



Article Quaternary Holey Carbon Nanohorns/SnO₂/ZnO/PVP Nano-Hybrid as Sensing Element for Resistive-Type Humidity Sensor

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Abstract: In this study, a resistive humidity sensor for moisture detection at room temperature is presented. The thin film proposed as a critical sensing element is based on a quaternary hybrid nanocomposite CNHox//SnO2/ZnO/PVP (oxidated carbon nanohorns-tin oxide-zinc oxidepolyvinylpyrrolidone) at the w/w/w/w ratios of 1.5/1/1/1 and 3/1/1/1. The sensing structure consists of a Si/SiO₂ dielectric substrate and interdigitated transducers (IDT) electrodes, while the sensing film layer is deposited through the drop-casting method. Morphology and composition of the sensing layers were investigated through scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction, and Raman spectroscopy. Each quaternary hybrid nanocomposite-based thin film's relative humidity (RH) sensing capability was analyzed by applying a direct current with known intensity between two electrodes and measuring the voltage difference when varying the RH from 0% to 100% in a humid nitrogen atmosphere. While the sensor with $CNHox/SnO_2/ZnO/PVP$ at 1.5/1/1/1 as the sensing layer has the better performance in terms of sensitivity, the structure employing $CNHox//SnO_2/ZnO/PVP$ at 3/1/1/1 (mass ratio) as the sensing layer has a better performance in terms of linearity. The contribution of each component of the quaternary hybrid nanocomposites to the sensing performance is discussed in relation to their physical and chemical properties. Several alternative sensing mechanisms were taken into consideration and discussed. Based on the measured sensing results, we presume that the impact of the p-type semiconductor behavior of CNHox, in conjunction with the swelling of the hydrophilic polymer, is dominant and leads to the overall increasing resistance of the sensing film.

Keywords: holey carbon nanohorns (CNHox); tin oxide; zinc oxide; polyvinylpyrrolidone (PVP); resistive humidity sensor; p-type semiconductor; swelling



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1. Introduction

In recent years, relative humidity (RH) sensors have been widely designed and developed due to their relevance in a large variety of industrial, commercial, and residential applications such as buildings heating, air conditioning and ventilating (HVAC systems), handheld devices, medical field (respirators, medical air lines, sterilizers), food processing, automotive industry (engine testbeds), pharmaceutical processing (storage, packaging, tablet coating, and compression), agriculture (soil moisture control, crop storage, conservation of seeds), diagnosis of corrosion and erosion in infrastructures and civil engineering, environmental and meteorological monitoring, mining industry, robotics and so forth. [1–5].

Apart from the sensing principle, fabrication technologies, and sensor design, the materials used as sensing elements play a cardinal role in developing an RH sensor with superior performances [6]. Thus, many different materials have been investigated as sensing layers within the design of RH sensors [7].

Due to their outstanding features, such as high sensitivity towards moisture, facile and versatile synthetic methods, low cost and tunable electric properties, as well as the ability to operate under severe conditions, semiconducting metal oxides (MOXs) have emerged as a promising choice in the RH sensor field [8]. Among MOXs, SnO₂ has received increased attention in the last decades due to its fast, linear, and high–sensitivity response towards relative humidity changes [9–13]. Kuang et al. developed a resistive RH sensor using a SnO₂ nanowire as a sensing film [14]. Tin (IV) oxide-based nanowires were synthesized by chemical vapor deposition using gold nanoparticles as catalysts. Both dynamic and static experiments emphasized that the manufactured sensor has a fast response and high sensitivity to RH changes in humid air. Parthibavarman et al. described the fabrication of a resistor-type humidity sensor using SnO₂-based spherical nanoparticles as a sensing layer [15]. The SnO₂ nanoparticles, synthesized by the microwave irradiation method, exhibit good sensitivity towards RH. The estimated response and recovery times were found to be of 32 s and 25 s, respectively.

Song et al. proposed an impedance sensor for RH detection at room temperature using KCl-doped SnO_2 nanofibers as a sensing thin film [16]. This RH sensor showed superior sensing performances, such as fast response time (6 s) and recovery time (7 s), good reproducibility, linearity, and stability. Furthermore, according to the authors, the addition of K⁺ ions led to an increase in the number of active sites for water molecules, thus improving the device sensitivity.

