Ab-initio Modeling of Functionalized 2D-Stanene nanostructure in context of FET based Toxic Gas Sensor

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Abstract. Detecting toxic gases in the environment cannot be minimized in today’s highly polluted world and the reality of global warming. Carbon monoxide is a highly toxic air pollutant and can cause serious health problems. Sensing materials plays a critical role in the performance of gas sensors. Nanostructure materials exhibit better performance as sensing channels in application for developing novel FET-based sensing devices. In the proposed work, the ab-initio study is performed to explore the performance of 2D-Stanene nano sheet as a sensing substrate for application of field-effect transistors as gas sensor. We explored CO gas-adsorption behaviour on pristine, hole-defective, and Pt-doped Stanene sheet and analyzed structural, charge-density, electronic and transport properties by first principles calculations and exploit its potential for high-performance gas sensing. Here in, to get the measure of sensing properties of Stanene nano sheet after the adsorption of gas molecule, first the molecular model of all the adsorption cases are modelled by considering all possible anchoring sites and optimized, and then calculations were performed based on density functional theory (DFT).

1. Introduction
From the beginning to the end of the day, we continuously sense something and our mind responds accordingly. We can see, the life of almost every individual across the world depend upon some automatic gadgets, in which sensor plays an important role[1].

It is interesting to see that sensor is a tool that identifies the existence and behavior of the physical environment and provides useful information in the form of signals. Due to this property of the sensor, we can study it at the nanoscale level[2]. Also, various technologies have been developed such as the nano-electromechanical system, nano-opto-electromechanical system, nano-photonics and the combination of nanotechnology with microtechnology[3].

Nano-sensors have a wide variety of applications in the field of healthcare, defense, homeland security, environmental monitoring and light-sensing electronics[4]. We can create more efficient and effective sensor networks through Tin(Sn) material because of its two-dimensional nature and excellent electronic and mechanical properties same as Graphene[5]. Sensing materials play a critical role in the performance of gas sensors. 2D nano-materials show much better performance as sensing channels in application for, sensing channels in application for developing novel FET-based sensing devices [6-8].

We first modeled a stanene sheet to be used as sensing substrate, to be used as channel of Field-effect transistors (FETs). Field-effect transistors (FETs) are the kind of transistors that control the flow of current through the electric field. Field-effect transistors (FETs) work on a principle that uses the field produced by the gate in a way that makes the channel conduct more or less. Here it consists of terminal, drain and gate where gate manipulates the channel conductivity [9]. The source is a terminal through which carrier (holes or electrons) enter the channel and drain allow the carriers to leave the channel. In bipolar transistors, the current that can be carried between the collector and emitter is modulated by the base current [10].

The working principle of FET sensor is to monitor the conductance change in the gate channel, before and after the adsorption of target molecules. Motivated by the applicability of 2D Graphene for gas sensing applications [11-13], we investigated the gas sensing properties of a monolayer of tin as stanene, in analogy with graphene.

In this work, first-principles methods based on DFT are employed to study the electronic and transport properties of the pristine, defected and Pt-doped Stanene to exploit its performance as a toxic gas sensor. It has been reported that functionalization, introducing dopants, and defects can tune the electronic and magnetic properties of the various nanomaterials[14-16]. Toxic gases are harmful gases and their reckless intake can cause harm to the respiratory system of the body. Carbon monoxide is an odorless toxic gas that is formed due to incomplete combustion of carbon and oxygen. Carbon monoxide is made up of one carbon atom and one oxygen atom with a bond order of 3, where it has one sigma bond and two pi bonds. It is also known as the invisible killer due to its poisonous nature and colorless character [17].

2. Computational Details

We exhibit the whole study of based on Density Functional Theory (DFT) which normally using electron density as a function of space and time. Here, We optimized and concluded all the results using Kohn-Sham coherent density functional method which further implements on computational package using open source software Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA). The SIESTA uses a basis set of strictly-localized atomic orbitals and employs norm-conserving pseudo potentials. All geometry optimizations and electronic structural calculations have been performed by using the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code [18].

Quantum transport theory as implemented in GOLLUM code these codes are based on the density functional theory (DFT) [19]. The exchange and correlation energies are treated within the generalized gradient approximation (GGA) [20] according to the Perdew-Burke-Ernzerhof (PBE) parameterization.

