

Article



Ternary Holey Carbon Nanohorns/TiO₂/PVP Nanohybrids as Sensing Films for Resistive Humidity Sensors

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Abstract: In this paper, we present the relative humidity (RH) sensing response of a chemiresistive sensor, employing sensing layers based on a ternary nanohybrids comprised of holey carbon nanohorns (CNHox), titanium (IV) oxide, and polyvinylpyrrolidone (PVP) at 1/1/1/(T1), 2/1/1/(T2), and with 3/1/1 (T3) mass ratios. The sensing device is comprised of a silicon-based substrate, a SiO₂ layer, and interdigitated transducer (IDT) electrodes. The sensitive layer was deposited via the dropcasting method on the sensing structure, followed by a two-step annealing process. The structure and composition of the sensing films were investigated through scanning electron microscopy (SEM), Raman spectroscopy, and X-ray diffraction (XRD). The resistance of the ternary nanohybrid-based sensing layer increases when H increases between 0% and 80%. A different behavior of the sensitive layers is registered when the humidity increases from 80% to 100%. Thus, the resistance of the T1 sensor slightly decreases with increasing humidity, while the resistance of sensors T2 and T3 register an increase in resistance with increasing humidity. The T2 and T3 sensors demonstrate a good linearity for the entire (0–100%) RH range, while for T1, the linear behavior is limited to the 0–80% range. Their overall room temperature response is comparable to a commercial humidity sensor, characterized by a good sensitivity, a rapid response, and fast recovery times. The functional role for each of the components of the ternary CNHox/TiO2/PVP nanohybrid is explained by considering issues such as their electronic properties, affinity for water molecules, and internal pore accessibility. The decreasing number of holes in the carbonaceous component at the interaction with water molecules, with the protonic conduction (Grotthus mechanism), and with swelling were analyzed to evaluate the sensing mechanism. The hard-soft acid-base (HSAB) theory also has proven to be a valuable tool for understanding the complex interaction of the ternary nanohybrid with moisture.

Keywords: holey carbon nanohorns (CNHox); titanium (IV) oxide; polyvinylpyrrolidone (PVP); nanohybrid; resistive RH sensor; swelling

1. Introduction

Humidity is a critical parameter for human life and other species, as its variation influences their vital activity. Thus, the interest for sustainable, reliable, low-cost, and highly sensitive humidity sensors increased in the last years due to their usefulness in a wide



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). variety of industrial, commercial, and residential applications such as in HVAC (heating, ventilation, and air conditioning), food/beverage processing, the medical field (incubators, respirators, and sterilizers), meteorology, structural health monitoring, agriculture, robotics, and so forth [1,2].

Devices used for humidity control and monitoring may include sensors with either a capacitive response [3], a gravimetric [4] or thermal conductivity change [5], and an optical [6] or a resistive signal [7].

Resistive sensors have received increased attention due to their constructive simplicity, low manufacturing cost, and low energy consumption. However, performances of the resistive humidity sensors, such as related to sensitivity, hysteresis, response time and recovery time, and reproducibility, are closely related to the properties of sensing materials [8]. Therefore, various sensing layers and their physical–chemical response to humidity change have been widely explored in the past.

Due to their excellent sensing properties toward water molecules, simplicity of use, low cost, flexibility in production, ability to operate in harsh environments, and tunable electric properties, semiconducting metal oxides (MOX) have gained considerable attention as promising candidates for RH monitoring [9]. Among these, TiO₂ is one of the most explored MOXs due to its fast, linear, and high response in electrical conductivity under analytic moisture exposure [10].

Wang et al. developed a facile template-assisted sol-gel process for preparing porous TiO_2 used as a sensing layer within the design of high-performance RH sensors [11]. The manufactured device shows high sensitivity, a very small hysteresis, and a rapid and highly reversible response (5 s for adsorption and 8 s for desorption).

Shinde et al. explored the RH sensing response of TiO_2 nanoflowers successfully synthesized by hydrothermal treatment. The study concluded that titania nanoflower-based sensor devices show good performance at room temperature [12].

