

Rh-doped carbon nanotubes as a superior media for the adsorption of O₂ and O₃ molecules: a density functional theory study

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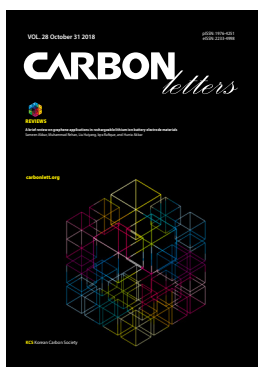
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Abstract

Transition-metal-embedded carbon nanotubes (CNTs) have been accepted as a novel type of sensing material due to the combined advantage of the transition metal, which possesses good catalytic behavior for gas interaction, and CNTs, with large effective surface areas that present good adsorption ability towards gas molecules. In this work, we simulate the adsorption of O₂ and O₃ onto Rh-doped CNT in an effort to understand the adsorbing behavior of such a surface. Results indicate that the proposed material presents good adsorbing ability and capacities for these two gases, especially O₃ molecules, as a result of the relatively large conductivity changes. The frontier molecular orbital theory reveals that the conductivity of Rh-CNT would undergo a decrease after the adsorption of two such oxidizing gases due to the lower electron activity and density of this media. Our calculations are meaningful as they can supply experimentalists with potential sensing material prospects with which to exploit chemical sensors.

Key words: Rh-doped carbon nanotubes, adsorption, density functional theory method

1. Introduction

Chemical sensors prepared with materials based on single-walled carbon nanotubes (CNTs) and applied for use with gaseous species are widely accepted to have numerous advantages, such as a small size, high sensitivity, and rapid response speeds at room temperature [1]. However, due to the weak interaction depending on the van der Waals force between the CNT surfaces and gas molecules, intrinsic CNTs with limited adsorption capacity cannot detect certain gaseous substances [2]. One feasible means of improving the adsorption and sensing capabilities of CNTs is to embed or dope foreign atom(s), in general transition metal (TM) atoms, on their sidewalls, making them capable of detecting a wider range of gases due to the strong activity and electron withdrawing/donating properties caused by such doping [3]. It has been recommended that one C atom on a CNT sidewall substituting a Pt or Pd atom can provide novel materials with good adsorption for gas molecules, including SO₂ and SOF₂ [4,5]. In addition, previous reports showed that Pt and Pd nanoparticle-functionalized CNTs are frequently employed as good room-temperature hydrogen sensors as a result of the strong binding energy and large electron charge transfer [6,7]. In addition, Rh is a notable TM in the same group with Pd and Pt which also reportedly has strong catalytic activity upon gas adsorption and sensing [8], also making it a viable candidate CNT dopant potentially for use in sensors.

Recently, we theoretically simulated the adsorption process of O₂ and O₃ molecules onto Rh-doped CNT (Rh-CNT) surfaces in order to investigate the geometric and elec-

tronic behavior of this modified surface in the presence of two gaseous species. To the best of our knowledge, there are few studies of the adsorption behavior of Rh-CNT surfaces towards O_2 and O_3 molecules or of the important roles of the abovementioned species in the atmosphere, and it appears to be essential to develop straightforward methods and introduce new adsorbent materials as adsorbents and sensors for these materials. Our calculations, including a geometric analysis, density-of-state (DOS) as well as frontier molecular orbital theory studies would offer fundamental evidence by which to suggest novel adsorbent or sensing materials which may be capable of O_2 and O_3 detection.

2. Computational Details

In the present density functional theory (DFT) calculation, the double numerical plus polarization basis sets, based on the Dmol³ package [9], were adopted. Generalized-gradient approximation with the Perdew-Burke-Ernzerhof functional and spin-unrestricted DFT [3] was utilized to obtain all the results reported below. In order to avoid interactions between adjacent cells, a single-walled CNT with a periodic boundary condition of $20 \text{ \AA} \times 20 \text{ \AA} \times 8.5 \text{ \AA}$ was defined [1]. One C atom on the sidewall of the CNT was replaced by an Rh atom to form Rh-CNT. The core treatment was set to DFT semi-core pseudopotentials to manage the interaction between the nucleus and valence electrons, whereas Brillouin zone k -point sampling was performed in a $1 \times 1 \times 2$ Monkhorst-Pack mesh [10], which presents good approximation for (8, 0) CNTs. The energy tolerance accuracy, maximum force, cut-off orbital and displacement were set as 10^{-5} Ha, 2×10^{-3} Ha/ \AA , 3.7 \AA and $5 \times 10^{-3} \text{ \AA}$, respectively [11].

