pollutants, food monitoring, and so forth [5]. Effective sensing of these poisonous species is challenging for the scientific community. The sensing substrate should have good sensitivity, selectivity, fast recognition, and reliability [6]. The catechol molecule also called pyrocatechol [7], is a phenolic substance [8] with the molecular formula of C₆H₄(OH)₂ [7]. It is used to prepare pharmaceuticals, cosmetics, insecticides, antioxidants, etc [7]. Since catechol is a toxic and low degradable molecule, its unchecked exposure to the environment for a long time is harmful and may negatively affect the environment and human health. Catechol may govern several health problems like skin irritation, eye damage, genetic defects, and so forth [9]. So, the advancement of sensing materials with high sensitivity, and fast recovery time, has become a strict necessity for catechol recognition.

There are many theoretical and experimental approaches reported for successful catechol detection. For instance, Maleki et al [8] introduced a novel enzyme-based biosensor using an artificial neural network successfully tested in natural water samples for catechol detection. They found that the catechol detection limit of 0.032 μM. Wang et al [10] investigated a reduced graphite oxide incorporated into a metal-organic framework MIL-101 (Cr) that is highly sensitive and reliable with the catechol detection limit of 4 μM. Yang et al [11] explored the sensing behavior of borophene for catechol compound using density functional theory (DFT) methods and obtained a suitable and concise recovery time of 7.6 ns. The sensing performance of ZnO/RGO nanocomposites toward catechol is investigated theoretically and experimentally [9]. The ZnO/RGO composites exhibit excellent sensitivity of 162.04 μA nM cm⁻² and a lower detection limit of 47 nM [9]. Using DFT simulation, the catechol detection behavior of metal-decorated two-dimensional (2D) dichalcogenide MoS₂ is studied by Lakshmy et al [7]. It has been found that the Ti-decorated MoS₂ system is a potential material for catechol sensing [7]. Manjunatha et al [12] fabricated a poly modified graphene electrode for catechol detection in a water sample with a lower detection limit of 8.7 × 10⁻⁷ mol L⁻¹. It has been reported that the boron-doped carbon quantum dots can detect the catechol molecule by an on-off fluorescent switching method with an ultrasensitive detection limit [13]. Qian et al [14] fabricated an electrochemical electrode-based high-performance polymeric film sensor with an excellent catechol detection performance. Zheng et al [15] obtained the N-doped carbon nanotube electrodes by heat treatment with the precursor of ZIF-67, which exhibits outstanding performance towards catechol sensing with a recovery range of 95.3%–105.0%. Zhao et al [16] prepared the nickel oxide deposited carbon nanotube sensor for catechol recognition, revealing remarkable sensitivity with a detection limit of 2.5 μM. Bansal et al [17] studied the synthesis and characterization of zirconia nanoparticles for catechol monitoring on water samples with an exquisite sensitivity of 0.14 μA μM⁻¹ cm². Vellaichamy et al [18] have synthesized an Au@NG-PPy nanocomposite for catechol determination, which shows excellent electrocatalytic activity towards catechol with a detection limit of 0.0016 μM. Yan et al [19] fabricated catechol photo electrochemical sensors, which offer a wide detectable range and low detection limit toward catechol. Chetankumar et al [20] investigated the electrochemical sensing of catechol, and they found excellent sensitivity and acceptable recovery with a low detection limit of 0.95 μM for catechol detection. It has been studied that the nanoporous gold thin films show a superb detection range for catechol [21].

Generally, the orbital interaction and charge transfer between the analyte and the host material is small, which is difficult to find out in experiments. By employing first-principles theoretical calculations, one can observe the change in the density of states, band structures, etc, and examine the charge transfer, which is one of the most crucial aspects of electrochemical sensing. From the theoretical point of view, the charge transfer makes some changes to the properties of the host material, such as resistivity, optical or electronic band gap, etc, which generates a signal to be detected by the sensor [5, 22]. The signal that is generated may be optical or chemical, according to which the sensor is designed. If the optical band gap, absorption, conductivity, etc, of the host material is changed after the signal generation, then it is an optical sensor [5]. One can also find suitable metals for the decoration purpose to enhance the sensing ability of the host material by theoretical modeling, which can help the experimentalist perform experiments.