Ghalamboran et al. reported a TiO_2 - TiO_2 composite-based resistive RH sensor [13]. From the structural point of view, the bead consists of micronic titania crystallites embedded in a matrix of TiO_2 nanoparticles. The experiments revealed that the best performances of the sensor based on the TiO_2 - TiO_2 composite as a sensing layer were recorded at RH < 25%. Moreover, as a distinctive feature, the manufactured sensor is insensitive to the presence of vapors' ethanol in dry air.

Biju et al. explored the sensing capabilities of the TiO_2 thin films prepared by sol-gel treatment on a glass substrate and sintered at different temperatures [14]. The authors reported an increase in the sensitivity just after the crystallization at 375 °C. These results are consistent with the increasing surface activity near crystallization.

Dubourg et al. developed an RH sensor using TiO_2 nanoparticles as sensing layer deposited onto the PET (Poly-Ethylene Terephthalate)-based flexible substrate through the screen-printing method [15]. The miniaturized device shows superior performances in terms of response/recovery time and linearity. Moreover, the sensor did exhibit a very good mechanical stability.

In addition, carbonaceous materials are extensively used as sensing layers within the design of the chemiresistive RH sensors. The large specific surface area, facile covalent/noncovalent functionalization, high conductivity, high mechanical strength, thermal stability, and low cost make these materials suitable candidates as sensitive coatings for resistive humidity monitoring. Graphene oxide and their nanocomposites [16,17], reduced graphene oxide [18], graphene [19], carbon nanotubes and their nanocomposites [20,21], carbon quantum dots [22], hydrogenated amorphous carbon [23], pyrolyzed bamboo [24], and carbon black [25] are well known carbonic nanomaterials studied for RH sensing applications.

In recent years, carbon nanohorns (CNHs), which are conical-shaped carbon nanostructures with a diameter of 2–5 nm, have been revealed as a suitable sensing layer in resistive RH monitoring [26]. Holey carbon nanohorns (CNHox), a type of carbon nanohorns with increased hydrophilicity, have proven to be promising alternatives as a sensitive coating within the design of the RH chemoresistors [27]. Moreover, binary nanocomposites such as CNHox/PEG-PPG-PEG (poly (ethylene glycol)-poly block (propylene glycol)-poly block (ethylene glycol), CNHox/PVP (polyvinylpyrrolidone), and ternary nanocomposites from the type CNHox/GO (graphene oxide)/PVP were successfully explored as sensing layers for RH monitoring [28–31].

All the CNHox-based manufactured sensors exhibit satisfactory sensing performances, comparable to those of a commercially capacitive RH device.

RH sensing capabilities of the ternary nanohybrid, such as CNHox/ZnO/PVP, CNHox/SnO₂/PVP, and the quaternary nanohybrid from the type CNHox/GO/SnO₂/PVP, were investigated within the design of the resistive humidity sensor using an interdigitated metal structure (IDT) deposited on the Si/SiO₂ structure [32–34]. For all the tested sensing layers, the resistance linearly increased when the sensors were exposed to a relative humidity ranging from 0 to 100%.

Finally, yet importantly, different TiO_2 /nanocarbonic materials' composites were used in resistive RH monitoring [35–38].

This paper presents the RH detection response of a resistive sensor that uses a sensitive layer based on a ternary nanocomposite comprised of CNHox-TiO₂-PVP in different weight/weight (w/w) ratios.

The ternary nanohybrid designed as a sensing layer for resistive RH monitoring includes constituents rigorously selected whose outstanding properties recommend them as components of the RH sensing film. CNHox shows high conductivity, high specific surface area/volume ratio, the facile synthesis method, internal pore accessibility, high purity, thermal stability, and hydrophilicity [39–42]. TiO₂ nanopowder exhibits a high affinity for water molecules and good chemical stability, while PVP is a dielectric hydrophilic polymer with excellent binding properties.

Experimental data were compared with detection data of sensitive layers based on the CNHox and PVP-CNHox binary mixture previously reported in the literature to highlight the effect of added TiO₂ on the sensing layer.

2. Materials and Methods

2.1. Materials

All the reagents used in the experimental section were purchased from Sigma-Aldrich (Redox Lab Supplies Com, Bucharest, Romania).

The details related to the composition and properties of the reagents are pointed out in the following paragraph.

