Disciplinarum Scientia. Série: Naturais e Tecnológicas, Santa Maria, v. 19, n. 3, p. 309-317, 2018.
Recebido em: 09.07.2018. Aprovado em: 28.09.2018.

ISSN 2176-462X

TOXIC GASES ADSORBED ON GRAPHENE OXIDE WITH VACANCY: A THEORETICAL STUDY[1]

GASES TÓXICOS ADSORVIDOS EM ÓXIDO DE GRAFENO COM VACÂNCIA: UM ESTUDO TEÓRICO

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ABSTRACT

Emission of toluene and formaldehyde emission is related to several health problems, such as cancer, cardiovascular and respiratory diseases. Studies show the use of graphene oxide as a gas sensor. Therefore, the aim of this study is to investigate the electronic and structural properties of the interaction between graphene oxide with vacancy (GOV) and toluene and formaldehyde. In this study, the SIESTA code was used, which is based on the Density Functional Theory (DFT). The interaction between toluene and the GOV that presented the lowest binding energy (-0.86 eV) was the one in which toluene was planarly approximated by vacancy. The interaction between formaldehyde and the GOV that presented a lower binding energy (-0.90 eV) is the one in which formaldehyde is planarly approximated by hydroxyl. For both cases, the electronic properties remained unchanged and the electronic density plots of charge are more concentrate on the nanostructure. All interactions occurred in a physical adsorption regime; thus, a possible application for GOV would be as a filter for industry vents.

Keywords: density function theory, formaldehyde, toluene.

RESUMO

A emissão de tolueno e formaldeído está associada a diversas doenças, como câncer e problemas no sistema nervoso central e respiratório. Estudos indicam que o óxido de grafeno pode ser usado como sensor de gases. Sendo assim, o objetivo deste estudo foi analisar as propriedades estruturais e eletrônicas da interação entre o óxido de grafeno com vacância (GOV) com tolueno e com formaldeído. Para este estudo foi utilizado o código computacional SIESTA, o qual é baseado na Teoria do Funcional da Densidade (DFT). A interação entre o tolueno e o GOV que apresentou menor energia de ligação (-0,86 eV) foi aquela em que o tolueno foi aproximado de forma planar pela vacância. A interação entre o formaldeído e o GOV que apresentou menor energia de ligação (-0,90 eV) foi aquela em que o formaldeído foi aproximado de forma planar pela hidroxila. Em ambos os casos, as propriedades eletrônicas permaneceram praticamente inalteradas e os plotes de densidade eletrônica de carga estão concentrados em maior quantidade na nanoestrutura. Todas as interações ocorreram em regime de adsorção física, sendo assim, uma possível aplicação do GOV seria utilizá-lo como filtro em chaminés de indústrias.

Palavras-chave: *teoria do funcional da densidade, formaldeído, tolueno.*

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INTRODUCTION

Roffael et al. (2018) indicated an increase in the emission of toxic gases such as toluene ($C_6H_5CH_3$) and formaldehyde (H_2CO), which, in association with environmental problems, is harmful. Toluene is an aromatic hydrocarbon, flammable, volatile, difficult to detect, introduced into the atmosphere by the production of gasoline and petroleum refinement. exposure to this gas is related to several health problems, such as cancer, cardiovascular and respiratory diseases (LIM et al., 2017). Formaldehyde is an organic volatile compound, classified as carcinogenic, present on the smoke released by textile, pharmaceutic, and plastic industry, and others; also, it is present on cigarette smoke and the smoke emitted by vehicles. Exposure to formaldehyde can cause serious harm to human health, which can lead to death It is classified by several agencies as a human carcinogen, it can exhibit mutagenic and teratogenic effects (DE SOUZA et al., 2017; NJOYA et al., 2009). Therefore, it is essential to detect and monitor the emission of toluene and formaldehyde in the environment.

Theoretical and experimental studies propose the use of carbon nanostructures for the adsorption of formaldehyde and toluene (KWON et al., 2016; YUAN; HE; CHEN, 2017). Li et al. (2016) detected formaldehyde with a film composed of reduced graphene oxide and molybdenum disulfide. Graphene oxide (GO) decorated with stannic oxide nanoparticles presented a great potential to detect formaldehyde (CAO et al., 2014). Su et al. (2016) found out that reduced graphene oxide and polyethylene oxide present a high sensibility in toluene detection.