ZnO is another semiconducting metal oxide, which has been intensively explored as a sensing layer in designing different types of devices [17–21]. For example, Qui et al. developed a chemoresistive RH sensor using ZnO nanotetrapods with faceted pores and large internal surfaces as the sensitive film [22]. This unique morphology of the sensing layer yields high sensitivity and rapid response and recovery time. Furthermore, Qi et al. studied an impedance-type humidity sensor based on flower-like ZnO nanorods as sensing elements [23]. The proposed sensor exhibits high sensitivity, the sensor's impedance decreasing by about five orders of magnitude with increasing relative humidity (RH) from 11% to 95%.

Tsai et al. investigated ZnO nanosheets as a sensing layer for resistive RH sensing at room temperature [24]. The surface-to-volume ratio and the porous-like surface are two features derived from the morphology of the film and were presented by the authors as the leading cause of the high sensitivity of the structure. In addition, a ZnO/SnO₂ cubic structure-based nanocomposite was also studied as a sensing layer for resistive RH monitoring [25].

Other types of MOXs that were studied as sensing layers in RH sensing include TiO₂ [26,27], CeO₂ [28,29], CuO [30,31].

At the same time, in the last two decades, a significant number of studies have explored the possibility of using carbon-based materials as sensing layers in the manufacturing of humidity sensors, thanks to the outstanding properties of these materials. Due to their multiple allotrope forms with different chemical and physical properties, carbonbased materials can be used as sensing films in a large variety of RH types of sensors. In addition, carbon-based-materials are of particular interest in RH sensors design due to their sensing capabilities at room temperature, large specific surface area, and chemical inertness. Moreover, facile hydrophilization of carbonic film through covalent functionalization enables modulation of sensitivity towards moisture. [32–34].

Among these types of materials, one can mention, *inter alia*, graphene oxide [35–37], carbon nanotubes [38–40], amorphous carbon [41], nanodiamond [42,43], nanocones [44], fullerenes and their derivatives [45,46], carbon nanocoils [47], holey carbon nanohorns (CN-Hox) and their nanocomposites [48–55], hydrogenated amorphous carbon [56], oxidized carbon nanoonions [57–60], carbon quantum dots [61].

Based on the information presented above, semiconducting metal oxides and nanocarbonic materials can form promising nanocomposites used as sensing layers for manufacturing high-performance RH sensors. Nanocomposites including SnO₂ and reduced graphene oxide [62], or multiwall carbon nanotubes [63], as well as nanocomposites of ZnO with graphene oxide [64,65], carbon nanotubes [66,67], or graphene quantum dots [68] may be included in this category.

Finally, yet importantly, polymers are widely used as sensing layers in designing RH sensors. Thus, dielectric polymers, such as polyvinyl alcohol [69], polyvinylpyrrolidone [70], or conductive polymers, such as polyaniline [71], are currently used as sensitive films in RH sensors with different detection principles.

This paper presents the response of a resistive RH sensor that uses a sensing layer based on quaternary hybrid nanocomposites $CNHox/SnO_2/ZnO/PVP$ at w/w/w/w ratios of 1.5/1/1/1, and, respectively, 3/1/1/1. The study emphasizes the relative humidity sensing capabilities of the newly developed quaternary organic–inorganic hybrid nanocomposites operating at room temperature.

2. Materials and Methods

Materials

All the materials used in the RH measurements were purchased from Sigma Aldrich (Redox Lab Supplies Com, Bucharest, Romania). Holey carbon nanohorns (CNHox, with the structure shown in Figure 1a) are characterized by lengths between 40 nm and 50 nm, diameters between 2 nm to 5 nm, and a specific surface area of around 1300–1400 m²/g. According to the supplier, CNHox used in experiments has no metal contamination, and graphite is their main impurity (around 10% w/w).

The polyvinylpyrrolidone (PVP) used has the structure depicted in Figure 1b and an average molar weight of 40,000 g mol⁻¹. Both tin (IV) oxide and zinc oxide were nanometric powders (averaged particle size lower than 100 nm), with a specific surface area of around 10–25 m²/g. Isopropyl alcohol, (CH₃)₂CHOH, is a solution of 70% w/w in water. All reagents were used as received without further purification.



Figure 1. The structure of (a) holey carbon nanohorns—CNHox, (b) PVP.