The adsorption energy (E_{ad}) of each system was calculated by the following equation [12]:

$$E_{ad} = E_{\text{Rh-CNT/gas molecule}} - E_{\text{Rh-CNT}} - E_{\text{gas molecule}} \quad (1)$$

In the formulation, $E_{\text{Rh-CNT/gas molecule}}$, $E_{\text{Rh-CNT}}$ and $E_{\text{gas molecule}}$ refer to the total energy levels of the system after adsorption, an isolated Rh-CNT and the optimized gas molecule, respectively.

Based on a Mullikan population analysis, the charge transfer number (Q_T) between the Rh-doped surface and the analytes can be obtained as the number of electrons carried by gas molecules after adsorption, as the carried electron value for molecules before adsorption is constant at 0. A negative Q_T indicates that charges transfer from Rh-CNT to gas molecules, whereas a positive Q_T indicates a reverse charge-transfer path.

3. Results and Discussion

3.1. Geometric structural analysis of Rh-CNT and gas species

To initiate the adsorption processes of O_2 and O_3 molecules onto the Rh-CNT surface, these models were preliminarily optimized with the lowest geometric energy levels, as shown in Fig.

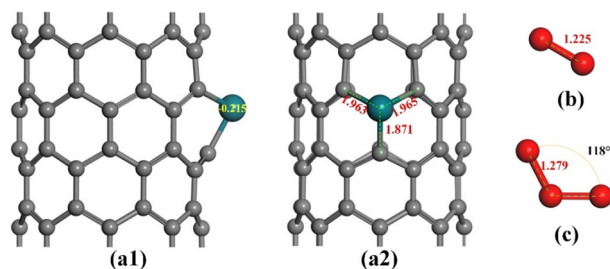


Fig. 1. Geometric structures of Rh-CNT and gas molecules. The gray, blue-green and red balls represent C, Rh and O atoms, respectively.

1. Fig. 1a illustrates how the doping Rh remarkably protrudes outward from the CNT sidewall with the Rh-C bonds measured at 1.963, 1.965, and 1.871 \AA , much larger than the C-C bond (1.411 \AA) of the intrinsic CNT due to the large radius of the Rh atom [5].

As depicted in Fig. 1b, the O-O bond inner O_2 molecule is measured to be 1.225 \AA , shorter than the inner O_3 molecule (1.279 \AA), as shown in Fig. 1c. This stems from the higher bond energy in the O_2 molecule.

3.2. Adsorption analysis of O_2 and O_3 onto the Rh-CNT surface

Two types of gas molecules were assessed to determine the possibility of approaching the Rh dopant of the proposed surface, which is considered to be an active area. We devised one- and two-molecule adsorbing systems to gain a comprehensive understanding of the adsorption properties and capacities of Rh-CNT with regard to the two gases.

Focusing on the O_2 adsorption system first, Fig. 2a and b indicate that the adsorbent has good adsorption performance towards one O_2 molecule, trapping both O atoms onto the Rh dopant with an adsorbing distance of 2.140 \AA , while performing in a weakened capacity upon two O_2 molecules, where only one molecule shows a good response towards the doping surface. In the one-molecule system, E_{ad} and Q_T are -1.384 eV and -0.371 e, respectively, greater than those in the B-CNT/ O_2 system published previously [13], suggesting better adsorption behavior in the Rh-doped case. This negative value in the former case suggests its chemisorption, whereas the latter strong case proves the chemical interaction between the O_2 molecule and the Rh-CNT [14], resulting in the considerable amount of electron transfer from the adsorbent surface to the adsorbate. In line with the adsorbing configuration of the system with two O_2 molecules, E_{ad} undergoes a slight change while Q_T of the second O_2 molecule is quite small, which we presume to stem from physisorption towards the second molecule [15].