Two-dimensional (2D) nanomaterials, including graphene [23], graphyne [24], porous nanomaterials [25–27], transition metal (TM) dichalcogenides [28, 29], etc, have gained a lot of scientific interest in sensing applications due to their large surface area, excellent electrochemical and optical properties. These properties are highly tunable by applying strain or decorating metal atoms at various possible sites, which make them a more promising substrate for hazardous gas or
biomolecule sensing [5]. The specificity of the 2D materials is high sensitivity and selectivity towards different biomolecules, lightweight, high charge mobility, long-term reusability, and portability, which are essential features, especially for sensing applications [5]. In addition, these porous nanomaterials provide various channels for gas diffusion that can reduce the recovery time of the sensor. Biphenylene (BP) is one of the novel 2D graphene-like carbon allotrope synthesized by Schlutter et al [30]. The BP sheet comprises square, hexagon, and octagon carbon rings [31], connected with sp2 and sp3 hybridization bonds. In the structure of BP, a large number of possible sites are presented for the decoration of metal atoms so that we can get the desired electrochemical properties [2, 32]. Because of the presence of a large number of adsorption sites in the BP structure, it possesses outstanding behavior in various fields such as energy storage [33], gas sensing [2], Li-ion batteries [34], and so forth [35]. Recently, a theoretical study on catechol sensing has been performed in a similar type of 2D nanomaterial holey graphene (hGY) decorated with an Sc atom [36]. This study reports the suitable catechol adsorption energy of ~3.22 eV and a total amount of 0.9e charge transfer from the catechol molecule to the host structure. BP sheet also contains six and eight-membered rings for the metal decoration; therefore, it will be interesting to study the catechol sensing properties of metal decorated BP monolayer. In the present study, first-principles density functional theory and ab-initio molecular dynamics simulations have been performed to explore the catechol sensing behavior of the pristine and metal decorated BP sheets. We have considered Ag, Au, Pd, and Ti TM atoms for the decoration purpose. We found that the Pd and Ti atoms are strongly bonded to the BP sheet with higher binding energies than Ag and Au. Hence, we have considered only Pd and Ti atom decoration on the BP sheet for catechol adsorption. Since the charge transfer mechanism is the central point to describe the sensing behavior of the substrate, we have performed the partial density of states (PDOS), Bader charge analysis [37], and charge density difference calculations. Ti-decorated BP sheet has more sensitivity towards the catechol detection due to the more charge transfer from the catechol molecule to the metal atom than the Pd decorated BP sheet. In addition to that, the recovery time is checked for the different temperatures at different frequencies. We found that the recovery time for the BP + Pd + catechol system is 0.90 s and 47 milliseconds, respectively, for the yellow and UV lights at 500 K, which is very suitable for practical applications. The results demonstrate that the Pd and Ti-decorated BP systems have promising potential in catechol sensing because of their excellent sensing attributes. The movement of a metal atom, thermal stability, and metal-metal clustering issues are treated by the diffusion energy barrier and ab-initio molecular dynamic (AIMD) calculation.

2. Computational details

We have used the density functional theory and ab-initio molecular dynamics methods as incorporated in Vienna Ab Initio Simulation Package [38]. The Projector Augmented Plane wave method within generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) [39] exchange-correlation functional is adopted, and the energy cut-off is chosen to be 500 eV. The Hellmann–Feynman force and energy convergence limit are set as 0.01 eV Å−1 and 10−5 eV, respectively. The Monkhorst-Pack k-point grid of 5 × 5 × 1 and 7 × 7 × 1 points are taken for geometry optimization and density of states calculations, respectively. A 2 × 2 × 1 supercell of BP containing 24 carbon atoms is considered, and the vacuum of 30 Å is taken perpendicular to the sheet to avoid interaction between periodic layers. Grimme’s dispersion correction DFT-D3 [34, 35] is applied with GGA-PBE to include weak van der Waals (vdW) interactions. The AIMD simulations [40] are performed to investigate the thermal stability of the system at room temperature. The system is placed in the microcanonical ensemble (NVE) followed by the canonical ensemble (NVT) for five ps time durations.

3. Results and discussion

3.1. Catechol detection in pristine BP sheet

We have considered a 2 × 2 × 1 supercell of BP containing 24 carbon atoms for all the calculations. The structure of BP comprises 4, 6, and 8 atoms of carbon rings, as presented in figure 1(a). The optimized lattice constants of the BP unit cell are a = 4.52 Å, and b = 3.75 Å, matching excellently with the reported literature values of 4.52 Å, and 3.76 Å [35]. We have obtained four different C–C bond lengths in the BP sheet, which have values of 1.452 Å, 1.446 Å, 1.459 Å, and 1.405 Å, consistent with the literature [35]. The unit cell of BP is presented in figure 1(b). To optimize the catechol molecule, we have placed it at the center of a cubic box with a lattice dimension of 20 Å, and geometry relaxation calculations are performed. The optimized structure of the catechol biomolecule is presented in figure 2(a). Here, we have performed DFT calculations within GGA approximations and DFT-D3 vdW corrections. People have also performed adsorption energy calculations of dopants by applying DFT along with the local density approximation and B3LYP functionals [11, 41, 42].

