Sensitivity of SnO$_2$ nanoparticles/reduced graphene oxide hybrid to NO$_2$ gas: a DFT study

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Abstract
The sensitivity of SnO$_2$ nanoparticles/reduced graphene oxide hybrid to NO$_2$ gas is discussed in the present work using density functional theory (DFT). The SnO$_2$ nanoparticle shapes are taken as pyramids, as proved by experiments. The reduced graphene oxide (rGO) edges have oxygen or oxygen-containing functional groups. However, the upper and lower surfaces of rGO are clean, as expected from the oxide reduction procedure. Results show that SnO$_2$ particles are connected at the edges of rGO, making a p-n heterojunction with a reduced agglomeration of SnO$_2$ particles and high gas sensitivity. The DFT results are in good agreement with the experimental characterization of both SnO$_2$ and rGO using energy gap and X-ray photoelectron spectroscopy (XPS) values. Gibbs free energy, enthalpy, and entropy of the various considered reactions are calculated. Results show that the sensitivity of the rGO/SnO$_2$ hybrid to NO$_2$ gas is the result of the interplay of the dissociation and oxidation reactions of NO$_2$ gas. The sensitivity of the rGO/SnO$_2$ hybrid to NO$_2$ increases with temperature until the NO$_2$ dissociation in the air reduces the concentration of NO$_2$.

Keywords NO$_2$ · Reduced graphene oxide · SnO$_2$ · Gas sensor

Introduction
Graphene is a material with high potential applications [1–3]. These applications include solar cells [1], light-emitting diodes (LEDs) [2], and many other applications [3]. The same is true for graphene oxide [4]. One contemporary application of graphene or graphene oxide is in gas sensing [5, 6]. Graphene is proved to be better than multi-wall carbon nanotubes (MWCNT) in gas sensing [7]. The large surface area of graphene is one of the important features that give graphene superiority in gas sensing operations. This superiority is also kept even after the mixture of graphene with other materials since the mixed materials are dispersed on graphene surfaces or edges that prevent agglomeration [8, 9]. Graphene oxide can be activated using materials that remove oxygen-containing functional groups on the surfaces of graphene oxide. Hydrazine is one of these materials that are used as an oxygen scavenger from graphene oxide surface [8]. The resultant material is called reduced graphene oxide (rGO). rGO is an n-type semiconductor [10]. In general, nanomaterials are now playing a vital role in the industry [11–13].

Tin oxide is one of the most used materials in gas sensing [14, 15]. It is a p-type semiconductor [16]. It has been used practically to detect various gases. The high number of oxygen vacancies in SnO$_2$ can enhance gas sensing operation by accepting or donating oxygen to the censored gas.

Nitrogen dioxide (NO$_2$) is an important polluting gas that is produced in large quantities due to vehicle engines and from smoking and kerosene heaters [17]. As a result, monitoring NO$_2$ is of vital importance. The use of graphene or graphene oxide has been suggested several times to build sensors for NO$_2$ gas [9, 18, 19]. Adding other sensing materials to graphene or its oxide is a common practice. SnO$_2$ is one of these materials that improve graphene sensitivity to NO$_2$ gas [7, 20–22]. In addition to SnO$_2$, other catalysts such as SnS$_2$, Ag, or Pd can also improve the sensitivity of graphene or its oxide [20–22].

The use of density functional theory has proved to give valuable information about gas sensing mechanisms,
including the various properties of materials used in the sensing operation [23, 24]. This includes related electronic structure properties such as the energy gap, vibrational properties of Raman and IR spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermodynamic properties such as Gibbs free energy, enthalpy, and entropy.

In the present work, DFT is used to analyze the gas sensing properties of SnO₂/rGO hybrid to NO₂ gas. The properties of the different materials used in this work are discussed. The results are compared with experimental findings of the various materials used in the sensing operation. Thermodynamic properties such as Gibbs free energy, enthalpy, and entropy of the various reactions are evaluated to estimate the reaction rates of NO₂ with the sensing materials.