Upon O_3 adsorption, Rh-CNT presents superior adsorbing behaviors and capacities. In the one-molecule system, two O atoms of O_3 are captured by the Rh atom with an adsorbing distance of 2.187 \AA , while in the two-molecule system, one O atom of each O_3 molecule is ensnared by the dopant with adsorbing distances of 2.231 and 2.234 \AA , respectively. One phenomenon similar to O_2 systems is that the Rh-C bonds of all adsorbing sys-

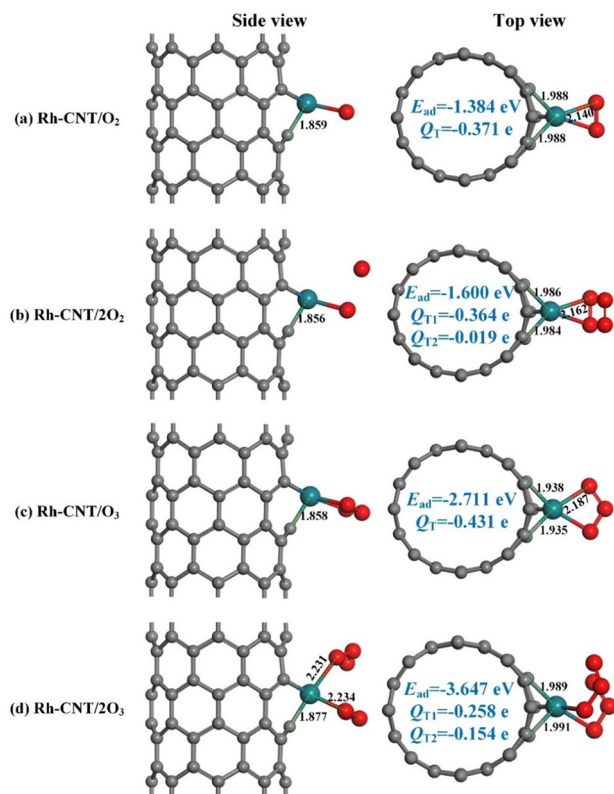


Fig. 2. Adsorption configurations and related parameters of various systems. (a) Ph-CNT/O₂, (b) Rh-CNT/2O₂, (c) Ph-CNT/O₃, and (d) Rh-CNT/2O₃.

tems experience different extents of prolongation, attributed to the adsorption process of the gas molecules. On the other hand, E_{ad} (-2.711 eV) in the Rh-CNT/O₃ system nearly doubled and Q_T (-0.431 e) is even larger compared to those in the Rh-CNT/O₂ system. Moreover, the pronouncedly enhanced E_{ad} (-3.647 eV) of the double O₃ molecule system, calculated to be -1.824 eV for the per-molecule adsorption, indicates chemisorption for both molecules, despite the slightly decreased Q_T values for the two molecules, which we assume to be a result of the fewer electron-transfer paths in comparison with the single O₃ molecule system.

3.3. Analyses of DOS and frontier molecular orbital theory

For a better understanding of the electronic behaviors and conductivity changes of Rh-CNT caused by the adsorption of molecules, the DOS and the frontier molecular orbital theories were considered.

Fig. 3 describes the DOS distribution of two types of gas systems. In Fig. 3a, where the DOS comparison of the O₂ systems is presented, it can be found that the DOS peaks of the Rh-CNT/O₂ system are obviously shifted towards a higher region, in good agreement with the loss of the electron for Rh-CNT [16,17], while the DOS of the Rh-CNT/2O₂ system is basically unchanged and even overlapped with that of the single-molecule system near the Fermi level due to the inactive electron property. According to the DOS distributions of O₃ systems displayed in Fig. 3b, it is clear that distinct shifts of the DOS curve can be found not only through a comparison between an isolated Rh-CNT and the related single O₃ molecule adsorbing system, but also in the comparison of the two adsorbing systems. Specifically, a noticeable shift of the peak in the Rh-CNT/O₃ system near the Fermi energy occurs compared to that in the isolated Rh-CNT system, and a further change, although relatively slight, can also be found in the Rh-CNT/2O₃ system compared with the single-molecule system. It should also be noted that according to the overlap of the Rh atom and O atom in the single-molecule system for O₂ and O₃ adsorption, we found that the Rh dopant is strongly hybridized with the adsorbed O₂ or O₃ molecule with the Rh-O bond, and a larger area of overlap in the Rh-CNT/O₃ system implies stronger chemisorption compared to that in the Rh-CNT/O₂ system [18,19]. This result is important when explaining the electronic behavior of adsorbent and gas species, as it sheds light on the mechanism of the change in the conductivity of Rh-CNT in a qualitative manner.