After optimizing the pristine BP and catechol molecule structure, the catechol molecule is placed at a 2 Å distance above the BP sheet at possible adsorption sites, and system is relaxed. The adsorption energy of the catechol molecule is calculated by using the following equation,

\[ E_{\text{ads}}(\text{catechol}) = E(\text{BP + catechol}) - E(\text{BP}) - E(\text{catechol}) \]

where \( E(\text{BP + catechol}) \) is the total energy of the BP + catechol system, \( E(\text{BP}) \) is the total energy of pristine BP sheet, and \( E(\text{catechol}) \) is the total energy of the catechol molecule. The maximum adsorption energy of the catechol molecule when it is placed above the hexagon is found to be ~0.35 eV, with C–O bond length of 3.32 Å. The relaxed structure of the BP + catechol system is presented in figure 2(b). The catechol adsorption energy for pristine VSe2 is reported to be ~0.25 eV by Chakraborty et al [41], and for pristine hGY, it is ~0.70 eV reported by Lakshmy et al [36]. We have performed the PDOS
Figure 1. Optimized structure of (a) 2 × 2 × 1 supercell of BP with different carbon–carbon bond lengths and possible adsorption sites. (b) Unit cell of BP. Here brown colour balls represent carbon atoms.

Figure 2. Optimized structure of (a) catechol molecule (b) catechol molecule attached to BP sheet at H2 site. Here brown, red and pink colour balls represent carbon, oxygen and hydrogen atoms, respectively.

3.2. Adsorption of transition metals (TMs) on pristine BP sheet

The adsorption energy of adsorbed biomolecule/gas on the host material is linked to the sensitivity of the sensing device such that the higher the adsorption energy, the better the sensitivity of the sensor [5]. Hence to elevate the sensitivity of pristine BP towards catechol, a suitable approach is to decorate the BP sheet with TMs. The TMs, including Ag, Au, Pd, and Ti having valence electron configuration 4d^{10} 5s^1, 5d^{10} 6s^1, 4d^{10}, and 3d^2 4s^2, respectively, are considered to decorate the BP sheet in this work. We have selected TMs of different d-series and having 1 and 2s-valence electrons for the thorough investigation of charge transfer. Although the metal (Ag/Au/Pd/Ti) decorated BP systems have not been fabricated, several noble metal-decorated nanomaterials are experimentally synthesized as an effective and low-cost sensor [43–45]. Metal decoration can be experimentally challenging and costly, however, in our proposed sensor the loading of metal atom is very small, so the designed sensor should be affordable for large scale synthesis. The possible adsorption sites for the decoration of TMs are H1, H2, H3, B1, B2, B3, and B4, as depicted in figure 1(a). To calculate the binding energy of the metal atom, the TMs are placed one by one at around a 2 Å distance above the all-possible adsorption sites, and each system is optimized. The optimized structures of Ti-decorated on the BP sheet at various adsorption sites are presented in figures S1(a)–(g). The

and Bader charge [37] calculations to study the charge transfer mechanism. The PDOS plots for C-2p orbitals and O-2p orbitals before and after the adsorption of the catechol molecule on a pristine BP sheet are presented in figure 3. When the catechol molecule is attached to the BP sheet, the states for the O-2p orbitals of the catechol molecule are depleted near the Fermi level (figure 3(d)), which signifies the charge loss from the O-2p orbital. Thus, the charge is transferred from the O-2p orbitals of the catechol molecule to the C-2p orbitals of the pristine BP sheet. From the Bader charge calculations, we found that a very less amount of charge 0.05e is going from the catechol biomolecule to the BP sheet. Hence, the adsorption of the catechol molecule on pristine BP is very weak, and the pristine BP may not be suitable for catechol detection.
following equation calculates the binding energy of the TM atoms on the BP sheet:

$$E_b(TM) = E(BP + TM) - E(BP) - E(TM)$$  \hspace{1cm} (2)$$

where $E(BP + TM)$ is the energy of the TM-decorated BP sheet, $E(BP)$ is the energy of the pristine BP sheet, and $E(TM)$ is the energy of the TM atom. The comparative study of binding energies of all the TMs, including their positions prior to and after the decoration on the BP sheet, is summarized in table 1. We found that the maximum binding energy for Ag atom is $-0.55$ eV at the H3 adsorption site, and for Au, it is $-1.18$ eV at the H3 site. When the Pd atom is placed above the H3 site, it moves to the H1 site after the relaxation, and the obtained maximum binding energy is $-1.90$ eV. In the case of the Ti atom, the maximum binding energy obtained is $-3.85$ eV at the B1 site, and at the H2 site, the binding energy is $-3.67$ eV, which is slightly smaller than the maximum binding energy. The binding energy of the Ag and Au atoms attached to the BP sheet is small, so we have not considered Ag and Au decorated BP sheets for the catechol adsorption.

