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The first-principles study on electronic transport mechanism in palladium decorated graphene

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ABSTRACT

Inert gases, despite various uses and industrial applications, may cause asphyxiation, so their detection and monitoring are essentially needed. However, the preparation of inert gas sensors is challenging due to the inactive chemical nature of these gases. This work was carried out to investigate the transport properties of inert gas sensors based on palladium-clusters-decorated-graphene-sheets (Pd-Gr) using Density Functional Theory (DFT) based methodology. The sensors comprising Pd clusters Pdₙ (n = 2-5) decorated graphene were simulated to investigate the structural stability, adsorption, sensitivity, and electronic characteristics. The transport properties were studied using current-voltage (I-V) curves obtained via non-equilibrium Green’s function (NEGF). The current appeared small at the start due to higher electrical resistance caused by charge transfer due to the adsorption of inert gases on the sensors. However, a voltage-dependent increase in the current took place afterward. The values of the resistance are found sensitive to the adsorption of the inert gases onto the sensors which helped to detect the gases. The energy difference of frontier molecular orbitals contributing to the conduction exhibited different responsive voltages which helped to points to the gas being adsorbed on the sensor. The findings of the work revealed that Pd₂ sensors are sensitive towards xenon and neon, Pd₃ and Pd₄ are suitable for the detection of krypton and helium respectively whereas the Pd₅ sensor is more appropriate for sensing argon and radon gases.
Keywords: Pd clusters; Graphene; Density Functional Theory; Inert gas sensor; NEGF

1. Introduction

Gas sensors are basically used to detect organic and hazardous gases in the human environment [1,2]. The sensors are useful in plenty of domains such as reducing pollution, defense purposes, civil safety, agriculture, industries, and pharmaceutical identification [3]. The functioning of the sensors relies on the materials involved such as semiconducting metal oxides [4-9], conducting polymers [10-18], and carbon nanotubes (CNTs) [19-25] which have been employed for gas identification [26]. The metal oxides have been frequently used due to their benefits of high sensitivity and low cost but these suffer from some serious drawbacks which include high pressure and temperature, a high power requirement, and low affinity [27]. The conducting polymers are easy to synthesize and can function at room temperature, but their incorporation into sensing devices is still constrained due to humidity effects and deterioration. Although carbon nanotubes have exceptional sensitivity and operate at room temperature their applications are still limited by their lengthy recovery times and intricate processing. Hence, the preparation of new gas-sensing materials which can operate at low temperatures and offer high sensitivity is at the heart of current research activities.

The principle of gas sensing and relevant techniques are categorized on the basis of differences in the electronic properties of the materials involved [28]. The detecting techniques are based on electronic fluctuation in the hosts such as metal oxide semiconductors, polymers, carbon nanotubes, and moisture absorption devices [29-31]. The technique based on other properties includes optical, calorimetric, auditory, and chromatographic changes in the materials upon detection of the gases. The two-dimensional (2D) nano-devices attracted a lot of research interest in gas detection because of their surface-to-volume ratio and gas adsorption properties [32]. The gas-identifying abilities of these materials have been abundantly predicted on the basis of theoretical investigations. The detecting mechanisms of 2D materials-based devices, from the perspective of theoretical calculations, include analysis of charge transfer and criterion for difference between chemical and physical adsorption [33-35].

The transfer of electric charge from the reactive species to sensing material is the main idea behind gas sensing where the host acts as a donor or acceptor. The sensing material's electrical
characteristics change due to this charge transfer. When oxidizing or reducing gases are present, for instance, an n-type (electron donor) sensing material experiences an increase in electrical resistance [36-40]. The opposite is demonstrated with p-type materials or electron acceptors. The devices for sensing gas are structurally based on field effect transistors (FETs) [41-47]. The sensing material in these devices is placed between the drain and source electrodes, which receive constant voltage power. The gas is detected by keeping track of variations in the electric current's value between the gate and the source as a consequence of a gas's exposure [48]. The main performance indicators for a gas sensor are durability, stability, quick response, selectivity, susceptibility, and recovery time. The 2D materials have the main advantage of making it simple to add catalytic materials, which can improve gas absorption and improve the properties of the gas sensor. Graphene has outstanding adsorption properties due to its vast surface area in this respect. However, we cannot use pristine graphene for sensing materials due to its zero bandgap. That’s why doping, decorating, or other band gap engineering strategies are often utilized to tune the band structure of graphene.

This work is carried out using a DFT-based methodology for designing inert gas sensors. The structures studied herein comprised pristine graphene, vacancy defect containing graphene, Palladium (Pd) clusters of different sizes, Pd clusters decorated defected graphene, and inert gases adsorbed Pd clusters-decorated-graphene (Pd\textsubscript{n}-Gr) sheets. The Pd\textsubscript{n}-Gr sheets (with n = 2-5) are the proposed inert gas sensors whose transport properties are comprehensively studied using a methodology based on non-equilibrium Green's function.