Zhou et at. (2014) show theoretically that the adsorption of formaldehyde on defective graphene is stronger than on pure graphene. Theoretical and experimental studies propose nanostructures as carbon nanotubes as sensors for formaldehyde and toluene (PARK et al., 2016; LIU et al., 2017). However, the adsorption of toluene and graphene oxide with vacancy is an unprecedented study. Graphene oxide has attracted attention because of its crucial importance in the detection of gases because it is a controllable and innovative nanomaterial (ZHAO et al., 2018). As there are no studies in the literature about the use of GOV as a sensor for toluene and formaldehyde, it is essential to understand the electronic and structural properties of GOV associated with these gases, thus, this is the aim of this study.

MATERIAL AND METHODS

Interactions between toxic gases and GOV were analyzed via calculations of first principles based on Density Function Theory (DFT) (HONENBERG; KOHN, 1964) which studied electronic properties of atoms, molecules and solids. Associated with the norm-conserving pseudopotential method by Troullier-Martins (TROUYLLIER; MARTINS, 1991), this theory is implemented on SIESTA code (Spanish Initiative for Electronic Simulations with Thousands of Atoms) (SOLER et al., 2002).

The Local density approximation (LDA) calss was used to describe the exchange-correlation of this study (CEPERLEY; ALDER, 1980).

In this study, the GO used is similar to the GO studied by Martinez (2013) whose structure has 164 atoms (144 are carbon atoms that form graphene sheet and 20 atoms belong to functional groups with three OH, two O, and three COOH). One carbon atom was removed from the graphene sheet to induce a defect, creating a vacancy. Toluene and formaldehyde were approximated to GOV by vacancy, the OH, and the COOH.

Binding energies between toxic gases and GOV were calculated using the equation:

$$E_b = [E_T (GOV + Gas) - E_T (GOV) - E_T(Gas)] \quad (1)$$

where the E_T(GOV+Gas) is the total energy of GOV interacting with toluene or formaldehyde, E_T(GOV) is the total energy of GOV, and E_T(Gas) represents the total energy of the respective gas.

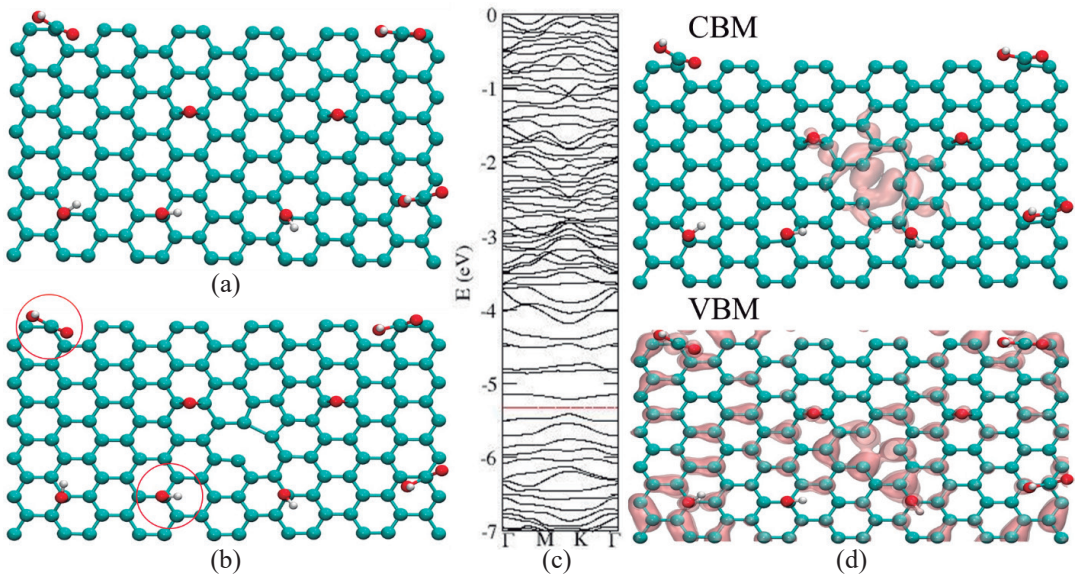
RESULTS AND DISCUSSION

The electronic and structural properties of GOV and of the lowest energy configuration of GOV interaction with toluene and formaldehyde are present next in the text.

