Institutul Național de Cercetare-Dezvoltare pentru Microtehnologie - IMT București

Chemiresistive ethanol sensor based on graphene and metal oxide nanocomposites and process for obtaining it

Romanian Patent Application 134143 RO OSIM din 30.01.2025

Assignees: National Institute for Research and Development in Microtechnologies - IMT Bucharest

Inventors: Cornel Cobianu, Bogdan- Catalin Serban, Octavian Buiu, Niculae Dumbravescu, Maria Roxana Marinescu, Narcis-Octavian Ionescu, Viorel Avramescu

Introduction

Ethanol is used intensively as an industrial solvent in the chemical, cosmetic and food industries for the preparation of various materials, being included in the class of volatile organic compounds with negative effects on the surrounding air and human health. For these reasons, measuring the concentration of ethanol both in industrial processes and in other medical applications or in traffic safety by measuring the concentration of ethanol in the exhaled air of drivers are conclusive examples of the need for such sensors with increasingly high sensitivity and selectivity.

Original approach

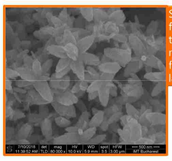
The invention presents a chemiresistive ethanol sensor and the new process for its manufacturing based on sensitive layers synthesized from zinc oxide (ZnO) and graphene nanocomposite. The nanocomposite was prepared by aqueous sonochemical synthesis of high acoustic radiation density. An original element of the method is the use of sodium hydroxide (NaOH), both as a reducing agent in the formation of ZnO from zinc nitrate $Zn(NO_3)_2$ and as an initiator of nanostructuring, thus obtaining hierarchically organized ZnO-graphene powders of nano-flower type (high porosity powders) for pH values equal to 14.

The method of manufacturing the sensitive layer consists of depositing the ZnO-graphene paste on a dielectric substrate by drop casting, followed by the subsequent heat treatment of the paste necessary for the thermal consolidation of the sensitive layer. On the opposite side, there is an electrical heating resistor of the sensitive structure. Functionalization of ZnO with graphene allows for increasing the sensitivity and reducing the electrical resistance of the sensitive layer and thus easier measurability of the ethanol sensor. The sensor substrate is made of Si/SiO_2 and has a size of 5 mm, the electrodes being made of gold. They can be linear or have an interdigitated configuration. The monitoring capacity of ethanol is investigated by applying a constant current between the two electrodes and measuring the voltage at different values of the ethanol concentration to which the sensitive layer is exposed.

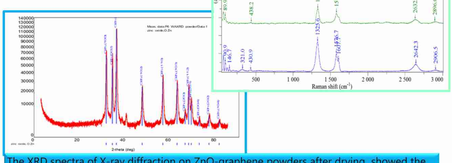
Sensor manufacturing

Obtaining and characterization of ZnO-graphene nanocomposite powders

- $Zn(NO_3)_2 \cdot 6H_2O$ was weighed with a microbalance to obtain the amount of 0.8940 g and then the measured amount was dissolved in 5 ml H_2O DI;
- Sodium hydroxide (NaOH) 1.59 g was weighed and was dissolved in 4 ml H_2O DI;
- 71.4 ml of aqueous graphene solution (1-4 layers, graphene having a concentration of 0.05 mg/ml) was measured; This amount of aqueous graphene contains 0.05 mg/ml (71.4 ml = 3.57 mg of graphene, about 0.4 wt% graphene in the final ZnO + graphene composition);
- The Zn salt solution was gradually poured into the measured graphene solution, stirring continuously;
- Drops of the basic NaOH solution were gradually poured into the synthesis beaker, stirring continuously; The pH of the solution was measured with litmus paper after each small addition of NaOH solution until reaching pH=14;
- The ultrasound installation was programmed at maximum power (200W) and a total time of 1.5 h;
- The ultrasound head (sonotrode) was inserted into the beaker with the ZnO + Gr solution and the ultrasound was started, the solution temperature was maintained in the range (64-67) ºC throughout the ultrasound; The acoustic power density applied to the solution was 2.5 W/mL of solution;
- The pH was measured again; it was maintained at 14;
- The solution was kept in the refrigerator for sedimentation for 24 h;
- The supernatant was replaced with water and the pH was measured again. After the first "wash procedure" the pH became 12;
- The process was repeated several times until reaching pH=7;
- The powder was dried in a microwave oven.



