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Abstract

Development of next-generation sensors based on graphene materials, especially epitaxial graphene (EG) as the most promising representative, with desirable cross-reactivity to heavy metals (HMs) is of great technological significance in the virtue of enormous impact on environmental sensorics. Nevertheless, the mechanisms by which EG responds to toxic HMs exposure and then produces the output signal are still obscure. In the present study, the nature of interaction of toxic HMs, e.g. Cd, Hg and Pb in neutral charge state and EG on Si-face SiC in the absence and in the presence of pure water solution has been investigated using density functional theory with the inclusion of dispersion correction and cluster model of EG. The gas-phase calculations showed that adsorbed electron-donating Cd and Hg adatoms on EG are most stable when bonded to hollow sites, while Pb species prefer to sit above bridge sites. By using non-covalent interaction analysis, charge decomposition analysis, overlap population density of states analysis and topological analysis, it was found that the interaction between Cd or Hg and EG is non-bonding in nature and is mainly governed by van der Waals forces, while Pb adsorption is followed by the formation of anti-bonding orbitals in vacuum conditions and bonding orbitals in water. The role of solvent in the adsorption behavior of HMs is studied and discussed. The present theoretical analysis is in good agreement with recent experimental results towards discriminative electrochemical analysis of the toxic HMs in aqueous solutions at critically low concentrations.

Supplementary material for this article is available online

Keywords: epitaxial graphene, heavy metals, interaction, DFT, solvent

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

1. Introduction

There is a long-standing interest in the development of highly-sensitive solid-state nanomaterials for fast, reliable and discriminative analysis of toxic heavy metals (HMs) in drinking water [1–4]. Possessing unique properties (large surface-to-volume ratio, high signal-to-noise ratio, controlled dimensionality, huge adsorption capacity, short response time to external stimulus) [5, 6] such materials could ultimately be used as core components in novel detection methods, which will become alternatives to traditional bulky detection techniques (chromatography [7], mass spectroscopy [8]) towards real-time monitoring of HMs permanently present in common sources of potable water (rivers, lakes) [9–11]. Particular attention is devoted to the detection of Cadmium (Cd), Mercury (Hg) and Lead (Pb) as the most hazardous representatives of HMs group [12, 13].

Recent huge progress in study of the two-dimensional graphene and its derivatives as sensors [14, 15] indicates the unprecedented possibility to detect even individual molecules and adsorbates due to extremely high sensitivity of graphene conductivity to local charge-transfer events [16]. In this regard, efforts to approbate state-of-the-art graphene-based...
materials and existing sensing principles for HMs identification seem not to be so surprising [17, 18]. In our previous works [19–26], we have outlined the main fundamentals underlying the detection of Cd, Hg and Pb using free-standing graphene. It was shown that the size of graphene, its thickness, defects status, and edge termination significantly affect the adsorption energy of HMs as well as electronic and optical properties of the nano-sized graphene, enabling simultaneous/selective detection. Furthermore, the integration of graphene epitaxially grown on SiC (EG) into both electrochemical cell and microfluidic chip allowed us to identify the nanomolar concentrations of Cd [20, 26], which is in line with modern World Health Organization requirements to Pb in drinking water [27]. In addition, chronamperometry measurements and comprehensive Raman study supported by density functional theory (DFT) calculations provided critical information on Lead behavior on epitaxial graphene (EG) (initial kinetics, diffusion rate, adsorption nature) [20, 21]. The unique properties of EG as a transducer system implies its fast response to external stimulus with improved signal-to-noise ratio, enabling the detection and discriminative analysis of critically low concentrations of HMs. While there has been a rising interest in developing electrochemical and conductometric sensing platform based on EG, several important issues related to factors limiting the sensing performance still need to be addressed. Particularly, despite the adsorption behavior of Cd, Hg and Pb on free-standing graphene is well established, there exists almost no fundamental knowledge on the influence of the supported substrate (buffer layer-covered Si-face SiC in our case) on the behavior of HMs locally adsorbed onto graphene surface. Buffer layer is the name of the C-rich surface reconstructed SiC, which has the same geometry as graphene but is partly bonded to the substrate, i.e. is not decoupled. It might be that the total interaction energies are predominantly determined only by the topmost graphene layer in the complexed EG structure and the contribution of the buffer layer and SiC layers is minimal or even negligible. Nevertheless, several authors reported on the redistribution of the charge-carrier density at the interface between SiC and graphene [28, 29]. Intuitively, such charge redistribution implies irreversible changes in electron-accepting or electron-donating ability of the substrate supported graphene compared to that of the free-standing counterpart. Furthermore, van der Waals forces between the buffer layer and the topmost graphene layer may also affect the adsorption energy of HMs. In a recent work, Caffrey et al [30] have emphasized the important role of the SiC substrate in the adsorption of molecules on monolayer graphene. Altogether this suggests that the substrate effect can not be ruled out in predicting the adsorption behavior of the toxic HMs.