GRAPHENE OXIDE WITH VACANCY

Figure 1 presents in (a) the optimized geometry of GO without defects, in (b) the optimized geometry of GOV, in (c) the electronic band structure of GOV and its electronic charge density plot in (d).

Figure 1 - (a) Optimized geometry of GO without defects, (b) optimized geometry of GOV, (c) GOV electronic band structure and (d) electronic charge density plot for CBM and VBM, respectively.

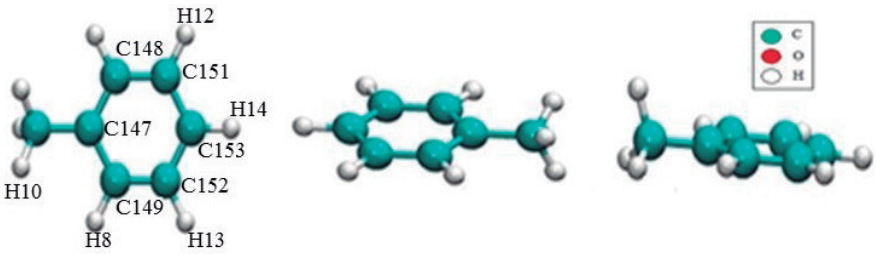


It is possible to see in Figure 1 (b) the OH and the COOH highlighted in red, these are the functional groups that toluene and formaldehyde are approximated. In figure 1 (c) it is seen a gap of 0.19 eV for GOV. In figure 1 (d) it is observed an electronic charge density associated with CBM (conduction band minimum) concentrated on the vacancy, for VBM (valence band maximum) it concentrates on functional groups. The CBM is more concentrated in carbon atoms next to the functional groups and VBM is delocalized for all atoms in a GO layer.

TOXIC GASES INTERACTING WITH GOV

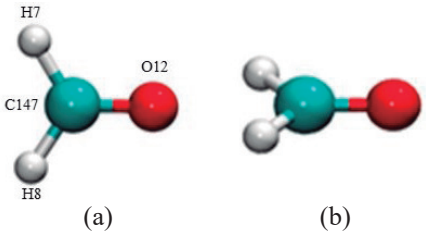
Five configurations for toluene interacting with GOV were studied, three configurations with toluene positioned vertically and two ones with toluene positioned horizontally, in parallel with GOV. All configurations were approximated to COOH, OH, and the vacancy, totalizing 15 interactions between toluene and GOV. In Figure 2 we presented the difference in Planar 1 and Planar 2.

Figure 2 - (a) Optimized geometry of toluene, (b) Planar 1 configuration and (c) Planar 2 configuration.



Three configurations of formaldehyde interacting with GOV were studied, two with formaldehyde position vertically, and one with formaldehyde positioned in horizontal, parallel with GOV. All configurations were approximate of the vacancy and functional groups totalizing 9 interactions between formaldehyde and GOV. In Figure 3 we present the Planar configuration of formaldehyde.

Figure 3 - (a) Optimize configuration of formaldehyde and (b) Planar configuration.



In all tables, we present the initial configuration, the optimized configuration, the smallest distance between atoms after the interaction, binding energies, and charge transfer. For the lowest energy interaction, we present the electronic band structure of GOV, energy levels of the gas, the electronic band structure, and the electronic charge density plots.

GOV INTERACTION WITH TOLUENE

Results associated with interactions between GOV and toluene are present in table 1.

Table 1 - Smallest distance between GOV and toluene (Å), binding energies (E_b) and charges transfer (ΔQ) of interactions. *Lowest energy configuration.