To understand the electronic properties of pristine and metal decorated BP systems, we have plotted the total density of states (TDOS) for pristine BP, BP + Pd, and BP + Ti systems as presented in figures S2(a)–(c). From the TDOS plot, the BP is metallic, and when metal atoms are attached to a BP sheet, the states near the Fermi level slightly increase. Hence, metal decoration alters the electronic property of the BP sheet which is a crucial feature for sensing applications. The spin-up and spin-down channels are symmetric for BP + Pd system while asymmetric for the BP + Ti system; hence the structure became magnetic in the case of Ti-decoration. This is due to the presence of the unpaired d-electrons in the valence sector of the Ti atom.

To get a qualitative picture of charge transfer and understand the interaction between TM atoms and the pristine BP sheet, we have calculated the PDOS for C-2p orbitals and Ti-3d orbitals before and after the adsorption of the Ti atom to the pristine BP sheet, as shown in figures 4(a)–(d). When the Ti atom is attached to pristine BP, the states of the C-2p orbital get enhanced near the Fermi level, which can be seen in figure 4(b), signifying the charge gain by C-2p orbitals of the BP sheet. To get a more precise insight into charge transfer, we have plotted the PDOS for Ti-3d orbital for isolated Ti atom and BP + Ti system, as presented in figures 4(c) and (d). For an isolated Ti atom, there is an intense state, as shown in figure 4(c), and the intensity of states decreases when the Ti atom is attached to BP. The decrease in intensity of states signifies that the Ti atom is losing some charge when it is attached to BP. Hence the charge is transferred from Ti-3d orbitals to C-2p orbitals, and this charge transfer is the reason behind the strong binding of the Ti atom with the BP. We have also plotted the PDOS for the C-2p orbitals and Pd-4d orbitals before and after the adsorption of the Pd atom on the BP sheet,
presented in figures S3(a)–(d). From the PDOS plots, we can observe that when the Pd atom is attached to the BP sheet, some charge is transferred to the C-2p orbitals from Pd-4d orbitals.

After getting the qualitative idea of the charge transfer, we have performed the Bader charge calculations [37] to get the quantitative idea of charge transfer. We report that a total amount of 1.19e charge is transferred from Ti-3d orbitals to C-2p orbitals when the Ti atom is attached to the BP sheet, while a small amount of charge 0.27e is transferred from the Pd-4d orbitals to the C-2p orbitals of the BP sheet.

We have drawn the charge density difference plot to visualize the charge transfer process when the Ti atom is attached to the BP sheet, as displayed in figures 5(a) and (b). The charge density difference is plotted between Ti-decorated BP and pristine BP system, i.e., \( \Delta \rho = \rho_{BP+Ti} - \rho_{BP} \) for isovalue 0.07e. The B-G-R colour pattern is adopted to plot the charge density difference. In the plot, the red colour region near the Ti atom indicates the charge loss region, and the green and blue colour regions in the BP sheet indicate the charge gain regions. Hence from the charge density difference plot, the charge is transferred from Ti-3d orbitals to C-2p orbitals. The charge density difference between BP + Pd and BP, i.e., \( \Delta \rho = \rho_{BP+Pd} - \rho_{BP} \) is presented in figures 5(c) and (d) for isovalue of 0.134e. In this plot, the red colour region near the Pd atom represents charge loss region, and the green and blue color regions in the BP sheet represent the charge gain regions.

### 3.3. Catechol detection in TM-decorated BP sheet

We have discussed in the previous section that we will consider only BP + Pd and BP + Ti systems for the catechol detection. To investigate the adsorption of the catechol molecule in the TM-decorated BP system, the catechol molecule is placed around 2 Å above the TM atom, and the relaxation calculations are performed. The geometry optimized structures of BP + Pd + catechol and BP + Ti + catechol is presented in figures 6(a) and (b). The following equation estimates the adsorption energy of the catechol molecule attached to metal decorated BP sheets,

\[
E_{ads}(\text{catechol}) = E(\text{BP + TM + catechol}) - E(\text{BP + TM}) - E(\text{catechol})
\]

where \( E(\text{BP + TM + catechol}) \) is the energy of BP + Pd/Pd + catechol system, \( E(\text{BP + TM}) \) is the energy of Ti/Pd-decorated BP system, and \( E(\text{catechol}) \) is the energy of the catechol molecule. The catechol adsorption energies for BP + Pd and BP + Ti systems are obtained to be -1.00 eV and -2.54 eV, respectively. The Pd–O and Ti–O bond distances are 2.42 Å and 2.21 Å, respectively. Chakraborty et al [41] have reported the catechol adsorption energy of -0.95 eV for Pd-decorated VSe2. The catechol adsorption energy for Sc-decorated hGY is reported to be -3.22 eV by Lakshmy et al [36] using the first-principles DFT method. Ponnusamy et al