To illuminate the conductivity change of Rh-CNT responding to the adsorption of molecules, the frontier molecular orbital theory is both essential and helpful, as, based on this theory, the energy gap (E_g) between the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) is widely accepted as a workable and effective indicator of the electrical conductivity of bulk

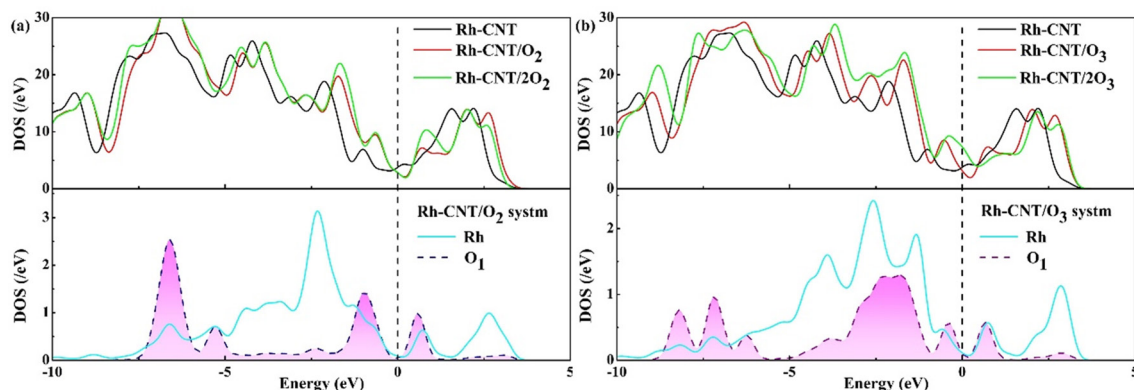


Fig. 3. DOS distributions of different adsorption systems. The dash lines are the Fermi levels.

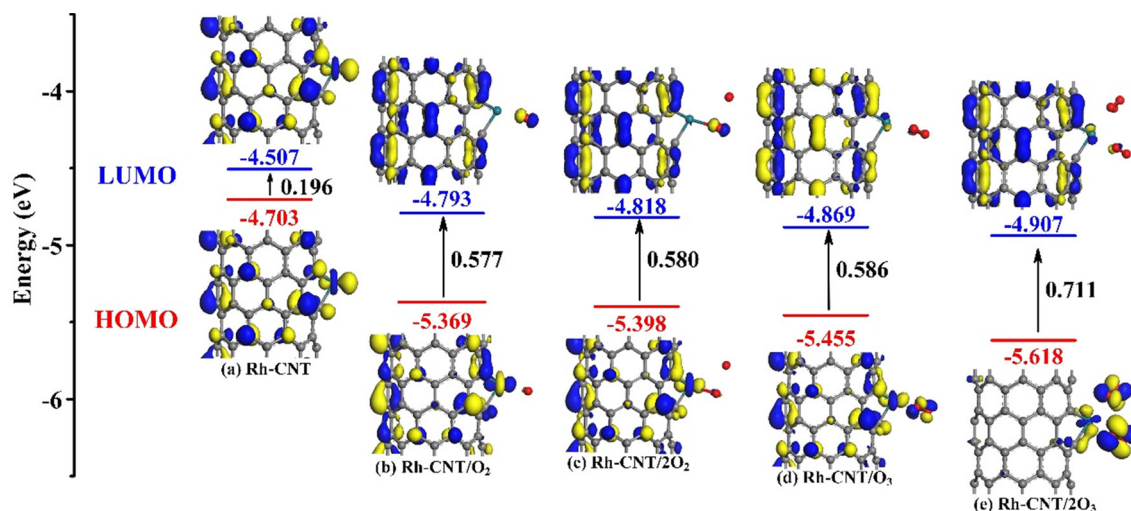


Fig. 4. HOMO and LUMO distributions and related energy levels.

materials [20,21]. Referring to a previous report, a lower E_g means higher electrical conductivity, whereas a higher E_g corresponds to lower electrical conductivity [22]. Fig. 4 indicates that the isolated Rh-CNT has an equally uniform density of the HOMO and LUMO characteristics of Rh atoms with E_g equal to 0.196 eV, a small gap indicating its excellent conductivity, while upon interaction with different species, significant changes were observed in both the HOMO and LUMO distributions and in the related energies in each system. Briefly, in terms of O_2 adsorption, HOMO is distributed mainly on Rh atoms, while LUMO is on O_2 molecules, unlike the O_3 adsorption system, in which HOMO and LUMO are both concentrated on Rh atom and analyte molecules. Such relocation of the orbitals for an adsorbing system corresponds to the increases of E_g in the Rh-CNT/ O_2 and Rh-CNT/ O_3 systems to 0.577 and 0.586 eV, respectively, which would lead to dramatic decreases in the conductivity of Rh-CNT after the adsorption of the two-gas species. Such results, in practice, are not difficult to understand. From the DOS of Rh-CNT, we can find that the Fermi level of this material is closer to LUMO than to HOMO, indicating its n-type property [8]. After the adsorption of the two types of oxidizing gases that are prone to electron withdrawing, the proposed surface would donate an electron, causing a decrease in the electron activity and density and thus leading to reduced conductivity.

