**ROMANIAN JOURNAL OF INFORMATION
SCIENCE AND TECHNOLOGY**
Volume **27**, Number 2, 2024, 137–150

Some Considerations about the Sensing Mechanisms and Electrical Response of Carbon Nanohorns–based Gas Sensors

Bogdan-Catalin SERBAN[1, 2, *], Octavian BUIU[1], Niculae DUMBRAVESCU[1],
Mihai BREZEZANU[3], Cornel COBIANU[4, 5], Marius BUMBAC[6], and
Mihaela NICOLESCU[7]

[1]National Institute for Research and Development in Microtechnologies, IMT-Bucharest, 126 A Str. Erou IancuNicolae, 077190, Voluntari, Ilfov, Romania
[2]Zentiva Romania S.A, Bulevardul Theodor Pallady 50, 032266 Bucharest, Romania
[3]Faculty of Electronics, Telecommunications and IT, National University of Science and Technology Politehnica Bucharest, Bd Iuliu Maniu 1-3, 061071, Bucharest, Romania
[4]Academy of Romanian Scientists (ARS), Str. Ilfov Nr. 3, Sector 5, Bucharest, Romnia
[5]Faculty of Business and Administration; University of Bucharest, Regina Elisabeta Street, No. 4-12, District 3, Bucharest, Romania
[6]Valahia University of Targoviste, Faculty of Sciences and Arts, Sciences and Advanced Technologies Department, Aleea Sinaia, nr 13, 130004, Targoviste, Dambovita, Romania
[7]Valahia University of Targoviste, Institute of Multidisciplinary Research for Science Technology, Aleea Sinaia, nr 13, 130004, Targoviste, Dambovita, Romania
`E-mails: bogdan.serban@imt.ro`*, `octavian.buiu@imt.ro`, `niculae.dumbravescu@imt.ro`, `mbrezeanu@upb.ro`, `cornel.cobianu@imt.ro`, `marius.bumbac@valahia.ro`, `cristina.nicolescu@valahia.ro`
* Corresponding author

Abstract. This paper aims to analyze the sensing mechanisms involved in the resistive detection of relative humidity, ethanol vapors, oxygen, ozone, ammonia, hydrogen sulfide, and hydrogen using carbon nanohorns (pristine and functionalized) and their nanocomposites/nanohybrids as sensing layers. Different alternative mechanisms are considered and discussed: decreasing holes in the carbonaceous component at the interaction with moisture, protonic conduction (Grotthuss mechanism), and swelling. The *hard-soft acid-base* (HSAB) theory's role is also highlighted as a valuable tool for understanding the essential interaction of nanocarbon materials with water molecules. The role of each constituent of the sensing layer is interpreted based on their chemical and physical properties and mutual interactions. For each tandem sensing layer – gas detected, the dominant sensing mechanism is associated with the electrical response of the sensor.

Key-words: Carbon nanohorns (CNHs); gas sensor; Hard Soft Acid Base (HSAB) theory.

1. Introduction

Along with carbon nanotubes [1], fullerenes [2], graphene [3], graphene oxide [4], reduced graphene oxide [5], *carbon nanohorns* (CNHs) have been intensively explored from an experimental and theoretical point of view in recent years, due to their potential application in a wide range of fields [6]. CNHs (Fig. 1a) are closed cages of sp^2-bonded carbon atoms, typically of 2–5 nm in diameter and 40–50 nm in length and were first synthesized using CO_2 laser ablation of carbon at room temperature in 1998 [7]. Following oxidation, the structure of CNHs is modified, and holes are formed on their sheaths (Fig. 1b). Beyond the changes in the physico-chemical properties, the net result of oxidizing the CNHs is increasing their surface area and providing access to their interior cavity.

Fig. 1. The structure of a) CNHs and b) oxidized carbon nanohorns (CNHox).

CNHs exhibit outstanding properties, such as high conductivity, high dispersibility, uniform size, excellent porosity, thermal and chemical stability, high adsorption capacity, superior permeability, exceptional catalytic properties, large specific surface area, low toxicity, clean synthesis process (no metal catalyst is involved in their synthesis; thus, the produced CNHs are free of metal impurities) [8]. Moreover, multiple and versatile covalent and noncovalent functionalization of CNHs can be performed to tailor their physical and chemical properties: oxidation (as described above), functionalization with photoactive units, grafting of bioactive units, decoration with nanoparticles, etc. [9], covalent attachment of organic fragments either to the open conical ends or to the sidewalls of the nanohorns. Noncovalent interactions are based on electrostatic interactions or $\pi - \pi$ stacking interactions between CNHs and aromatic organic molecules (such as pyrene and their derivatives) [10]. Given the above, CNHs are considered potential alternatives to carbon nanotubes and graphene in different applications [11]. Recently, CNHs (pristine and functionalized) and their nanocomposites/nanohybrids have been intensively studied and explored for different applications, such as gas storage devices [12], supercapacitors [13], rechargeable batteries [14], compounding material [15], electrochemical biosensing [16], gas adsorption [17], and catalyst support [18]. Specifically, CNHs were employed as sensing layers in resistive detection of *relative humidity* (RH) and some gases, such as ethanol, oxygen, ozone, ammonia, H_2S, and CO_2 .

This paper aims to analyze the sensing mechanisms involved in the resistive detection of different gases by sensing structures employing CNHs and their nanocomposites/nanohybrids as sensing layers. Different alternative mechanisms are considered and discussed. The role of each constituent of the sensing layer is interpreted based on chemical and physical properties and mutual interactions. For each sensing layer – detected gas tandem, the dominant sensing mechanism is discussed concerning the electrical response of the sensor.

The paper is structured as follows: RH detection is presented in Section 2, O_2 detection in Section 3, H_2S sensing in Section 4, H_2 detection in Section 5, ethanol sensing in Section 6, NH3 detection in Section 7, ozone sensing in Section 8, while Section 9 is dedicated to conclusions.