2. Computational Details

The electronic transport properties of the proposed inert gas sensors are thoroughly examined in this work. The entire calculations were carried out using a linear combination of atomic orbitals (LCAO) method implemented in BAND and DFTB modules of the Amsterdam Density Functional (ADF) package. The input was set up using the graphical user interface (GUI) and calculations under periodic boundary conditions were performed. The ADF creates the molecular orbitals using the built-in Slater-type orbitals (STO) to model atomic basis. To establish the exchange correlation between electrons the level of theory employed consisted of a TZ2P basis set and hybrid functional B3LYP. To incorporate all electron interactions, the frozen core was set to none and relativistic
effects were into account with spin-orbit coupling. The energy convergence criteria of $1 \times 10^{-6}$ eV were adopted in the numerical integration whereas the gradient convergence criterion was $10^{-3}$ Hartree/Å, and the step convergence criterion was $10^{-1}$ Hartree/Å. The maximum allowed energy and stress energy change was $7.3 \times 10^{-4}$ Hartree/Å and $5 \times 10^{-4}$ Hartree/Å respectively. The van der Waals interactions between the interface and adsorbed gases were also taken into account by considering the empirical dispersion correction DFT-D3 [49, 50]. The delocalized modes updated method was used to optimize the geometry of the coordinates.

Pristine graphene, vacancy defect containing graphene, Pd clusters, Pd clusters decorated defected graphene (Pd$_n$-Gr), and inert gases adsorbed Pd$_n$-Gr were structurally optimized using the self-consistent-charge density-functional tight-binding (SCC-DFTB) method [51]. The atomic charges are used to address self-consistency in SCC-DFTB and charge density is expressed in terms of Hirshfeld charges whereas the quasi-Newton optimization technique with delocalized coordinates was used for the optimization.

The adsorption energy of inert gases on Pd$_n$-Gr sensors is calculated by using equation (6),

$$\Delta E_{\text{adp}} = (E_{\text{gas/surf}} - E_{\text{gas}} - E_{\text{surf}})$$

Non-equilibrium Green’s function (NEGF) is a useful method for studying the transport properties of gas sensors. This method initially invented in the 1960s by Martin, Schwinger, Kadanoff, Baym, Keldysh, and others was later merged with the Landauer methodology upon the emergence of mesoscopic physics in the 1980s [52]. Hence, ‘The NEGF Landauer method’ has become a resourceful technique in the field of nano-electronics for device modeling and technology development. The FET, which is used in billions of smartphones, is the most recognizable component of contemporary electronics. A schematic diagram of a FET is depicted in Figure 01, where the active region, known as the channel, is situated between the source and drain and two highly conductive sections. FET also includes a third terminal that can be utilized to regulate the channel's resistance $R = V/I$. The attention to the issue of computing the steady-state charge current $I$ at a given voltage $V$ is worthwhile when quantum effects are taken into account. The NEGF method has been established to study quantum transport in nanomaterials like sensors, transistors, etc.
The permissible energy levels in quantum mechanical formulations are typically determined by the eigenvalues of the channel which is characterized by the Hamiltonian Matrix $H$ in the NEGF technique. However, if we interpret the structure as a closed system denoted just by $H$, an applied voltage will result in the accumulation of opposing charges in the source and drain, and hence a capacitor may be considered instead of a resistor.

![Diagram](image)

**Figure 01**: A resistor in the form of a mechanical device with a channel and two contacts named source and drain. The channel is characterized by a Hamiltonian $H$ in the NEGF method. $\Sigma_1$ and $\Sigma_2$ represent the source and drain with $\mu_1$ and $\mu_2$ as respective electrochemical potentials. while $\Sigma_0$ denotes abstract contacts, such as the phonon bath [53].

The external battery continuously removes electrons from the drain and moves them to the source to keep the electro-chemical potential difference as given in equation (1),

$$\mu_1 - \mu_2 = qV$$  \hspace{1cm} (1)

It distinguishes the situation as a resistor. Such an open system can be explained, for example, by describing the two connections 1 and 2 by functions $\Sigma_{1,2}$ and $\Sigma_{1,2}^{in}$. The first of these $\Sigma_{1,2}$, gives the rate of escape of electrons from the channel the second $\Sigma_{1,2}^{in}$ denotes the rate of incoming electrons from the contacts into the channel. Additionally, there are ‘abstract contacts’, characterized by $\Sigma_0$ and $\Sigma_0^{in}$ self-energy functions, which indicate the interaction of electrons with the channel's lattice and with one another as they move through it. There are two steps to applying
the NEGF approach to a specific problem [53, 54]. (i) Choose the proper functions $\Sigma_m$ and $\Sigma_m^\text{in}$, (ii) Calculate the relevant quantities using equations (2) to (5):