Preparation of the quaternary organic–inorganic—holeycarbon nanohorns hybrid sensing films and the experimental setup are described in detail in the supplementary material.

3. Results and Discussions

3.1. Surface Topography

Surface topography of the sensing layers based on the quaternary hybrid nanocomposite was investigated by scanning electron microscopy (SEM). For surface inspection, a field emission gun scanning electron microscope/FEG-SEM-Nova NanoSEM 630 (Thermo Scientific, Waltham, MA, USA) (FEI), with superior low voltage resolution and high surface sensitivity imaging, was employed.

At first glance, regions with a discontinuous character of particles' distribution can be distinguished in all presented SEM images (Figures 2 and 3). However, the nanoscale images reveal a broad particle size distribution, from about 10–30 nm to 100 nm. Particles of much larger sizes (100–200 nm) can also be visualized due to the aggregation of both nanocarbonic particles and semiconducting metal oxides of different sizes and crystallographic orientations.



Figure 2. Scanning electron micrographs of the CNHox/SnO₂/ZnO/PVP = 1.5/1/1/1, w/w/w/w ratio.



Figure 3. Scanning electron micrographs of the CNHox/SnO₂/ZnO/PVP = 3/1/1/1, w/w/w/w ratio.

3.2. Surface Composition

Figure 4 shows the elemental composition on the sensing layers surface (expressed in both atomic and weight percentages), obtained through EDX spectroscopy coupled with SEM. The method confirmed the presence of the elements C, Sn and Zn, according to the chemical design of both of the quaternary hybrid nanocomposites prepared. However, these numerical evaluations suffer from errors specific to the EDX method, which reach up to 50%–60% in the case of Sn and Zn atoms, and from errors due to the inhomogeneity of the distribution of carbon and oxide materials in the sensitive layer. Nevertheless, from Figure 4a,b, it can be noted that sample "1.5" has a lower amount of carbon than sample "3", which is in agreement with the proposed preparation procedure.

1μπ	elected Area 3	Selected Area		1µm			
Element	Weight %	Atomic %		Element	Weight %	Atomic %	
СК	13.15	21.17		СК	22.32	35.33	
OK	37.44	45.24		OK	30.14	35.82	
SiK	48.43	33.34		SiK	39.74	26.91	
SnL	0.32	0.05		SnL	2.52	0.4	
ZnK	0.65	0.19		ZnK	5.29	1.54	
	(a)		_		(b)		

Figure 4. Surface composition of sensitive quaternary layers, depending on the content of nanocarbon material and semiconductor metal oxides obtained by EDX spectroscopy coupled with SEM: (a) Sample "1.5" Ox-SWCNH/SnO2/ZnO/PVP = 1.5/1/1/1, and (b) Sample "3" Ox-SWCNH/SnO₂/ZnO/PVP = 3/1/1/1.

3.3. X-ray Diffraction Results

X-ray diffraction measurements were performed using a 9 kW Rigaku Smart Lab diffractometer (Osaka, Japan) operated at 40 kV and 75 mA. A PSA 0.5° soller slit was employed to ensure an appropriate divergence of the X-ray beam at the detector. Grazing incidence X-ray diffraction (GIXRD) patterns were recorded by maintaining the incidence angle ω at 0.5°, while the detector scanned in the 20 range of 5 to 60°. The peak indexing was made using the ICDD database—International Center for Diffraction Data. GIXRD patterns are shown in Figure 5a–d for each component of quaternary holey carbon nanohorn-based hybrid nanocomposite and for the nanohybrid CNHox/SnO₂/ZnO/PVP at 1.5/1/1/1 mass ratio (Figure 5e).



Figure 5. Diffractogram GIXRD for: (a) CNHox, (b) ZnO, (c) SnO₂, (d) PVP, nanocomposite CNHox/SnO₂/ZnO/PVP (e) (1.5/1/1/1 mass ratio) and (f) (3/1/1/1 mass ratio).