2. Relative Humidity Detection

2.1. Introduction

Different types of CNHs and their nanocomposites were used as key sensing elements in the design of resistive *relative humidity* (RH) sensors: pristine CNHs [19], CNHox [20], CNHs-polyvinylpyrrolidone (PVP) [21], CNHox-poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG) [22], GO-CNHox-PVP at several mass ratios (i.e., 1/1/1, 1/2/1, and 1/3/1 w/w/w) [23,24]. Moreover, several organic-inorganic nanohybrids, such as CNHox-SnO_2-ZnO-PVP [25], CNHox-TiO_2-PVP [26, 27], CNHox-KCl-PVP [28] and CNHox-ZnO-PVP [29] were employed to obtain sensing films for resistive monitoring of the RH. In all the cases mentioned above, the sensing capability of a novel sensing layer was investigated by applying a direct current with known intensity between the two electrodes of the sensing structure and measuring the resulting voltage difference while varying the RH from 0% to 100% in humid nitrogen/air atmosphere, at constant room temperature (t=23°C). The thin film's resistance increased when the sensors were exposed to RH, with no exception. Regardless of the composition of the CNHs nanohybrids or nanocomposites used as sensing elements, several sensing mechanisms can be considered and are detailed below.

2.1.1. Protonic conduction (Grotthuss mechanism)

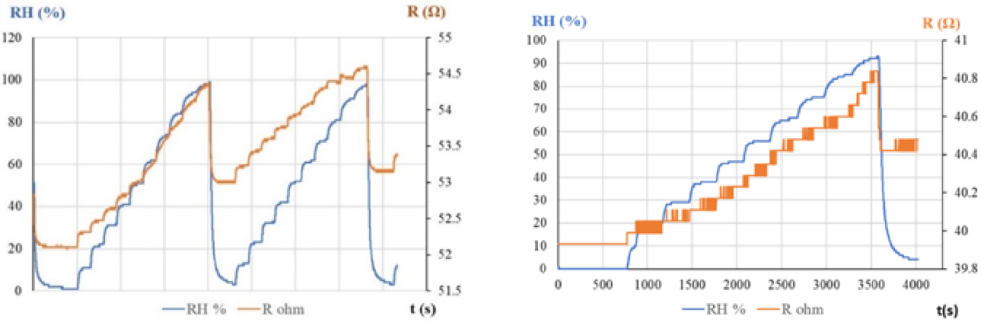
This sensing mechanism considers the dissociation of water and the ionization of carboxylic acids. The adsorbed water molecules on the surface of CNHox (and of the GO, for ternary mixtures such as GO-CNHox-PVP) may dissociate to H^+ and OH^- ions at the edges of both nanocarbonic materials. Moreover, the carboxylic groups grafted onto the molecular architecture of both CNHox and GO may dissociate. The protons generated by the water dissociation process may tunnel from one water molecule to another through hydrogen bonding, increasing the overall electrical conductivity of the sensitive film. However, even if it seems plausible, it is evident that the increasing resistance of the sensing layer, as measured experimentally, cannot result from this type of mechanism. In other words, without completely excluding this scenario, proton conduction cannot play a dominant role in resistive RH detection.

2.1.2. Water as electron donor for p-type semiconducting materials such as CNHox

This sensing mechanism considers the fact that CNHox is a p-type semiconducting material. Therefore, when interacting with them, the water molecules donate their electron pairs, thus decreasing the number of holes in CNHox and increasing the distance between its Fermi level and valence band. Consequently, the conductivity of the CNHox-based sensing layer decreases with RH concentration, confirming the experimental measurements.

One can also assess this mechanism from the perspective of the Hard-Soft Acid-Base (HSAB) theory. This concept, introduced by Ralph Pearson in the early 1960s, operates with Lewis acids and bases. According to this classification, a molecule capable of donating electrons pair is a base, while a molecule capable of accepting electrons is an acid. Pearson classified Lewis acids and bases as soft, hard, and borderline [30–33]. According to the HSAB theory, strong bases prefer to interact with strong acids, soft bases prefer strong acids, while borderline bases have an affinity for borderline acids. Considering the HSAB theory perspective in the sensing process, water molecules (classified as hard Lewis bases) will interact with the holes of the p-type semiconducting material CNHox (hard Lewis acids), and they will be nulling each other by multiple recombination processes.

Another important aspect is the role the hydrogen bonds play in explaining the increased RH sensitivity of CNHox-based sensing layers in humid air compared to that measured in humid nitrogen. This phenomenon, reported in [20] (21 mΩ/RH unit sensitivity in humid air – Fig. 2a - versus 9.1 mΩ/RH unit sensitivity in humid nitrogen – Fig. 2b), is in accordance with Watts et al. [1]. Most oxygen molecules in humid air are mainly absorbed into the polar carboxyl groups on the CNHox. The oxygen molecules are rather polarizable and can generate hydrogen bonding with the hydroxide (–OH) on the carboxyl group. Thus, the electron-withdrawing effect of the carboxyl group is attenuated. Consequently, hole concentration on the CNHox decreases, yielding a minor overall increase in resistance of the carbonaceous sensing film, even though oxygen molecules' physisorption could cause an antithetical electrical response. The presence of carboxylic groups on the backbone of SWCNHs is a key structural feature, and the hydrogen bond formation to each carboxyl group is a dominant factor.



(a)

(b)

Fig. 2. RH response of: a) single-walled CNHox (SWCNHox)-based sensor in humid air (orange curve) vs the RH response of a reference sensor (blue curve), and b) sensing structure with single-walled CNHox (SWCNHox) - based sensing layer in humid nitrogen (orange curve) vs. the RH response of a reference sensor (blue curve) [22]

2.1.3. The swelling of the dielectric, hydrophilic polymer

Despite their dielectric properties, the contribution of PVP and PEG-PPG-PEG polymers, when used together with CNHox in sensing layer matrices for resistive monitoring of RH, is very interesting and may have a significant impact on the behavior and performance of the sensor. PVP has essential properties recommended for manufacturing sensing layers: solubility in various solvents (alcohol, water), high thermal resistance, high hygroscopicity, and excellent film-forming properties. In addition, PVP can significantly contribute to the sensing mechanism through swelling. Moisture absorption (up to 25% moisture at RH = 75%) increases the distance between CNHox nanoparticles, leading to a decrease of electrically percolating pathways. Accordingly, the sensitive layer should become less conductive [48, 49]. The sensing structure based on PVP-based nanocomposite as sensing film exhibits a linear characteristic and good sensitivity when varying RH from 0% to 100% in a humid nitrogen gas. The manufactured device displays a fast response time and good stability over time [22].