Nowadays, Researcher follows the GGA approximation because there are so many advantages over LDA, Local Density Approximation (LDA) have such limitations it does not account for van der Waals bonding, not suitable for strongly correlated system and gives a poor description of hydrogen bonding and over binding error for solids and molecules significantly reduces[21].
Numerical atomic orbital’s (NAOs) with double zeta polarization (DZP) basis set have been used for geometry optimization. Minimization of energy has been carried out using standard conjugate-gradient (CG) technique until the forces on each atom are less than 0.005 eV/Å, the mesh cut-off energy is taken equal to 250 Ry.

3. Results and discussion
3.1 Structural Analysis

To explore the interaction of CO gas molecule with defect functionalized stanene systems, we firstly modeled and optimized the atomic structures of gas molecules and all Stanene systems. We have considered three sensing substrate systems:

1. Sn - the pristine Stanene nanostructure, consisting of 40 Tin (Sn) atoms.
2. Sn_V - defective Sn system, by creating a vacancy at the center of Stanene nanosheet.
3. Sn_Pt - doped Sn system, by replacing one Sn atom with dopant Pt atom at the center of Stanene nanosheet.

We have designed pristine 2D Stanene nanostructure sheet by repeating the unit cell 5 times along Z direction making it a nanosheet of 40 Tin atoms. After initial relaxation of the pristine sheet, the relaxed lattice constant of a unit cell is 4.647 Å, and the length of Sn-Sn bond is 0.279 nm. These computed parameters are in good agreement with the previous reported results. After doping of Pt, we have analyzed the change in atomic structure, bond length between Sn-Sn increases to 0.282 nm and the bond between Sn-Pt decreases to 0.265 nm, which supports the strong interaction between the dopant atom and the sheet. In defective Sn system, we have created a vacant space due to creation of vacancy or hole at the center, the bond length between Sn-Sn decreases to a value of 0.275 nm, as compared to pure stanene sheet.

In figure 1(a) represents the unit cell of Stanene. In figure 1(b), a pure stanene sheet is formed due to the repetition of the unit cell of stanene, appearing as a honeycomb-like structure in the 2D plane. In figure 1(c) one atom of Platinum is doped in the center of the pure Stanene sheet because it provides a two-dimensional Sn sheet with a vacant space formed because of the removal of Sn atom which was at the same place where Pt was doped.

![Figure1](a) 2D unit cell (b) 2D-Stanene 5*5 sheet (c) 2D-Pt doped Sn-sheet (d) 2D-Sn sheet with a vacancy. Dark and white spheres represent Sn and P atoms, respectively.
After the optimization of CO molecule, the bond length of CO is 0.116 nm, which is in accordance with the published results. In the case of CO adsorption, there are six possible coordination configurations depending on the different atoms of CO molecule above three adsorption sites.

![Adsorption Sites](image1)

(a) Different absorption sites of Stanene sheet (b,c) CO molecules interact with Sn sheet and Sn_Pt sheet with two different orientation at 3 location, respectively

![Carbon Atom Oriented towards sheet](image2)

We allow CO molecules to interact with the Stanene sheet in all possible ways and found that there are three different adsorption sites of interaction, which are, i) T-site, on the top of Sn atom (T), ii) C-site, center of the Sn hexagon (C) in which the molecule is placed in the hollow space region of a honeycomb-like structure of the sheet., and iii) B-site, the bridge point of a Sn-Sn bond (B), where the molecule is placed above the bond of the two atoms of Sn-Sn molecules of the sheet. Figure 2 (a) represents the three different adsorption sites. In case of Sn_V sheet, we have placed the molecule on the vacant site.
The CO molecule has a diatomic structure. Due to the presence of three absorption sites, we can get six different coordination configurations depending upon the orientation of carbon and oxygen. In figure 3(b) the CO molecules interact with three different absorption sites, the top row figure shows the carbon atom orientation, forming a bond with a pure Sn sheet. The down row shows the oxygen atom orientation, forming a bond with a pure Sn sheet. In figure 3(c) the CO molecules interact with three different absorption sites, the top row figure shows the carbon atom orientation, forming a bond with pure Platinum, doped in Sn sheet. The down row shows the oxygen atom orientation, forming a bond with the Platinum, doped in the Sn sheet.

The side view of CO molecules that interacts with three different sheets with pure Sn sheet, Sn sheet doped with Pt and Sn sheet with vacant space is represent in below figure. When the CO molecules interact with the pure Sn sheet, it makes two bonds between Sn-O with a bond length of 0.216 nm and the length of bond between C-O is 0.141 nm. In figure 3(b) oxygen atom of the CO molecule is bonded with Platinum which is doped in Sn sheet, forming the bond length of 0.248 nm between Pt-O and the bond length between C-O is 0.12nm. Figure 3(c) represents the vacant Sn sheet where the CO molecule formed a bond with Sn, having a bond length of 0.258 nm and C-O molecules having a bond length of 0.127nm.