The metal-free CNHox are characterized by the specific surface area around 1300–1400 m²/g (BET) with lengths between 40 nm and 50 nm and diameters between 2 nm and 5 nm (TEM). According to the supplier, oxidized carbon nanohorns contain 10% amorphous graphite. Their structure, as shown in Figure 1a, emphasizes so-called "nanowindows" and carboxilic groups, both created through the oxidation of pristine carbon nanohorns [43,44]. Titania nanopowder exhibits a primary particle size of around 21 nm (TEM) with a surface area of between 35 and 65 m²/g (BET). Polyvinylpyrrolidone (the molecular structure shown in Figure 1b) has an average molecular weight of 40,000. Ethyl alcohol is pure and of ACS spectroscopic grade, 95%.



Figure 1. The structure of (a) CNHox and (b) PVP.

All chemicals were used as received without further purification.

2.2. Methods

The surface topography of the sensing films based on $TiO_2/CNHox/PVP$ ternary nanohybrid were investigated by scanning electron microscopy (SEM, Thermo Scientific, Waltham, MA, USA). For surface visualization, 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 used.

The Raman spectra have been collected at room temperature with a Witec Raman spectrometer (Alpha-SNOM 300S, WiTec GmbH, Ulm, Germany) using 532 nm as an excitation. The 532 nm diode-pumped solid-state laser has a maximum power 145 mW. The incident laser beam with a spot-size of about 1.0 μ m was focused onto the sample with 6 mm working distance objective attached to a Thorlabs MY100X-806 microscope (Thorlabs Elliptec GmbH, Dortmund, Germany). The Raman spectra were measured with an exposure time of 20 s accumulation and the scattered light was collected by the same objective in the back-scattering geometry with 600 grooves/mm grating. The calibration of the Raman systems was carried out using the 520 cm⁻¹ Raman line of a silicon wafer. The spectrometer scanning data collection and processing were carried out by a dedicated computer using WiTec Project Five software (versionProject five).

X-ray diffraction measurements were performed using a 9 kW Rigaku Smart Lab diffractometer (Osaka, Japan) operated at 40 kV and 75 mA. To ensure a good divergence of the X-ray beam at the detector, a PSA 0.5° Soller slit was used. Grazing incidence X-ray diffraction (GI-XRD) patterns were recorded, keeping the incidence angle ω at 0.5°, while the detector scanned from $2\theta = 5^{\circ}$ to 60° . The peak indexing was made using the ICDD International Center for Diffraction Data database.

The scanning electron microscopy (SEM) was performed on TESCAN VEGA II LMU-General Purpose equipment (resolution: 3 nm at 30 kV; accelerating voltage 200 V–30 kV; electron gun source: tungsten filament; magnification: $13 \times -1,000,000 \times$; and detectors: SE, BSE, LVSTD) (TESCAN ORSAY HOLDING, a.s., Brno, Czech Republic).

2.3. The Preparation of the Ternary Nanocarbonic Materials-Based Nanocomposite Sensing Films

For the investigation of the relative humidity-sensing capabilities of the nanocarbonic materials-based nanocomposites, the following chemical compositions of the sensing films (mass ratios, w/w/w) were designed and tested: CNHox-TiO₂-PVP (1/1/1), CNHox-TiO₂-PVP (2/1/1), and CNHox-TiO₂-PVP (3/1/1). A standard preparation procedure for all the three ternary compositions mentioned above was designed and performed. For example, the preparation of the solid-state sensing films based on CNHox/TiO₂/PVP = 1/1/1 (mass ratio, w/w/w) is described below.

PVP (10 mg) was dispersed in 10 mL ethanol and subjected to stirring in an ultrasonic bath for 30 min at room temperature. CNHox powder (10 mg) was added to the previously prepared solution and the resulting mixture is ultrasonicated for 4 h at room temperature. An amount of 10 mg TiO₂ nanopowder was added to the previous suspension and continuous stirring was performed in the ultrasound bath for 6 h at room temperature. The homogenization of the dispersions was achieved by employing a mild sonication bath (FS20D Fisher Scientific, Dreieich, Germany) at 42 kHz (output power 70 W). This process ensured a uniform dispersion of the CNHox and TiO₂ in the PVP matrix.