The contribution of the PEG-PPG-PEG polymer matrix to the RH sensing mechanism is more complex and requires a subtle interpretation. PEG-PPG-PEG is less hydrophilic than PVP and needs more water molecules to start the swelling. For RH $< 40\%$, its resistance has a relatively low increase with RH. However, experimental findings show that for RH $> 65\%$, its resistance sharply increases with RH. This might be an effect of a considerable number of hydrogen bonds being broken, leading to the fast swelling of the host PEG-PPG-PEG (switch-type behavior). Consequently, the distance between CNHox moieties increases, electrically percolating pathways are reduced, and the sensing layer becomes less conductive.

2.1.4. Individual contribution of other components to RH sensing mechanism

Graphene oxide (GO) seems to be an appropriate candidate as a sensing element for resistive RH detection due to several outstanding properties: hydrophilic properties, good charge carrier, low-cost synthesis, excellent dispersant for CNHox and long-term stability. Moreover, GO is a p-type material and exhibits a decrease in electrical conduction (similar to CNHs - pristine and functionalized) when to exposed to moisture.

SnO_2 (as nanometric powder) shows good sensitivity towards RH. Water molecules can be adsorbed by physisorption or hydrogen bonding and react with the Lewis acid site and Lewis base site on the SnO_2 surface (according to the HSAB theory, Sn^{4+} is a hard acid and H_2O is a hard base) and then release electrons. According to this approach, the sensitive layer should become more conductive, a result that does not follow overall experimental results.

ZnO (used as nanopowder) is a typical n-type semiconducting metal oxide with good RH sensing performance. Water dissociation provides protons as charge carriers of the hopping transport. Thus, the RH sensing film based on CNHOx and ZnO could become less resistive.

KCl was also used with CNHox as part of the hybrid nanocomposite employed for the resistive RH sensors. The presence of K^+ cations confers the ternary nanohybrid an increased RH sensitivity by increasing the number of active sites available to interact with water molecules. According to the HSAB theory, K^+ cations are hard acids, and water is a hard base, leading to a hard acid-hard base interaction between water molecules and the sensing layer.

TiO_2 was employed as an element of the CNHox-based sensing film for resistive RH monitoring. The presence of Ti^{4+} cations confer to CNHox-TiO_2-PVP at 1/1/1, 2/1/1/, and 3/1/1 mass ratios nanohybrids an increased RH sensitivity by increasing the number of active sites available for interactions with water molecules. According to the HSAB theory, Ti^{4+} cations are hard acids, while water is classified as a hard base. Furthermore, the generated protons may tunnel from one water molecule to another through hydrogen bonding. This proton hopping could lead to an increase in the sensing film conduction. A higher mass percentage of TiO_2 (to synthesize more protons as charge carriers) and the formation of a continuous film of water at the surface of the sensing layer are two *sine qua non* – conditions to have predominant ionic conduction. However, it is plausible to assume that the increasing resistance of the sensing layer employing CNHox-TiO_2-PVP cannot fully correlate with this type of sensing mechanism.

2.1.5. Mutual interactions of the sensing elements that may influence the sensing mechanism and performance of the CNHs-based resistive RH sensors

CNHox, CNHox-PVP, and GO-CNHox-PVP-based sensing layers were proven to be excellent solutions as sensing layers in the design of RH sensors, with the ternary nanocomposites showing the best performance. The GO-CNHox-PVP sensing layer (1/1/1, 1/2/1, and 1/3/1 w/w/w mass ratios) showed better RH sensitivity and linearity than the CNHox-PVP nanocomposite [23, 24]. The proposed explanation for this phenomenon relies on the behavior of GO as a constituent of the ternary nanocomposite. Thus, through $\pi - \pi$ stacking interactions and intermolecular hydrogen bonds, GO may act as a dispersant for CNHox. The higher the concentration of CNHox in the nanocomposite, the more compact and the lower the specific surface area of the aggregates will be obtained. The performance of RH sensors that use CNHox-based sensing layers is correlated with the hydrophilicity and p-type semiconducting properties of GO (Table 1).

The overall linearity of the ternary nanocarbonic materials-based resistive RH sensors – in humid nitrogen, when varying RH from 0% to 100% – is very good, as shown in Fig. 3. In terms of linearity, sensor 121 (GO-CNHox-PVP at 1/2/1 w/w/w mass ratio) seems to have the best performance (R^2 = 0.9988) compared to sensor 111 and 131 (GO-CNHox-PVP at 1/1/1 and 1/3/1 w/w/w mass ratio, respectively). This comparison shows that an optimum mass ratio between CNHox, GO and PVP should be used to maximize the performance of the resistive RH sensor.

Moreover, adding metal oxides (such as ZnO or SnO_2) to CNHox-PVP or CNHs-PVP-GO led to sensing structures with increased RH sensitivity (by one order of magnitude) compared to that shown by CNHox-PVP [25-27]. Three possible explanations can be considered:

(a) CNHox has p-type electrical conduction, while both ZnO and SnO_2 are n-type metallic oxide semiconductors. By adding SnO_2 and/or ZnO to the CNHox, islands of p-n semiconductor heterojunctions embedded in PVP may be formed in the nanohybrid, thus increasing the sensitivity of the RH sensing layer.

(b) It is plausible to assume that both SnO_2 and ZnO interact differently with the CNHox, leading to a change in the pore distribution and thus increasing the specific surface area.

(c) The free volume of the polymer within the nanohybrid is higher than that of the pure polymer [51]. That means that the nanohybrid possesses a higher swelling degree when compared to the CNHox-PVP or CNHox-GO-PVP matrix nanocomposites.