| System        | Initial position | Final position | Binding energy (eV) | C–metal bond length (Å) |
|---------------|------------------|----------------|--------------------|-------------------------|
| Biphenylene + Ag | H1               | H1             | -0.29              | 3.41                    |
| Biphenylene + Ag | H2               | H2             | -0.31              | 3.65                    |
| Biphenylene + Ag | H3               | H3             | -0.55              | 2.77                    |
| Biphenylene + Ag | B1               | B1             | -0.29              | 2.56                    |
| Biphenylene + Ag | B2               | Moved slightly towards H3 | -0.54              | 2.52                    |
| Biphenylene + Ag | B3               | Moved slightly towards H3 | -0.54              | 2.43                    |
| Biphenylene + Au | H1               | B2             | -0.85              | 2.37                    |
| Biphenylene + Au | B1               | H2             | -0.60              | 3.72                    |
| Biphenylene + Au | B2               | H2             | -1.18              | 2.17                    |
| Biphenylene + Au | B1               | B1             | -0.82              | 2.37                    |
| Biphenylene + Au | B2               | Moved slightly towards H3 | -1.18              | 2.17                    |
| Biphenylene + Au | B3               | Moved slightly towards H3 | -1.18              | 2.17                    |
| Biphenylene + Pd | H1               | H1             | -1.90              | 2.27                    |
| Biphenylene + Pd | H2               | H2             | -1.44              | 2.39                    |
| Biphenylene + Pd | H3               | H1             | -1.90              | 2.27                    |
| Biphenylene + Pd | B1               | H1             | -1.90              | 2.27                    |
| Biphenylene + Pd | B2               | H1             | -1.90              | 2.27                    |
| Biphenylene + Pd | B3               | B3             | -1.77              | 2.15                    |
| Biphenylene + Pd | B4               | B4             | -1.77              | 2.15                    |
| Biphenylene + Ti | H1               | H1             | -2.79              | 2.17                    |
| Biphenylene + Ti | H2               | H2             | -3.67              | 2.17                    |
| Biphenylene + Ti | H3               | H3             | -2.99              | 2.24                    |
| Biphenylene + Ti | B1               | B1             | -3.85              | 2.09                    |
| Biphenylene + Ti | B2               | B1             | -3.85              | 2.09                    |
| Biphenylene + Ti | B3               | B3             | -3.85              | 2.09                    |
| Biphenylene + Ti | B4               | B4             | -2.18              | 2.07                    |
[9] investigated the RGO-supported ZnO system experimentally and theoretically and obtained the catechol adsorption of $-4.09 \text{ eV}$. Lakshmy et al [7] reported the catechol adsorption energy of $-1.79$ and $-2.23 \text{ eV}$ for the MoS$_2 + \text{Pd}$ and MoS$_2 + \text{Ti}$ systems, respectively.

The changes in electronic structure properties in pristine BP and metal-decorated BP after the catechol adsorption are determined by the TDOS plots, which is presented in figures S4(a)–(c). For both the configurations, the states near the Fermi level are enhanced, which signifies that the catechol molecule attached to the BP + Pd and BP + Ti systems. Up and down spin states are symmetric for the BP + Pd + catechol system, whereas the spin states are asymmetric for BP + Ti + catechol system; hence the latter possess the magnetic attributes. The magnetic behaviour is due to unpaired 3d electrons in the Ti atom. The catechol adsorption energies and bond lengths on pristine and TM-decorated BP sheets are summarized in table 2.

The charge transfer mechanism is the central point of the sensing behaviour. So, to get a clear picture of charge transfer after the catechol adsorption on BP + Ti system, we have investigated the PDOS of outer shell orbitals. The PDOS is plotted for Ti-3d orbitals and O-2p orbitals before and after the adsorption of the catechol molecule to the Ti-decorated BP sheet and presented in figure 7. From figure 7(b), we can see the enhancement in states near the Fermi level compared to figure 7(a), which signify the transfer of charge to Ti-3d orbitals when the catechol molecule is attached to BP + Ti system. To get a clearer insight into charge transfer, we further calculated the PDOS for the O-2p orbitals of catechol, as presented in figures 7(c) and (d). Some intense states are present in PDOS for the O-2p orbitals of the isolated catechol molecule, as shown in figure 7(c). The intensity of these states decreases, and states near the Fermi level are depleted after the adsorption of the catechol molecule on the BP + Ti system, as seen in figure 7(d). These reductions in states signify the transfer of charge from O-2p orbitals of the catechol molecule to Ti-3d orbitals, and this charge transfer is the reason for the strong binding of catechol to the BP + Ti system. Furthermore, we have plotted the PDOS for the Pd-4d orbitals and O-2p orbitals before and after the adsorption of the catechol molecule on the BP + Pd system, as presented in figures S5(a)–(d). We may conclude from this PDOS plot that the charge is transferred from the O-2p orbitals of the catechol molecule to the Pd-4d orbitals of the BP + Pd system.