It is worth noting that commonly used approaches for detection of HMs imply recognition of the divalent cations, namely Cd\(^{2+}\), Hg\(^{2+}\), and Pb\(^{2+}\), which are most popular chemical forms of HMs existing in nature. Except in the oxidized form (HM\(^{2+}\)), HMs can also exist in two other chemical forms [31–34]: particulate-bound form (HM\(_p\)) and elemental HM\(_0\). Even though HM\(^{2+}\) and HM\(_p\) forms can be easily detected by means of traditional tools, the recognition and discrimination of elemental HM\(_0\) are still challenging tasks. The main reason complicating the detection of HM\(^{2+}\) is poor solubility/reactivity of neutral HM atoms in water/electrolyte solutions [35–37] and, as a result, their weak interaction with the majority of known sensitive materials. There is another important aspect of the interaction between neutral metals and EG that we should highlight as a key stage of electrochemical detection of HMs by using anodic stripping voltammetry (ASV) technique. Particularly, ASV measurements consist of two stages. The first stage in the detection process is so-called preconcentration step, when divalent metals cations first adsorb on the inert EG surface and then they readily reduce to their zero oxidation states (elemental HM\(_0\)) at a specific potential. Reduced metal absorbates cover the electrode surface, causing the charge transfer to graphene layer. During the second stage—stripping step—accumulated metal species re-oxidize to HM\(^{2+}\) form and diffuse from the electrode to bulk solution/electrolyte. In this case, metal adatoms lose two electrons, facilitating the generation of the stripping current. It is obvious that there is a direct relationship between the resulting stripping current and the concentration of the adsorbed metal species: larger number of the metal ions plated at the electrode surface as neutral metal species will lead to a higher stripping peak current. Taking the abovementioned into account, it is reasonable to assume that the preconcentration step primarily determines the response of EG towards HMs exposure. Therefore, a fundamental knowledge about the solvent-mediated interaction between EG and elemental HMs is a cornerstone for understanding the nature of the HMs detection by EG at the atomic level.

Due to a lack of available benchmark data on adsorption of HMs on EG, it is indubitably important to mimic realistic sensing conditions, considering as many influential factors as possible (especially the surrounding dielectric medium and substrate effects). Such complex approach is anticipated to be a more effective way to predict the correct adsorption order/priority for different HMs than exploiting free-standing graphene in vacuum as a sensor model. A holistic understanding of the EG structural changes under HMs exposure and physics underlaying the sensing mechanisms may bring innovative and creative solutions for signal processing, improvement of detection limit, and enhancement of selectivity.

Here, we extend our previous discussion on the interaction between free-standing graphene and HMs to cover the case of adsorption of Cd, Hg and Pb on EG immersed in water. For the first time, we comprehensively study the EG–HMs bonding nature through performing extended charge decomposition analysis (ECDA), non-covalent interaction (NCI) analysis, overlap population density of states (OPDOS) analysis and topological analysis. The obtained results allow us to shed light on the solvent-mediated adsorption of neutral metal species onto EG surface and to link the calculated adsorption characteristics with experimental sensing performance.

