

# Ternary Oxidized Carbon Nanohorns/TiO<sub>2</sub>/PVP Nanohybrid as Sensitive Layer for Chemoresistive Humidity Sensor <sup>†</sup>

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**Abstract:** The relative humidity (RH) sensing response of a chemoresistive sensor using a novel ternary hybrid nanocomposite film as a sensing element is presented. The sensitive layer was obtained by employing the drop-casting technique for depositing a thin film of nanocomposite between the electrodes of an interdigitated (IDT) structure. The sensing support structure consists of an IDT dual-comb structure fabricated on a oSi-SiO<sub>2</sub> substrate. The IDT comprises chromium, as an adhesion layer (10 nm thickness), and a gold layer (100 nm thickness). The sensing capability of a novel thin film based on a ternary hybrid made of oxidated carbon nanohorns–titanium dioxide–polyvinylpyrrolidone (CNHox/TiO<sub>2</sub>/PVP) nanocomposite 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 a humid nitrogen atmosphere. The ternary hybrid-based thin film's resistance increased when the sensors were exposed to relative humidity ranging from 0 to 100%. It was found that the performance of the new chemoresistive sensor is consistent with that of the capacitive commercial sensor used as a benchmark. Raman spectroscopy was used to provide information on the composition of the sensing layer and on potential interactions between constituents. Several sensing mechanisms were considered and discussed, based on the interaction of water molecules with each component of the ternary nanohybrid. The sensing results obtained lead to the conclusion that the synergic effect of the p-type semiconductor behavior of the CNHox and the PVP swelling process plays a pivotal role in the overall resistance decrease of the sensitive film.

**Keywords:** oxidized carbon nanohorns (CNHox); titanium (IV) oxide (TiO<sub>2</sub>); polyvinylpyrrolidone (PVP); chemoresistive humidity sensor; swelling

## 1. Introduction

Relative humidity (RH) sensors have received increasing attention in the last decades due to their importance in many areas of daily life, such as HVAC (heating, ventilation, and air conditioning), food storage, biomedical, climatology, structural health monitoring, agriculture, microelectronics and so forth [1]. The sensing principle, fabrication technology, temperature operating capability, and the sensitive layer play a cardinal role in obtaining superior sensing performances [2]. Due to their excellent sensing properties toward water molecules, abundance and ease of manufacture, low cost, tunable electric properties, and ability to operate under adverse conditions, semiconducting metal oxides (SMOX) have emerged as promising candidates for sensing humidity with high accuracy [3].  $\text{TiO}_2$  is one of the most-used SMOXs and has received increased attention in the last decades due to its fast, linear and sensitive response towards RH changes [4].

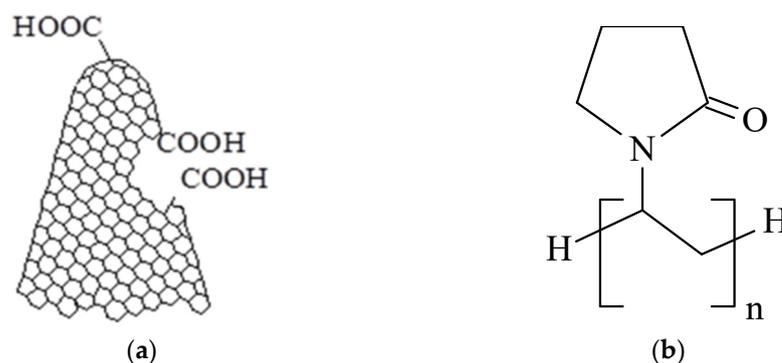
At the same time, a lot of recently reported work focused on using carbon-based nanomaterials as sensitive layers within the design of humidity sensors [5]. Among these, in the last years, oxidized carbon nanohorns—single—graphene tubules with oxygen functionalities, mostly carboxylic groups (CNHox) and their nanocomposites, have been extensively explored and have proven to be an attractive option [6–10]. Interestingly, the oxidized carbon nanohorns– $\text{TiO}_2$  nanohybrid was recently used for enhanced photocatalytic hydrogen production [11].

This paper presents, for the first time to our knowledge, the synthesis and characterization of a film based on a ternary nanocomposite comprising oxidized carbon nanohorns–titania–polyvinylpyrrolidone CNHox/ $\text{TiO}_2$ /PVP at 2/1/1 w/w/w ratio. Furthermore, the room temperature RH sensing response of a resistive sensor employing the synthesized sensing film was investigated.