The sensitivity of a sensing substrate is related to the adsorption energy of the target molecule and the amount of charge transfer. Higher adsorption energy and a large number of charge transfers result in a strong chemical bond between the sensing substrate and the target molecule. From the Bader charge portioning, we found that the charge transfer amount from the catechol molecule is amplified to 0.10e for BP + Ti substrate, which was very less than 0.05e for pristine BP. For a pristine BP system, the catechol adsorption energy is very
weak (−0.35 eV), leading to low sensitivity toward catechol. The strong interaction between BP + Ti with catechol leading to high adsorption energy −2.54 eV and significant charge transfer of 0.10e which can transform into a detectable signal and enhance sensitivity toward catechol.

The charge density difference plot between BP + Ti + catechol, BP + Ti, and pristine BP, i.e. \( \Delta \rho = \rho_{\text{BP+Ti+catechol}} - \rho_{\text{BP+Ti}} - \rho_{\text{BP}} \), for the isovalue of 0.060e, is presented in figures 5(e) and (f). We have taken the B-G-R colour pattern to draw these plots where the red colour region on the catechol
molecule represents the charge loss region, while the green colour regions near the Ti atom represent the charge gain regions, respectively. Hence, the charge is transferred from the catechol molecule to the metal Ti atom.

### 3.4. Practical viability of the system

#### 3.4.1. Diffusion energy barrier calculations.

Metal clustering is a crucial issue for metal decorated nanomaterials that can reduce the sensing ability drastically. If the metal atom diffuses with ease from its adsorption site, then there is a huge possibility that the system may form the metal cluster. The experimental cohesive energy of the Ti and Pd atom is 4.85 eV/atom and 3.89 eV/atom, respectively [46]. The cohesive energy of the metal atoms is higher than the binding energies of $\approx 3.67$ eV and $\approx 1.90$ eV for Ti and Pd atoms, respectively. Thus, we have computed the diffusion energy barrier for the metal atoms by performing the climbing-image nudged elastic band (CI-NEB) calculations [47] to check the possibilities of the clustering of metal atoms into the BP sheet. We have calculated the energy barrier for the diffusion of the Ti atom from one hexagon site to the nearest hexagon site, while for the case of the Pd atom energy barrier is computed for the displacement along with one square site to the next square site as these are the most stable sites for the decoration of Ti and Pd atoms on BP sheet. The CI-NEB plots of the energy barrier versus diffusion coordinates for the movement of Ti and Pd atoms are presented in figures 8(a) and (b). The diffusion characteristics of doxorubicin on silica surfaces are studied by all-atom molecular dynamics simulation [48]. The authors have shown an analysis to calculate the diffusion coefficient from the classical Brownian motion equations. We have computed the diffusion energy barrier for the diffusion of metal atoms on the BP sheet by employing the standard CI-NEB method, which comes out to be $4.29$ eV and $2.39$ eV for the Ti and Pd atoms, respectively. There are various studies on the diffusion barrier of Ti and Pd atoms by applying CI-NEB method. For instance, Valencia et al [49] have studied the adsorption of Ti atom onto graphene surface and calculated the diffusion energy barrier of $0.74$ eV for the Ti atom. The diffusion barrier for the Ti atom on the MoS$_2$ surface is obtained at $5.96$ eV [7]. The energy barrier for diffusion of the Ti atom over the graphene flake is reported to be $3.42$ eV [50]. In divacancy defective graphene surface, the diffusion barrier of $5.82$ eV exists for the Ti atom [51]. The diffusion barrier of $1.04$ eV is found for the Pd atom on the graphene surface [52]. The energy barrier of $1.90$ eV for diffusion of the Pd atom is reported by Chen et al [53]. Our calculated energy barriers are comparable with these previous reports and large enough to restrict the clustering metal adatoms.

Moreover, the thermal energy of the metal atoms should also be smaller than the value of their diffusion energy barrier so that the system may remain prevented from clustering [54, 55]. We have calculated the thermal energy of the metal atoms by using the relation, $E = \frac{1}{2} k_B T$, where $E$ is the thermal energy, $k_B$ is the Boltzmann constant, and $T$ is the temperature. We have taken $T = 700$ K; the maximum considered temperature for the recovery time calculation. The obtained thermal energy of the metal atoms is to be $0.09$ eV. Thus, the computed energy barriers for the metal atoms are much higher than the thermal energy of the metal atoms, indicating that the metal atoms will remain attached to the BP sheet, and the metal decorated BP structures are prevented from metal-metal clustering.