2. Computational details
The interaction between HMs in neutral charge state (Cd, Hg and Pb) and EG on Si-face 4H-SiC has been investigated based on hybrid gas-phase and solvated density-functional
theory calculations performed by using Gaussian 16 Rev. B.01 program package [38]. To represent the EG surface, we have used a cluster model as a basic structure. In brief, our cluster consists of 4 × 5 first graphene layer located above 4 × 5 buffer layer on 4 × 4 Si-face surface of hexagonal SiC. It is important to note that at least 26% of carbon atoms belonging to buffer layer is covalently bonded to SiC surface, forming $sp^3$ bonds. Thus, the present chemical environment is similar to the respective experimental observation [39, 40], according to which one third of the carbon atoms in the buffer layer is $sp^3$-hybridized. To avoid a high concentration of the dangling bonds at the carbonized SiC surface, in buffer layer optimization of Cd, Hg and Pb species located on EG adsorption of HMs was simulated by full geometrical thermore, since electrochemical detection of HMs is pre-

However, since we consider the adsorption of individual metals at adsorption sites on graphene surface, one can argue that output signal from graphene after metal adsorption depends on the density of surface electroactive sites in a stronger manner than on intrinsic properties of graphene. The adsorption of HMs was simulated by full geometrical optimization of Cd, Hg and Pb species located on EG (the details of optimization procedure are presented in supplementary information, see figure S1 is available online at stacks.iop.org/NANO/30/294002/mmedia), with the same initial Cartesian coordinates and with self-consistent field convergence criterion of $10^{-8}$. All calculations were carried out without symmetry restrictions, but in such a way as to make possible the comparison of the adsorption behavior of different metals. In ideal, the adsorption of HMs on EG should be modeled by using the periodic boundary conditions calculations to avoid the edge effect on the metal binding. However, since we consider the adsorption of individual atoms, using the cluster model is believed to be an effective approach to describe adequately the local adsorption phenomena. All the calculations were carried out using PBE1PBE-D3 level of theory [41, 42] with consideration of split basis set and empirical dispersion correction, which was included as Grimme’s dispersion term [43]. In other words, dispersion-corrected DFT functional PBE1PBE includes explicitly London forces, thereby allowing a prediction of the weak van-der Waals forces. 6-31G basis set was used for carbon, silicon and hydrogen atoms, while basis set developed by the Stuttgart–Dresden–Bonn group (SDD) was utilized for the HM species [44]. The self-consistent reaction field method combined with the polarizable continuum model was chosen to study the effect of water medium on the complexation between HMs and EG [45]. To get deep insights into charge distribution within EG structures interacting with HMs, we performed Mulliken population analysis [46] and Hirshfeld analysis [47]. To better understand the role of the van-der-Waals (vdW) interaction in adsorption of HMs, NCI and topological analyses were carried out using Multiwfn program [48]. Quantum theory of atoms in molecules method [49] and extended charge transfer analysis (CDT) scheme implemented in Multiwfn program [50] were also applied to investigate the nature of metal-EG bonding and orbital interaction for all considered complexes. To shed more light on the interaction between EG and metallic adsorbates, OPDOS were calculated and analyzed.

To estimate the energetics of the interacting complexes, we calculated the adsorption ($E_{\text{ads}}$), interaction ($E_{\text{int}}$) and deformation ($E_{\text{def}}$) energies by the following relationships:

$$
\begin{align*}
E_{\text{ads}} &= (E_{\text{tot}}^{\text{iso}} - E_{\text{tot}}^{\text{EG}}) - E_{\text{rel}}^{\text{HM} \oplus \text{EG}} \\
E_{\text{int}} &= (E_{\text{tot}}^{\text{iso}} - E_{\text{tot}}^{\text{EG}}) - E_{\text{rel}}^{\text{HM} \oplus \text{EG}} \\
E_{\text{def}} &= E_{\text{int}} - E_{\text{ads}}
\end{align*}
$$

where $E_{\text{tot}}^{\text{iso}} - E_{\text{tot}}^{\text{EG}}$ is the total energy of the EG after complexation with HMs, $E_{\text{rel}}^{\text{HM} \oplus \text{EG}}$ are the total energies of non-relaxed isolated HM species and EG, respectively. While $E_{\text{rel}}^{\text{HM} \oplus \text{EG}}$ are the total energies of the HM species and EG in the relaxed geometry. Counterpoise correction for basis set superposition error [51] was considered for accurate calculation of the adsorption/interaction energy. The adsorption height of HM adatom on EG defined was determined the difference between the $z$ coordinate of the HM adatom and the average value of the $z$ coordinates of neighboring C atoms in graphene plane (more details can be found in supplementary information).