SEM for ZnO/ graphene nanocomposite obtained from the synthesis carried out at pH=14 shows that under these synthesis conditions nanostructuring was obtained in the form of nano-flowers which thus ensure good porosity and a large specific area for the sensitive film.



The XRD spectra of X-ray diffraction on ZnO-graphene powders after drying showed the specific X-ray diffraction maxima, 15-26 of ZnO according to material standards and also demonstrated the obtaining of very well-defined ZnO crystallites, which demonstrates the capability of sonochemical synthesis to produce polycrystalline powders even after the drying step and before the calcination thermal treatment.

Treatment of ZnO-graphene nanocomposite powder

Considering that graphene is oxidized in air by heating at high temperatures specific to calcination, to preserve the graphene incorporated in the nanocomposite, the structural consolidation of the powder was performed by a heat treatment at 450 ºC in nitrogen.

Deposition of the sensitive layer

To obtain the sensitive layer, ZnO-graphene powder was used after calcination in nitrogen at 450 ºC, which was dispersed in deionized water to form a sufficiently consistent paste that could be positioned in a controlled manner over the interdigitated platinum electrodes of the sensor. After thermal consolidation of the deposited layer, the sensor is ready for functional tests.

Advantages of the proposed sensing layer

The use of ZnO/ graphene nanocomposite as sensing layers presents several advantages:
- sonochemical method used for synthesis of the ZnO-graphene nanocomposite provide a high specific surface/volume ratio, affinity for ethanol molecules as well as a significant percentage variation in the resistance of the sensitive layer upon contact with them,
- room temperature detection, reversibility, fast response.

Quaternary Oxidized Carbon Nanohorns - Based Nanohybrid for Resistive Humidity Sensor

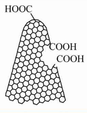
ES2958943T3, Spain, 16. 02. 2024

Assignees: National Institute for Research and Development in Microtechnologies - IMT Bucharest

Inventors: Bogdan-Cătălin Serban, Octavian Buiu, Cornel Cobianu, Viorel Avramescu, Niculae Dumbravescu

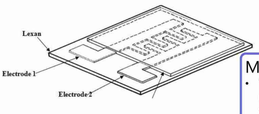
Introduction

- The present invention relates to the RH sensing response of a resistive sensor employing a sensing layer based on quaternary nanohybrid composition comprising or consisting of $CNHOX/SnO_2/ZnO/PVP$ at 1.5/1/1/1 w/w ratio to 3/1/1/1 w/w ratio. When employed as RH sensing layers, these quaternary nanohybrid compositions exhibit several significant advantages:
- Oxidized carbon nanohorns (CNHOX) (Figure 1) have high specific surface area/volume ratio, water molecules affinity and show rapid electrical resistance variation when RH varies from 0% to 90%.
- The nanometric tin (IV) oxide (SnO_2) nanopowder exhibits good RH sensitivity. CNHOX have p-type electrical conduction (through holes), while SnO2 is a n-type metallic oxide semiconductor (through electrons). By adding SnO_2 to CNHOX, one will obtain islands of p-n semiconductor heterojunctions embedded in PVP (a dielectric material) that increase the sensitivity of the sensitive layer.
- Zinc oxide (ZnO) nanopowder exhibits good RH sensitivity. Both ZnO and SnO2 are n-type electrical conductors. The ZnO – SnO_2 nanocomposite has sensing properties superior to each of the single oxides, because each of the oxides interacts differently with the oxidized carbon nanohorn material, leading to alterations in the pore distribution, which increase the specific surface area;
- Polyvinylpyrrolidone (PVP) is a hydrophilic polymer with excellent binding properties, which enables its employment in sensing structures with either flexible or rigid substrates;
- Detection at room temperature, low response time, low cost, small size, simplicity in manufacture.