Table 1. Correlation and comparison between different CNHox-based RH sensing layers, sensing mechanism and sensing performance

Sensing layer (mass ratio)	**Sensitivity $\left(S = \frac{\Delta R}{\Delta RH}\right)$ (Ω / % RH)**	**Dominant sensing mechanisms**	**Ref.**
CNHox	(/%RH)	Water acts as an electron donor for CNHox	[20]
CNHox/PVP 1/1	0.020–0.058	Water acts as an electron donor for CNHox; Swelling of PVP leads to a decrease of electrically percolating pathways	[22]
CNHox/PVP 1/2	0.017–0.025	Water acts as an electron donor for CNHox; Swelling of PVP leads to a decrease of electrically percolating pathways	[22]
CNHox/GO/PVP 1/1/1	0.150–0.200	Water acts as an electron donor for CNHox and GO; Swelling of PVP leads to a decrease of electrically percolating pathways; Dispersion of CNHox through hydrogen bonds and $\pi - \pi$ stacking interaction with GO enhances surface area and improves RH sensing	[23, 24]
CNHox/GO/PVP 2/1/1	0.063–0.070	Water acts as an electron donor for CNHox and GO; Swelling of PVP leads to a decrease of electrically percolating pathways; Dispersion of CNHox through hydrogen bonds and $\pi - \pi$ stacking interaction with GO enhances surface area and improves RH sensing	[23, 24]
CNHox/GO/PVP 3/1/1	0.043–0.051	Water acts as an electron donor for CNHox and GO; Swelling of PVP leads to a decrease of electrically percolating pathways; Dispersion of CNHox through hydrogen bonds and $\pi - \pi$ stacking interaction with GO enhances surface area and improves RH sensing	[23, 24]

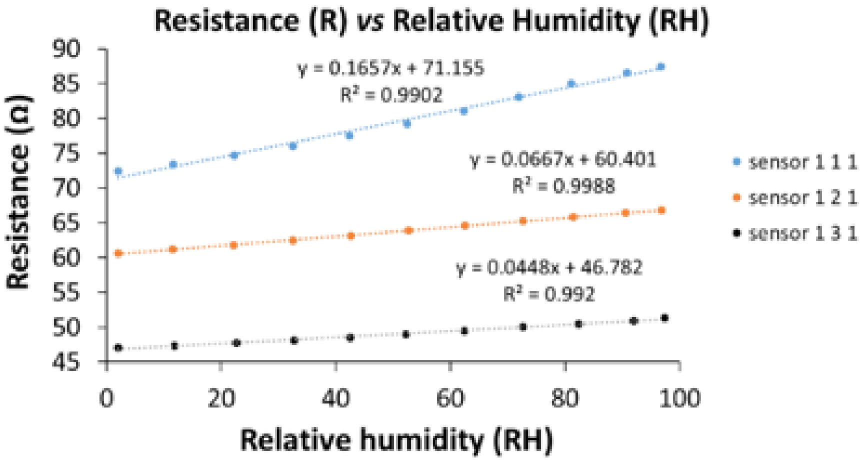


Fig. 3. The transfer functions of the studied CNHox-based RH sensors in humid nitrogen.

3. Oxygen Detection

Nanocomposite matrices of CNHox-PVP and CNHs-PVP have been proposed as sensing layers for detecting O_2 within resistive structures. A mass ratio of 9:1 between the CNHs material and the polymer was used in both cases. PVP is an excellent binder for nanocarbonic material, but with low permeability for O_2. Experimental results revealed interesting details; in the case of CNHox, the resistance of the sensitive layer decreased with O_2 concentration, while in the case of CNHs, the opposite trend was recorded. On the one hand, since the O_2 molecules are electron acceptors (electron affinity between 0.4-0.5 eV [38]) and CHNox are p-type semiconductors, the chemisorbed O_2 molecules accept electrons from CHNox, leading to the generation of new holes, thus decreasing the resistance of the sensing layer. On the other hand, several research studies demonstrated that pristine CNHs might be n-type semiconductors. This conclusion is based on the change in the electrical resistance of the pristine CNHs-based sensing layer upon exposure to CO_2, a typical electron donor. This conclusion is consistent with the measured O_2 detection experimental results mentioned above. By being an n-type semiconductor, when exposed to O_2 (an electron acceptor), CNHs decrease the sensing layer's electrical conductivity (increase in resistance).

4. H_2S Detection

In_2O_3-CNHs nanocomposite was used as a key sensing element in the resistive hydrogen sulfide (H_2S) sensor design [54]. Unlike all the other sensitive layers discussed above, where CNHs (either pristine or oxidized) were the major component of the nanocomposite/nanohybrid sensing layer, in the case of In_2O_3-CNHs nanocomposite, the nanocarbonic material was only used as an additive (a mass concentration of 2 wt%). When exposed to H_2S, the resistance of the In_2O_3-CNHs sensing layer decreased. Experiments showed show excellent selectivity and good reproducibility of the manufactured sensors, which might be due to:

(a) Using CNHs increased the specific surface area from 12.79 m^2/g for In_2O_3 to 26.33 m^2/g for In_2O_3/CNHs (2wt%). Once specific surface area increases, gas molecules may easily diffuse and adsorb, thus enhancing the H_2S response.

(b) The formation of p-n heterojunctions between the CNHox and In_2O_3 increases the surface band bending and the H_2S response.

5. H_2 Detection

SWCNHs dispersed with Pd, Ni and Pd-Ni alloy nanoparticles were used as sensing layers in the design of resistive H_2 sensors [40], with SWCNHs dispersed with Pd-Ni showing the highest sensitivity. The thin film resistance increased when the sensors were exposed to H_2-containing nitrogen and decreased to the initial level when pure N_2 was purged. This behavior repeated for more than 20 cycles with no influence on the sensor performance. A two-step sensing mechanism was proposed to describe these measurements. The initial step consists of a weak chemisorption of H_2 molecules onto the Pd surface [41]. This phenomenon could induce charge transfer from the metal (or alloy, as the case) to CNHs. Considering the p-type semiconducting behavior of the CNHs, a decreased number of holes yields a higher resistance. The charge transfer from the metallic particles to the nanocarbon material is accelerated for CNHs dispersed with Pd-Ni alloy nanoparticles.