3. Results and discussion

First, the structures composed of EG and metal adsorbates (Cd, Hg, and Pb, respectively) were optimized in the gas phase. As can be seen from figure 1, Cd and Hg adatoms tend to occupy hollow sites (center of the hexagonal ring in honeycomb structure), while Pb adatom prefers to be adsorbed above the bridge site (center of C–C bond). As we have shown previously for adsorption of HMs on free-standing nanosized graphene [23], these reactive sites are the most stable ones. One can argue that BL-covered SiC substrate, which supports a graphene cluster does not affect significantly the type of the most favorable binding site in the vacuum conditions. The binding height of the metal adsorbates decreases gradually in the order of Cd $>$ Hg $>$ Pb. In particular, the height of the Cd and Hg are found to be 3.10 and 3.05 Å, while the height of the Pb adatom is equal to 2.59 Å. From the fundamental point of view, such a difference can be understood in terms of both atomic size dependence and difference in electron-donating ability. Then, by using equation (1) we have determined the main adsorption characteristics (adsorption energy, interaction energy and deformation energy) and made a comparative charge transfer analysis for all considered structures. The results are given in table 1. Binding to EG increases in the order Cd $<$ Hg $<$ Pb.
and is followed by increasing metal-to-EG charge transfer in the same order. It can be explained by the fact that Pb donates electrons to EG more easily than Cd and Hg adatoms. Since the ionization potential of Pb is approximately equal to 7.41 eV \[52, 53\], which is much lower than the ionization energies of 8.99 eV and 10.43 eV for Cd and Hg, respectively \[53\], an enhanced charge transfer from Pb to EG is observed. In addition, the interaction/adsorption energy of Pb is higher than the chemisorption limit (generally such limit is considered to be equal approximately to \(\sim 0.5\) eV). Although, there is general consensus on the charge transfer magnitude and direction determined by both Mulliken analysis and ECDA method, Hirshfeld charge analysis gives slightly different results for some adsorption configurations, especially regarding the charge transfer direction between Cd/Hg and EG. Nevertheless, we believe that the charge transfer in those cases makes a minor contribution to the total interaction energy compared to the contribution of the dispersion forces and can be, therefore, ruled out as a main driving force of the complexation. In other words, the physisorption mechanism of Cd and Hg species onto EG surface under gas-phase conditions is mainly governed by van der Waals interaction. As was mentioned before, we estimated both adsorption and interaction energies. The difference between them can be used as an energy, which is required to deform the EG structure during the adsorption of metallic adsorbates. According to our estimations, this energy is very small for Cd and Hg adsorption. In this case, EG undergoes no observable deformation. On the other hand, this parameter was found to increase to 0.18 eV for Pb adsorption, implying that larger energy penalty needs to be paid to accommodate neutral Lead adatom onto the EG surface. One can argue that the chemisorption of Pb occurs by involving additional driving forces underlying the complexation between EG and Pb. It is important to note that the distance between the metals adatom and EG surface decreases with increasing the atomic number in the periodic table, which is consistent with the adsorption energy trend. Indeed, the adsorption height is inverse proportional to the adsorption energy. Similar trend was found for the adsorption of metals on free-standing graphene \[54\].