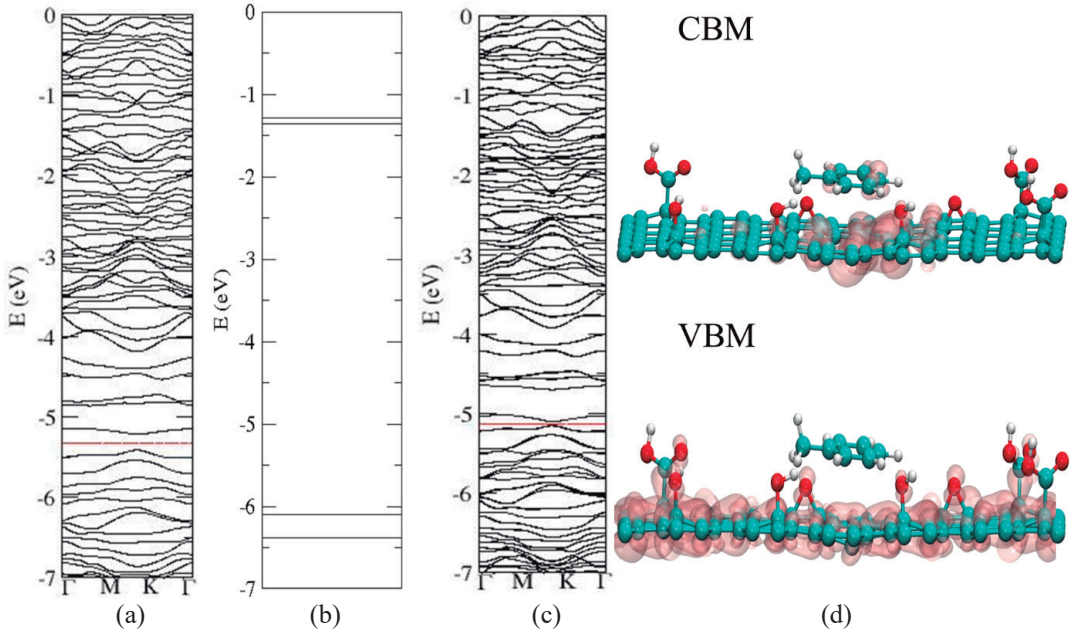
Initial configuration	Optimized Configuration	d (Å)	E_b (eV)	ΔQ (e^-)
Vacancy_H8	C33_H8	C - H = 1.93	-0.33	+0.09
Vacancy _H10	C38_H10	C - H = 2.80	-0.21	+0.02
Vacancy _H14	C33_H14	C - H = 2.29	-0.27	+0.10
Vacancy _Planar1	O6_H13	O - H = 2.23	-0.80	+0.14
Vacancy _Planar2*	O10_ H12	O - H = 2.16	-0.86	+0.11
COOH_H8	H4_H8	H - H = 2.02	-0.42	-0.06
COOH _H10	H4_H10	H - H = 1.71	-0.32	-0.09
COOH _H14	H4_H14	H - H = 1.73	-0.09	+0.01
COOH _Planar1	H4_C149	H - C = 1.90	-0.78	-0.13
COOH _Planar2	H4_ C147	H - C = 2.00	-0.79	-0.13
OH_H8	H2_H8	H - H = 1.93	-0.11	+0.01
OH_H10	H2_H10	H - H = 2.80	-0.12	-0.01
OH_H14	H2_H14	H - H = 2.29	-0.06	+0.01
OH_Planar1	H2_C152	H - C = 2.29	-0.62	+0.01
OH_Planar2	H2_C148	H - C = 2.14	-0.79	-0.05

Binding energies range from -0.06 to -0.86 eV, smallest distances range from 1.71 Å to 2.80 Å. Positive values for charge transfer indicate a transfer from GOV to toluene, and negative values indicate a charge transfer from toluene to GOV.

The lowest energy configuration is the Vacancy_Planar2, in which the gas is approximated to the parallel position of the vacancy. This interaction presents a binding energy of -0.86 eV, the smallest distance between toluene and GOV is 2.16 Å, between H atom from toluene and O atom from GOV, the H-O bond length is 0.96 Å. A charge transfer of +0.11 e- occurred from GOV to toluene. Electronic band structure and electronic charge density plot of this interaction are present in figure 4 (c)-(d).

In figure 4 (c) it is possible to observe the electronic band structure of GOV interacting with toluene, with a gap of 0.10 eV, and after the interaction, no significant modifications around Fermi level were noticed. The electronic charge density, figure 4 (d), is concentrated on GOV and toluene for CBM and VBM, the results show that the electronic charge density is concentrated only in GOV. These results indicate that this interaction is characterized as physical adsorption.

Figure 4 - (a) Electronic band strucutre of GOV, (b) energy levels of toluene, (c) electronic band structure of the interaction (gap of 0.10 eV) and (d) electronic charge density plot.



GOV INTERACTION WITH FORMALDEHYDE

Results associated with interactions between GOV and formaldehyde are present in table 2.

Table 2 - Smallest distance between GOV and formaldehyde (Å), binding energies (E_b) and charge transfer (ΔQ) of interactions. *Lowest energy configuration.

