Sensitivity of SnO₂ nanoparticles/reduced graphene oxide hybrid to NO₂ gas: A DFT study

Shaima K. Abdulridha

University of Baghdad

Mudar Ahmed Abdulsattar (✉ mudarahmed3@yahoo.com)

Iraq Ministry of Science and Technology <https://orcid.org/0000-0001-8234-6686>

Mohammed T. Hussein

University of Baghdad

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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 nanoparticles 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 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.

Introduction

Graphene is a material with high potential applications [1–3]. These applications include solar cells [1], 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 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].

Tin oxide is one of the most used materials in gas sensing [11, 12]. It is a p-type semiconductor [13]. 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. 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 [9,14,15]. 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 [7,16–18]. In addition to SnO_2 other catalysts such as SnS_2 , Ag, or Pd can also improve the sensitivity of graphene or its oxide [16–18].

The use of density functional theory (DFT) has proved to give valuable information about gas sensing mechanisms, including the various properties of materials used in the sensing operation [19,20]. 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 SnO_2/rGO hybrid to NO_2 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 NO_2 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 SnO_2/rGO hybrid and their interaction with NO_2 gas. Previous works on SnO_2 surveyed different methods and bases to perform electronic structure calculations such as GGA, LDA, B3LYP, and PBE0 [21]. B3LYP 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 [22, 23]. 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. SDD basis is used for heavy Sn atoms that cannot be represented by 6-311G** basis. Dispersion corrections are important for the present calculations because of long-range forces between the interacting molecules. GD3BJ dispersion correction version is added [24]. Gaussian 09 molecular facilities program is used to perform present calculations [25].

Previous works on SnO_2 relied on the pyramid structure of its surface [20,23,26]. Pyramids on the SnO_2 surface are also confirmed experimentally [22]. Figure 1a shows the pyramid SnO_2 cluster used in the present calculations. The stoichiometry of this cluster ($\text{Sn}_{10}\text{O}_{16}$) is carefully chosen so that adding more oxygen to this cluster (such as $\text{Sn}_{10}\text{O}_{17}$) will make the Gibbs free energy of reaction positive, and the cluster will return to the optimum stoichiometry $\text{Sn}_{10}\text{O}_{16}$ in a specific reaction rate. This is in agreement with experimental results that SnO_2 has a lot of vacancies [23]. The Sn-O bond length is in the range of 1.9 to 2.1 Å, which is in agreement with the literature [27].

Graphene has a well-known hexagonal honeycomb structure. Coronene ($\text{C}_{24}\text{H}_{12}$) is used frequently to represent graphene [28–30]. However, we use oxygen instead of hydrogen (C_{24}O_6) 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 [31]. A lower range for C = O and C-O (1.22 to 1.45 Å) is also in agreement with the experiment [31]. C_{24}O_6 (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):

ΔG 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 [14] so are the 365 nm (3.397 eV) radiation as in reference [9].

NO₂ gas at low temperatures decomposes to NO and O₂ [32, 33] in an endothermic reaction as in the reaction:

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 [34]:

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

4

In the above equation, [NO₂] is the concentration of NO₂ gas. C₁ is an empirical coefficient that can be found experimentally. k(T) is the temperature-dependent part:

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

5

T is the temperature, ΔG_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 between NO₂ gas and the SnO₂/reduced graphene oxide hybrid:

$$\frac{d[\text{NO}_2]}{dt} = -C_2[\text{NO}_2][\text{Sn}_{10}\text{O}_{16}/\text{C}_{24}\text{O}_6]k(T).$$

6

Solving Eq. (4) and Eq. (6) for the concentration of NO_2 (assuming $[\text{NO}_2]$ is not appreciably affected by the two reactions):

$$[\text{NO}_2] = [\text{NO}_2]_0 \exp^{-C_1 k(T) t} \quad (7)$$

$$[\text{NO}_2] = [\text{NO}_2]_0 \exp^{-C_2 [\text{Sn}_{10}\text{O}_{16}/\text{C}_{24}\text{O}_6] k(T) t} \quad (8)$$