- Density of Quantum States
  \[
  A = i[G^R - G^A]
  \]  
  \[
  (2)
  \]

- Green function
  \[
  G^R = [E I - H - \Sigma]^{-1}
  \]  
  \[
  (3)
  \]

- Electron Density
  \[
  G^n = G^R \Sigma^\text{in} G^A
  \]  
  \[
  (4)
  \]

- Current per unit energy
  \[
  \bar{I}_m = \frac{q}{\hbar} \text{Trace} \left[ \Sigma^\text{in}_m A - \Gamma_m G^n \right]
  \]  
  \[
  (5)
  \]
  Where $\Gamma_m = i[\Sigma_m - \Sigma_m^\dagger]$

In this work, we studied the graphene layer decorated with palladium clusters $\text{Pd}_n$ (where $n = 2-5$) for sensing inert gases via calculating the electrical transport properties. A schematic diagram showing the junction and system's geometry for studying the transport properties of the proposed sensor is shown in Figure 02.

**Figure 02:** Schematic diagram of the system’s geometry for electronic transport in the inert gas sensor. The gold leads and central scattering region comprising of the $\text{Pd}_n$ decorated graphene sheet are shown.

Transport properties are investigated by NEGF calculations, performed on the DFTB package. Non-Equilibrium Green's Functions formalism (NEGF) is used to model electron transport through
nanoscale devices. In the "scattering region," electron transport is viewed as a coherent one-dimensional scattering process for electrons entering from the electrodes.

Our objective is to calculate the transmission function $T(E)$, which describes the rate at which electrons of energy $E$ travel through the scattering region from the left electrode to the right electrode. We can determine the electric current for a given bias voltage $V$ applied between the electrodes using the transmission function.

The electronic current provided through the connected region is determined by given Landauer–Buttiker [55,56] formulas given in equations (7) and (8);

$$I(V_b) = G_0 \int_{\mu_L}^{\mu_R} T(E,V_b) dE \quad (7)$$

$$T(E,V_b) = T_R \left[ \Gamma_L(E)G_R(E)\Gamma_R(E)G_A(E) \right] \quad (8)$$

$G^{A/R}$ is a green function in the scattering region, $\Gamma_{R/L}$ is the coupling matrix between one of the leads and the central region and $T(E,V_b)$ is transmission spectra, it tells about the probability of electrons having energy $E$ can transmit from one lead to another. $G_0$ is quantum conductance having value $G_0 = \frac{2e}{h}$.

The solution for the scattering region's Green's function, $G^{A/R}$ is carried out using equation (9);

$$(E_S - H) G^{A/R} = I \quad (9)$$

where $H$ is the Hamiltonian, $I$ is the identity matrix, $S$ is the overlap matrix, and Hamiltonian is constructed per equation (10) with $L$, $C$, and $R$ representing the center, left, and right leads, respectively;

$$H = \begin{pmatrix} H_L - \Sigma_L & H_{LC} & 0 \\ H_{CL} & H_C & H_{RC} \\ 0 & H_{CR} & H_R - \Sigma_R \end{pmatrix} \quad (10)$$

The Fermi energies at equilibrium were calculated and the Hamiltonian and overlap matrices of electrode/channel regions were modeled with the help of the DFTB module. For transport calculations, periodic boundary conditions within the point approximation were used to represent
crystals in this method. Self-consistent Crystal Orbital Overlap Population (COOP) calculation were performed to analyze electronic properties on the BAND module using the TZ2P basis set.

3. RESULT AND DISCUSSION

In the starting phase of the work, we optimized the most stable configuration of inert gases adsorbed on Pd\(_n\) (n = 2-6) decorated graphene and studied the structural and electronic properties. The structures were simulated in three steps (i) Pd\(_n\) clusters with n= 2 to 6 were optimized (ii) The perfect graphene sheet 6x6x1 was optimized (iii) The defected graphene sheet 6x6x1 having single vacancy defect, was optimized (iv) The clusters were decorated one-by-one on pristine graphene (v) The clusters were decorated one-by-one on defect-containing-graphene to prepare series of gas sensors Pd\(_n\)-Graphene. The optimized structures of the inert gas sensor were then used to investigate the adsorption of inert gases [51] and the calculated transport properties of the materials are elaborated in the following sections.