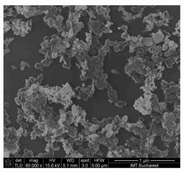
Oxidized carbon nanohorns (CNH_{ox})

Figure 1



IDT sensing structure

Figure 2



SEM image for $CNHOX/SnO_2/ZnO/PVP$ at 1.5/1/1/1 nanohybrid composition

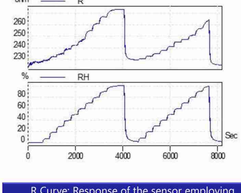
Figure 3

Materials, Methods, Results

- The interdigitated (IDT) sensing structure (Figure 2) can be manufactured on Lexan, Kapton, or glass. The dielectric substrate may have a thickness from 5 to 50 μm. The electrodes can be made from the same material or can be formed of different materials. The electrodes can be made from conductive materials such as gold and chromium.
- A dispersion formed in isopropyl alcohol of a nanohybrid sensing layer described above, at different w/w ratios, was deposited on the IDT structure using the drop casting method (Figure 3).
- The RH sensing capability of the proposed sensitive layers was investigated by applying a current between the two electrodes and measuring the voltage at different RH values.
- Measurements were performed in humid nitrogen at RT and compared with the response of a commercial capacitive RH humidity sensor, provided with signal-processing and signal-amplifying electronics (Figure 4 and Figure 5). From the detection principle point of view, the resistance of the sensitive layer varies with the RH level.

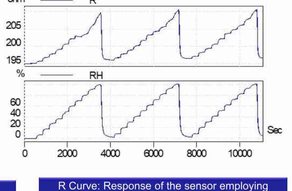
Conclusions

- The IDT sensing structure presented in this work exhibits a linear response and good RH sensitivity when varying RH from 0% up to 90% in humid N2 environment.
- The sensor response time and stability are comparable to that of a commercially available RH sensor



R Curve: Response of the sensor employing $CNHOX/SnO_2/ZnO/PVP$ at 1.5/1/1/1 as sensing layer
RH Curve: Response of Sensirion RH sensor

Figure 4



R Curve: Response of the sensor employing $CNH_{ox}/SnO_2/ZnO/PVP$ at 3/1/1/1 as sensing layer
RH Curve: Response of Sensirion RH sensor

Figure 5

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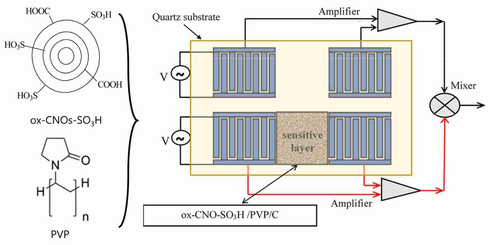
Surface Acoustic Wave Sensor for Relative Humidity Monitoring

Romanian Patent Application A00623, RO, OSIM, 21.10.2024

Assignees: National Institute for Research and Development in Microtechnologies - IMT Bucharest
Valahia University of Targoviste
Inventors: Bogdan-Cătălin Serban, Octavian Buiu, Marius Bumbac, Cristina Mihaela Nicolescu

Introduction

Carbon nano-onions (CNOs) were first synthesized by Ugarte in 1992 by electron irradiation of carbon black. The standard procedure for the synthesis of CNOs is based on the annealing of diamond nanoparticles at high temperatures, in an inert atmosphere, under high vacuum conditions. Structurally, CNOs are zero-dimensional nanoparticles (with a diameter between 1.4 and 50 nm), characterized by closed multilayer shells (interlayer distance of approximately 3.4 Å and with a C60 or C80 fullerene included in their core). CNOs synthesized by traditional methods (vacuum heat treatments, electrical discharges between two carbon electrodes, etc.) are hydrophobic. Oxidations with dilute nitric acid or ozone lead to the formation of onion-type nanocarbon structures, functionalized with polar groups such as carboxyl, hydroxyl, carbonyl, which substantially increase the solubility of CNOs in polar solvents such as methanol, water, tetrahydrofuran, propanol, etc.



Original approach

The present invention relates to the RH sensing response of a surface acoustic wave sensor employing a sensing layer based on new ternary nanocomposite matrices of the polyvinylpyrrolidone type / oxy sulfonated onion-type nanocarbon materials (ox-CNOs-SO_3H)-carbon black. The oxy sulfonated onion-type nanocarbon materials used are found in the ternary nanocomposite in a mass percentage ranging between 60 - 70%, while carbon black is found in a mass percentage ranging between 5-10%.
The sensor used is of the "delay line" type, dual, made on a piezoelectric quartz substrate. The sensor has a double delay line to compensate for thermal drift. Thus, one delay line is covered with the ternary nanocomposite sensitive to RH variation, the second delay line being the piezoelectric substrate without a sensitive layer. The sensitive films are deposited on the piezoelectric quartz substrate by the "spin coating" method.