Results And Discussion

Figure 2 shows the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of both SnO_2 (represented by the $\text{Sn}_{10}\text{O}_{16}$ cluster) and the rGO (represented by the C_{24}O_6 cluster) and their energy gaps. The experimental energy gap of SnO_2 is 3.6 to 3.92 eV [27, 35] which is around our calculated 3.875 eV value. The experimental energy gap of rGO is in the range between 1.00 to 1.69 eV [16]. The present calculated gap of rGO represented by C_{24}O_6 is 1.336 eV which is nearly the average of the experimental range. The p-n heterojunction formed between rGO and SnO_2 [36] is of the straddling gap since the HOMO and LUMO energy levels of rGO are within that of SnO_2 , as shown in Fig. 2. If the two materials (SnO_2 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 SnO_2 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/ SnO_2 hybrid, which is some kind of a composite at the molecular or nanoscale [37]. The final calculated gap of the rGO/ SnO_2 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 $\text{Sn}_{10}\text{O}_{16}$ and C_{24}O_6 clusters and hybrid reveal other quantities such as XPS that match the experimental values of SnO_2 and rGO as in Table 1. As an example, O1s energy level in rGO alone is in the range - 520.716 to -524.302 eV, which is in good agreement with experimental XPS spectra of reference [38]. The O1s energy level in $\text{Sn}_{10}\text{O}_{16}$ is in the range - 520.139 to -521.808 eV, which is only 2% different than experimental 531.1 eV value. The O1s theoretical energy level in the rGO/ SnO_2 hybrid is in the range - 519.511 to -524.308 eV, which incorporates both $\text{Sn}_{10}\text{O}_{16}$ 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.

Table 1
Some present calculated properties of rGO and SnO₂ clusters and their rGO/SnO₂ hybrid in comparison with experimental references.

Quantity	Theoretical	Experimental	Experimental references
rGO energy gap eV	1.336	1.00 to 1.69	[16]
SnO ₂ energy gap eV	3.875	3.6 to 3.92	[27, 35, 39]
rGO/SnO ₂ energy gap eV	1.534	-	-
XPS rGO O1s eV	-520.716 to -524.302	-531.19 to -533.8	[38]
XPS SnO ₂ O1s eV	-520.139 to -521.808	531.1	[40]
XPS rGO/SnO ₂ O1s eV	-519.511 to -524.308	-	-
XPS rGO C1s eV	-278.790 to -280.899	-284.83 to -291.2	[38]
XPS rGO/SnO ₂ C1s eV	-278.321 to -282.307	-	-

Figure 3a shows our initial theoretical arrangement of attaching the SnO₂ cluster (Sn₁₀O₁₆) to the rGO cluster (C₂₄O₆). In this attachment, the base of the SnO₂ pyramid is put on the rGO surface. However, after performing self-consistent field calculations of the present density functional theory, the SnO₂ 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 SnO₂ 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 FESEM and SEM images in which SnO₂ nanoparticles are stacked on rGO sides and edges [8,9].

NO₂ sensitivity is only triggered by its interaction with either rGO or SnO₂ in the rGO/SnO₂ hybrid. This interaction changes the energy gap value that ultimately changes the resistivity of rGO/SnO₂. The oxidation of the SnO₂ cluster in the rGO/SnO₂ hybrid can be described by the equation:

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 ΔG_a should be determined as in the following reaction:

In the above reaction, $[\text{C}_{24}\text{O}_6/\text{Sn}_{10}\text{O}_{16} - \text{NO}_2]^\ddagger$ 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:

$$\Delta G = \Delta H - T\Delta S$$

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ΔH is the change in enthalpy or the enthalpy of reaction. ΔS 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 interacting molecules and, consequently, positive entropy energy. The two exceptions are reactions number 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.