The sensing layer was obtained by depositing the dispersion over the IDT sensing structure using the drop-casting method, with the contact area being masked.

The sensing device consists of a metallic interdigitated (IDT) dual-comb structure fabricated on a Si substrate (470 μ m thickness), covered by a SiO₂ layer (1 μ m thickness) (Figure 2). The metal stripes of the IDT were made of chromium (10 nm thickness) and gold (100 nm thickness). The digits' width and spacing were equal to 10 microns, with a 0.6 mm separation between the digits and bus bar. The thickness of the coatings varied between 175 and 225 nm, without affecting the response of the sensing structures [45].



Figure 2. The layout of the (interdigitated) IDT sensing structure.

After the deposition, a two-step annealing scheme was performed as follows: (1) heating for 48 h at 70 $^{\circ}$ C under low pressure (1 mbar) and (2) heating for 24 h at 100 $^{\circ}$ C under low pressure (1 mbar).

The performances of the tested devices (indicated as DUT, meaning "device under test") were compared with those provided by a reference humidity sensor (REF); REF is an industrial-grade capacitive sensor with a typical accuracy of \pm 2% in the humidity range of 0–100% RH for a working temperature domain of 0–90 °C.

The relative humidity-sensing measurements were performed in an appropriate experimental setup (Figure 3), in which, for varying the relative humidity in the testing chamber from 0% to 100% RH, the dry nitrogen was purged through two recipients (Carl Roth GmbH + Co. KG, Karlsruhe, Germany) in series containing deionized water. The humidity in the testing chamber (the size of the chamber is $10 \times 8 \times 4$ cm³) was changed by mixing dry nitrogen passing through the containers with deionized water in different ratios.



Figure 3. Experimental setup employed for RH measurements. Abbreviations: M.F.C., mass flow controller; DUT, device under testing; and REF, reference sensor.

In the mixing chamber (the purple cub in Figure 3), the gases flowing on both paths formed a homogenous mixture that passed to the testing chamber. The chamber included two types of sensors: the designed resistive sensing structures (the DUT), which uses $CNHox/TiO_2/PVP$ as sensing layer, and the reference capacitive relative humidity sensor, namely REF. The commercial sensor used in the experiment was a Sensirion Digital Humidity Sensor SHT4x sensor (Sensirion AG, Stäfa, Switzerland). The capacitive sensor was used to double-check the RH level indicated by the mass flow controller (MFC) system. The MFCs 4850 series (Brooks Instrument, Hatfield, PA, USA) with a flow range of 50 sccm–40 slpm (full scale), an accuracy of 3.0% FS, and a response time of 300 ms were used. The proximity between the two sensors and the gas inlet, which were both exposed to the identical gas, ensured quasi-identical experimental conditions and thus led to valid conclusions.

A Keithley 6620 current source (Keithley Instruments GmbH, Germering, Germany), ensuring a current variation between 0.01 and 0.1 A was employed; the data were collected and analyzed with a PicoLog data logger (PICO Technology, Neots, Cambridgeshire, UK). All the measurements were recorded at constant room temperature (21-22 °C)

3. Results and Discussion

Scanning electron micrographs show that the surface morphology of the coating mixture is relatively homogenous in all the cases (Figures 4–6). The outstanding physical and chemical properties of carbon nanohorns make them ideal for the construction of hybrid nanostructures. Thenon-covalent bonds formed between TiO₂, CNHox, and PVP are, probably, the main interactions responsible for these results [46].

The interaction between the nanocarbonic materials with TiO_2 and PVP has been proven using Raman spectroscopy.

Figure 7a–c present the recorded Raman spectra for the $CNHox/TiO_2/PVP$ mixtures drop-casted on glass (measured in four points of the material).



(a)



Figure 4. Scanning electron micrographs of the CNHox/TiO₂/PVP at the 1:1:1 w/w/w ratio: (**a**) ×600,000 magnification and (**b**) ×150,000 magnification.



(a)

(b)

Figure 5. Scanning electron micrographs of the CNHox/TiO₂/PVP at the 2:1:1 w/w/w ratio: (**a**) ×600,000 magnification and (**b**) ×150,000 magnification.