#### 3.4.2. Stability of the structure at room temperature.

To investigate the stability of the metal-decorated BP system
at room temperature, we have performed the *ab-initio* molecular dynamic (AIMD) simulations. The metal-decorated BP systems are placed in the microcanonical ensemble (NVE) for a time duration of 5 ps, and the temperature is raised up to 300 K in a time step of 1fs. Then resultant system from the microcanonical ensemble is placed into the canonical ensemble (NVT) for a time duration of 5 ps. The final MD replications of the BP + Ti and BP + Pd systems at 300 K are depicted in figures 9(a) and (b), respectively. After the MD simulation, the Ti–C bond length changed to 2.52 Å, which was 2.17 Å before the MD simulation. Similarly, Pd–C bond length changes from 2.27 Å to 2.73 Å. So, we observe a minor modification in metal–C bond lengths; therefore, both systems are stable at room temperature.
Next, we have performed the AIMD simulations to check the integrity of the BP + metal (Pd, Ti) + catechol systems at ambient temperature. The final MD snapshots of BP + Ti + catechol and BP + Pd + catechol systems are presented in figures 9(c) and (d). After the MD simulations, we got that both the structures are stable at room temperature. In the case of BP + Pd + Catechol, the orientation of catechol molecules changes with the rise in temperature, but the catechol molecule remains intact with the Pd decorated BP system even at room temperature. We have also plotted the bond length fluctuations between the carbon atom of biphenylene and the oxygen atom of catechol for the BP + catechol system (C–O), as presented in figure 10(a). We found that the C–O bond length between catechol and pristine BP increases with the increase in temperature and becomes around 10 Å at 100 K. The C–O bond length remains more than 6 Å up to room temperature, indicating that the catechol molecule is desorbed from the pristine BP sheet even at the 100 K. Therefore, the pristine BP sheet is not suitable for catechol detection. Similarly, we have also plotted the Ti/Pd–O and Pd–C
bond lengths for the catechol adsorbed on metal decorated BP systems, as shown in figures 10(b) and (c). We have observed small thermal fluctuations in the Ti–O bond length, as shown in figure 10(b), indicating that the catechol molecule remains intact to the Ti-decorated BP even at room temperature. In the case of Pd-decorated BP, we noticed that the orientation of the catechol molecule changes after around 200 K. Therefore, we have plotted two bond lengths (Pd–O) and (Pd–C) atoms for the BP + Pd + Catechol system because when the orientation of catechol molecule changes the Pd–O bond length will increase, but the bond distance between Pd and the carbon atom of catechol will decrease, indicating that the catechol molecule is still attached to the Pd atom. The bond length fluctuations for the BP + Pd + Catechol system are displayed in figure 10(c).

3.5. Recovery time calculations

The recovery time is the possible time duration in which an adsorbed biomolecule is desorbed from its host material. The recovery time necessarily consigns the reusability of the sensing material or device. For the practical feasibility of the system, recovery time should be less at ambient temperatures. The recovery time for the catechol molecule is calculated by using the transition state theory [56],

\[ \tau = \vartheta^{-1} \exp \left( -\frac{E_b}{kT} \right) \]  \hspace{1cm} (4)

where \( \tau \) is the recovery time, \( \vartheta \) is the attempt frequency, \( E_b \) is the binding energy, \( K \) is the Boltzmann constant, and \( T \) is the temperature. We have calculated the recovery time for BP + catechol, BP + Pd + catechol, and BP + Ti + catechol systems at different frequencies and temperatures [7, 57]. To compare the recovery time of all systems precisely, namely, yellow light of frequency around 5.2 \times 10^{14} \text{ Hz} and UV light of frequency 1 \times 10^{16} \text{ Hz} are considered for the calculations.

In addition to that, three different temperatures of 300 K, 500 K, and 700 K are considered. The calculated recovery times for yellow and UV light at all different temperatures are depicted in table 3.

Although, the recovery time of pristine BP is minimum, but the catechol adsorption energy on pristine BP is very less such that the catechol molecule gets desorbed even at 100 K. Hence, pristine BP is not feasible for detecting the catechol molecule. If we look at the case of yellow light frequency and 300 K temperature, the recovery time of BP + Pd + catechol and BP + Ti + catechol is quite high (\( \sim 10^9 \)); hence their reusability will not be feasible. When the temperature is raised to 500 K, the recovery time for BP + Pd + catechol system is 900 milli-second for the yellow light and 47 milli-second for UV light, which is suitable for reusability. But the BP + Ti + catechol system has a very high recovery time even at 500 K for both the frequencies and therefore, we further raised the temperature to 700 K, at which the recovery time for BP + Ti + catechol system decreases significantly so that the system may become feasible for reusability. The recovery time of BP + Ti + catechol at 700 K is 8 min for yellow light and 25.2 s for UV light.