6. Ethanol Detection

Different types of CNHox-based nanohybrids were used as sensing layers within resistive vapor ethanol sensors: ternary nanohybrids, such as CNHox-SnO_2-PVP at 1/1/1 and 2/1/1 mass ratio, CNHox-ZnO-PVP at 5/2/1 and 5/3/2 mass ratio [42, 43], and quaternary nanohybrids, such as CNHox-GO-SnO_2-PVP at 1/1/1/1 w/w/w/w mass ratio [44]. In all cases, the ethanol sensing capability of the sensing layers was investigated at room temperature by applying a direct current with known intensity between the two electrodes of the sensing structure and measuring the resulting voltage difference for ethanol vapor concentration varying between 0 to 50 mg/L in dry air. The resistance of the layers increased with the ethanol concentration. This suggests that the overall behavior for all ternary and quaternary nanohybrids used as sensing layers is equivalent to p-type semiconducting material.

Two distinct ethanol sensing mechanisms were identified by examining the potential interactions between ethanol and the components of the nanohybrid sensing layers. The first sensing mechanism relies on ethanol as an electron donor for p-type semiconductor materials, such as CNOx or GO. While interacting with CNHox or GO, ethanol molecules donate their electron pairs, thus decreasing the number of holes in CNHox or GO. Consequently, the sensing film becomes more resistive. This mechanism can also be explained via the HSAB theory perspective. Ethanol is a hard Lewis base, while CNHox is a hard Lewis acid. By nulling each other out through multiple recombination processes, the conductivity of the sensing layer decreases. At the same time, according to the HSAB theory, the Sn^{4+} ion is a hard acid, so one may anticipate a hard acid-hard base type of interaction between the ethanol and the SnO_2.

The second sensing mechanism is based on the electron trapping and generation caused by the *metal oxide semiconductor* (MOX) – O_2 - ethanol interaction. When in contact with SnO_2 or ZnO nanoparticles, residual O_2 molecules are adsorbed on the surface of the MOX. The electrons in the SnO_2/ZnO nanoparticles are attracted by the adsorbed O_2 molecules. Consequently, O_2 molecules convert to oxygen ions, according to the scheme of reactions (1-4), and form a depletion region that increases sensor resistance.

$$O_2(\text{gas}) \rightarrow O_2(\text{ads}) \tag{1}$$

$$O_2(\text{ads}) + e^- \rightarrow O_2^-(\text{ads}) \tag{2}$$

$$O_2^-(\text{ads}) + e^- \rightarrow 2O^- \tag{3}$$

$$O^- + e^- \rightarrow O^2- \tag{4}$$

After the reductive ethanol molecules are injected into the testing chamber, and the device is exposed to ethanol vapors at room temperature, the adsorbed ethanol molecules react with oxygen-negative ions and release electrons according to two reactions (5–6).

$$CH_3CH_2OH(\text{ads}) + 6O^-(\text{ads}) \rightarrow 2CO_2(g) + 3H_2O(g) + 6e^- \tag{5}$$

$$CH_3CH_2OH(\text{ads}) + 6O^{2-}(\text{ads}) \rightarrow 2CO_2(g) + 3H_2O(g) + 12e^- \quad (6)$$

Ethanol removes the O_2 ions, the potential energy barrier is shortened, and the depletion layer is reduced. As a result, electrons move easily from one nanoparticle to another, and the resistance of the sensing structure decreases [45]. However, the overall increase in the resistance of the sensing layer, as measured and reported above, cannot be explained through this second sensing mechanism. This sensing mechanism cannot play a key role in resistive ethanol detection without completely neglecting it. It is worth mentioning that PVP does not change its structure upon contact with ethanol molecules, acting only as a binder [46].

Beyond the two sensing mechanisms described above, two types of interactions between the sensing layer components might have a role in ethanol sensing. First, both ZnO and SnO_2 are n-type semiconductors, while CNHox has p-type electrical conduction. Therefore, by adding SnO_2 and/or ZnO to CNHox, islands of p-n semiconductor heterojunctions embedded in PVP may be formed, leading to increased ethanol sensitivity. Secondly, it is plausible to assume that both SnO_2 and ZnO interact separately with the CNHox, altering the sensing layer's porosity and increasing its specific surface area.

In conclusion, it can be assumed that the p-type semiconducting behavior of CNHox (and GO, when used) is the key mechanism that increases the overall resistance of the discussed sensing layers when exposed to ethanol.

7. Ammonia Detection

SWCNHs produced by the gas-injected arc-in-water method were used as key sensing elements in the design of resistive ammonia sensors, for which the resistance of the sensing layer increased when exposed to NH_3 molecules [47]. The sensing mechanism involved relies on CNHox being a p-type semiconducting material and NH_3 being an electron donor, which donates its electron pairs, thus decreasing the hole concentration in CNHox and lowering the conductivity of the sensing layer. According to the HSAB theory, ammonia is a hard Lewis base that strongly interacts with the holes of the CNHs, which are hard Lewis acids.

8. Ozone Detection

Similarly, with ammonia detection, SWCNHs were used as key sensing elements in the design of resistive ozone sensors, for which the resistance of the sensing layer increased when exposed to O_3 molecules [48]. Such a behavior can be explained by the charge transfer from O_3 molecules to the CNHox–based sensing layer. O_3 molecules are a classic example of an electron acceptor; therefore, in contact with the CNHox-based sensing layer, they lead to lowering its resistance.