In the case of CNHox (Figure 5a), the GIXRD pattern shows three broad diffraction peaks, characteristic for CNHox, located at 23.86°, 43.11°, and 53.26°, correspondent with the (002), (100), and (004) facet of CNHs [72]. Further, in Figure 5b,c, one can be observed that the GIXRD pattern exhibits multiple diffraction peaks, which can be ascribed unambiguously to wurtzite ZnO and SnO₂. First, the zinc oxide phase belongs to the 186: P63*mc* spatial group with card no. 079-0208, having the lattice constant: a = b = 0.32 nm and c = 0.52 nm. Second, tin oxide belongs to the 136: P42/*mnm* spatial group according to card no. 210-1853 with the following lattice parameters: a = b = 0.47 nm, c = 0.31 nm. Finally, for the polymeric component, the GIXRD pattern of polyvinylpyrrolidone (Figure 5d) exhibited two broad characteristic peaks at 20 of 11.25° and 21.21°, corresponding to d-values of 7.96 and 4.18 Å, respectively. These results are in good agreement with reported literature data [73].

Further, the GIXRD pattern of $CNHox/SnO_2/ZnO/PVP$ at 1.5/1/1/1 mass ratio shows multiple diffraction peaks, assigned as carbon nanohorns, SnO_2 and ZnO phases exhibit different crystallization. The size of the crystalline domains, also called the mean crystallite size, which represents a measure of the crystal quality, was evaluated with the

Scherrer formula. This gives a straightforward correlation between the mean crystallite size (τ) and the Full Width at Half Maximum (β) in the following way [74]:

$$\tau = \frac{k\lambda}{\beta\cos\theta'},\tag{1}$$

where k is a shape factor usually equal to 0.9, θ is the peak angular position, and λ is the wavelength. The following values for the mean crystallite size were obtained: 2.35 nm for carbon, 19.7 nm for SnO₂, and 39.7 nm for ZnO. Moving forward to higher CNHox concentration (e.g., 3/1/1/1 mass ratio), the characteristic diffraction peaks for ZnO disappear, while the ones for SnO₂ indicate poor crystallization. Our findings suggest that the crystal quality of the individual components is strongly correlated to the CNHox concentration.

3.4. Raman Spectroscopy

The interaction between the holey carbon nanohorns, metal oxides, and polyvinylpyrrolidone has been proven using Raman spectroscopy. Raman spectra have been acquired by Lab Ram HR 800 Raman spectrometer, using a He-Ne laser excitation (633 nm). The Raman spectra of the quaternary nanocomposites based on CNHox/SnO₂/ZnO/PVP highlighted the complexity of the chemical interactions between the four components.

Thus, Figure 6 shows three Raman spectra recorded in three different film positions deposited from the quaternary nanocomposite CNHox/ZnO/SnO₂/PVP at 3/1/1/1 (w/w/w/w) ratio, plotted in red, green, and blue color, respectively. It can be observed that three active Raman bands (D, G, 2D) were recorded, at the wavenumbers of 1316.0, 1589.6, and 2630.8 cm⁻¹ which are characteristic for sp^2 defected carbon nanomaterials [48,49].

One can also identify one specific SnO_2 band (629.5 cm⁻¹) having a low intensity, explainable by the small size of the related crystallites, according to the GIXRD results.

Furthermore, Raman signals at 441 cm⁻¹ (E high 2), 575 cm⁻¹ (A1(LO)), and 585 cm⁻¹ (E1(LO)) were observed for ZnO [75].



Figure 6. Raman spectra of solid-state films of CNHox $/SnO_2/ZnO /PVP = 3/1/1/1$ (mass ratio) deposited on a silicon substrate in three different film positions, plotted in red, green, and blue color.

3.5. RH Monitoring Capability of the Quaternary Nanocomposite

The relative humidity monitoring capability of each quaternary hybrid nanocompositebased thin film was explored by applying a direct current at the two electrodes and measuring the voltage difference when varying the RH from 0% to 100%. For convenience, we will use the following abbreviations: sensor "1.5"—an RH resistive sensor using as sensing layer a quaternary nanohybrid based on CNHox//SnO₂/ZnO/PVP at 1.5/1/1/1 The behavior of both manufactured RH sensors is presented below (Figure 7a,b). According to results shown in Figure 7a,b, the resistance of the quaternary hybrid nanocompositebased sensing layer increases when RH increases in the range from 0% to 100% RH; measurements have been performed in steps of 10% RH. In addition, it was observed that the resistance of the sensitive layer for the RH value "0" increases with the decrease of the CNHox content in the quaternary nanohybrid. This is an expected behavior caused by the fact that CNHox is a nanocarbonic material with high conductivity. Increasing their concentration leads to decreasing the nanocomposite's electrical resistance. The overall linearity of both quaternary hybrid nanocomposites-based resistive sensors—in humid nitrogen, when varying RH from 0% to 100%—is good, as shown in Figure 8.