In addition, in the double-molecule systems, E_g of the Rh-CNT/ $2O_2$ system is slightly enlarged while that of the Rh-CNT/ $2O_3$ system shows only a moderate increase. This is in accordance with the contention above that Rh-CNT has better adsorption behavior and capacity of O_3 compared to O_2 , resulting in a larger change of E_g in the O_3 system (0.381 eV) compared to the O_2 system (0.390 eV) with respect to the one-molecule system against the pure Rh-CNT system. It also has a much more enlarged gap of O_3 adsorption (0.125 eV) compared to O_2 adsorption (0.003 eV) when the number of molecules increases from one to two.

4. Conclusions

In this paper, we utilized the DFT method and investigated the adsorption behavior of O_2 and O_3 molecules onto the proposed Rh-CNT surface. Rh dopant as an active catalytic center presents good adsorption ability for the targeted gases, especially O_3 molecules. With regard to the adsorption of the two molecules, Rh-CNT possesses better adsorption of O_3 molecules than of O_2 , leading to higher E_{ad} and Q_T values in the O_3 system with decreased parameters in the O_2 system. This confirms the stronger adsorption performance of Rh-CNT towards O_3 as compared to O_2 . After adsorption, the proposed material would undergo a decrease in conductivity, which provides a workable method for further study and exploitation efforts to make such material an excellent sensing material. Our calculations are meaningful as they suggest novel materials to be examined by experimentalists for use as gas adsorbents or chemical sensors.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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Author contribution: Hao Cui performed this work and wrote this manuscript, Xiaoxing Zhang guided this work, Qiang Yao and Yulong Miao helped analyze the data, while Hanyan Xiao and Ju Tang modified the writing in order to improve its quality.