Figure 6. Scanning electron micrographs of the CNHox/TiO₂/PVP at the 3:1:1 w/w/w ratio: (a) ×600,000 magnification and (b) ×150,000 magnification.



Figure 7. Cont.



Figure 7. Raman spectra of the solid-state films of the CNHox/TiO₂/PVP nanocomposite of: (a) 1/1/1, (b) 2/1/1, and (c) 3/1/1 (*w/w/w*), deposited on glass and measured in four points of the material.

For instance, Figure 7b shows Raman spectra recorded in four different positions of the CNHox/TiO₂/PVP = 2/1/1 (*w/w/w*) film plotted in red, grey, green, and blue colors. It can be observed that three active Raman bands (D, G, and 2D) were recorded at the wavenumbers of 1318.3, 1591.9, and 2627.8 cm⁻¹, which confirms the presence of the nanocarbonic material (CNHox) [27,30,34]. One can also identify specific anatase TiO₂ bands as follows: E_{g1} mode at 149.1 cm⁻¹ (very sharp and intense in all the samples, except for 1/1/1), B_{1g} at 397.6 cm⁻¹, A_{1g} at 513.9 cm⁻¹, and E_{g3} at 634.7 cm⁻¹ [47–49]. It must be noted that B_{1g} , A_{1g} , and E_{g3} are faded in the 1/1/1 sample. The peaks associated with PVP are undetectable, most probably being covered by CNHox. The shift of the Raman peak positions of each of the two materials considered separately is the most interesting result shown in Figure 7a–c. A plausible explanation for this result can be related to the hydrogen bonds formed between all the components of the synthesized ternary nanohybrid.

Each X-ray diffraction pattern shows a broad feature at 21.08° , which becomes more intense at greater CHN concentrations (Figure 8). This can be attributed to the (002) reflection of CNHox nanoparticles [34,50]. In addition, other diffraction peaks are visible at 25.25° , 37.78° , 48.01° , 54.00° , and 55.13° for the sample with the lowest concentration of CNHox. According to the ICDD (International Crystallography for Diffraction Data) database, one can unambiguously assign these diffraction features to the (101), (004), (200), (105), and (211) reflections of wurtzite anatase-TiO₂ with the following unit cell parameters: a = b = 0.37 nm and c = 0.94 nm. The narrow intense peak from 51.20° is given by the Si substrate.



Figure 8. X-ray diffraction pattern for solid-state films of the $CNHox/TiO_2/PVP$ nanocomposite with weight ratios (w/w/w) of (1) 1/1/1 (black line), (2) 2/1/1 (red line), and (3) 3/1/1 (blue line).

The relative humidity monitoring capability of each carbonaceous nanohybrid-based thin film was explored by applying a constant current between the two electrodes and measuring the voltage difference when varying the RH from 0% to 100%. For the convenience of our analysis, we use the following abbreviations:

- the T1-chemiresisitive sensor, which employed the sensing layer based on CNHox/TiO₂/PVP at the 1/1/1 ratio (w/w/w);
- the T2-chemiresisitive sensor, which employed the sensing layer based on CNHox/TiO₂/PVP at the 2/1/1 ratio (w/w/w); and
- the T3-chemiresisitive sensor, which employed the sensing layer based on CNHox/TiO₂/PVP at the 3/1/1 ratio (w/w/w).

The behavior of all the three manufactured sensors is presented below in Figures 9–11:



Figure 9. The response of the sensor T1 (the blue curve) as a function of time for the three full measurement cycles when RH varies between 0% and 100%. The "RH curve-red" shows the variation of the RH in the testing chamber, as indicated by the reference sensor.



Time (s)

Figure 10. The response of the sensor T2 (the blue curve) as a function of time for the three measurement cycles when RH varies between 0% and 100%. The "RH curve-red" shows the variation of the RH in the testing chamber, as indicated by the reference sensor.



Figure 11. The response of the sensor T3 (the blue curve) as a function of time for the three measurement cycles when RH varies between 0% and 100%. The "RH curve-red" shows the variation of the RH in the testing chamber, as indicated by the reference sensor.