The optimization of a pure unit cell of graphene produced a lattice constant of 2.46 Å and a C-C bond length of 1.42 Å, which is well consistent with the literature [57,58]. A 6x6x1 supercell was created using the relaxed unit cell. The bond length of optimized palladium clusters (Pd-Pd) is 2.71 Å, 2.49 Å, 2.60 Å, and 2.68 Å for Pd\(_n\) (2-5), respectively. Bond lengths of Pd-Pd are in good agreement with reported results [59,60]. The structural optimization of inert gases He, Ne, Xe, Kr, Ar, and Rn adsorption on already optimized sensors Pd\(_2\)-gr, Pd\(_3\)-gr, Pd\(_4\)-gr, Pd\(_5\)-gr, and Pd\(_6\)-gr and Pd\(_5\)-gr were independently carried out and studied in detail. As a representative diagram, the structures of the Pd\(_5\)-gr sensors showing the adsorption of the inert gases on the surface of the Pd\(_5\) cluster (six Pd atoms) decorated graphene sheets are given in Figure 03.
3.1. Adsorption Energy

In order to study the adsorbate-adsorbent adhesion, the values of adsorption energy are calculated to understand the interaction of gas molecules with the slabs [51]. The value of adsorption energy is found using equation (6) and the negative values point to exothermic process. The sensitivity of the sensors is determined on the basis of adsorption energies in such a way that higher the adsorption energy (negative), the more sensitive the sensor [57].

The findings of the work indicated that the sensor Pd$_2$-Gr is more sensitive toward the detection of Ne and Xe gases. Kr gas is more effectively detected by the Pd$_3$-Gr sensor, which has adsorption energy of $-1.185$ eV. The sensor Pd$_4$-Gr is more sensitive to He which exhibited an adsorption energy of $-1.194$ eV. The sensor Pd$_5$-Gr is more effective for the detection of Rn and Ar gases. The calculated values of the adsorption energy in the case of different sensors are given in Table 01.

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**Table 01:** Adsorption energies of inert gases
3.2 Transport Properties of the Sensors

The response of a sensor can be studied via NEGF method by applying voltage to examine the electronic transport properties [61-65]. The primary principle underlying gas sensing is the transfer of electric charge between the chemical species to be detected and the sensing material which acts as acceptor or donor. The changes in the electrical character of the sensing material upon the charge transfer help the detection of the gases. The resistive [66], optical [67], electrochemical [68], and field-effect transistor (FET) type gas sensors [69, 70] are basic forms of gas sensors out of which the FET type gas sensors are studied in this work. FET has three regions: drain, source, and gate as schematically shown in Figure 04.

![Figure 04: Schematic of FET-based gas sensor with Au as source and drain leads whereas the optimized Pd₅-gr sheets are used as gate.](image-url)

<table>
<thead>
<tr>
<th>Sensors</th>
<th>Adsorbed Inert gases</th>
<th>Adsorption Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd₂-Gr</td>
<td>Neon</td>
<td>-0.363eV</td>
</tr>
<tr>
<td></td>
<td>Xenon</td>
<td>-0.645eV</td>
</tr>
<tr>
<td>Pd₃-Gr</td>
<td>Krypton</td>
<td>-1.185eV</td>
</tr>
<tr>
<td>Pd₄-Gr</td>
<td>Helium</td>
<td>-1.194 eV</td>
</tr>
<tr>
<td>Pd₅-Gr</td>
<td>Argon</td>
<td>-0.902 eV</td>
</tr>
<tr>
<td></td>
<td>Radon</td>
<td>-0.669 eV</td>
</tr>
</tbody>
</table>
The Pd$_{2}$-Gr sheets are placed between the drain and source metallic to trigger the basic functioning of a transistor. To pass the current, the potential is applied in the form of gate potential and the bias voltage. The former is applied to the active region of the sensor which acts as a gateway for the passage of electrons whereas the latter is used to vary the voltage in the transistor.

The sensor in the form of Pd decorated graphene is connected to gold leads and electronic current is passed through the drain to the source. The transmission spectra T(E) represents the probability of electron movement through a system at different energy levels. The conductance peaks in these spectra indicate resonant transmission at specific energy levels. The position, height, and width of these peaks provide valuable information about the resonant states' energy levels and coupling strengths. The analysis of the conductance peaks allows the identification of quantum resonances and resonant tunneling phenomena. Low transmission regions indicate energy barriers or localized states, while high transmission regions suggest efficient charge transport. The broadening of a conductance peak reflects a stronger coupling between the resonant state and the surrounding environment, such as phonons, impurities, or defects. Conversely, a narrower peak indicates weaker coupling and reduced scattering effects [71-76].

The electrons whose energies fall within the bias window are responsible for contributing to the total current integral, as per the Landauer-Buttiker formula. The configuration with the Fermi level set to zero and the bias window's region taken as [V/2, V/2] for the transmission of electrons, the integral area of the transmission spectra gives the current [56,77].