Table 1 also reports the calculated adsorption and interaction energies for metal adsorbates complexed with EG in the solvent (water medium). Similar to gas phase calculations, the adsorption and interaction energies for Cd and Hg are lower than the physisorption limit, indicating that the van der Waals force is a key factor, which regulates the adsorption of Cd and Hg species onto EG immersed in pure water solution. Nevertheless, solvent changes the binding sites from hollow sites to bridge/on-top sites and gives rise to increase in adsorption/interaction energies. Indeed, when the bridge sites become more energetically favored only two/one carbon atoms, instead of six for hollow site adsorption, are involved in the binding process. Therefore, due to the fact that Cd and Hg share their electrons with smaller number of C atoms the interaction/adsorption energies in comparison

| HM | Adsorption energy, eV | Interaction energy, eV | Deformation energy, eV | Charge on atom |
|----|----------------------|-----------------------|-----------------------|----------------|
|    | Gas | Water | Gas | Water | Gas | Water | Gas | Water | Gas | Water |
| Cd | 0.217 | 0.293 | 0.223 | 0.302 | 0.005 | 0.008 | 0.23 | 0.07 | -0.07 | 0.02 | 0.08 | 0.07 |
| Hg | 0.246 | 0.384 | 0.252 | 0.394 | 0.005 | 0.010 | 0.26 | 0.08 | -0.01 | 0.03 | 0.15 | 0.08 |
| Pb | 0.641 | 1.57 | 0.827 | 0.533 | 0.185 | -1.037 | 0.45 | 0.11 | 0.22 | -0.01 | 0.45 | 0.11 |

Figure 1. Side view and zoomed top view of the gas-phase relaxed adsorption configurations of Cd (a), Hg (b) and Pb (c) on epitaxial graphene surface.

Table 1. Parameters describing the behavior of elemental heavy metals adsorbed onto epitaxial graphene surface in the absence of water and in the presence of water.
with the gas phase have been increased. Deformation energies for these two structures are slightly higher than the gas-phase values. The last adsorption configuration we have examined is the Pb adsorption. The preferred binding site in the presence of water has a certain similarity to the gas-phase environment, but we noticed a solvent-mediated decrease in the interaction energy from 0.827 to 0.533 eV, which is in good agreement with the decrease in the charge transfer magnitude \((\text{table 1})\). Nevertheless, some important difference still exists. In particular, the adsorption energy of Pb in water becomes much higher in comparison to gas-phase value, which can be explained by solvent-induced deformation of EG interacted with Pb. This is evidenced by the large deformation energy.

To get deeper insights into the nature of the interaction between HMs and EG, we have also examined the OPDOS spectra (figure 2). It is worth noting that the sign of the OPDOS can indicate the type of the interaction (bonding, anti-bonding and non-bonding). In particular, the positive and negative values of OPDOS point out to a bonding and anti-bonding interaction, respectively \([55, 56]\). While the zero value of OPDOS suggests a dominant role of the non-bonding interaction in the complexation between adsorbates and a surface \([55, 56]\). Since only the nature of the frontier molecular orbitals and lowest energy levels of the interacting complexes mostly determines the strength of the interaction, we are mainly interested in understanding the OPDOS features in the energy range from \(-3\) to \(0\) eV (which is near the Fermi level). A closer look at this region (figure 2(a)) indicates that the Pb adatom significantly contributes to the formation of frontier orbitals, which is confirmed by the presence of the intense anti-bonding OPDOS peak. Another observation is that the energy levels of Cd and Hg adsorbates do not participate in the formation of the highest and lowest orbitals of complex, which is evidenced by the zero overlap population in the considered region. It is obvious that the anti-bonding OPDOS peaks for these two metals are observed only within the regions, which are far from

![Figure 2. Overlap population density of states (OPDOS) for epitaxial graphene interacted with elemental heavy metals under gas-phase conditions (a) and in the presence of water solution.](image-url)
the Fermi level and Cd (Hg) only contributes to deeper-lying molecular orbitals. The most important finding is that the pure water solution has considerable effect on the OPDOS spectra of the interacting complexes. For example, while in the gas phase OPDOS features for all three metals demonstrate mostly anti-bonding character, their nature undergoes conversion from anti-bonding to bonding due to the solvent effect (figure 2(b)). It can be explained by changes of the nature of the hybridized molecular orbitals of the complex. Nevertheless, the overlap population near the Fermi level region is non-zero only for Pb adsorption, while the adsorption of the Cd and Hg remains non-bonding in nature.