Theory

DFT at the B3LYP/6-311G** is used in the present work to simulate the structure and different properties of the sensing materials of the SnO₂/rGO hybrid and their interaction with NO₂ gas. Previous works on SnO₂ surveyed different methods and bases to perform electronic structure calculations such as GGA, LDA, B3LYP, and PBE0 [25]. B3LYP (see reference [26] for the abbreviations) was found to give a bandgap that is more consistent with experimental results. Previous use of B3LYP in gas sensor calculations gave satisfactory results in comparison with experiments [27, 28]. The basis 6-311G** reflects the size of molecules and the total number of atoms in the present work. A small number of atoms can give us the freedom to use a more intricate basis, while a large number of atoms can restrict the use of a detailed and complicated basis. Stuttgart/Dresden (SDD) basis is used for heavy Sn atoms that cannot be represented by the 6-311G** basis. Dispersion corrections are important for the present calculations because of the long-range forces between the interacting molecules. GD3BJ dispersion correction version is added [29]. Gaussian 09 molecular facilities program is used to perform present calculations [30]. It is interesting to calculate the calculate basis set superposition error (BSSE) for the system of atoms in Fig. 1a and b, which is of the order of 0.007 atomic units per atom. This number represents the difference between the use of the complete set and the present set. The percentage of HF in B3LYP is 20%. This percentage seems to give an advantage for B3LYP present calculations.

Previous works on SnO₂ relied on the pyramid structure of its surface [24, 28, 31]. Pyramids on the SnO₂ surface are also confirmed experimentally [27]. Figure 1a shows the pyramid SnO₂ cluster used in the present calculations. The stoichiometry of this cluster (Sn₉O₁₆) is carefully chosen so that adding more oxygen to this cluster (such as Sn₁₀O₁₇) will make the Gibbs free energy of reaction positive, and the cluster will return to the optimum stoichiometry Sn₁₀O₁₆ in a specific reaction rate. This is in agreement with experimental results that SnO₂ has a lot of vacancies [28]. The Sn–O bond length is in the range of 1.9 to 2.1 Å, which is in agreement with the literature [32].

Graphene has a well-known hexagonal honeycomb structure. Coronene (C₂₅H₁₂) is used frequently to represent graphene [33–35]. However, we use oxygen instead of hydrogen (C₂₅O₉) to simulate the real existence of oxygen in the air and not the rare hydrogen. A variation of C–C bond length in the range (1.32 to 1.5 Å) according to bond distance from edges is in agreement with the experiment [26]. A lower range for C=O and C-O (1.22 to 1.45 Å) is also in agreement with the experiment [26]. C₂₅O₉ (as in Fig. 1b) is called reduced graphene oxide since no oxygen-containing functional groups exist on the surface of this cluster. Practically, the edges of the graphene cluster of atoms are terminated by oxygen, hydroxyl, or oxygen-containing functional groups. The upper and lower surfaces of graphene can also be terminated by oxygen or oxygen-containing groups. However, the functional groups on graphene surfaces can be removed easily, which is not the case for functional groups at the edges. The removal of an OH group by hydrazine (N₂H₄) from the surface and edges of reduced graphene oxide in Fig. 1b can be given by the following reactions (in all the following reactions we use the standard conditions of 25 °C and 1 atm unless mentioned otherwise):

\[
C_{24}O_6 + 1/4N_2H_4 \rightarrow C_{24}O_6 + 1/4N_2 + H_2O \quad (\text{Surface } \Delta G = 1.681 \text{ eV}),
\]

\[
C_{24}O_6 + 1/4N_2H_4 \rightarrow C_{24}O_6 + 1/4N_2 + H_2O \quad (\text{Edge } \Delta G = 4.632 \text{ eV})
\]

\(\Delta G\) is the Gibbs free energy of the reaction. We can see from the upper two equations that removing the OH functional group from the edge of graphene requires three times the energy required to remove the OH group from the surface. The same is not true for removing oxygen from the surface and edge. Oxygen can be completely removed using hydrazine [8]. The UV radiation can break the OH bond to graphene at the surface only. The energy of a 532 nm (2.331 eV) can break this bond [18] so are the 365 nm (3.979 eV) radiation as in reference [9].