3.2.1 Pd$_{2}$-Gr sensor

The transmission spectra calculated for the sensor Pd$_{2}$-Gr at varying voltages are shown in Figure 05 (left panel). At zero bias some current is found which increased with an increase in bias voltage. Due to a phenomenon involving thermal or thermal-equilibrium currents, a minor current can still flow at zero voltage. The electrons have thermal energy even when no voltage is applied and the Fermi levels of the electron reservoirs at the ends of the wire are aligned. Hence, the thermal equilibrium current is produced by the occupation imbalance of electron states close to the Fermi level. This permits a few electrons to defeat the expected obstructions inside the wire and travel through it, bringing about a little current stream. The temperature and the properties of the wire material influence the magnitude of this thermal current which is typically very low [78,79]. When
the voltage increases (0V-1V), the conductance decreases ($G = I / V$). However, on reaching 1.2V the electron got enough energy to overcome the potential barrier, and conductance increases which is shown in Figure 05 (Left panel). Thus, the voltage 1.2V is the operating voltage for the Pd$_2$-gr sensor. Figure 06 shows the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) showing conductance channels in the sensor Pd$_2$-Gr.

**Figure 05:** (Left panel) The calculated transmission spectra of inert gas sensor Pd$_2$-gr, calculated at varying voltages 0V-1.4V. (Middle panel) The calculated transmission spectra of neon adsorbed gas sensor Pd$_2$-gr, calculated at varying voltages 0V-1.4V. (Right Panel) The calculated transmission spectra of Xenon adsorbed gas sensor Pd$_2$-gr, calculated at varying voltages 0V-1.4V.

It was found that LUMO +1 is a major contributor to the conductance. It is consistent with the transmission spectra shown in Figure 05(Left panel) where we get broad peaks after the Fermi
level which indicates that the states in LUMO are playing a major role in the transmission of electrons [80].

Figure 06: The calculated frontier molecular orbitals contributing to the conductance in case of sensor Pd$_2$-Gr. (a) HOMO (b) HOMO-1 (c) LUMO and (d) LUMO+1 with energy -0.353 eV, -0.341 eV, -0.392 eV and -0.393 eV respectively.

Figure 05 (Middle panel) shows transmission spectra in the case of neon gas adsorption on the Pd$_2$-gr sensor. Except for 1.2V transmission spectra of neon gas adsorption on Pd$_2$-gr, the remaining spectra show more conduction when compared with that of pristine Pd$_2$-gr. However, at 1.2V (operating voltage for Pd$_2$-gr) neon adsorbed sensor shows less conduction than that of pristine. Before the adsorption, the neon gas sensor has localized states. However, after the adsorption of neon gas, electron density gets redistributed, and states became delocalized which is revealed from the transmission spectra given in Figure 05 (Middle panel).

The frontier orbitals HOMO and LUMO of neon adsorbed on Pd$_2$-gr are shown in Figure 07. Before the adsorption of neon gas mostly LUMO is participating in electronic transport. But after the adsorption of neon gas, HOMO also appeared contributing to the conduction which can be seen from transmission spectra given in Figure 05 (Middle panel) and HOMO, LUMO density given in Figure 06. The resonating peaks observed in HOMO are still localized. The majority of the delocalized resonating peaks are present away from the Fermi level which indicates the major
role of LUMO+1 and LUMO+2 in transmission. The difference in energy is 0.038 eV, 0.052 eV, 0.001 eV, and 0.003 eV for HOMO, HOMO-1, LUMO, and LUMO+1, respectively [81].

Figure 07: The calculated frontier molecular orbitals contributing to the conductance in case of neon adsorbed sensor Pd$_2$-Gr. (a) HOMO (b) HOMO-1 (c) LUMO and (d) LUMO+1 of neon adsorbed on Pd$_2$-gr with energy -0.392 eV, -0.393 eV, -0.391 eV and -0.390 eV respectively.

Figure 05 (Right panel) shows transmission spectra calculated in case of xenon gas adsorbed Pd$_2$-gr. The transmission spectra of Xe adsorbed on Pd$_2$-gr shows same behavior as neon gas adsorbed on Pd$_2$-gr except that sharp resonating peaks obtained in 0V to 1V region in comparison to that of neon on Pd$_2$-gr spectra as per figure 05 (Middle panel). More delocalized peaks were obtained between 3V to 5V for the Xe adsorbed Pd$_2$-gr sensor. The transmission spectra (at 0V-1.4V except for 1.2V) of Xe gas adsorbed on Pd$_2$-gr reveal increased conductivity compared to pristine Pd$_2$-gr. However, the operating voltage (1.2V) of the Pd$_2$-gr sensor, the Xe gas adsorbed on the sensor exhibits reduced conductivity compared to the pristine sensor. Prior to adsorption, the sensor possesses localized states. Nevertheless, after the adsorption of Xe gas, redistribution of electron density leads to a more delocalized nature of the states, as evidenced by the transmission spectra depicted in 05 (Right panel).

The calculated HOMO and LUMO of Xe adsorbed Pd$_2$-gr are shown in Figure 08. The HOMO and LUMO are contributing to electronic transport which cooperates with transmission spectra given in figure 05 (right panel). Xenon adsorbed Pd$_2$-gr give more response at 0V to 1V than Ne adsorbed Pd$_2$-gr and the difference in energy is 0.037 eV, 0.051 eV, 0.002 eV, and 0.782 eV for HOMO,
HOMO-1, LUMO, and LUMO+1, respectively. This difference in energy and different responsive voltage points to the gas is being adsorbed on the sensor.