Sensor manufacturing

The steps required to synthesize oxysulfonated onion-type nanocarbon materials (generically denoted ox-CNOs-SO_3H) are as follows:

Onion-type nanocarbon materials synthesis:
1) Onion-type nanocarbon materials (CNOs) are synthesized from nanodiamond, by heat treatment at 1650ºC, in a helium atmosphere.
2) Oxidation of CNOs is achieved by treatment in Ar-O_2 plasma (2/1 volumetric mixture), in a quartz tube, at a pressure of 10 torr, at room temperature. The injection time is 5 minutes, the exposure time varying between 5 and 10 minutes.
3) Ox-CNOs-SO_3H are prepared by dispersing 50 mg of ox-CNOs in 10 mL of 95% sulfuric acid in a Teflon autoclave and heating the obtained dispersion at 200ºC for 20 hours
4) The obtained product is washed with deionized water until neutral and heated in vacuum at 150ºC for six hours.

Sensitive layer preparation:
1) The quartz substrate is cleaned for 10 minutes in an ultrasonic bath using equal volumes of ethanol and demineralized water sequentially.
2) 3 mg of polyvinylpyrrolidone is added to 15 mL of deionized water, under magnetic stirring, for 20 minutes, at room temperature.
3) Subsequently, 6 mg of ox-CNOs-SO_3H is added to the previously prepared solution and magnetic stirring is continued for 90 minutes, at room temperature.
4) 1 mL of aqueous carbon black dispersion (10% concentration) is added to the dispersion prepared in item 3 and magnetic stirring is continued for 180 minutes, at room temperature.
5) The obtained dispersion is deposited by the "spin coating" method, using a quartz substrate (3000 rpm, for 40 s).
6) The obtained film is subjected to heating at 100ºC for 60 minutes.
7) The obtained film is subjected to a final heat treatment at 200ºC for 30 minutes.
8) The obtained sensitive layer, deposited on the substrate, is dried in an oven at 50ºC, in vacuum, for 24 hours.

Advantages of the proposed sensing layer

The use of the previously described ternary nanocomposite presents several notable advantages:
• the presence of ox-CNOs-SO_3H confers a high specific surface area/volume ratio, affinity for water molecules ("mass loading"), as well as a variation in the resistance of the sensitive layer upon contact with them ("electric loading");
• excellent mechanical properties;
• detection over a wide temperature range;
• the hydrophilic character of PVP and ox-CNOs-SO_3H facilitates the interaction with water molecules;
• carbon black improves the dispersion of ox-CNOs-SO_3H in the polymer matrix and modulates the conductivity of the moisture-sensitive layer, being an excellent filler.
• rapid response of the sensor to variations in RH levels;
• reversibility;

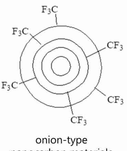
Chemiresistive Ethanol Sensor

Romanian Patent Application A00644, RO, OSIM, 21.10.2024

Assignees: National Institute for Research and Development in Microtechnologies - IMT Bucharest
Valahia University of Targoviste
Inventors: Bogdan-Cătălin Serban, Octavian Buiu, Marius Bumbac, Cristina Mihaela Nicolescu

Introduction

Monitoring ethanol concentration is an important process in various industrial fields such as the wine industry (e.g., monitoring fermentation processes), the biofuel industry, traffic management and safety (sensors for measuring alcohol levels, portable or even included in the dashboard of cars), the food industry, industrial monitoring (the sensor can be used in various industrial environments to monitor alcohol levels, thus ensuring worker safety), the medical field (breath monitoring). Highly concentrated ethanol is extremely flammable and has high toxicity, which can affect human health.

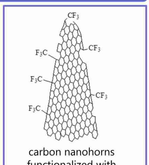


onion-type nanocarbon materials functionalized with trifluoromethyl groups

Figure 1

Original approach

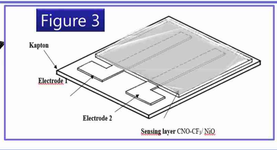
The sensitive films described in this invention, which are used to obtain resistive ethanol sensors, are binary nanohybrids of the type of onion-type nanocarbon materials functionalized with trifluoromethyl groups (CNO-CF_3- Fig.1) - Ni oxide (NiO) and carbon nanohorns functionalized with trifluoromethyl groups (CNH-CF_3) – NiO. From the point of view of the detection principle, the conductivity of the sensitive layer decreases with the level of ethanol concentration. The increase in the resistance of the film sensitive to ethanol vapors can be explained taking into account the physicochemical properties of the two components and their mutual interaction. The sensor substrate is made of polyimide (Kapton) and has a size of 5 mm, the electrodes being made of gold. The width of the electrodes is approximately 200 microns, with a separation of 5 mm between them (Fig.3). The ethanol monitoring capacity is investigated by applying a constant current between the two electrodes and measuring the voltage at different values of the ethanol concentration to which the sensitive layer of the type CNO-CF_3 / NiO, CNH-CF_3 / NiO, CNO-CF_3 / CNH-CF_3 / NiO is exposed.