![Side view of interaction of CO molecules with (a) Pure Sn sheet (b) Sn_Pt sheet (c) Sn_V sheet](image)

**Figure 3.** Side view of interaction of CO molecules with (a) Pure Sn sheet (b) Sn_Pt sheet (c) Sn_V sheet

### 3.2 Charge Density Analysis

Charge Density Analysis plays an important role in determining electronic properties. It gives a clear description of electron density by explaining the interaction between the atoms of the molecules and the process of bond formation which helps in predicting the most reactive position for any electron charge distribution of a molecule. It also provides quantitative information about the different regions of charge distribution for a molecule. In the charge scale, we can observe a higher electron density at
the inner-most region (magenta) with a value of +1.0239 and the lowest electron density at the outermost region (red).

The values of the charge density of colors are given in the center of figure 4. In figure 4(a), the pure Sn sheet forms a concentric circle in the center of the hexagonal structure of the sheet and the presence of magenta color, that is visible in the Sn-Sn bond formation region, shows high electron density and indicates the formation of a strong covalent bond.

**Figure 4.** The Charge Density Plot of (a) Pure Sn sheet (b) Platinum doped Sn sheet (c) Sn sheet with one atom vacant (d) CO molecules

Figure 4(b), a higher charge density is observed around Platinum atoms of the platinum doped Sn sheets that means the ionization energy of Platinum (Pt) is higher than Tin(Sn) atom. The formation of concentric circles around the platinum atoms represents the ionic nature and indicates maximum charge concentration, which forms magenta circular structures.

In between the Sn-Sn vacant sheet, in figure 4(c), there are concentric circles around the central region and deformed dumb-bell shapes of the triangular shape formed around the atoms. Hence there is a partially covalent and ionic bond. From figure 4 (d), it is visible that the CO molecules bond forms the dumb-bell shape which indicates the sharing of equal charge between atoms and the charge density in most of the parts are of blue color that shows the presence of the covalent bond.

### 3.3 Electron Properties Analysis

The forbidden energy gap is the energy difference between the HOMO of the valance band and LUMO of the conduction band in the density of states (DOS) plotting. In any system, the conduction band provides enough energy to the electrons which allows them to move freely and this movement of electrons creates an electric current. The transition of an electron from HOMO of the valance band to the LUMO of the conduction band is very important to understand the Density of States (DOS) plot and Projected Density of states (PDOS) plot. DOS plots show the concentration of states for a particular energy level that an electron can occupy.
In Figure 5(a), the DOS plot shows the variation for all the different types of sheets and their concentration of states is demonstrated, where the pure Sn sheet has lower peaks in the forbidden gap region as compared to the vacant Sn (Sn_V) sheet and doped Platinum Sn (Sn_Pt) sheet. On the other hand, the vacant Sn sheet has higher peaks in the forbidden gap region. On the same figure, continuous waves are visible, which means that there is no energy gap in all three sheets. At the forbidden energy region, the sequence for the formation of lower peaks is Sn<Sn_Pt<Sn_V.

In the LUMO or conduction region, higher peaks are formed with the sequence of Sn>Sn_Pt>Sn_V. In Figure 5(b) graph represents the DOS plot of pure Sn sheet and pure Sn sheet interacting with CO (Sn_CO) molecules. In the LUMO or conduction region, the Sn_CO sheet shows high absorbance as compared to the pure SN sheet. In the forbidden energy gap region, the Sn_CO has a lower peak as compared to the pure Sn sheet, without interacting with CO molecules which means that the concentration of electron gets decreases in the region where we interact the CO molecules with the pure Sn sheet.

In Figure 5(c), the graph represents the DOS plot of the vacant Sn sheet which does not interact with CO molecules (Sn_V) versus the vacant Sn sheet which interacts with CO molecules (Sn_V_CO). The forbidden energy gap region of the Sn_V_CO sheet has a higher peak as compared to the Sn_V sheet, which means that the concentration of electron gets increase in the region when we interact with the CO molecules with pure SN sheet. In the LUMO or conduction region, Sn_CO interaction with the sheet shows high absorbance as compared to the pure SN sheet.