NO₂ gas at low temperatures decomposes to NO and O₂ [36, 37] in an endothermic reaction as in the reaction:

\[
NO_2 \rightarrow NO + 1/2O_2 \quad (\Delta G = 0.416 \text{ eV})
\]

The decomposition of NO₂ near the surfaces of catalysts affects the ability to sensor NO₂ since it decreases the concentration of the gas near the sensor surface. The rate of decomposition is given by [38]:

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In the above equation, \([\text{NO}_2]\) is the concentration of \(\text{NO}_2\) gas. \(C_1\) is an empirical coefficient that can be found experimentally. \(k(T)\) is the temperature-dependent part:

\[
\frac{d[\text{NO}_2]}{dt} = C_1 [\text{NO}_2] k(T).
\]  

(4)

\[
k(T) = T \exp \left( \frac{-\Delta G_a}{k_B T} \right).
\]

(5)

\(T\) is the temperature, \(\Delta G_a\) is the Gibbs free energy of activation, and \(k_B\) is the Boltzmann constant. The same method of Eq. (4) can be used to calculate the reaction.

Fig. 1  a Sn10O16 cluster molecule and b reduced graphene oxide (rGO) cluster molecule

Fig. 2  Heterojunction between \(\text{SnO}_2\) and rGO clusters to form the rGO/\(\text{SnO}_2\) hybrid
between NO₂ gas and the SnO₂/reduced graphene oxide hybrid:

\[
\frac{d[NO_2]}{dt} = -C_2[NO_2] \frac{[Sn_{10}O_{16}/C_{24}O_6]}{C_2} k(T) \tag{6}
\]

Solving Eq. (4) and Eq. (6) for the concentration of NO₂ (assuming [NO₂] is not appreciably affected by the two reactions):

\[
[NO_2] = [NO_2]_0 \exp^{-C_1 k(T)t} \tag{7}
\]

\[
[NO_2] = [NO_2]_0 \exp^{-C_2 [Sn_{10}O_{16}/C_{24}O_6] k(T)t} \tag{8}
\]

**Results and discussion**

Figure 2 shows the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of both SnO₂ (represented by the Sn₁₀O₁₆ cluster) and the rGO (represented by the C₂₄O₆ cluster) and their energy gaps. The experimental energy gap of SnO₂ is 3.6 to 3.92 eV [32, 39] which is around our calculated 3.875 eV value. The experimental energy gap of rGO is in the range of 1.00 to 1.69 eV [22]. The present calculated gap of rGO represented by C₂₄O₆ is 1.336 eV which is nearly the average of the experimental range. The p-n heterojunction formed between rGO and SnO₂ [40] is the straddling gap since the HOMO, and LUMO energy levels of rGO are within that of SnO₂, as shown in Fig. 2. If the two materials (SnO₂ and rGO) do not interact at all, the final gap should be that of rGO. However, this is not the case. The high affinity of carbon atoms drags oxygen atoms from SnO₂ because of the lower affinity of Sn atoms, as in Fig. 3b. In addition, a bond is formed between carbon and tin atoms. Due to these interactions, the final material is called the rGO/SnO₂ hybrid, which is some kind of a composite at the molecular or nanoscale [41]. The final calculated gap of the rGO/SnO₂ hybrid is 1.534 eV, with the HOMO and LUMO energy levels moved to be higher than that of rGO as in Fig. 2.