## 2. Materials and Methods

### 2.1. Materials

All the materials used in the experiments described below were purchased from Sigma Aldrich (Redox Lab Supplies Com, Bucharest, Romania). CNHox (structure shown in Figure 1a) is characterized by diameters between 2 and 5 nm, lengths between 40 and 50 nm, and a specific surface area around 1300–1400  $\text{m}^2/\text{g}$ . PVP, with the structure depicted in Figure 1b, has an average molar weight of 40,000 Da.  $\text{TiO}_2$  is a nanometric powder (averaged particle size lower than 25 nm), while isopropyl alcohol,  $(\text{CH}_3)_2\text{CHOH}$ , is a solution 70% w/w in water.



**Figure 1.** The structure of: (a) CNHox; (b) PVP.

### 2.2. Synthesis of the Ternary Hybrid Nanocomposite Sensing Films and Experimental Setup

The synthesis of the sensitive film based on the ternary nanohybrid CNHox/ $\text{TiO}_2$ /PVP at 2/1/1 w/w/w ratios is described below.

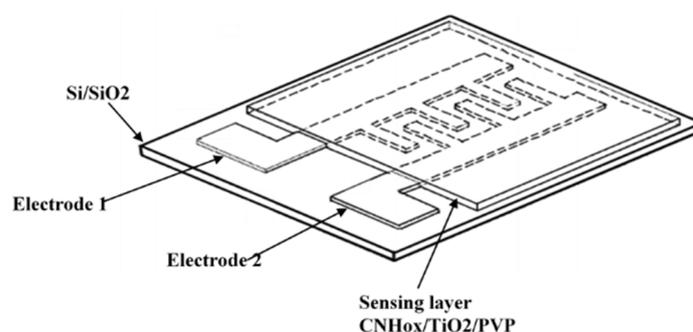
PVP powder (2 mg) was dissolved in 5 mL isopropyl alcohol solution (70% w/w in water) and subjected to stirring in an ultrasonic bath for one hour at room temperature (RT). CNHox (4 mg) was added to this solution, followed by stirring in the ultrasonic bath for

three hours at room temperature. An amount of 2 mg  $\text{TiO}_2$  nanopowder was added to the previous dispersion, and continuous stirring was performed in the ultrasound bath for 6 h at RT. The dispersions' homogenization was achieved by employing a mild sonication bath (FS20D Fisher Scientific, Dreieich, Germany) at 42 kHz (output power 70 W). This treatment facilitated a relatively uniform distribution of the CNHox and  $\text{TiO}_2$  in the PVP network. The film was annealed in a two-step sequence according to the following procedure:

- Heating for 24 h at 90 °C under low pressure (2 mbar);
- Heating for 24 h at 120 °C under low pressure (2 mbar).

Using the drop-casting method, the sensitive film was obtained by depositing the dispersion of CNHox/ $\text{TiO}_2$ /PVP in isopropanol solution over the IDT sensing structure (contact area being masked).

The sensing device consists of a metallic IDT dual-comb structure fabricated on a Si substrate (470  $\mu\text{m}$  thickness) covered by  $\text{SiO}_2$  (as passivation layer, 1  $\mu\text{m}$  thickness) (Figure 2). The IDT's metal stripes were made by successive deposition of 10 nm chrome (Cr) and 100 nm gold (Au). The sensor has dimensions of  $20 \times 11 \text{ mm}^2$  [6,7,10].

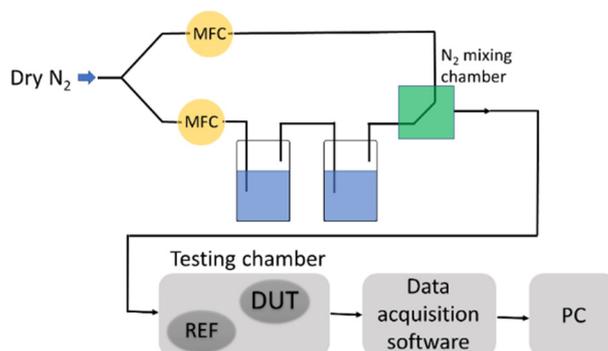


**Figure 2.** This is a figure. Schemes follow the same formatting.

Raman spectra of the sensing layer were acquired by Lab Ram HR 800 Raman spectrometer (Horiba Europe, Antwerp, Belgium), using a He-Ne laser excitation (633 nm).