**Figure 5.** Density of States plotting (a) with all different three Sn, Sn_Pt and Sn_V sheet, (b,c,d) with or without interaction of CO molecules with Sn sheet, Sn_V sheet and Sn_Pt sheet, respectively.
In Figure 5, the lower right graph represents the DOS plot of the Platinum doped Sn (Sn_Pt) sheet and platinum doped Sn sheet interaction with CO (Sn_Pt_CO) molecules. While in the forbidden energy gap region, the Sn_Pt show a lower concentration of electrons and in the case of Sn_Pt_CO, it shows a higher concentration of electrons and their antagonistic behavior is visible. The absorbance of CO molecules through the LUMO band of the Sn_Pt_CO sheet shows high energy after 1.5 eV but in the case of Sn_Pt sheet, the LUMO band shows the high peak at 1 eV that denotes the acceptance of electrons in orbital shifting, which means that high energy is required for the bond formation of Planiunm and CO molecules. PDOS plots depict the energy of any particular orbitals and the concentration of states that an electron can occupy.

![Figure 5](image_5.png)

**Figure 5.** The lower right graph represents the DOS plot of the Platinum doped Sn (Sn_Pt) sheet and platinum doped Sn sheet interaction with CO (Sn_Pt_CO) molecules.

In all the three possibilities with the CO molecules (in Figure 6) interaction with sheets of pure Sn sheet, platinum doped Sn (Sn_Pt) sheet and vacancy Sn sheet PDOS are shown in figure 6(a,b,c). In all the cases, the Carbon atom of the CO molecule has shown high absorption in the conduction band as compared to the oxygen atom when they interact with the sheets.

**Figure 6.** Projected Density of States with interaction of CO molecule with Sn, Sn_Pt and Sn_V sheet.

3.4 Electron Transport Analysis

To study the transport properties of our system, we used the GOLLUM code which is based on the equilibrium transport theory. GOLLUM code gives the electronic and thermal transport properties of nanostructured materials. GOLLUM code generates Hamiltonian through Density Functional Theory(DFT) which corresponds further to generate the S-matrix which gives the physical quantities such as current by using additional theory in DFT that is equilibrium Green Function (EGF).

The GOLLUM code helps to analyzed and study the first principle behavior of any nanostructure material through their I-V characteristics by using the DFT-EGF approach. For transport calculation, the system is divided into three parts that include the left electrode, nanostructured material (scattering region) and right electrode, which are attached in a consecutive matter in series to fulfill the valency of each atom. The electrodes which are used for transport analysis are periodic in structure while the contact nanostructured material is non-periodic in structure.

![Figure 7](image_7.png)

**Figure 7(a).** shows the comparative plotting of three different sheets that include pure Sn sheet, platinum doped Sn (Sn_Pt) sheet and vacant Sn(Sn_V) sheet and these sheets are represented in terms...
of their I-V characteristics. From the graph, it is clear that before the supply of 1V, the output current in the vacant Sn(Sn_V) sheet shows high peaks as compared to the other two different sheets. After the supply of 1V, the Platinum doped Sn (Sn_Pt) sheet shows an efficient current with a magnitude scale of 10-5 Ampere. It can be easily concluded that by adding the functionality to the Sn sheet, in terms of adding vacancy and dopant Pt atom, we can modulate the conductivity of the sheet. Here, considerable rise in the current as shown in figure 7(a) indicates the increase in conductivity of our considered functionalized sheets.

![Figure 7](image-url)

**Figure 7.** I-V Characteristics with/ without interaction of CO molecules with Sn, Sn_Pt and Sn_V sheet.

For exploring the adsorption of CO molecule with pure Sn sheet, platinum doped Sn (Sn_Pt) sheet and vacant Sn(Sn_V) sheet, we have obtained I-V curves which are plotted in figure 7(b),(c),and (d) respectively. For all the three considered systems, we have compared the I-V curves both in absence and presence of the adsorbed CO gas molecule. The sharp rise in value of current clearly indicates the strong interaction between the adsorbed CO gas with the sensing sheets

4. Conclusion

Structural analysis exhibits the variation in adsorption distance relative to system. High peaks in DOS represents to charge donating nature of adsorbed molecule. Adsorption bond formation nature is found highly with C atom of CO molecule.

Covalent bonds are formed in Sn hexagonal rings/between C & Sn and partially ionic and covalent between Pt & Sn.I-V curves exhibit metallic nature with high rise in current with the adsorption of CO with all considered Sn sheets.

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