From the simulation results, an essential advantage of using the BP sheet as a catechol sensing material is its suitable catechol adsorption energy. It is apparent from the recovery time calculation that the catechol adsorption energy should not be

| System                  | Yellow light 300 K | Yellow light 500 K | Yellow light 700 K |
|-------------------------|--------------------|--------------------|--------------------|
| BP + catechol           | 1.4 × 10^{-9}      | 6.0 × 10^{-12}     | 6.2 × 10^{-13}     |
| BP + Pd + catechol      | 5.9 × 10^{9}       | 0.90               | 4.2 × 10^{-11}     |
| BP + Ti + catechol      | 5.1 × 10^{28}      | 2.3 × 10^{11}      | 4.8 × 10^{2}       |

| System                  | Yellow light 300 K | Yellow light 500 K | Yellow light 700 K |
|-------------------------|--------------------|--------------------|--------------------|
| BP + catechol           | 7.2 × 10^{-11}     | 3.3 × 10^{-13}     | 3.2 × 10^{-14}     |
| BP + Pd + catechol      | 3.1 × 10^{9}       | 4.7 × 10^{-2}      | 2.2 × 10^{-12}     |
| BP + Ti + catechol      | 2.6 × 10^{27}      | 1.2 × 10^{10}      | 25.2               |

| Host material          | Catechol adsorption energy (eV) | Maximum charge transfer | Recovery time at room temperature for visible light frequency (in seconds) |
|------------------------|---------------------------------|------------------------|--------------------------------------------------------------------------|
| hGY + Sc [36]          | −3.22                           | 0.9e                   | —                                                                         |
| MoS_{2} + Ti [7]       | −2.23                           | 0.10e                  | 5.59 × 10^{22}                                                          |
| MoS_{2} + Pd [7]       | −1.79                           | —                      | 2.26 × 10^{15}                                                          |
| VSe_{2} + Pd [41]      | −0.95                           | 0.08e                  | 11.8                                                                     |
| BP + Pd (present work) | −1.00                           | 0.15e                  | 5.9 × 10^{9}                                                            |
too high or too less. The previous study for catechol sensing on Sc embedded hGY system reports the catechol adsorption energy of $-3.22$ eV [36]. Although the large adsorption energy provides high sensitivity for catechol molecules, from a reusability point of view, it may lead to a very high recovery time and affect the reversibility of the system. The calculated recovery time for the MoS$_2$ + Pd system is $1.1 \times 10^2$ s at 500 K for UV light [7]. At the same condition, the recovery time for the BP + Pd system is 47 milliseconds. The sensing properties of various 2D materials for catechol detection are tabulated in table 4.

4. Conclusions

We have performed the first principles-based simulations to investigate the catechol detection properties of pristine and TM-decorated BP systems. We have selected Ag, Au, Pd, and Ti atoms for the decoration as they belong to different d-series and possess 1 and 2 s valence electrons. The adsorption energy of catechol molecule on pristine BP sheet is $-0.35$ eV, which gets improved to $-1.00$ eV, and $-2.54$ eV with the decoration of Pd and Ti-atoms, respectively. By performing molecular dynamics simulations, we found that the catechol molecule gets desorbed at around 100 K from the pristine BP sheet but remains intact at room temperature when pristine BP is decorated with Pd and Ti atoms. From the Bader charge portioning, we found that O-2p orbitals of the catechol molecule transfer 0.1e charge to Ti-3d orbitals upon catechol adsorption on the Ti-decorated BP sheet. We calculated the diffusion energy barrier by performing the CI-NEB calculations to study the formation of metal–metal clusters in metal-decorated BP systems. The systems may be protected from metal–metal clustering with high diffusion energy barriers of 4.29 and 2.39 eV for Ti, and Pd atom, respectively. The stabilities of the BP + Pd + catechol and BP + Ti + catechol systems at room temperature are verified by performing the first-principles MD simulations. We calculated the recovery time at different frequencies and temperatures to investigate the reusability of the metal-decorated BP systems for catechol detection and found that the recovery time of the Pd decorated BP sheet is optimum at 500 K. In comparison, it is suitable for Ti-decorated BP sheet at an elevated temperature of 700 K.

Data availability statement

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

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Conflict of interest

There are no conflicts to declare.

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