Surface topography of the sensing films based on the  $\text{TiO}_2$ /CNHox/PVP ternary nano hybrid was investigated by scanning electron microscopy (SEM-Nova NanoSEM 630, 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) (F.E.I.), with superior low voltage resolution and high surface sensitivity imaging, was used.

The RH sensing measurements were conducted in a suitable experimental setup (Figure 3). The dry nitrogen was purged through two vessels in series containing deionized water for varying the RH in the testing chamber from 0% to 100% RH.



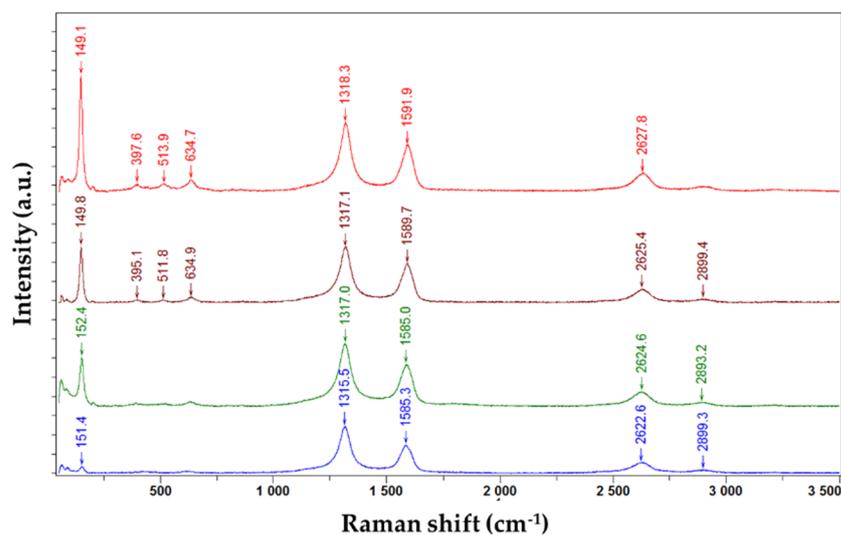
**Figure 3.** Experimental setup employed for RH measurements.

The experimental chamber included a tandem of sensors: the resistive sensing structure (abbreviated as DUT—device under testing, Figure 3) using the CNHox/TiO<sub>2</sub>/PVP-based sensitive film and a capacitive RH commercial sensor (abbreviated as REF, Figure 3). During all measurements, the RH was continuously monitored by the REF sensor. A Keithley 6620 current source (Keithley Instruments GmbH, Germering, Germany), providing current variation between 0.01 and 0.1 A, was employed. The data were collected and analyzed with a PicoLog data logger (PICO Technology, Neets, Cambridgeshire, UK). All experiments were conducted at the ambient temperature [6,7,10].

### 3. Results

#### 3.1. Raman Spectroscopy

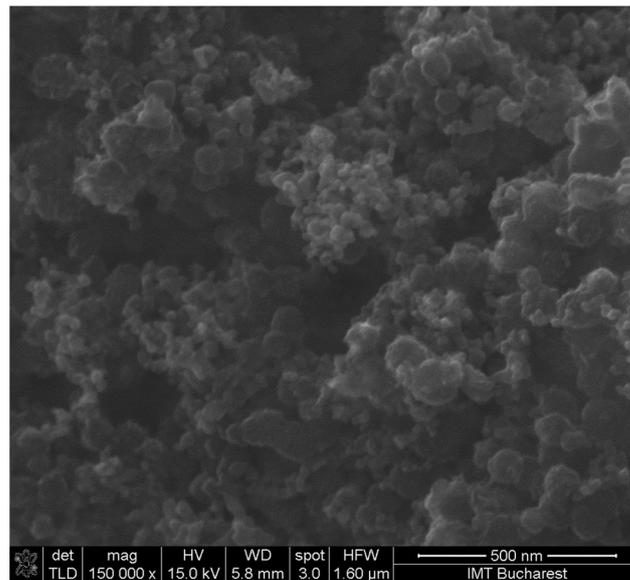
The interaction between CNHox, TiO<sub>2</sub>, and PVP was proven using Raman spectroscopy. Figure 4 shows four Raman spectra recorded in four different positions of the CNHox/TiO<sub>2</sub>/PVP = 2/1/1 (w/w/w) film, plotted in red, gray, green, and blue color. It can be observed that three active Raman bands (D, G, 2D) were recorded at the wavenumbers of 1318.3, 1591.9, and 2627.8 cm<sup>-1</sup>, which confirm the presence of the nanocarbonic material (CNHox). One can also identify specific TiO<sub>2</sub> bands as follows: Eg mode at 149.1 cm<sup>-1</sup> (very sharp and intense), B<sub>1g</sub> at 397.6 cm<sup>-1</sup>, A<sub>1g</sub> at 513.9 cm<sup>-1</sup>, and Eg at 634.7 cm<sup>-1</sup>. The peaks associated with PVP are undetectable, most probably being covered by CNHox. The shift of the Raman peak positions of both CNHox and TiO<sub>2</sub> within the ternary nanohybrid compared to the Raman peak positions of each of the two materials considered separately is the most interesting result shown in Figure 4. A plausible explanation for this result can be related to the hydrogen bonds formed between all the components of the synthesized ternary nanohybrid.