Table 2

Gibbs free energies of reactions and activation and their components (enthalpy and entropy) at standard temperature and pressure (temperature 298.15 Kelvin and pressure 1 atm). (S) represents surface reactions and (E) represents edge reactions.

n	Reaction	ΔG (eV)	ΔH (eV)	$T\Delta S$ (eV)
1	$C_{24}O_6(OH) + \frac{1}{4}N_2H_4 \rightarrow C_{24}O_6 + \frac{1}{4}N_2 + H_2O$ (S)	1.681	2.075	0.393
2	$C_{24}O_6(OH) + \frac{1}{4}N_2H_4 \rightarrow C_{24}O_6 + \frac{1}{4}N_2 + H_2O$ (E)	4.632	5.063	0.431
3	$C_{24}O_7 + \frac{1}{2}N_2H_4 \rightarrow C_{24}O_6 + \frac{1}{2}N_2 + H_2O$ (S)	-0.199	0.159	0.358
4	$C_{24}O_6 + \frac{1}{2}N_2H_4 \rightarrow C_{24}O_5 + \frac{1}{2}N_2 + H_2O$ (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	$C_{24}O_6/Sn_{10}O_{17} \rightarrow C_{24}O_5/Sn_{10}O_{17} + \frac{1}{2}O_2$ (E)	1.224	1.474	0.250

Finally, Fig. (5) summarizes the reactions that take place when NO_2 gas reacts with $C_{24}O_6/Sn_{10}O_{16}$ cluster hybrid. The first reaction is the dissociation of NO_2 gas to NO and O_2 gases (the upper arrow in Fig. (5)). This reaction can take place even before NO_2 reaches the surface of the $C_{24}O_6/Sn_{10}O_{16}$ cluster, in which the hybrid can be considered as a catalyst for the dissociation reaction. Due to this reaction, the

concentration of NO_2 decreases as it approaches the $\text{C}_{24}\text{O}_6/\text{Sn}_{10}\text{O}_{16}$ surface (the arrow on the left side of Fig. (5)). The remaining NO_2 concentration reacts with both rGO and SnO_2 parts of the rGO/ SnO_2 hybrid. At room temperature, the interaction with both rGO and SnO_2 does not change the concentration of NO_2 appreciably. The interaction of NO_2 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 SnO_2 /rGO sensor to increase even after stopping NO_2 gas from flowing. This does not happen for the oxygen connected to the SnO_2 cluster due to negative Gibbs energy of separation of oxygen from SnO_2 as in reaction number 8 in Table 2. The ability of NO_2 gas to oxidize the rGO/ SnO_2 hybrid can make it easily distinguished from other gases that mainly reduce oxygen from the sensor, such as NH_3 , CO, acetone, ethanol, methanol gases [8,37].

The sensitivity of the rGO/ SnO_2 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 NO_2 [8,41,42]. However, examining Eqs. (5) and (8), we can see that the reaction rate should increase with temperature. The reason for the drop of sensitivity in high temperatures is that the concentration of NO_2 decreases rapidly in high temperatures due to dissociation before reaching rGO/ SnO_2 hybrid surface, as we discussed in Fig. 5.

Conclusions

The interaction of NO_2 gas with rGO/ SnO_2 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 SnO_2 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/ SnO_2 hybrid is in between that of SnO_2 and rGO due to the reaction between them. The present results also show that the sensitivity of the rGO/ SnO_2 hybrid to NO_2 is mostly due to SnO_2 interaction with NO_2 gas. The effect of rGO is to distribute SnO_2 nanoparticles evenly on rGO edges and to reduce agglomeration of SnO_2 . 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 reaching the surface of rGO/ SnO_2 appreciably and decreases the sensitivity.

Declarations

Author contribution: Conceptualization: Abdulsattar; formal analysis:

Abdulridha; investigation: Hussein; methodology: Abdulsattar, and Abdulridha;

project administration: Abdulsattar; supervision: Abdulsattar; writing—

original draft: Abdulsattar

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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Figures

Figure 1

(a) Sn₁₀₀₁₆ cluster molecule, (b) reduced graphene oxide (rGO) cluster molecule.

Figure 2

Heterojunction between SnO_2 and rGO clusters to form the rGO/ SnO_2 hybrid.

Figure 3

(a) our initial $\text{Sn}_{10}\text{O}_{16}$ molecular cluster connection with C_{24}O_6 molecular cluster, (b) the formation of rGO/ SnO_2 hybrid.

Figure 4

The transition state and the steps of the reaction of rGO/SnO₂ hybrid with NO₂.