The resistance of the ternary coating mixture-based sensing layer increases when RH increases in the range from 0% to 80% RH. When the humidity increases from 80% RH to 100% RH, different behavior of the sensitive layer is registered. Thus, the resistance of the T1 sensor slightly decreases with increasing humidity, while the resistance of sensors T2 and T3 register an increase in resistance with increasing humidity. Therefore, we can conclude that the behavior of the sensors at high humidity levels is mediated by the relative mass percentage of the TiO₂ in the coating of the tested devices.

The most reasonable interpretation of the present data is related to both the type of predominant conduction in different humidity ranges and the mass ratio of $TiO_2/CNHox$ in the ternary nanohybrid. The adsorbed water molecules at the surface of the CNHox donate their electron pairs, decreasing the number of holes in the carbonaceous component of the RH sensitive layer [51,52]. As the electron density increases, the oxidized carbon nanohorns become more resistive (as we can see, up to RH = 80%, the predominant conduction is ensured through the holes) [27,28]. In addition, the interaction of water molecules with the surface of TiO₂ yields protonic conduction (Grotthus mechanism), which should increase the sensing film's conduction. However, this type of conduction is achievable only if a continuous film of water is formed on the surface [53,54]. Obviously, this condition is met only at high RH levels. Thus, once the 80% RH level is achieved, combined with increasing the mass percentage of TiO₂ (from the T1 composition in comparison with T2 and T3), this

leads to a switch in the overall conduction (i.e., the protons-based conduction becomes predominant), resulting in an overall decrease of the sensing film's electrical resistance.

From the Figures 9–11, the drift of the sensor when returning to the "0" point of relative humidity is noticable. The measured resistance of the sensing layer at the 0% RH between the measurement cycles has the smallest drift when sensor T1 was used. It is clear that the increased mass percentage of the oxidized carbon nanohorns in the ternary nanohybrid (T2 and T3) is related with the increased possibility to generate more water clusters and may decelerate the desorption process with detrimental effects from the drift point of view. This is a direct consequence of the high porosity of the oxidized carbon nanohorn.

Moreover, it was observed that the resistance of the sensitive layer for the RH value "0" decreases with the increase of the CNHox content in the nanohybrid. This is a natural behavior because CNHox is a nanocarbonic material with high conductivity and increasing its concentration leads to the decreasing of the electrical resistance of the nanohybrid.

Figure 12a–c presents the resistance of the tested sensing layers vs. the RH values recorded by the commercial sensor when humidity was varied from 0% to 100% in the first three run cycles presented in Figures 9–11. The T2 and T3 sensors showed good linearity, while for the T1 sensor, the linearity range is limited to RH = 0–80%. These data show that the stability in time was relatively good for sensors T2 and T3 (Figure 12) for more than 3 h of continuous functioning when humidity was varied from 0% to 100% RH, while sensor T1 had good stability at humidities lower than 80%.



(c)

Figure 12. The transfer function of the sensor (a) T1, (b) T2, and (c) T3 in humid nitrogen (RH = 0-100%).

For the comparison of the sensing performances of the RH resistive sensors with different initial resistance values, a relative sensitivity (Sr) to relative humidity variations (RH) was defined.

The sensitivity of the sensor was defined as follows:

$$S = \frac{\Delta R_x}{\Delta R H_x} = \frac{R_x - R_0}{R H_x} \tag{1}$$

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 indicates it). R_0 is the estimated resistance from the graph calibration line, which equals the relative humidity determined by extrapolation for the value at RH 0%. The comparison is summarized in Table 1.

Table 1. Sensitivity of CNHox-TiO₂-PVP compared with previously tested sensing layers.

Sensing Layer	Sensitivity
CNHox [27]	0.013–0.021
CNHox-PVP 1/1 [28]	0.020–0.058
CNHox-PVP 2/1 [28]	0.017–0.025
CNHox-TiO ₂ -PVP 1/1/1*	0.150–0.300
CNHox-TiO ₂ -PVP 2/1/1	0.010–0.040
CNHox-TiO ₂ -PVP 3/1/1	0.010-0.035

* The values calculated for sensor T1 when humidity varies from 0% RH to 80% RH.