**Figure 4.** Raman spectra recorded in four different positions of the film deposited from the ternary nanocomposite CNHox/TiO<sub>2</sub>/PVP.

#### 3.2. SEM Analysis

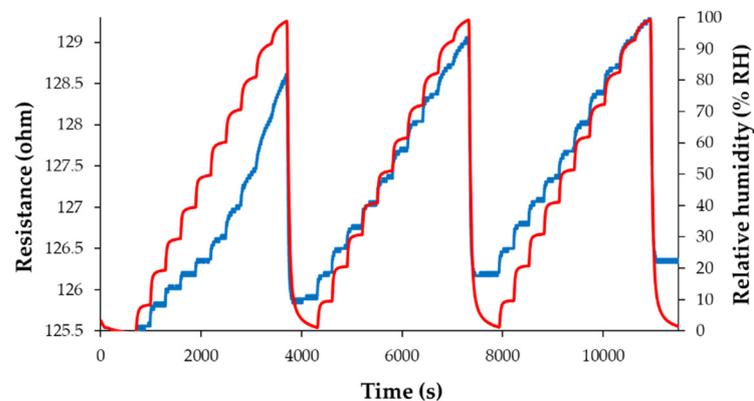
Scanning electron micrographs show that the surface morphology of the coating mixture is relatively homogenous in all the cases (Figure 5).



**Figure 5.** Scanning electron micrographs of the  $\text{TiO}_2/\text{CNHox}/\text{PVP}$  at X150,000 magnification.

### 3.3. RH Monitoring Capability of the Ternary Hybrid Nanocomposite

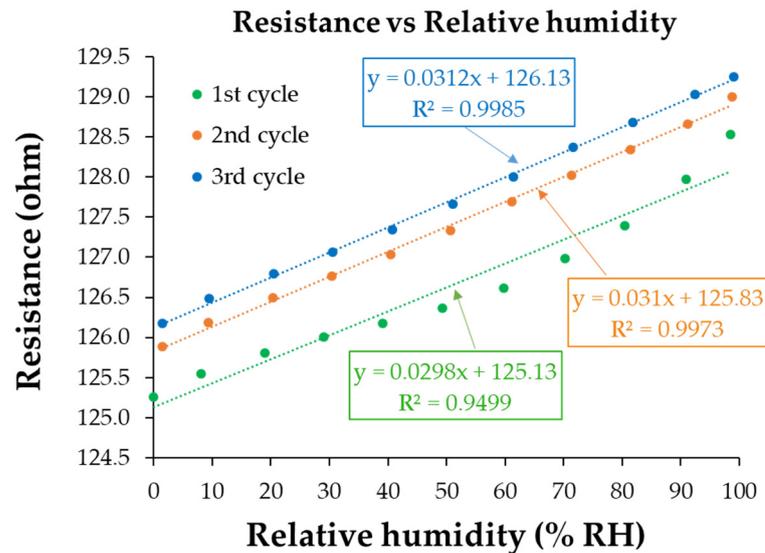
The RH sensing capability of the ternary hybrid nanocomposite-based sensing layer was investigated by applying a current between the two electrodes and measuring the voltage difference when varying the RH from 0% to 100%. A notable characteristic of these sensors is low power consumption, below 2 mW. The behavior of the manufactured sensors is presented in Figure 6.