To shed more light on the orbital interaction in HMs–EG complex, we performed charge decomposition analysis (CDA). The results are presented in figure 3 only for Pb adsorbrates on EG, since no orbital interaction is observed for Cd and Hg species. Whenever the Lead adsorption happens, the strong orbital interactions between the highest occupied and degenerate unoccupied levels of Lead adatom (HOMO, LUMO, L + 1) and the orbitals of EG occurs under gas phase conditions (figure 3(a)). The solvent weakens this orbital interaction (figure 3(b)), which is accompanied by a decrease in the interaction energy and charge transfer magnitude (table 1). This finding suggests that the independently of the dielectric media the adsorption of Cd and Hg on EG is driven by weak long-range van der Waals forces, while the bonding between Lead and EG is governed by orbital interaction.

We have also performed NCI analysis for all considered adsorption configurations. The results are shown in figure 4. It is clearly seen that the NCI iso-surfaces (at constant reduced density gradient, RDG = 0.5) for Cd and Hg species adsorbed onto EG are characterized by the presence of green-colored non-bonding interaction region, which is located at the center of the hexagonal ring (figures 4(a) and (b)). It may originate from the presence of ring critical points (RCPs) with vanishing density gradient. More complicated picture is observed for EG interacted with Pb (figure 4(a)). More specifically, there is a competitive contribution of different components to the total interaction energy: steric repulsion (red color), strong attraction (blue color) and vdW interaction (green color). Consideration of the solvent effect in the calculations slightly modifies the NCI iso-surfaces (figure 5), causing the redistribution of the non-bonding interaction green-colored region in the case of the Cd and Hg adsorption (due to change of the binding site) and a decrease of the attractive interaction for Pb adatom on to EG surface.

To better understand the nature of bonding, topological properties of critical points describing the interaction between EG and HMs were examined. Corresponding topological parameters of bond critical points (BCPs), RCPs and cage critical points (CCPs) are listed in table 2. The aforementioned discussions suggest that the adsorption sites determine the type of critical points. In particular, we noticed the absence of the RCPs and CCPs for Pb adsorption under gas-phase conditions and for all metals on EG immersed in water. We have identified that the electron density $\rho$ at BCPs is the highest for the Pb–C bonds. Laplacians of the electron densities are positive for all metals, indicating weak interaction of HMs with EG, except Pb. The relationship between potential energy density, $V(r)$, and Lagrangian kinetic energy density, $G(r)$, can be considered as an additional indicator of the bond type. Our data suggest that the $-V(r)/G(r)$ ratio is smaller than 1 for Cd–C and Hg–C bonds (RCPs and CCPs), while this ratio reaches much higher values for BCPs describing the Pb–C bonding. This implies that the interaction between Cd and Hg with EG is non-bonding in nature, while Pb–C exhibits much stronger chemical bonding (weak chemisorption). It is also confirmed by the negative value of the energy density, $H(r)$, and the higher values of electron localization function and localized orbital locator. Therefore, topological analysis also indicates that the adsorption of Cd and Hg onto EG is regulated by long-range dispersion forces, while the

Figure 3. Orbital interaction diagrams determined using CDA analysis for two considered cases: (a) neutral Lead adatom adsorbed on epitaxial under gas-phase conditions and (b) neutral Lead adatom adsorbed on epitaxial in the presence of water. Occupied and empty molecular orbitals are represented as solid and dashed lines.
orbital interaction is responsible for the Pb–C bonding formation.