Besides the energy gap, calculations of the electronic structure of Sn₁₀O₁₆ and C₂₄O₆ clusters and hybrid reveal other quantities such as XPS that match the experimental

| Quantity                | Theoretical | Experimental              | Experimental references |
|-------------------------|-------------|---------------------------|-------------------------|
| rGO energy gap eV       | 1.336       | 1.00 to 1.69              | [22]                    |
| SnO₂ energy gap eV      | 3.875       | 3.6 to 3.92               | [32, 39, 43]            |
| rGO/SnO₂ energy gap eV  | 1.534       | -                         | -                       |
| XPS rGO O1s eV          | -520.716 to -524.302 | -531.19 to -533.8         | [42]                    |
| XPS SnO₂ O1s eV         | -520.139 to -521.808 | 531.1                     | [44]                    |
| XPS rGO/SnO₂ O1s eV     | -519.511 to -524.308 | -                         | -                       |
| XPS rGO C1s eV          | -278.790 to -280.899 | -284.83 to -291.2         | [42]                    |
| XPS rGO/SnO₂ C1s eV     | -278.321 to -282.307 | -                         | -                       |
values of SnO$_2$ and rGO as in Table 1. As an example, O1s energy level in rGO alone is in the range of $-520.716$ to $-524.302$ eV, which is in good agreement with experimental XPS spectra of reference [42]. The O1s energy level in Sn$_{10}$O$_{16}$ is in the range of $-520.139$ to $-521.808$ eV, which is only 2% different from the experimental 531.1 eV value. The O1s theoretical energy level in the rGO/SnO$_2$ hybrid is in the range of $-519.511$ to $-524.308$ eV, which incorporates both Sn$_{10}$O$_{16}$ and C$_{24}$O$_6$ within its range. Although carbon atoms exist only in the C$_{24}$O$_6$ cluster, the C1s level in the hybrid is wider than that of the C$_{24}$O$_6$ cluster alone, as in Table 1.

Figure 3a shows our initial theoretical arrangement of attaching the SnO$_2$ cluster (Sn$_{10}$O$_{16}$) to the rGO cluster (C$_{24}$O$_6$). In this attachment, the base of the SnO$_2$ pyramid is put on the rGO surface. However, after performing self-consistent field calculations of the present density functional theory, the SnO$_2$ cluster is repelled so that the attachment is made between one of the carbon atoms at the edge of rGO and one Sn atom at the edge of SnO$_2$ as in Fig. 3b. This arrangement is consistent with the above-mentioned high and powerful reactivity of rGO edges with respect to the rGO surface. This is also consistent with experimental findings in field emission scanning electron microscope