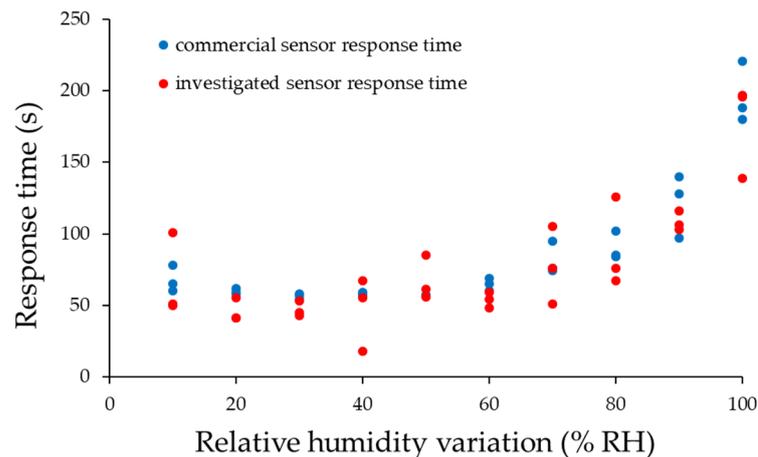
**Figure 6.** The response of sensor: “RH curve-blue” presented as a function of time for three measurement cycles, when relative humidity was increased in ten steps from 0% RH to 100% RH; “RH curve-red” shows the characteristic measured for a commercial, capacitive sensor.

The resistance of the ternary hybrid-based thin film increases when RH increases. The ternary nanohybrid-based resistive sensors’ overall linearity—in humid nitrogen when varying RH from 0% to 100%—is very good, as shown in Figure 7.

An important parameter, such as response time (in seconds), was estimated for both manufactured and commercial RH sensors (Figure 8). It has been observed that, between 10 and 70% RH, comparable response times for either DUT or REH are measured. Differences appear at an RH below 10% and higher than 70%.



**Figure 7.** The transfer function of the quaternary nanohybrid-based resistive sensors in humid nitrogen (RH = 0–100%).



**Figure 8.** Response time of the tested sensor variation for relative humidity jumps.

### 3.4. Analysis of the Sensing Mechanism

The most plausible sensing mechanism considers the *p*-type semiconducting material properties of CNHox and the swelling of the hydrophilic polymer. At the interaction with oxidized carbon nanohorns, H<sub>2</sub>O molecules donate their electron pairs, decreasing the number of holes in the nanocarbonic materials. Thus, the ternary nanohybrid-based sensing film becomes less conductive. In the same line, the swelling of the hydrophilic polymer PVP increases the distance between the CNHox particles and diminishes the electrically percolating pathways. However, the interaction of water molecules with the surface of TiO<sub>2</sub> yields protonic conduction (Grotthuss mechanism), which should increase the sensing film's conduction. Without completely excluding the later mechanism, one can come to the conclusion that the first two effects prevail and play a pivotal role in the overall increasing resistance of the sensitive film.

## 4. Conclusions

The RH sensing response of a resistive detector using sensing layers based on a ternary hybrid nanocomposite of CNHox/TiO<sub>2</sub>/PVP (2/1/1) was reported. The novel sensitive film used within the design of the chemoresistive sensor exhibited an RT response comparable to that of a commercial capacitive humidity sensor. The ternary nanohybrid-

based resistive sensors' overall linearity—in humid nitrogen when varying RH from 0% to 100%—was shown to be excellent. The estimated response times were comparable to those of the commercial sensor. Several sensing mechanism hypotheses were discussed according to the possible chemical interaction between oxidized carbon nanohorn, titania, PVP, and water molecules. Although the Grotthuss mechanism cannot be excluded, the hole conduction ability of CNHox in conjunction with the swelling of hydrophilic polymer prevails and leads to the overall decreasing conduction of the sensing films.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/CSAC2021-10616/s1>.

**Author Contributions:** Conceptualization, B.-C.S., C.C. and O.B.; methodology, B.-C.S., C.C., V.A., N.D. and O.B.; software, M.B. (Marius Bumbac), C.M.N. and M.B. (Mihai Brezeanu); validation, B.-C.S., C.C., N.D., O.B. and M.B. (Marius Bumbac); investigation, N.D., B.-C.S., V.A., C.C., R.M. and F.C.; resources, O.B.; writing—original draft preparation, B.-C.S., C.C., O.B. and M.B. (Marius Bumbac); writing—review and editing, all co-authors; visualization, O.B.; supervision, B.-C.S., C.C. and M.B. (Marius Bumbac); project administration, B.-C.S. and O.B.; funding acquisition, C.R., O.B. All authors have read and agreed to the published version of the manuscript.

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