Let us discuss the obtained results with two possible sensing approaches related to detection of HMs: (i) electrochemical detection and (ii) conductometric detection. In the first case, the sensing performance is strongly dependent on the redox potential of each metal and the electron transfer kinetics at the EG electrode surface. If the electron transfer kinetics is fast, the equilibrium redox reaction causes generation of the stripping current even at low concentrations of metal species in aqueous solution. Taking our results into account, one can assume that the electron transfer rate for Pb on EG will be higher than for Cd and Hg on EG. This means that the sensitivity to Pb at low concentrations will be better than to Cd and Hg. Nevertheless, due to the unique redox behavior of each metal three clearly separated stripping peaks occur, making the simultaneous detection of Cd, Hg and Pb possible at moderate and high concentrations. Considering the second approach, it is obvious that the sensing mechanism will be regulated by EG resistance changes induced by the adsorption of elemental HMs. Earlier it was argued that graphene is very sensitive to external adsorbates, enabling detection of changes in a local concentration by less than one electron charge [16]. Despite the minimal charge transfer
Table 2. Results of topological analysis for critical points (CPs), which describe the interaction between elemental heavy metals and epitaxial graphene under gas-phase conditions and in the presence of pure water solution (values in the brackets). Three different types of the CPs namely bond critical points (BCPs), ring critical points (RCPs) and cage critical points (CCPs) are considered for each adsorption configuration.

| Topological parameters | Critical points | Critical points | Critical points |
|------------------------|-----------------|-----------------|-----------------|
|                        | (3, -1) BCP     | (3, +1) RCP     | (3, +3) CCP     |
|                        | Cd              | Hg              | Pb              | Cd              | Hg              | Pb              | Cd              | Hg              | Pb              |
| \( \rho(r) \)         | 0.0118 (0.0125) | 0.0122 (0.0130)| 0.0382 (0.0299)| 0.00798 (--)| 0.0102 (--)| 0.00759 (--)| 0.00873 (--)|          |
| \( \nabla^2 \rho \)    | 0.0287 (0.0282)| 0.0334 (0.0330)| 0.0895 (0.0764)| 0.0218 (--)| 0.0287 (--)| 0.0273 (--)| 0.0341 (--)|          |
| \( K(r) \)            | 0.0000653 (0.000197)| -0.000129 (-0.000619)| 0.00523 (0.00305)| -0.000249 (--)| -0.000205 (--)| -0.000466 (--)| -0.000492 (--)|          |
| \( G(r) \)            | 0.00724 (0.00725)| 0.00822 (0.00819)| 0.0155 (0.01333)| 0.00521 (--)| 0.00699 (--)| 0.00637 (--)| 0.00805 (--)|          |
| ELF                    | 0.0558 (0.0670)| 0.0489 (0.0606)| 0.312 (0.2144)| 0.0298 (--)| 0.0378 (--)| 0.0171 (--)| 0.0170 (--)|          |
| LOL                    | 0.195 (0.2111)| 0.185 (0.202)| 0.382 (0.328)| 0.149 (--)| 0.165 (--)| 0.116 (--)| 0.116 (--)|          |
| \( V(r) \)            | -0.00731 (-0.00744)| -0.00809 (-0.00813)| -0.0207 (-0.0164)| -0.00496 (--)| -0.00678 (--)| -0.00591 (--)| -0.00756 (--)|          |
| \( H(r) \)            | -0.0000653 (-0.000197)| 0.000129 (0.000619)| -0.00523 (-0.00305)| 0.000249 (--)| 0.000205 (--)| 0.000466 (--)| 0.000492 (--)|          |
| \( -V(r)/G(r) \)      | 1.01 (1.02)| 0.98, 098 (0.99)| 1.33 (1.23)| 0.95 (--)| 0.96 (--)| 0.92 (--)| 0.93 (--)|          |
observed in our work, one can still anticipate EG conductivity changes after metal adsorption. It is important to note that Cd and Hg adatoms are always physisorbed on the EG independently of the medium type, while the interaction between Pb adatoms and EG can be attributed to a weak form of chemisorption. This finding is in good agreement with generally accepted chemisorption limit, according to which the equilibrium distance between the metal adsorbate and EG must be shorter than 3 Å, while the interaction energy has to be higher than 0.5 eV. Keeping this in mind, it is reasonable to assume that the charge transfer from HMs to EG will dominate the electron transport in the EG only in the case of Pb chemisorption, whereas physisorbed Cd and Hg species can be regarded as impurities acting as Coulomb scattering centers that limit the transport through EG. Indeed, Sun et al. [57] proved that large adsorbates captured by suspended graphene through van der Waals interaction can be detected as a step-like resistance change. This suggests the principal possibility to identify the presence of the Cd, Hg, and Pb species dissolved in water, with preferential sensing and response to Pb species. Knowledge of the adsorption characteristics also enable to predict the recovery time of EG-based sensors. There is a fundamental relationship between recovery time and adsorption energy, which can be represented as follows [58]:

\[
\tau = \frac{1}{\nu_0} e^{-E_{ads}/\hbar k_B T},
\]

where \(\nu_0\) is the attempt frequency, \(k_B\) is the Boltzmann constant, and \(T\) is the temperature. It is obvious that the recovery time \(\tau\) increases with the increasing adsorption energy \(E_{ads}\). According to our estimations, Cd on EG will have the shortest recovery time followed by Hg and Pb.

It is important to note that the present results are in good agreement with experimental findings. Indeed, as was shown in our previous work by using anodic stripping voltammetry (SWASV) technique [20, 59], EG as a working electrode exhibits a very intensive stripping peak current for Lead species with sensitivity as high as \(2.3 \times 10^3\) A cm\(^{-2}\) mole\(^{-1}\) and good linearity over a concentration range from 1 nM to 1 \(\mu\)M. Furthermore, it was revealed that the sensitivity of EG towards Pb was much better than that to Cd and Hg. Such a difference can be definitely explained by the different accumulation ability of the metals on EG surface, which is governed by interaction strength in the complex composing of EG and HMs. The higher interaction energy causes the larger accumulation ability and enhanced electrochemical response of EG.

4. Conclusions

In this study, we presented vdW-corrected DFT investigation of the interaction between monolayer EG on (0001) SiC and toxic HMs (Cadmium, Mercury, Lead) in neutral charge state. It is noteworthy that using homogeneous graphene monolayers on SiC is imperative to design high performance sensors enabling single HM adatom detection. Our results indicate that the adsorption of electron-donating Cd and Hg species on the hollow sites of the EG under vacuum conditions is predominantly governed by long-range intermolecular forces, while the most favorable adsorption configuration of Lead is found to be above the bridge site. Such adsorption configuration and high electron-donating ability of Lead cause strong orbital interaction, which is evidenced by enhanced values of topological parameters for BCPs, formation of the hybridized frontier orbitals in interacting complex, and observation of the anti-bonding OPDOS feature near to Fermi level. We revealed that both adsorption characteristics of the HMs and nature of the interaction between metals and EG are strongly affected by the solvent. In particular, water solution changed the preferred binding site of Cd and Hg adatoms from hollow site to bridge and on-top sites, respectively. The dispersion forces are expected to be the dominant factor in the interaction between EG and Cd/Hg. It was predicted that the solvent weakens the interaction energy of Pb and changes the nature of the interaction from antibonding to bonding.

Non-bonding character of the interaction of EG with cadmium and mercury points to slow rate charge transfer reactions at the electrode surface and, as a result, a weak electrochemical signal is expected in the low concentration regime. Rather, our theoretical results suggest that physisorbed Cd and Hg species can be regarded as massive Coulomb scattering centers influencing the carrier transport through graphene. In this regard, HMs identity may be determined by the unique shape of the output conductometric signal. In contrast to the Cd and Hg, the interaction of the elemental Lead with EG remains its bonding nature even in water solution, thereby implying fast charge-transfer reactions at extremely low Pb concentrations and enabling reliable and real-time Pb identification by unique reduction-oxidation peaks. A comparison of the interaction mechanisms that underly the EG response to single HM adatoms suggests an exclusive selective reaction towards Pb species as the most feasible scenario of the EG-based sensor operation under simultaneous presence of three considered metals. This study allowed to uncover the nature of bonding between individual HMs and EG under realistic conditions, thereby facilitating a better understanding of the sensing mechanisms and promoting conceptualization of sensors of HMs.

The present results have a significant importance because of their fundamental relevance to sensing applications, especially to electrochemical discriminative analysis of HMs in drinking water. Moreover, they clearly support and explain in detail our experimental results of electrochemical sensing of Pb by EG, which shows much stronger signal than that of Cd and Hg.

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