Figure 7. The response of (**a**) Sensor "1.5", and (**b**) Sensor "3", ("R curve"-blue) as a function of time for two measurement cycles when relative humidity was increased in ten steps from 0% RH to 100% RH; "RH curve-red" shows the similar characteristic measured for a commercial, capacitive sensor.



Figure 8. The transfer function of the new sensors in humid nitrogen (RH = 0%–100%).

The sensor response is defined as:

Response (%) =
$$\frac{\Delta R}{R_{dry nitrogen}} \times 100 = \frac{R_{humid} - R_{dry nitrogen}}{R_{dry nitrogen}} \times 100$$
, (2)

where R_{humid} and $R_{dry nitrogen}$ are the measured resistances exposed to humid conditions and dry nitrogen, respectively. By analyzing the % response of the sensors with the composite sensing layer when exposed to different RH levels, one can observe that the humidity sensing response varies with the amount of deposited CNHox, that is, the calculated response (%) increases for the studied sensing layers with RH, and that sensor "1.5" has better % response when compared with the sensor "3".

To compare the sensing performances of the RH resistive sensors with different initial resistance values, a relative sensitivity (S_r) to relative humidity variations (RH) was defined:

$$S_r = \frac{R_x - R_0}{(RH)_x}, \tag{3}$$

where: R_x is the resistance of the sensitive layer measured in the test chamber for the RH_x value indicated by the commercial sensor (measured with $\pm 2\%$ accuracy as the producer suggests it). R_0 is the estimated resistance from the graph calibration line resistance = *f* (relative humidity) by extrapolation for the value at RH = 0%.

The newly designed RH resistive sensors were compared with those previously reported in terms of the value of relative sensitivity. The comparison is summarized in Table 1. Different hybrids such as metal oxides semiconductor/nanocarbonic materials could yield heterojunctions beneficial for relative humidity monitoring. The purpose of the study was to investigate the qualitative effect of metal oxides added in the composite along with CNHox and PVP. Additionally, the combination ratios chosen are similar to the previously tested composites based on CNHOx and PVP as presented in Table 1. As can be seen from Table 1, the CNHox and CNHox/PVP-based sensitive films were proven suitable for RH resistive monitoring with better sensitivity for the nanocomposite. Thus, the favorable effect of the hydrophilic and dielectric PVP addition was demonstrated in terms of swelling effect [48,49].

On the other hand, both quaternary nanohybrids which contain graphene oxide (Table 1) are superior in terms of sensitivity. Graphene oxide has a pivotal role in the dispersion of holey carbon nanohorn, increasing surface area and, finally, improving humidity sensing. Furthermore, the metal oxides added to the mixture resulted in a better sensitivity for the sensing layer compared with the binary mixture CNHox/PVP with one order of magnitude. In all situations, the sensing layer showed a decrease of sensitivity of the sensing layer with the increase of nanocarbonic material content except the case of mixing graphene oxide along with CNHox and tin oxide in the composite. In terms of sensitivity, the results presented in Table 1 shows that the quaternary mixture of CNHox/GO/SnO₂/PVP are the most promising materials for resistive sensors.

Sensing Layer	Relative Sensitivity		
CNHox [48]	0.013-0.021		
CNHox-PVP 1/1 [49]	0.020-0.058		
CNHox-PVP 2/1 [49]	0.017–0.025		
Graphene-PVP inkjet printed [50]	0.21–0.30		
GO-CNHox-PVP 1/1/1 [51]	0.150-0.200		
GO-CNHox-PVP 1/2/1 [51]	0.063-0.070		
GO-CNHox–PVP 1/3/1 [51]	0.043-0.051		
CNHox/GO/SnO ₂ /PVP 0.75/0.75/1/1 [76]	0.548-0.770		
CNHox/GO/SnO ₂ /PVP 1/1/1/1 [76]	0.798–0.980		
$CNHox/SnO_2/ZnO/PVP = 1.5/1/1/1$ -present study	0.320-0.489		
$CNHox/SnO_2/ZnO/PVP = 3/1/1/1$ -present study	0.105-0.242		

Table 1. Sensitivity CNHox–SnO₂-ZnO–PVP compared with previous tested sensing layers.