References

- [1] Zhang X, Cui H, Gui Y, Tang J. Mechanism and application of carbon nanotube sensors in SF₆ decomposed production detection: a review. *Nanoscale Res Lett*, **12**, 177 (2017). <https://doi.org/10.1186/s11671-017-1945-8>.
- [2] Yoosefian M, Zahedi M, Mola A, Naserian S. A DFT comparative study of single and double SO₂ adsorption on Pt-doped and Au-doped single-walled carbon nanotube. *Appl Surf Sci*, **349**, 864 (2015). <https://doi.org/10.1016/j.apsusc.2015.05.088>.
- [3] Zhang X, Cui H, Zhang J, Tang J. Adsorption characteristic of Pd-4 cluster carbon nanotube towards transformer oil dissolved components: a simulation. *Appl Surf Sci*, **419**, 802 (2017). <https://doi.org/10.1016/j.apsusc.2017.05.004>.
- [4] Zhang X, Dai Z, Wei L, Liang N, Wu X. Theoretical calculation of the gas-sensing properties of Pt-decorated carbon nanotubes. *Sensors*, **13**, 15159 (2013). <https://doi.org/10.3390/s131115159>.
- [5] Jiang HR, Lu Z, Wu MC, Ciucci F, Zhao TS. Borophene: a promising anode material offering high specific capacity and high rate capability for lithium-ion batteries. *Nano Energy*, **23**, 97 (2016). <https://doi.org/10.1016/j.nanoen.2016.03.013>.
- [6] Rangel E, Sansores E. Theoretical study of hydrogen adsorption on nitrogen doped graphene decorated with palladium clusters. *Int J Hydrogen Energy*, **39**, 6558 (2014). <https://doi.org/10.1016/j.ijhydene.2014.02.062>.
- [7] Ferrari AC, Bonaccorso F, Fal'Ko V, Novoselov KS, Roche S, Bøggild P, Borini S, Koppens FH, Palermo V, Pugno N, et al. Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. *Nanoscale*, **7**, 4598 (2015). <https://doi.org/10.1039/c4nr01600a>.
- [8] Zhao JX, Ding YH. Theoretical study of the interactions of carbon monoxide with Rh-decorated (8,0) single-walled carbon nanotubes. *Mater Chem Phys*, **110**, 411 (2008). <https://doi.org/10.1016/j.matchemphys.2008.02.036>.
- [9] Zhang X, Cui H, Dong X, Chen D, Tang J. Adsorption performance of Rh decorated SWCNT upon SF₆ decomposed components based on DFT method. *Appl Surf Sci*, **420**, 825 (2017). <https://doi.org/10.1016/j.apsusc.2017.05.127>.
- [10] Zhao Q, Buongiorno M, Lu W, Bernholc J. Carbon nanotube-metal cluster composites: a new road to chemical sensors? *Nano Lett*, **5**, 847 (2005). <https://doi.org/10.1021/nl050167w>.
- [11] Wang R, Zhang D, Zhang Y, Liu C. Boron-doped carbon nanotubes serving as a novel chemical sensor for formaldehyde. *J Phys Chem B*, **110**, 18267 (2006). <https://doi.org/10.1021/jp061766+>.
- [12] Boys SF, Bernardi F. The calculation of small molecular interactions by the differences of separate total energies: some procedures with reduced errors. *Mol Phys*, **19**, 553 (2002). <https://doi.org/10.1080/00268977000101561>.
- [13] Azam MA, Alias FM, Tack LW, Seman RNAR, Taib MFM. Electronic properties and gas adsorption behaviour of pristine, silicon-, and boron-doped (8, 0) single-walled carbon nanotube: a first principles study. *J Mol Graphics Modell*, **75**, 85 (2017). <https://doi.org/10.1016/j.jmkgm.2017.05.003>.
- [14] Rad AS, Zareyee D. Adsorption properties of SO₂ and O₃ molecules on Pt-decorated graphene: a theoretical study. *Vacuum*, **130**, 113 (2016). <https://doi.org/10.1016/j.vacuum.2016.05.009>.
- [15] Berahman M, Sheikhi MH, Zarifkar A, Gebauer R, Taheri M, Asad M. H₂S gas sensor based on thin film graphene nanoribbons decorated with copper: a first principles study, in Proceedings of the Ultrafine Grained and Nano-Structured Materials, Tehran, Iran, (2013).
- [16] Cuong NT, Chi DH, Kim YT, Mitani T. Structural and electronic properties of Ptn (n=3, 7, 13) clusters on metallic single wall carbon nanotube. *Phys Status Solidi*, **243**, 3472 (2006). <https://doi.org/10.1002/pssb.200669166>.
- [17] Ganji MD, Sharifi N, Ardjmand M, Ahangari MG. Pt-decorated graphene as superior media for H₂S adsorption: a first-principles study. *Appl Surf Sci*, **261**, 697 (2012). <https://doi.org/10.1016/j.apsusc.2012.08.083>.
- [18] Garadkar KM, Shirke BS, Hankare PP, Patil DR. Low cost nanostructured anatase TiO₂ as a H₂S gas sensor synthesized by microwave assisted technique. *Sens Lett*, **9**, 526 (2011). <https://doi.org/10.1166/sl.2011.1507>.
- [19] Li Y, Hodak M, Lu W, Bernholc J. Mechanisms of NH₃ and NO₂ detection in carbon-nanotube-based sensors: an ab initio investigation. *Carbon*, **101**, 177 (2016). <https://doi.org/10.1016/j.carbon.2016.01.092>.
- [20] Kim HS, Lee H, Han KS, Kim JH, Song MS, Park MS, Lee JY, Kang JK. Hydrogen storage in Ni nanoparticle-dispersed multiwalled carbon nanotubes. *J Phys Chem B*, **109**, 8983 (2005). <https://doi.org/10.1021/jp044727b>.
- [21] Yoosefian M, Etminan N, Moghani MZ, Mirzaei S, Abbasi S. The role of boron nitride nanotube as a new chemical sensor and potential reservoir for hydrogen halides environmental pollutants. *Superlattices Microstruct*, **98**, 325 (2016). <https://doi.org/10.1016/j.spmi.2016.08.049>.
- [22] Rad AS, Abedini E. Chemisorption of NO on Pt-decorated graphene as modified nanostructure media: a first principles study. *Appl Surf Sci*, **360**, 1041 (2016). <https://doi.org/10.1016/j.apsusc.2015.11.126>.