9. Conclusions

An extensive review of experimental data regarding the resistive detection of RH, O_2, H_2S, H_2, ethanol vapors, ammonia, and O_3 using CNHs (either pristine or oxidized) and their nanocomposites/nanohybrids as sensing layers was performed. In each case, various sensing mechanisms (such as the decreasing number of holes in the nanocarbon material (CNHs) at the interaction with water, ammonia, and ethanol, the protonic conduction (Grotthuss mechanism), the swelling of hydrophilic polymer (such as PVP), the charge transfer from a metal (or alloy) to the CNHs, the electron trapping and generation from the MOX – oxygen - ethanol interaction) were considered and discussed. The hard-soft acid-base (HSAB) theory also has proven to be a valuable tool for understanding the essential interaction between the nanocarbon materials and other components of the analyzed sensing layers (such as KCl, TiO_2, SnO_2), on the one hand, and RH, ethanol or ammonia, on the other. The role of each component of the sensing layers was discussed based on its chemical and physical properties. Mutual interactions between components of the sensing layers (such as the formation of p-n semiconductor heterojunctions embedded in PVP, alteration of the pore distribution with increasing the specific area, generation of supermolecules through $\pi - \pi$ stacking interactions, and intermolecular hydrogen bonds) were also considered. Last but not least, subtle aspects (such as the role of hydrogen bonds in obtaining better sensitivity of CNHox towards RH in humid air in comparison with humid nitrogen) were also discussed. For each sensing layer-gas tandem analyzed, the dominant sensing mechanism associated with the electrical response of the sensor was identified and presented.

Acknowledgements. The authors from IMT Bucharest would like to acknowledge the financial support of Contract No. 673 PED/2022 (PN-III-P2-2.1-PED-2021-4158) - UEFISCDI and the Core program Micro-Nnano-SIS PLUS PN19160201 - Nanocarbon materials - unconventional processes and technologies, test applications, contract 14N, 2019 (Ministry for Research, Innovation, and Digitalization).

References

[1] P. C. WATTS, N. MUREAU, Z. TANG, Y. MIYAJIMA, J. D. CAREY and S. R. P. SILVA, *The importance of oxygen-containing defects on carbon nanotubes for the detection of polar and non-polar vapours through hydrogen bond formation*, Nanotechnology, **18**(17), 2007, paper 175701.

[2] K. N. SEMENOV, E. V. ANDRUSENKO, N. A. CHARYKOV, E. V. LITASOVA, G. G. PANOVA, A. V. ENKOVA, I. V. MURIN and L. B. PIOTROVSKIY, *Carboxylated fullerenes: Physico-chemical properties and potential applications*, Progress in Solid State Chemistry **47–48**, 2017, pp. 19–36.

[3] C. N. COBIANU, N. DUMBRAVESCU, B.-C. SERBAN, O. BUIU, C. ROMANITAN, F. COMANESCU, M. DANILA, R. MARINESCU, V. AVRAMESCU and O. IONESCU, *Sonochemically synthetized ZnO-Graphene nanohybrids and its characterization*, Reviews on Advanced Materials Science **59**(1), 2020, pp. 176–187.

[4] A. M. DIMIEV and E. SIEGFIED, Eds., *Graphene Oxide: Fundamentals and Applications*, John Wiley & Sons, Chichester, 2017.

[5] R. TARCAN, O. TODOR-BOER, I. PETROVAI, C. LEORDEAN, S. ASTILEAN and I. BOTIZ, *Reduced graphene oxide today*, Journal of Materials Chemistry C **8**(4), 2020, pp. 1198–1224.

[6] N. KAROUSIS, I. SUAREZ-MARTINEZ, C. P. EWELS and N. TAGMATARCHIS, *Structure, properties, functionalization, and applications of carbon nanohorns*, Chemical Reviews **116**(8), 2016, pp. 4850–4883.

[7] S. IIJIMA, M. YUDASAKA, R. YAMADA, S. BANDOW, K. SUENAGA, F. KOKAI and K. TAKAHASHI, *Nano-aggregates of single-walled graphitic carbon nano-horns*, Chemical Physics Letters **309**(3-4), 1999, pp. 165–170.

[8] S. ZHU and G. XU, *Single-walled carbon nanohorns and their applications*, Nanoscale **2**(12), 2010, pp. 2538–2549.

[9] N. RUBIO, M. A. HERRERO, M. MENEGHETTI, A. DIAZ-ORTIZ, M. SCHIAVON, M. PRATO and E. VAZQUEZ, *Efficient functionalization of carbon nanohorns via microwave irradiation*, Journal of Materials Chemistry **19**(25), 2009, pp. 4407–4413.

[10] G. PAGONA, J. FAN, A. MAIGNÈ, M. YUDASAKA, S. IIJIMA and N. TAGMATARCHIS, *Aqueous carbon nanohorn–pyrene–porphyrin nanoensembles: controlling charge-transfer interactions*, Diamond and Related Materials 16(4–7), 2007, pp. 1150–1153.

[11] B. C. SERBAN, M. BUMBAC, O. BUIU, C. COBIANU, M. BREZEANU and C. M. NICOLESCU, *Carbon nanohorns and their nanocomposites: Synthesis, properties and applications. A concise review*, Annals of the Academy of Romanian Scientists: Series on Mathematics and its Applications **11**, 2018, pp. 5–18.

[12] C. RUNGNIM, K. FAUNGNAWAKIJ, N. SANO, N. KUNGWAN and S. NAMUANGRUK, *Hydrogen storage performance of platinum supported carbon nanohorns: A DFT study of reaction mechanisms, thermodynamics, and kinetics*, International Journal of Hydrogen Energy **43**(52), 2018, pp. 23336–23345.

[13] C. M. YANG, Y. J. KIM, M. ENDO, H. KANOH, M. YUDASAKA, S. K. IIJIMA and K. KANEKO, *Nanowindow-regulated specific capacitance of supercapacitor electrodes of single-wall carbon nanohorns*, Journal of the American Chemical Society **129**(1), 2007, pp. 20–21.

[14] Y. HUANG, Z. Li, S. JIN, S. ZHANG, H. WANG, P. HIRALAL, G. A. J. AMARATUNGA and H. ZHOU, *Carbon nanohorns/nanotubes: An effective binary conductive additive in the cathode of high energy-density zinc-ion rechargeable batteries*, Carbon **167**, 2020, pp. 431–438.

[15] S. B. KADAMBI, K. PRAMODA, U. RAMAMURTY and C. N. T. RAO, *Carbon-nanohorn reinforced polymer matrix composites: synergetic benefits in mechanical properties*, ACS Applied Materials & Interfaces **7**(31), 2015, pp. 17016–17022.