The tested devices were prepared and tested by following the same procedures; from the preparation of the sensitive layer (where the mild ultrasonication was used), to the testing protocol, after the sensitive layer was deposited by the same method and using the same quantity of sensing material. The drop-casting method is a facile and low-cost technique that does not lead to layers with a very ordered and homogeneous structure, but the response of the sensitive layer is comparable to the response given by the sensors whose sensing layer that was obtained by inkjet printing [50].Two essential parameters,

If R(t) is the response of the device in time, the t_r can be evaluated as:

resistive sensors.

$$t_r = t_{90} - t_{10},$$
 (4)

where t_{90} and t_{10} represent the moments when the response R(t) reaches 90% and 10%, respectively, from the total variation of the sensor's resistance due to a change in the RH value (as in the example presented in Figure 9).

the response and recovery time (in seconds), were calculated for both manufactured RH



Figure 9. Calculation of response time between two steps of relative humidity.

The response time varied from 35 to 100 s for both sensors when relative humidity was changed in the testing chamber (Figure 10). The highest values of response time were registered when the relative humidity exceeded 70%. A longer response time corresponding to the high level of RH can be explained by decreasing the number of active sites.



Figure 10. Response time for sensor 1.5 and sensor 3 when relative humidity increased with 10% RH steps in the second run of the sensor.

Water molecules are adsorbed in the hydrophilic sensing layer based on CNHox/SnO₂/ ZnO/PVP. At a higher level of RH, besides the adsorption process, a second process will occur, that is, the condensation around the vicinity of the hydrophilic groups. As a result, the balance of these two processes is reducing the number of active sites, resulting in a blockage of the active sites.

Figure 11 presents a recovery pattern for the two resistive sensing layers tested when the relative humidity from the testing chamber dropped from 100% to 0%. The calculated recovery times ranged from 65 s to 100 s.



Figure 11. Recovery times of the resistive sensor after the second cycle; the recovery time was measured from 100% to 0% RH (clean, dry nitrogen): (**a**) sensor "1.5" and (**b**) sensor "3".

3.6. Analysis of Sensing Mechanism

Each component of the quaternary organic–inorganic hybrid nanocomposite used for resistive monitoring of RH has a specific contribution to the sensing performance. Thus, considering the properties of materials included in quaternary hybrid nanocomposites, several possible sensing mechanisms are proposed hereafter.

CNHox have outstanding intrinsic properties, such as facile synthesis, high conductivity (*p*-type semiconductor), high dispersibility in water and organic solvents (such as ethanol and isopropyl alcohol), hydrophilicity (their affinity for water molecules could be attributed to the presence of the oxygen-containing functional groups), high chemical stability, superior porosity, and a large surface area (1300 to 1400 m²/g). All these features make CNHox a suitable material for the resistive monitoring of RH at room temperature.

At contact with the surface of the CNHox, the water molecules donate their electrons pairs to the valence band, decreasing the number of holes and increasing the separation between the Fermi level and valence band in oxidized carbon nanohorns. Therefore, the RH sensing layer based on quaternary hybrid nanocomposite becomes more resistive. Several studies reported in the literature support this hypothesis [77,78].

Related to the CNHox, a second sensing mechanism can be analyzed. The adsorbed water molecules could dissociate to H⁺ and OH⁻ ions. In addition, the generated proton may tunnel from one water molecule to another through hydrogen bonding, decreasing the overall electrical resistance of the quaternary hybrid-based sensing film [79].

The nanometric tin (IV) oxide (SnO₂) powder exhibits good sensitivity towards relative humidity.

According to the literature data, water molecules can be adsorbed by hydrogen bonding or physisorption. At higher temperatures (>100 °C), water molecules can react with the Lewis acid sites onto the surface of the SnO₂ (according to the Hard Soft Acid Base (HSAB) theory, Sn⁴⁺ is a hard acid and H₂O is a hard base) and then release electrons. Consequently, the RH sensing layer based on quaternary hybrid nanocomposite becomes

less resistive [80,81]. However, since all the RH sensing experiments were performed at room temperature, this sensing mechanism can be excluded. However, at sensor operation temperature, displacement of the pre-adsorbed oxygen located at the surface onto SnO_2 by the water molecules is plausible and could lead to decreased resistance [82].