CNHox and CNHox/PVP-based sensitive films were proven appropriate for RH resistive monitoring but the nanocomposite shows to have an increased sensitivity. Thus, the favorable effect of the hydrophilic polymer addition in terms of the higher sensing performance of the chemiresistor for almost the entire relative humidity range was demonstrated [27,28].

The data presented in Table 1 show that the presence of TiO_2 in the sensing layer improves the sensitivity of the tested device when the ratio $CNHox/TiO_2/PVP$ is 1/1/1 (w/w/w) at humidity levels ranging from 0% to 80%. If the CNHox content from the sensing layer is increased, the sensitivity decreases and the values are in the range presented for CNHox and CNHox/PVP, as presented in the literature.

Thus, the presence of TiO_2 improves the humidity sensing in the 0%–80% RH domain. This comparative analysis suggests that there is an optimum ratio of CNHox/TiO₂, which should be used for maximizing the sensitivity of ternary nanocomposites towards moisture. This is a good starting point for further optimization of the CNHox/TiO₂ ratio.

The response and recovery time measured at room temperature (RT) are two important parameters for the estimation of sensing performance of a device. Both adsorption and desorption of water molecules to and from the sensitive nanohybrid film may be very slow under room temperature.

The response time (t_r) is evaluated by using Equation (2), where t_{90} and t_{10} represent the moments in time at which the response R(t) reaches 90% and 10%, respectively, from the total variation of the sensor's resistance because of a change in the value of the RH (Figure 13) [27]. Similarly, the recovery times were calculated by substracting t_{90} from t_{10} when the sensor is recovering from 100% RH to 0% RH.

$$t_r = t_{90} - t_{10} \tag{2}$$



Figure 13. Example for calculation of response time.

Figure 14 presents the response and recovery times of the investigated sensor containing coatings with CNHox/TiO₂/PVP at a mass ratio of 1/1/1 (*w/w/w*) when relative humidity is increased from 40% to 50% (Figure 14a) and from 100% to 0% RH for the recovery time (Figure 14b).



Figure 14. Response and recovery times of the T1 humidity sensors with sensing coatings kept at room temperature, where (**a**) is the response time and (**b**) is the recovery time for sensor T1. Response time was measured for the case when relative humidity is increased from 40% to 50%, while the recovery time was measured from 100% to 0% RH (clean dry nitrogen).

The reference sensor had response time ranging from 40 to 90 s with higher values when RH was over 60% RH, while the response of the investigated sensors was between 30 and 150 s. It was observed that the sensor T1 showed values of response times in the range of 60–120 s for RH values ranging from 0 to 80% RH, while sensors T1 and T2 had response times between 30 and 150 s for the relative humidity ranging from 0 to 100% (Figure 15).

The values of the response time were under 100 s when relative humidity was less than 60% RH for all sensors. The smallest values of the response time were recorded for sensor T3 at an RH below 60% and the highest values of response time were registered for the sensor T1 in the relative humidity range of 0–80% RH.

The recovery time varied between 20 and 25 s (for the T1 sensor) and was doubling (40–50 s) for the T2 and T3 sensors.



Response time vs relative humidity variation

Figure 15. Response time vs. relative humidity (%) for sensor T1, sensor T2, and sensor T3.

Analysis of Sensing Mechanism

In order to explain the behavior of the three manufactured sensors in the whole range of RH, we brought into analysis two distinct sensing mechanisms. As we will see, these approaches explain how the interaction of water with ternary nanohybrid-based sensing layers yield opposing effects on its resistance.

The first assumption refers to the p-type semiconductor-nature of the holey carbon nanohorns [27,28]. According to the HSAB (hard–soft acid-base) theoretical interpretation, water is a well-known electron donor [55]. Upon moisture exposure, the sensing resistance increases, suggesting a recombination between electron donors (water molecules) and CNHox holes as positive charge carriers. Thus, the CNHox conductive network seems to be the major carriers' transport path in the composite. It is worth mentioning that the water-affinity and high porosity of CNHox (gained through oxidative treatment of pristine carbon nanohorns–CNHs) are extremely beneficial for the humidity-sensing film capabilities.