| Table 2 | Gibbs free energies of reactions and activation and their components (enthalpy and entropy) at standard temperature and pressure (temperature 298.15 K and pressure 1 atm). (S) represents surface reactions and (E) represents edge reactions |
|---------|---------------------------------------------------------------------------------|
| $n$     | Reaction                                                                            | $\Delta G$ (eV) | $\Delta H$ (eV) | $T\Delta S$ (eV) |
| 1       | C$_{24}$O$_6$(OH)$_n$$\rightarrow$C$_{24}$O$_6$+$\frac{1}{2}$N$_2$+$\frac{1}{2}$H$_2$O (S) | 1.681           | 2.075             | 0.393             |
| 2       | C$_{24}$O$_6$(OH)$_n$$\rightarrow$C$_{24}$O$_6$+$\frac{1}{2}$N$_2$+$\frac{1}{2}$H$_2$O (E) | 4.632           | 5.063             | 0.431             |
| 3       | C$_{24}$O$_6$+$\frac{1}{2}$N$_2$+$\frac{1}{2}$H$_2$O (S) $\rightarrow$C$_{24}$O$_6$+$\frac{1}{2}$N$_2$+$\frac{1}{2}$H$_2$O (E) | -0.199          | 0.159             | 0.358             |
| 4       | C$_{24}$O$_6$+$\frac{1}{2}$N$_2$+$\frac{1}{2}$H$_2$O (E) $\rightarrow$C$_{24}$O$_6$+$\frac{1}{2}$N$_2$+$\frac{1}{2}$H$_2$O (E) | -1.542          | -1.095            | 0.446             |
| 5       | NO$_2$ $\rightarrow$NO+$\frac{1}{2}$O$_2$                                        | 0.416           | 0.626             | 0.209             |
| 6       | C$_{24}$O$_6$/Sn$_{10}$O$_{16}$+NO$_2$ $\rightarrow$C$_{24}$O$_6$/Sn$_{10}$O$_{17}$ + NO | 1.255           | 1.244             | -0.011            |
| 7       | C$_{24}$O$_6$/Sn$_{10}$O$_{16}$+NO$_2$ $\rightarrow$[C$_{24}$O$_6$/Sn$_{10}$O$_{16}$ + NO$_2$]$^\ddagger$ | -0.0595         | -0.447            | -0.387            |
| 8       | C$_{24}$O$_6$/Sn$_{10}$O$_{17}$ $\rightarrow$C$_{24}$O$_6$/Sn$_{10}$O$_{16}$+$\frac{1}{2}$O$_2$ (S) | -0.838          | -0.618            | 0.220             |
| 9       | C$_{24}$O$_6$/Sn$_{10}$O$_{17}$ $\rightarrow$C$_{24}$O$_6$/Sn$_{10}$O$_{17}$+$\frac{1}{2}$O$_2$ (E) | 1.224           | 1.474             | 0.250             |

Fig. 4 The transition state and the steps of the reaction of rGO/SnO$_2$ hybrid with NO$_2$
(FESEM) and scanning electron microscope (SEM) images in which SnO$_2$ nanoparticles are stacked on rGO sides and edges [8, 9].

NO$_2$ sensitivity is only triggered by its interaction with either rGO or SnO$_2$ in the rGO/SnO$_2$ hybrid. This interaction changes the energy gap value that ultimately changes the resistivity of rGO/SnO$_2$. The oxidation of the SnO$_2$ cluster in the rGO/SnO$_2$ hybrid can be described by the equation:

$$C_{24}O_6/Sn_{10}O_{16} + NO_2 \rightarrow C_{24}O_6/Sn_{10}O_{17} + NO \ (\Delta G = 1.255 \text{ eV})$$  \hspace{1cm} (9)

The reaction in the upper equation is endergonic, and we can use Eqs. (4) and (5) to determine the reaction rate. To determine the reaction rate, the Gibbs free energy of activation $\Delta G_a$ should be determined as in the following reaction:

$$C_{24}O_6/Sn_{10}O_{16} + NO_2 \rightarrow [C_{24}O_6/Sn_{10}O_{16} \sim NO_2]^+ \ (\Delta G_a = -0.0595 \text{ eV})$$  \hspace{1cm} (10)

In the above reaction, $[C_{24}O_6/Sn_{10}O_{16} \sim NO_2]^+$ is the transition state. The value of the activation energy ($\Delta G_a = -0.0595 \text{ eV}$) is negative, which means that the formation of the transition state is an exergonic reaction. The steps of this reaction are shown in Fig. 4.

Gibbs free energy, enthalpy, and entropy of a reaction are connected via the relation:

$$\Delta G = \Delta H - T \Delta S$$  \hspace{1cm} (11)

$\Delta H$ is the change in enthalpy or the enthalpy of reaction. $\Delta S$ is the change in entropy, while the term $T \Delta S$ is the entropy energy of the reaction. As we have seen before in Eq. (5) that Gibbs free energy of activation determines the rate of reaction. The enthalpy of reaction is the heat produced or absorbed in the reaction. The entropy of reaction is usually related to the difference between the number of reacting molecules and the number of product molecules. In Table 2, we listed the different reactions encountered in this work, including their Gibbs free energy, enthalpy, and entropy. We can see from Table 2 that most of the reactions have a higher number of product molecules than the number of reactants.
interacting molecules and, consequently, positive entropy energy. The two exceptions are reaction numbers 6 and 7 in Table 2. Reaction number 6 has an equal number of reactants and products and very small entropy energy. Reaction number 7 has the number of products less than the reactants and hence negative entropy energy. The sign of the entropy energy affects the value of Gibbs free energy and the final rate of reaction.