Figure 08: The calculated frontier molecular orbitals contributing to the conductance in case of Xenon adsorbed sensor Pd_2-Gr. (a) HOMO (b) HOMO-1 (c) LUMO and (d) LUMO+1 with energy -0.391 eV, -0.392 eV, -0.390 eV and -0.389 eV respectively.

Figure 9 shows the characteristics curves calculated for the sensors pristine Pd_2-gr, Ne- Pd_2-gr, and Xe-Pd_2-gr. At V = 0, there is no electronic current, only small amount of current flows through sensor due to diffusion or thermal phenomenon. When voltage is increased, current would increase until threshold voltage is arrived at which the current gets constant; this is active region of sensor where sensor normally operates. The current will remain constant until the breakdown voltage is applied. It’s a region where the current drastically gets increased and the sensor gets short-circuited [81-84]. At the voltage of -0.88V, -1.05V, and -1.37V the respective active regions for pristine Pd_2-gr, Ne-Pd_2-gr, and Xe-Pd_2-gr get started. The other sensors also show same behavior as observed from their respective characteristics curves. This difference in voltage is an important parameter which leads to differentiate the adsorbed gases.
Figure 9: The calculated characteristics IV-curves for pristine Pd$_2$-gr, Ne-Pd$_2$-gr, and Xe-Pd$_2$-gr sensors.

3.2.2 Transport properties of Pd$_3$-Gr

The transmission spectra of pristine Pd$_3$-Gr are shown in Figure 10 (Left panel).
Figure 10: (Left Panel) The calculated transmission spectra of sensor Pd₃-gr, calculated at varying voltages 0V-1.4V. (Right Panel) The calculated transmission spectra of Krypton adsorbed gas sensor Pd₃-gr, calculated at varying voltages 0V-1.4V

At 0V and 1.4V no peaks were obtained before the Fermi level which indicates absence of involvement of HOMO in the transmission. While for other voltages, HOMO peaks were obtained which indicates its participation in the transmission of electrons. The bias voltage 0.8V is the operating voltage for the Pd₃-gr sensor as it has more delocalized peaks than the other voltages. While for the Pd₂-gr sensor operating voltage was 1.2V. For 0.8V, Pd₂-gr sensor has localized transmission spectra because of the different distribution of electrons for the Pd₂-gr sensor and Pd₃-gr sensor. For good response, the delocalized resonance peaks are required, no matter how high is the amplitude of peaks and thus if it is localized it will not effective for the transmission of electrons [84-87].

HOMO and LUMO calculated for the pristine sensor Pd₃-gr are shown in Figure 11 which shows that HOMO, HOMO-1, LUMO and LUMO+1 contribute to the transmission of electrons in the sensor. In comparison to that of the sensor Pd₂-gr, the rich involvement of HOMO in the transmission of electrons is noted in the Pd₃-gr sensor.
Figure 11: The calculated frontier molecular orbitals contributing to the conductance in case of the sensor Pd$_2$-Gr. (a) HOMO (b) HOMO-1 (c) LUMO and (d) LUMO+1 with energy -0.354 eV, -0.354 eV, -0.352 eV, and -0.352 eV respectively at 0.8V.

The transmission spectra of Krypton adsorbed on Pd$_3$-Gr are shown in Figure 10 (Right panel). The conduction is smaller in Kr-Pd$_3$-gr when compared to the pristine Pd$_3$-gr. After the adsorption of Krypton gas, the electronic distribution takes place in such a way that total resistance in the sensor increases which leads to decreases in current as transmission spectra that indicates the transfer of current; therefore, the peaks in transmission spectra for Kr-Pd$_3$-gr are less intense than that of the pristine Pd$_3$-gr. For Pd$_3$-gr, the HOMO also takes part in conduction but after the adsorption of Krypton only LUMO contributes to the transmission of electrons [81].

The calculated orbitals HOMO and LUMO in case of Krypton adsorbed by Pd$_3$-gr sensor are shown in Figure 12. The difference in energy appeared as 0.031 eV, 0.031 eV, 0.030 eV, and 0.031 eV for HOMO, HOMO-1, LUMO, and LUMO+1, respectively. The IV-curve calculated for the sensor Pd$_3$-Gr is shown in Figure 13.

![Figure 12](image1.png)

Figure 12: (a) HOMO (b) HOMO-1 (c) LUMO and (d) LUMO+1 with energy -0.385 eV, -0.385 eV, -0.383 eV and -0.383 eV respectively at 0.8V for Krypton adsorbed Pd$_3$-gr sensor.
Figure 13: The calculated IV- characteristics curves for pristine Pd$_3$-gr and Kr-Pd$_3$-gr sensors.