carbon nanohorns functionalized with trifluoromethyl groups (CNH-CF_3)s

Figure 2

Figure 3



Sensor manufacturing

PVP

The steps required to obtain the CNO-CF_3/NiO sensitive film are presented bellow:
1) The Kapton substrate was cleaned for 10 minutes in an ultrasonic bath using equal volumes of ethanol, acetone, and finally deionized water sequentially.
2) Onion-type nanocarbon materials (CNOs) are synthesized from nanodiamond by thermal treatment at 1650°C in a helium atmosphere.
3) The synthesis of onion-type nanocarbon materials functionalized with trifluoromethyl groups (CNO-CF_3) is performed by treatment in CF4 plasma at a pressure of 1 bar in a nickel reactor at room temperature. The injection time is 3 minutes, and the exposure time varying between 2 and 20 minutes.
4) The CNO-CF_3 dispersion is prepared by dissolving 1 mg of CNOs-CF_3 in 5 mL of isopropyl alcohol, under magnetic stirring for five hours, at room temperature.
The synthesis of NiO nanopowder involves the following sequence of steps:
5) 0.237 g (1.0 mmol) of NiCl2·6H2O and 0.06 g of Na2C2O4 are dissolved under magnetic stirring in 15 mL of H2O and 2.0 mL of ethylene glycol.
6) the obtained solution is transferred to a stainless steel autoclave and heated at 200 °C for 12 hours.
7) the autoclave is cooled to room temperature.
8) the solid product is separated by centrifugation, washed with deionized water, respectively ethanol, then dried in air.
9) the solid product is gradually heated to 300ºC (3 degrees/min), maintained for one hour at this temperature, then gradually cooled to room temperature.
10) To the dispersion prepared in item 4, 1 mg of NiO nanopowder prepared in item 9 is added.
11) The obtained dispersion is deposited by the "drop casting" method using a Kapton substrate with linear electrodes or interdigitated electrodes (after previously masking the contact area).
12) Densification of the sensitive layer is carried out in a nitrogen atmosphere, for 120 minutes, at a temperature of 100 ºC.

Advantages of the proposed sensing layer

The use of binary and ternary nanohybrids as sensitive films presents several advantages:
- nanocarbon materials functionalized with trifluoromethyl groups present a high specific surface/volume ratio, affinity for ethanol molecules (by forming hydrogen bonds) as well as a variation in the resistance of the sensitive film upon contact with them;
- NiO nanopowder is a p-type semiconductor with a wide conduction band, a large specific surface area. It presents a synergistic effect with oxidized nanocarbon materials such as CNO-CF_3 and CNH-CF_3, also p-type semiconductors, upon contact with ethanol molecules;
- the metal oxide modifies the pore distribution at the interface with the oxidized onion-type nanocarbon materials, increasing their specific surface area;
- trifluoromethyl groups, through their marked electron-withdrawing effect, increase the number of carriers in CNO-CF_3 and CNH-CF_3. Conduction is achieved by holes (p-type carriers), and the sensitivity of the material for ethanol molecules increases;
- room temperature detection;

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Surface Acoustic Wave Sensor for Relative Humidity Monitoring

Romanian Patent Application A00645, RO, OSIM, 21.10.2024

Assignees: National Institute for Research and Development in Microtechnologies - IMT Bucharest
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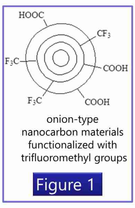
Inventors: Bogdan-Cătălin Serban, Octavian Buiu, Marius Bumbac, Cristina Mihaela Nicolescu