Initial Configuration	Optimized Configuration	d (Å)	E_l (eV)	ΔQ (e^-)
Vacancy_Planar	C38_H8	C - H = 2.49	-0.33	+0.08
Vacancy _ H8	O10_H7	O - H = 2.05	-0.27	+0.10
Vacancy _O12	C33_O12	C - O = 2.77	-0.18	-0.04
COOH_Planar	H4_O12	H - O = 1.49	-0.57	-0.17
COOH_ H7	H4_H7	H - H = 1.58	-0.07	+0.06
COOH_O12	H4_O12	H - O = 1.53	-0.60	-0.21
OH_Planar*	H2_O12	H - O = 1.67	-0.90	-0.13
OH_ H8	H2_H8	H - H = 2.01	-0.24	+0.00
OH_O12	H2_O12	H - O = 1.63	-0.69	-0.14

Binding energies range from -0.07 to -0.90 eV, smallest distances range from 1.49 Å to 2.77 Å. Positive values for charge transfer indicate a transfer from GOV to formaldehyde, and negative values indicate a charge transfer from formaldehyde to GOV.

The lowest energy configuration is the OH_Planar, in which the gas is approximate in the parallel position of the OH, with binding energy of -0.90 eV, the smallest distance between formaldehyde and GOV is 1.67 Å, between O atom from formaldehyde and H atom from OH, the H-O bond length is 0.96 Å. A charge transfer of -0.13 e- occurred from formaldehyde to GOV. Electronic band structure and electronic charge density plot of this interaction are present in figure 5 (c)-(d).

Figure 5 - (a) Electronic band structre of GOV, (b) energy levels of formaldehyde, (c) electronic band structure of the interaction (gap of 0.20 eV) and (d) electronic charge density plot.

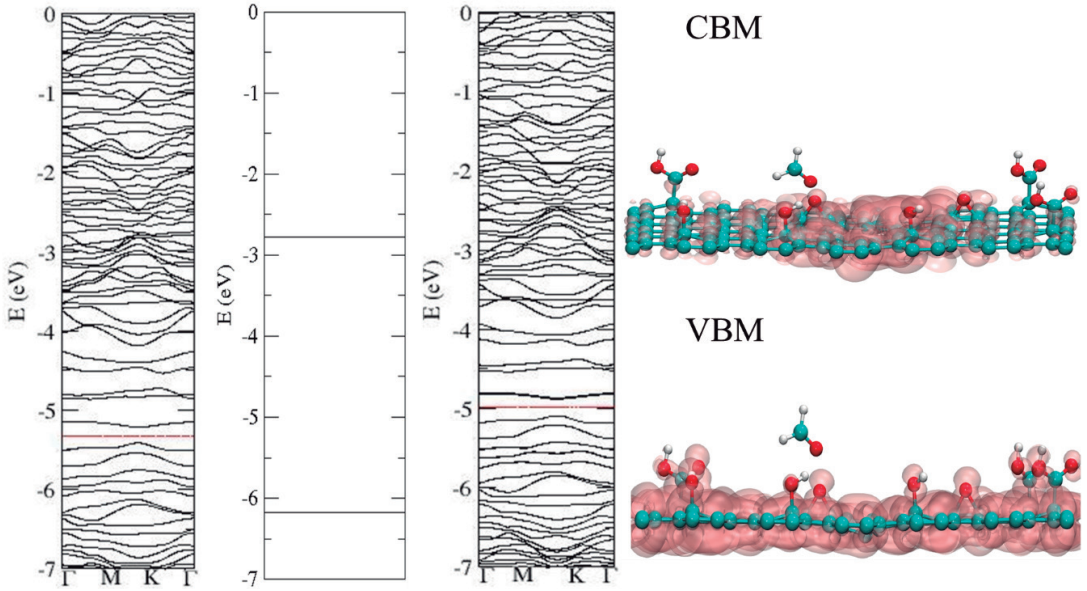


Figure 5 (c) presents the electronic band structure of the lowest configuration, in which it is possible to observe a gap of 0.20 eV and a shift of the Fermi level. The electronic charge density, Figure 5 (d), is concentrated on GOV for CBM and for VBM.