3.2.3 Transport properties of sensors Pd$_4$-Gr and Pd$_5$-Gr

The calculated transmission spectra of the sensors Pd$_4$-Gr, He-Pd$_4$-Gr, Pd$_5$-Gr, Ar-Pd$_5$-Gr and Rn-Pd$_5$-Gr, are shown in figures 14 and 15 respectively.
**Figure 14: (Left Panel)** The calculated transmission spectra of the Pd$_4$-gr sensor at varying voltages 0V-1.4V. **(Right Panel)** The calculated transmission spectra of helium adsorbed on Pd$_4$-gr varying voltages 0V-1.4V.

The values of the operating voltage found in case of the sensor Pd$_4$-Gr is 1V and 0.8V for the sensor Pd$_5$-Gr. The response of these sensors appeared the same as observed and discussed previously for the sensors Pd$_2$-Gr and Pd$_3$-Gr.

**Figure 15: (Left panel)** Transmission spectra of Pd$_5$-gr varying voltages (0V-1.4V). **(Middle panel)** Transmission spectra of argon adsorbed on Pd$_5$-gr varying voltages (0V-1.4V). **(Right panel)** Transmission spectra of radon adsorbed on Pd$_5$-gr varying voltages (0V-1.4V).
The characteristics IV-curve calculated for the pristine Pd\textsubscript{4-gr}, Pd\textsubscript{5-gr}, He-Pd\textsubscript{4-gr}, Ar-Pd\textsubscript{5-gr}, and Rn-Pd\textsubscript{5-gr} are shown in Figure 16.

### 3.3 Recovery time

Recovery time refers to the amount of time taken by the sensor to reset or return to its baseline reading after being exposed to a gas. The sensor technology, gas concentration, and presence of any contaminating substances play important role in determining this time [88,89]. It is important factor to check the sensor capacity that can be calculated using formula (11):

\[
t = A^{-1} \exp \left( \frac{-E_{\text{adp}}}{2K_BT} \right)
\]

The Boltzmann constant (K\textsubscript{B}) is (8.62 \times 10^{-5} \text{eV} \text{K}^{-1}), the attempt frequency (A) is constant at 10^{12} \text{s}^{-1}, and the system's temperature is T. The Langmuir-Hinshelwood model for gas-surface interactions serves as the foundation for the recovery time of the gas sensor [90-93]. The recovery time is only few seconds for the inert gas which depicts good capacity of sensors and also found consistent with the relevant literature [94,95]. Table 02 shows the calculated values of the recovery time for inert gases on different sensors.

### Table 02: Recovery time of inert gases adsorbed on Pd\textsubscript{n-gr} (n = (2-5)) at 300K
<table>
<thead>
<tr>
<th>Gases</th>
<th>Adsorbed gases</th>
<th>$\tau$ (sec) At $T = 300K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_2$-Gr</td>
<td>Neon</td>
<td>1.11E-9</td>
</tr>
<tr>
<td></td>
<td>Xenon</td>
<td>2.6E-7</td>
</tr>
<tr>
<td>Pd$_3$-Gr</td>
<td>Krypton</td>
<td>8.92E-3</td>
</tr>
<tr>
<td>Pd$_4$-Gr</td>
<td>Helium</td>
<td>1.062E-2</td>
</tr>
<tr>
<td>Pd$_5$-Gr</td>
<td>Argon</td>
<td>3.75E-5</td>
</tr>
<tr>
<td></td>
<td>Radon</td>
<td>4.14E-7</td>
</tr>
</tbody>
</table>

### 3.4 Sensitivity

One of the key objectives in designing a gas sensor is to achieve high responsiveness and selectivity. The change in conductance is a crucial factor in determining a sensor's response to various gas adsorbate, particularly in the linear regime. As a result, the proportional change in conductance, which serves as an indicator of the sensor's response to various gas adsorbate, can be used to define a sensor's sensitivity [96,97] as per equation (12):

$$S = \left| \frac{G_0 - G}{G} \right| (100\%) \quad (12)$$

The conductance of the Pd decorated graphene sheets with and without the gas adsorbate is denoted by $G$ and $G_0$ respectively. At a given bias step, the electrical conductance is found as change in current with respect to voltage $G = \frac{dI}{dV}$, approximately using $G = \frac{I}{V}$ [98-100]. The sensitivity for Xenon and Neon based Pd$_2$-gr sensors are found 84% and 67% whereas Krypton detection using Pd$_3$-gr and Helium detection using Pd$_4$-gr are found to have respective values of sensitivity as 73% and 91%. Argon and radon shows 49% and 61% sensitivity towards Pd$_5$-gr sensor. The designed sensors show good sensitivity for detection of the inert gases which agrees with the relevant literature [101-103].
4. Crystal Orbital Overlap Population (COOP)