[16] X. LIU, H. Li, F. WANG, S. ZHU, Y. WANG and G. XU, *Functionalized single-walled carbon nanohorns for electrochemical biosensing*, Biosensors and Bioelectronics **25**(10), 2010, pp. 2194–2199.

[17] D. PUTHUSSERI, D. J. BABU, S. OKEIL and J. J. SCHNEIDER, *Gas adsorption capacity in an all carbon nanomaterial composed of carbon nanohorns and vertically aligned carbon nanotubes*, Physical Chemistry Chemical Physics **19**(38), 2017, pp. 26265–26271.

[18] M. KOSAKA, S.KUROSHIMA, K. KOBAYASHI, S. SEKINO, T. ICHIHASHI, S. NAKAMURA, T. YOSHITAKE and Y. KUBO, *Single-wall carbon nanohorns supporting Pt catalyst in direct methanol fuel cells*, The Journal of Physical Chemistry C **113**(20), 2009, pp. 8660–8667.

[19] K. P. SELVAM, T. NAKAGAWA, T. MARUI, H. INOUE, T. NISHIKAWA and Y. HAYASHI, *Synthesis of solvent-free conductive and flexible cellulose–carbon nanohorn sheets and their application as a water vapor sensor*, Materials Research Express **7**(5), 2020, 056402.

[20] B. C. SERBAN, O. BUIU, N. DUMBRAVESCU, C. COBIANU, V. AVRAMESCU, M. BREZEANU, M. BUMBAC and C. M. NICOLESCU, *Oxidized carbon nanohorns as novel sensing layer for resistive humidity sensor*, Acta Chimica Slovenica **67**(2), 2020, pp. 469–475.

[21] B. C. SERBAN, O. BUIU, N. DUMBRAVESCU , V. AVRAMESCU, M. BREZEANU, M. R. MARINESCU, M. BUMBAC and C. M. NICOLESCU, *Carbon nanohorns-based matrix nanocomposite for relative humidity sensor in EMERGEMAT*, Proceedings of 2022 International Conference on Emerging Technologies in Engineering Materials, Bucharest, Romania, 2022, pp. 90.

[22] B. C. SERBAN, O. BUIU, N. DUMBRAVESCU, C. COBIANU, V. AVRAMESCU, M. BREZEANU, M. BUMBAC, C. PACHIU and C. M. NICOLESCU, *Oxidized carbon nanohorn-hydrophilic polymer nanocomposite as the resistive sensing layer for relative humidity*, Analytical Letters **54**(3), 2021, pp. 527–540.

[23] B. C. SERBAN, O. BUIU, C. COBIANU, V. AVRAMESCU, N. DUMBRVESCU, M. BREZEANU, M. BUMBAC, C. M. NICOLESCU and R. MARINESCU, *Ternary carbon-based nanocomposite as sensing layer for resistive humidity sensor*, Multidisciplinary Digital Publishing Institute Proceedings **29**(1), 2019, paper 114.

[24] B. C. SERBAN, C. COBIANU, O. BUIU, M. BUMBAC, N. DUMBRAVESCU, V. AVRAMESCU, C. M. NICOLESCU, M. BREZEANU, C. PACHIU, G. CRACIUN and C. RADULESCU, *Ternary nanocomposites based on oxidized carbon nanohorns as sensing layers for room temperature resistive humidity sensing*, Materials **14**(11), 2021, paper 2705.

[25] B. C. SERBAN, C. COBIANU, O. BUIU, M. BUMBAC, N. DUMBRAVESCU, V. AVRAMESCU, C. M. NICOLESCU, M. BREZEANU, C. RADULESCU, G. CRACIUN, C. ROMANITAN and F. C. COMANESCU, *Quaternary holey carbon nanohorns/SnO_2/ZnO/PVP nano-hybrid as sensing element for resistive-type humidity sensor*, Coatings **11**(11), 2021, paper 1307.

[26] B. C. SERBAN, O. BUIU, M. BUMBAC, N. DUMBRAVESCU, V. AVRAMESCU, M. BREZEANU, C. RADULESCU, G. CRACIUN, C. M. NICOLESCU, C. ROMANITAN and F. COMANESCU, *Ternary holey carbon nanohorns/TiO_2/PVP nanohybrids as sensing films for resistive humidity sensors*, Coatings **11**(9), 2021, paper 1065.

[27] B. C. SERBAN, O. BUIU, M. BUMBAC, R. MARINESCU, N. DUMBRAVESCU, V. AVRAMESCU, C. COBIANU, C. M. NICOLESCU, M. BREZEANU, C. RADULESCU and F. COMANESCU, *Ternary oxidized carbon nanohorns/TiO_2/PVP nanohybrid as sensitive layer for chemoresistive humidity sensor*, Chemistry Proceedings **5**(1), 2021, paper 12.

[28] B. C. SERBAN, N. DUMBRAVESCU, O. BUIU, M. BUMBAC, M. BREZEANU, C. COBIANU, R. MARINESCU, C. PACHIU, V. AVRAMESCU and C.M. NICOLESCU, *Oxidized carbon nanohorns/KCl/PVP nanohybrid as sensing layer for chemiresistive humidity sensor*, Proceedings of 2023 International Semiconductor Conference, Sinaia, Romania, 2023, pp. 75–80.

[29] B. C. SERBAN, N. DUMBRAVESCU, O. BUIU, M. BUMBAC, M. BREZEANU, C. COBIANU, R. MARINESCU, C. PACHIU, V. AVRAMESCU and C.M. NICOLESCU, *Ternary holey carbon-based nanohybrid for resistive relative humidity sensor*, Proceedings of 2023 International Semiconductor Conference, Sinaia, Romania, 2023, pp. 25–30.

[30] R. G. PEARSON, *Hard and soft acids and bases, HSAB, part II: Underlying theories*, Journal of Chemical Education **45**(10), 1968, paper 643.

[31] B.C. SERBAN, A.S. KUMAR, S. COSTEA, M. MIHAILA, O. BUIU, M. BREZEANU, N. VARACHIU, C. COBIANU, *Surface acoustic wave CO_2 sensing with polymer-amino carbon nanotube composites*. In 2008 International Semiconductor Conference, 2008 **1**, pp. 73–76, IEEE event.