CONCLUSION

The interactions between the GOV and toxic gases under study were analyzed using computational simulations. The GOV presents gap of 0.19 eV, and the electronic charge density plot concentrates on the vacancy for CBM and in the functional groups for VBM. It was analyzed fifteen interactions between toluene and the GOV, the interaction with the lowest energy is the one in which toluene was approximated in the parallel position of the vacancy. For the interaction between formaldehyde and the GOV, it was analyzed nine interactions, and the one that presents the lowest energy is with formaldehyde approximated in parallel to the OH. In both cases, a physical adsorption occurred between the systems, indicating that the GOV could be a potential filter of toluene and formaldehyde for industry vents.

REFERÊNCIAS

CAO, Y. et al. Solid-state synthesis of SnO2-graphene nanocomposite for photocatalysis and formaldehyde gas sensing. **RSC Advances**, v. 4, n. 86, p. 46179-46186, 2014.

CEPERLEY, D. M.; ALDER, B. J. Ground State of the Electron Gas by a Stochastic Method. **Phys. Rev. Lett.**, v. 45, p. 566-569, 1980.

DE SOUZA, A. et al. Use of Mass Spectrometry for the Determination of Formaldehyde in Samples Potentially Toxic to Humans: A Brief Review. **Mass Spectrometry InTech**, v. 9, p. 253-271, 2017.

HOHENBERG, P.; KOHN, W. Inhomogeneous electron gas. **Physical Review**, v. 136, n. 3B, p. 864-871, 1964.

KWON, Y. et al. Selective detection of low concentration toluene gas using Pt-decorated carbon nanotubes sensors. **Sensors and Actuators B: Chemical**, v. 227, p. 157-168, 2016.

LI, J. et al. Study on photocatalytic performance of cerium-graphene oxide-titanium dioxide composite film for formaldehyde removal. **Physica status solidid. A**, v. 213, n. 12, p. 3157-3164, 2016.

LIM, J. H. et al. Comparative analysis of microRNA and mRNA expression profiles in cells and exosomes under toluene exposure. **Toxicology in Vitro**, v. 41, p. 92-101, 2017.

LIU, Y. et al. Progress on sensors based on nanomaterials for rapid detection of heavy metal ions. **Science China Chemistry**, v. 60, n. 3, p. 329-337, 2017.

MARTINEZ, V. **Estudio de la estabilidad del óxido de grafeno con el tiempo.** 2013. 72f. Dissertação (Mestrado em Ciência dos Materiais e Engenharia Metalúrgica) - Universidad de Oviedo, Asturias, 2013.

NJOYA, H. K. et al. Histopathological effect of exposure of Formaldehyde vapour on the trachea and lung of adult wistar rats. **Int. J. Integ. Bio**, v. 7, p. 160-165, 2009.

PARK, C. S.; YOON, H.; KWON, O. S. Graphene-based nanoelectronic biosensors. **Journal of Industrial and Engineering Chemistry**, v. 38, p. 13-22, 2016.

ROFFAEL, E. et al. Influence of pulping technology on the release of formaldehyde and volatile organic acids from oak fibres and medium density fibreboards (MDF) prepared therefrom. **European Journal of Wood and Wood Products**, v. 76, p. 397-399, 2018.

SOLER, J. M. et al. The SIESTA method for ab initio order-N materials simulation. **Journal of Physics: Condensed Mat**ter, v. 14, n. 11, p. 2745-2779, 2002.

SU, Y. et al. Reduced graphene oxide-polyethylene oxide hybrid films for toluene sensing at room temperature. **RSC Advances**, v. 6, n. 100, p. 97840-97847, 2016.

TROULLIER, N.; MARTINS, J. L. Efficient pseudopotentials for plane-wave calculations. **Phys. Rev. B**, v. 43, n. 3, p. 1993-2006, 1991.

YUAN, M.; HE, X.; CHEN, H. First-principles Studies of Formaldehyde Molecule Adsorption on Graphene Modified with Vacancy, -OH, -CHO and -COOH Group. In: ASIA_PACIFIC ENGINEERING AND TECHNOLOGY CONFERENCE, 2017, Malaysia. **Anais.** Malaysia, 2017, p. 1929-1934.

ZHAO, C. et al. Facile synthesis of SnO2 hierarchical porous nanosheets from graphene oxide sacrificial scaffolds for high-performance gas sensors. **Sensors and Actuators B: Chemical**, v. 258, p. 492-500, 2018.

ZHOU, Q. et al. DFT study of formaldehyde adsorption on vacancy defected graphene doped with B, N, and S. **Chemical Physics**, v. 440, p. 80-86, 2014.