We employed Crystal Orbital Overlap Population (COOP) to examine the bonding between atoms in a crystal. Quantitatively, it shows how strong the bonding interactions between atoms are by measuring the overlap between crystal orbitals. Positive (negative) COOP population indicates bonding (antibonding) respectively [104,105]. Additionally, the specific orbitals involved in the adsorbate-surface bond can be identified with COOP analysis. In the case of physisorption, for instance, the COOP curve may have a peak that corresponds to the non-bonding orbitals of the surface or the adsorbate, indicating their role in the interaction. The electronic structure of the material can have an impact on the shape of the non-bonding peaks in the COOP curve. Non-bonding peaks can be lone-pair or non-bonding electrons, and they typically occur at energies where there is little to no overlap between the atoms' valence orbitals [106].

Palladium has a closed shell electronic configuration 4d\(^{10}\). However, electron delocalization occurs in cluster form, resulting in electron transfer from 4d to 5s and 5p orbitals via sp-d hybridization. One s, 3 p, and 2 d orbitals of pd\(_2\)-decorated graphene overlap, resulting in sp\(_3\)d\(_2\) hybridization as reported in the literature [107,108], depicted in figure 17.

![Hybridization (sp\(_3\)d\(_2\)) of Pd\(_2\)-gr](image)

**Figure 17:** Hybridization (sp\(_3\)d\(_2\)) of Pd\(_2\)-gr

A palladium atom doped on graphene has four unpaired electrons, 3 electrons make the covalent bond with three carbon atoms of graphene, and one remaining atom is bound with one of 2 unpaired electrons of another palladium atom. which is also depicted in COOP Figure 08(a). One remaining unpaired free and delocalized electron interacts with inert gas. Carbon in graphene has a delocalized pi bond, which also attracts adsorbed inert gases. Because of this small charge is
transferred from inert gases to palladium and then to carbon in the pd$_2$-gr sensor. The shape of the COOP curve can be used to estimate the degree of covalence between two atoms in a crystal. A large peak in the COOP curve that is centered at a particular energy, for instance, indicates that the valence orbitals of the two atoms significantly overlap, indicating a high degree of covalence. On the other hand, a lower degree of covalence and a weaker overlap is suggested by a COOP curve with a narrow peak [109]. Figure 18(a) indicates the strong overlapping of the orbital of a palladium atom with the orbital of a carbon atom which indicates a covalent bond between palladium and carbon atoms. A small peak of Neon also appears in COOP which shows weak interaction between gas and sensor. Inert gas peaks weakly overlap with the p orbital of the carbon atom and the s orbital of the palladium atom which indicates the weak interaction between gases and palladium as reported in the previous study [110,111].

In Pd$_3$-Gr, Pd$_4$-Gr, and Pd$_5$-Gr sensor palladium atom decorated on graphene connected with further tow palladium atoms therefore they have sp$_3$d$_3$ hybridization. One s, 3 p, and 3 d orbital overlap to form a hybrid orbital. Pd$_3$-Gr sensor has one free electron while no. of free electron increases to 2 and 3 for Pd$_4$-Gr and Pd$_5$-Gr sensors, respectively. Figure 08 (b) show COOP for the Pd$_3$-Gr-Kr in which sharp peaks of the d orbital of palladium atoms clearly overlap with the s and p orbital of a carbon atom which depict that there is a covalent bond between the carbon and palladium atoms which is well consistent with the previous study [112]. As no. of free electrons increases for Pd$_4$-Gr, and Pd$_5$-Gr sensors, charge density is more diffuse on palladium clusters compared to graphene. The COOP peaks for inert gases clearly indicate that gases are physisorbed on sensors. Furthermore, no antibonding peaks for any sensor which indicates the good stability of the material as studied in the literature [113].
Figure 18: COOP of inert gases adsorbed on Pd$_2$ doped graphene (a) Neon adsorbed Pd$_2$ doped graphene (b) Krypton adsorbed Pd$_3$ doped graphene (Fermi level set at zero)

5. Summary

The detailed investigations were made on the transport characteristics of sensors based on a series of palladium clusters Pd$_n$ ($n = 2$-5) decorated graphene sheets for the detection of inert gases. Utilizing density functional theory with non-equilibrium Green's function (NEGF) formalism, the calculations for transport properties were performed. The work comprised of findings on adsorption mechanism and transport properties of the most stable structures of the sensors for inert gas sensors. The Pd$_5$ sensor appeared more suitable for the detection of argon and radon gases whereas the Pd$_2$ sensor is more sensitive to xenon and neon. The detection of krypton and helium gases is effectively carried out using Pd$_3$ and Pd$_4$-based sensors respectively. The characteristic IV curves and transmission spectra are used to discuss the conduction phenomenon in the sensors.

Declarations

Ethical Approval
Not applicable

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

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