Finally, Fig. 5 summarizes the reactions that take place when NO₂ gas reacts with C₂₄O₆/Sn₁₀O₁₆ cluster hybrid. The first reaction is the dissociation of NO₂ gas to NO and O₂ gases (the upper arrow in Fig. 5). This reaction can take place even before NO₂ reaches the surface of the C₂₄O₆/Sn₁₀O₁₆ cluster, in which the hybrid can be considered a catalyst for the dissociation reaction. Due to this reaction, the concentration of NO₂ decreases as it approaches the C₂₄O₆/Sn₁₀O₁₆ surface (the arrow on the left side of Fig. 5). The remaining NO₂ concentration reacts with both rGO and SnO₂ parts of the rGO/SnO₂ hybrid. At room temperature, the interaction between both rGO and SnO₂ does not change the concentration of NO₂ appreciably. The interaction of NO₂ with rGO takes place only one time, after which the oxygen atom attached to rGO will not be able to escape due to the high Gibbs energy of separation as in reaction number 9 in Table 2. This causes the resistance of the SnO₂/rGO sensor to increase even after stopping NO₂ gas from flowing. This does not happen for the oxygen connected to the SnO₂ cluster due to negative Gibbs energy of separation of oxygen from SnO₂ as in reaction number 8 in Table 2. The ability of NO₂ gas to oxidize the rGO/SnO₂ hybrid can make it easily distinguished from other gases that mainly reduce oxygen from the sensor, such as NH₃, CO, acetone, ethanol, methanol gases [8, 41]. The sensitivity of the rGO/SnO₂ hybrid increases as we increase the temperature until the temperature reaches between room temperature to 150 °C after which it drops depending on the method of manufacturing and concentration of NO₂ [8, 45, 46]. However, examining Eqs. (5) and (8), we can see that the reaction rate should increase with temperature. The reason for the drop in sensitivity in high temperatures is that the concentration of NO₂ decreases rapidly in high temperatures due to dissociation before reaching rGO/SnO₂ hybrid surface, as we discussed in Fig. 5.

Conclusions

The interaction of NO₂ gas with rGO/SnO₂ hybrid is analyzed using the DFT method and compared with available experimental findings. The calculated energy gaps and XPS levels are in good agreement with the experiment. DFT calculations show that SnO₂ and rGO are connected by their edges due to the high reactivity of rGO edges with respect to their surface. The energy gap of the rGO/SnO₂ hybrid is in between that of SnO₂ and rGO due to the reaction between them. The present results also show that the sensitivity of the rGO/SnO₂ hybrid to NO₂ is mostly due to SnO₂ interaction with NO₂ gas. The effect of rGO is to distribute SnO₂ nanoparticles evenly on rGO edges and to reduce the agglomeration of SnO₂. The sensitivity of the rGO/SnO₂ hybrid to NO₂ increases with temperature until the NO₂ dissociation in the air reduces the concentration of NO₂ reaching the surface of rGO/SnO₂ appreciably and decreases the sensitivity. The results are in good agreement with previous experimental findings, including energy gaps and XPS values.

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Author contribution Conceptualization: Abdulsattar; formal analysis: Abdulridha; investigation: Hussein; methodology: Abdulsattar and Abdulridha; project administration: Abdulsattar; supervision: Abdulsattar; writing—original draft: Abdulsattar.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication All co-authors have seen and approved the manuscript.

Conflict of interest The authors declare no competing interests.

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