PVP can absorb up to 25% moisture at 75% and consequently result in the swelling of this hydrophile polymer. This swelling causes the movement of oxidized nanohorns, increases the intercones distance, and reduces the electrically percolating pathways. Therefore, the sensor resistance increases upon exposure to higher amounts of moisture because more water molecules will permeate into the bulk of the ternary nanohybrid.

In addition, the role of hydrophilic TiO_2 in increasing the resistance of ternary nanohybrids at the exposure to humidity should not be ignored. The $CNHox/TiO_2/PVP$ nanohybrid has a better response than the CNHox/PVP nanocomposite [28]. Considering PVP is the major contributor in water sorption of nanohybrids, any microstructural change of the polymer may be of paramount importance in the diffusion of water molecules and may finally affect the sensing performance [56,57]. As a rule, the free volume of polymer/inorganic nanohybrids is larger than that of pure polymer [58–60]. Therefore, in comparison with the CNHox/PVP nanocomposite, the $CNHox/TiO_2/PVP$ nanohybrid should possess a larger degree of swelling. The diffusion of higher amounts of water yields an increasing resistance [61].

This mechanism sensing interpretation shows why the resistance of the ternary nanohybrid-based sensitive film increases when RH increases in the range from 0% to 80% RH for T1 and in the range from 0% to 100% RH for both T2 and T3. Moreover, it clearly emphasizes the role of each component in the overall results concerning the resistance of the sensing layer.

However, a question remains: how can we explain the behavior of the T1 sensor above 80% RH?

Firstly, according to the HSAB theory, the Ti⁴⁺ ion is classified as a hard acid and can electrostatically interact with water molecules according to the process [53]:

$$4H_2O + Ti^{4+} \iff [Ti^{4+} - 4HO^-] + 4H^+$$
(3)

These H⁺ ions may tunnel from one water molecule to another through hydrogen bonding. This phenomenon counterbalances all the factors discussed above and potentially leads to a decrease of the sensing layer resistance. However, two conditions must be met to have a predominant ionic conduction: (1) generation to a continuous film of water at the surface of the sensing layer (possible at high RH levels) and (2) a significant amount of TiO₂ (T1 sensor has the highest mass percentage of TiO₂ as compared with the other two sensors).

These two factors could reasonably explain the "switch behavior" of the T1 sensor above 80% RH.

Obviously, the second mechanism can, at least partially, operate in all the cases at high RH levels but prevails only in the case mentioned above.

4. Conclusions

This paper reports the RH sensing response of a chemiresistive sensor employing sensitive films based on a ternary nanohybrid comprised of CNHox, titanium (IV) oxide, and PVP at 1/1/1/(T1), 2/1/1/(T2), and 3/1/1 (T3) mass ratios. The sensing device is comprised of a silicon-based substrate, a SiO₂ layer, and interdigitated transducer (IDT) electrodes. The sensing layer was deposited via the drop-casting method on the sensing structure and was annealed following a two-step procedure. The morphology and composition of the sensing films were investigated through scanning electron microscopy (SEM), Raman spectroscopy, and X-ray diffraction (XRD). The RH monitoring capability of each ternary nanohybrid-based thin film was explored by applying a current between the two electrodes and measuring the voltage difference when varying the RH from 0% to 100%. The resistance of the ternary nanohybrid-based sensing layer increased when RH increased in the range from 0% to 80% and was measured with 10% RH steps. When the RH rose from 80% to 100%, a different behavior of the sensitive layer was registered. Thus, the resistance of the T1 sensor slightly decreased with increasing humidity, while the resistance of sensors T2 and T3 registered an increase in resistance with increasing humidity. The manufactured sensors exhibited a room temperature response comparable to that of a commercial capacitive humidity sensor and was characterized by rapid response and recovery times as well as good sensitivity. The T2 and T3 sensors showed good linearity, while for the T1 sensor, the linearity area was limited to relative humidity from 0% to 80% RH. The sensing role of each component of the ternary $CNHox/TiO_2/PVP$ nanohybrid was explained based on their electronic properties, hydrophilicity, and porosity. The decreasing number of holes in the holey carbon nanohorns at the interaction with water molecules, with the protonic conduction (Grotthus mechanism), and with the swelling of the PVP were taken into account in order to investigate the sensing mechanism. The hard-soft acid-base (HSAB) theory also supports this interpretation.

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