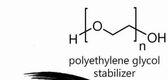
Introduction

Trimethylamine (TMA), an organic compound of primary importance in industrial organic synthesis, is a colorless, hygroscopic amine that is gaseous at room temperature. Trimethylamine has a fish-like odor at low concentrations and an ammonia-like odor at higher concentrations. Given that it is hazardous to human skin, eyes, and respiratory tract, the National Institute for Occupational Safety and Health (NIOSH) suggests that the upper limit of exposure to TMA be 10 ppm for 10 hours of exposure and 15 ppm for 15 minutes of exposure. Microbial degradation of trimethylamine N-oxide during spoilage of fish and marine organisms leads to the accumulation of trimethylamine. Consequently, the concentration of trimethylamine is widely used as one of the relevant indicators for assessing the freshness of fish and seafood intended for human consumption. Thus, there is increased interest in the design and manufacture of trimethylamine sensors with low detection limits.



onion-type nanocarbon materials functionalized with trifluoromethyl groups

Figure 1



polyethylene glycol stabilizer

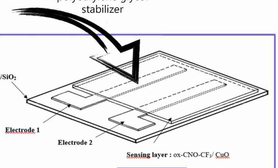


Figure 2

Original approach

The sensitive film described in this invention, which is used to obtain resistive trimethylamine sensors, is a binary nanohybrid of the type of oxidized onion-type nanocarbon materials functionalized with trifluoromethyl groups (Figure1) / CuO.
From the detection principle's point of view, the sensitivity film's resistance increases with the trimethylamine concentration level.
The increase in resistance is explained by the fact that trimethylamine donates electrons to the sensitive layer, decreasing the concentration of holes.
The sensor substrate is made of Si/SiO_2 and has a size of 5 mm, the electrodes being made of gold. They can be linear (Figure 2) or have an interdigitated configuration. The monitoring capacity of trimethylamine is investigated by applying a constant current between the two electrodes and measuring the voltage at different values of the trimethylamine concentration to which the sensitive layer is exposed.

Sensor manufacturing

ox-CNOs-CF_3 synthesis:
1) Onion-type nanocarbon materials (CNOs) are synthesized from nanodiamond, by heat treatment at 1650ºC, in a helium atmosphere.
2) The synthesis of nanocarbon materials functionalized with trifluoromethyl groups (CNO-CF_3) is performed by treatment in CF_4 plasma at a pressure of 1 bar, in a nickel reactor, at room temperature. The injection time is 5 minutes, the exposure time varies between 2 and 20 minutes.
3) The synthesis of ox-CNOs-CF_3 is performed by oxidation of CNO-CF_3 in Ar-O_2 plasma (volumetric mixture 3/1), in a quartz tube, at a pressure of 4 torr, at room temperature. The injection time is 10 minutes, and the exposure time varies between 2 and 10 minutes.

ox-CNO-CF_3/CuO sensitive layer preparation:
The raw materials required for the synthesis of the sol are: the precursor- $Cu(CH_3COO)_2 \cdot 2H_2O$, the solvent (mixture of ethanol and ethanolamine), the stabilizer (polyethylene glycol with molecular weight M=5,000), ox-CNO-CF_3. The molar ratio of $Cu(CH_3COO)_2 \cdot 2H_2O$ - ethanol is 1: 4.
1) Magnetic stirring is performed sequentially, in two stages:
   - at a temperature of 50ºC, for 2h;
   - at a temperature of 70ºC, for 2h.
2) In the second stage of magnetic stirring, ox-CNO-CF_3, synthesized in item 3, is added.
3) The solution is stabilized at room temperature for 12h.
4) The deposition of the formed solution is carried out by the drop casting method, after previously masking the contact area.
5) The densification of the sensitive layer is carried out sequentially, in two stages, by thermal treatment, as follows:
   - in air, for 10 minutes, at a temperature of 300ºC;
   - in air, for 1 h, at a temperature of 400ºC.

Advantages of the proposed sensing layer

The use of binary and ternary nanohybrids as sensitive films presents several advantages:
The use of the described sensing film presents advantages such as:
- onion-type oxidized nanocarbon materials functionalized with trifluoromethyl groups provide a high specific surface/volume ratio, affinity for trimethylamine molecules as well as a significant percentage variation in the resistance of the sensitive layer upon contact with them;
- trifluoromethyl groups, through their marked electron-attracting effect, increase the number of carriers in nanocarbon materials.
- the presence of fluorine atoms, through their hydrophobic effect, reduces the affinity for water molecules.
- CuO changes the pore distribution at the interface with oxidized onion-type nanocarbon materials functionalized with trifluoromethyl groups, increasing their specific surface area;
- room temperature detection;
- reversibility;
- fast response.