[32] V. AVRAMESCU, C. BOSTAN, B. C. SERBAN, I. GEORGESCU, S. COSTEA, N. VARACHIU and N. C. COBIANU, *Surface acoustic wave devices and their sensing capabilities*, Proceedings of 2009 International Semiconductor Conference, Sinaia, Romania, 2009 **1**, pp. 27–36.

[33] B. C. SERBAN, A. KUMAR, C. COBIANU, O. BUIU, S. COSTEA, C. BOSTAN and N. VARACHIU, *Selection of gas sensing materials using the Hard Soft Acid Base theory; application to Surface Acoustic Wave CO_2 detection*, Proceedings of 2010 International Semiconductor Conference, Sinaia, Romania, 2010 **1**, pp. 247–250.

[34] B. C. SERBAN, C. COBIANU, N. DUMBRAVESCU, O. BUIU, M. BUMBAC, C. M. NICOLESCU, C. COBIANU, M. BREZEANU, C. PACHIU and M. SERBANESCU, *Electrical percolation threshold and size effects in polyvinylpyrrolidone-oxidized single-wall carbon nanohorn nanocomposite: The impact for relative humidity resistive sensors design*, Sensors **21**(4), 2021, paper 1435.

[35] B. C. SERBAN, C. COBIANU, N. DUMBRAVESCU, O. BUIU, V. AVRAMESCU, M. BUMBAC, C. M. NICOLESCU, C. COBIANU and M. BREZEANU, *Electrical percolation threshold in oxidized*

single wall carbon nanohorn-polyvinylpyrrolidone nanocomposite: A possible application for high sensitivity resistive humidity sensor, Proceedings of 2020 International Semiconductor Conference, Sinaia, Romania, 2020, pp. 239–242.

[36] Z. WANG, L. SHI, F. WU, S. YUAN, Y. ZHAO and M. ZHANG, *The sol–gel template synthesis of porous* TiO_2 *for a high-performance humidity sensor*, Nanotechnology **22**(27), 2011, paper 275502.

[37] S. SHOJAI NASAB and S. ZAHMATKESH, *Preparation, structural characterization, and gas separation properties of functionalized zinc oxide particle filled poly (ether-amide) nanocomposite films*, Journal of Plastic Film & Sheeting **33**(1), 2017, pp. 92–113.

[38] K. URITA, S. SEKI, S. UTSUMI, D. NOGUCHI, H. KANOH, H. TANAKA, Y. HATTORI, Y. OCHIAI, N. AOKI, M. YUDASAKA, S. IIJIMA and K. KANEKO, *Effects of gas adsorption on the electrical conductivity of single-wall carbon nanohorns*, Nano Letters **6**(7), 2006, pp. 1325–1328.

[39] M. ZHOU, Y. YAO, Y. HAN, L. XIE, X. ZHAO, N. BARSAN and Z. ZHU, *Ultrasensitive gas sensor based on nanocube* In_2O_3*-CNH composite at low operating temperature*, Sensors and Actuators B: Chemical **354**, 2022, paper 131224.

[40] N. SANO, T. ISHII, H. MORI, Y. IKEYAMA and H. TAMON, *One-step synthesis of single-walled carbon nanohorns dispersed with Pd-Ni alloy nanoparticles by gas-injected arc-in-water method and effects of synthesis factors on their hydrogen sensor sensitivity*, Journal of Applied Physics **112**(4), 2012, paper 044301.

[41] H. NAKATSUJI, M. HADA and T. YONEZAWA, *Theoretical study on the chemisorption of a hydrogen molecule on palladium*, Journal of the American Chemical Society **109**(7), 1987, pp. 1902–1912.

[42] C. COBIANU, B. C. SERBAN, N. DUMBRAVESCU, O. BUIU, V. AVRAMESCU, C. PACHIU, B. BITA, M. BUMBAC, C. M. NICOLESCU and C. COBIANU, *Organic–inorganic ternary nanohybrids of single-walled carbon nanohorns for room temperature chemiresistive ethanol detection*, Nanomaterials **10**(12), 2020, paper 2552.

[43] C. COBIANU, B. C. SERBAN, N. DUMBRAVESCU, O. BUIU, V. AVRAMESCU, M. BUMBAC, C. M. NICOLESCU and C. COBIANU, *Room temperature chemiresistive ethanol detection by ternary nanocomposites of oxidized single wall carbon nanohorn (ox-SWCNH)*, Proceedings of 2020 International Semiconductor Conference, Sinaia, Romania, 2020, pp. 13–16.

[44] B. C. SERBAN, N. DUMBRAVESCU, O. BUIU, M. BUMBAC, M. BREZEANU, C. COBIANU, R. MARINESCU, C. PACHIU, V. AVRAMESCU, C. M. NICOLESCU and F. COMANESCU, *Quaternary oxidized carbon nanohorns–based nanohybrid as sensing layer for room temperature resistive ethanol sensing*, Proceedings of 2023 International Semiconductor Conference, Sinaia, Romania, 2023, pp 67–70.

[45] K. S. CHOI, S. PARK and S. P. CHANG, *Enhanced ethanol sensing properties based on* SnO_2 *nanowires coated with* Fe_2O_3 *nanoparticles*, Sensors and Actuators B: Chemical **238**, 2017, pp. 871–879.

[46] P. C. GRIFFITHS, N. HIRST, A. PAUL, S. M. KING, R. K. HEENAN and R. FARLEY, *Effect of ethanol on the interaction between poly (vinylpyrrolidone) and sodium dodecyl sulfate*, Langmuir **20**(16), 2004, pp. 6904–6913.

[47] N. SANO, M. KINUGASA, F. OTSUKI and J. SUEHIRO, *Gas sensor using single-wall carbon nanohorns*, Advanced Powder Technology **18**(4), 2007, pp. 455–466.

[48] N. SANO and F. OHTSUKI, *Carbon nanohorn sensor to detect ozone in water*, Journal of Electrostatics **65**(4), 2007, pp. 263–268.