Moreover, the holey carbon nanohorns have p-type electrical conduction (through holes), while SnO₂ is an n-type metallic oxide semiconductor (through electrons). Therefore, by adding SnO₂ to the CNHox, islands of p-n semiconductor heterojunctions embedded in the polyvinylpyrrolidone will appear in the nanocomposite that could virtually increase the sensitivity towards moisture.

ZnO nanopowder is an *n*-type electrical conductor and exhibits good sensitivity towards relative humidity. Again, the water dissociation provides protons as charge carriers of the hopping transport. Consequently, the RH sensing layer based on quaternary hybrid nanocomposites could become more conductive [83,84].

It is supposed that both metal oxides semiconducting interact differently with the oxidized carbon nanohorns material, leading to alterations in the pore distribution and thus increasing the specific surface area.

Last but not least, swelling of the PVP can significantly contribute to the sensing mechanism. PVP is a dielectric polymer with hydrophilic properties, absorbing up to 25% moisture at RH = 75%. Moisture absorption increases the distance between CNHox particles, leading to a reduction of electrically percolating pathways.

As a general rule, the free volume of polymer/ inorganic nanohybrid is larger than that of the pure polymer [85]. Therefore, in comparison with $CNHox//SnO_2/ZnO/PVP$ at 3/1/1/1, $CNHox/SnO_2/ZnO/PVP$ at 1.5/1/1/1 nanohybrid should possess a higher degree of swelling.

According to this analysis, the interaction of the quaternary hybrid-based sensing layer with water molecules has two opposite effects on resistance. First, without completely excluding the proton-tunneling mechanism, the interaction of CNHox and PVP tandem with water plays a cardinal role in the overall decreasing resistance of the sensing layer.

4. Conclusions

The experimentally measured RH sensing response of resistive sensors using sensing layers based on an organic–inorganic quaternary hybrid nanocomposite of $CNHox/SnO_2/ZnO/PVP$ at 1.5/1/1/1 and 3/1/1/1 mass ratios was reported in this paper. While the sensor with $CNHox//SnO_2/ZnO/PVP$ at 3/1/1/1 as a sensing layer has the better performance in terms of linearity, the structure employing the $CNHox//SnO_2/ZnO/PVP$ at 1.5/1/1/1 has a better performance in terms of sensitivity. The estimated recovery times ranged from 65 s to 100 s.

The sensing role of each component of the quaternary hybrid nanocomposite was explained based on their chemical, physical properties, and mutual interactions. Several sensing mechanisms were considered and analyzed. Based on the sensing results, it was concluded that the *p*-type semiconductor behavior of CNHox, in conjunction with the swelling of PVP, prevails and leads to the overall increasing resistance of the sensing films. The low power consumption of the manufactured sensors, below 2 mW, the sensing performances at room temperature, and the manufacturing simplicity are the essential benefits of the presented sensors.

The results of the present study highlight that the RH sensitivity of the quaternary nanohybrid sensing layer is substantially improved compared to the previous results reported by the authors on CNHox and CNHox with PVP. Therefore, the beneficial effect of SnO_2 and ZnO in the composition of the nanohybrids was confirmed. However, these values are smaller than those associated with the nanohybrid based on CNHox and graphene oxide (such as CNHox/GO/SnO2/PVP: 0.75/0.75/1/1/ and CNHox/GO/SnO2/PVP: 1/1/1/1). This conclusion does highlight the impact of the GO presence in the nanohybrid's composition to achieve a higher sensitivity; we associate this impact with the "p" type semiconducting properties of the GO, in conjunction with better hydrophilicity.

5. Patents

Serban B. C., Buiu O., Cobianu C., Avramescu V., Dumbravescu N., Quaternary oxidized carbon nanohorns—based nanohybrid for resistive humidity sensors, EPO Application, nr. EP20465581.5, 13.11/2020.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/coatings11111307/s1, S1. Preparation of the quaternary organic-inorganic holey carbon nanohorns- based hybrid sensing films and experimental setup, Figure S1: The layout of the (interdigitated) IDT sensing structure, S2. RH monitoring experimental setup, Figure S2: Experimental setup employed for RH measurements.

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