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Highly Selective Detection of Hydrogen Sulfide by Simple Cu-CNTs Nanocomposites

Nahida Musayeva [1,*], Hadiya Khalilova [1], Bakhtiyar Izzatov [1], Giovanna Trevisi [2], Shahla Ahmadova [1] and Muhammad Alizada [1,3]

1 Institute of Physics, Azerbaijan Ministry of Science and Education, H. Javid Ave, 131, AZ1143 Baku, Azerbaijan
2 Institute of Materials for Electronics and Magnetism (IMEM), Consiglio Nazionale delle Ricerche, Parco Area delle Scienze 37/A, 43124 Parma, Italy
3 Department of Physics and Electronics, Khazar University, Mehseti Str., 41, AZ1096 Baku, Azerbaijan
* Correspondence: nmusayeva@physics.science.az; Tel.: +994-503025647

Abstract: The presented work is devoted to the preparation of nanocomposites based on multiwall carbon nanotubes (MWCNTs) and copper (Cu) nanoparticles by a simple chemical method, and to study their sensing properties to hydrogen sulfide (H_2S) gas. The Cu decorated multiwall carbon nanotubes (MWCNTs/Cu) were prepared by the deposition of very thin Cu layers on the pristine and functionalized multiwall carbon nanotubes (f-MWCNTs) using both physical (electron beam evaporation (EBE)) and chemical (electrochemical deposition) methods. MWCNTs/Cu prepared in the two above-mentioned ways, their sensing properties were studied, and the results were comparatively analyzed. The effect of the chemical functionalization of MWCNTs by oxygen-containing groups on the sensing properties of these f-MWCNT/Cu nanocomposites has been investigated. All the prepared sensors demonstrated high sensitivity and selectivity to H_2S in the air at room temperature. The f-MWCNT/Cu structure obtained by the chemical method demonstrated about 5 times (~400%) higher sensitivity ($\Delta R/R_0$) to H_2S gas compared to the similar structure obtained by the physical method. The temperature effect on sensory characteristics (response and self-recovery time) of the f-MWCNTs/Cu structure was also studied.

Keywords: carbon nanotubes; MWCNTs; Cu; H_2S; sensor; nanocomposite; decoration

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1. Introduction

It is known that every year a large amount of toxic discharges are released into the environment from different anthropogenic sources, including industrial operations, transport infrastructure, and domestic activities. Over time, the continuously increasing the amount of toxic pollutants has become a serious threat to both the natural environment and all living organisms. In the industrially developed countries of the world, the natural environment has long been exposed to various anthropogenic discharges. Fossil fuel production, transportation, and use, as well as chemical enterprises have significantly contributors of pollution to the ecosystem pollution, particularly of atmospheric pollution. The pollution of the atmosphere has led to such global problems as climate change, ozone layer depletion, acid rains, and deforestation, and is also causing harm to all of the ecosystem's components, including human health [1–3].

The utilization of fossil fuel resources results in the release of a huge amount of harmful gases into the atmosphere. These pollutants include total hydrocarbons, carbon oxides (CO_2, CO), sulfur dioxide (SO_2), hydrogen sulfide (H_2S), nitrogen oxides (NO_x), chlorine (Cl_2), ammonia (NH_3), volatile organic compounds, dioxins, and solid particulates [4].

In order to prevent the pollution of the atmosphere by anthropogenic emissions, and to ensure the safety of both industrial operations and transport facilities while minimizing their environmental impact in general, it is important to develop new monitoring methods.

The preparation of new sensors comprised of different nanocomposites for use in remote air pollution controlling systems is one of the most prominent potential solutions for this problem.

H_2S is a highly reactive toxic gas. The main anthropogenic sources of H_2S are sulfur-containing fuels, including power plants, refineries, vehicles, and various production enterprises working with fossil fuels. Crude oil containing H_2S causes corrosion of pipelines and equipment. Prolonged exposure to H_2S even at low concentrations may result in headache, nausea, collapse, coma, and death, despite the low toxicity of H_2S gas concentration for humans. The standard threshold limit value is about 10 ppm of this pollutant. A concentration of 150 ppm H_2S may cause conjunctivitis and irritation of mucus membranes. This gas readily passes through alveolar membrane of the lung and penetrates the blood stream. Death can occur as a result of respiratory failures [5,6].

All of the above stated reasons make it necessary to prevent H_2S pollution, while reducing its concentration to the maximum permissible level in air in the densely populated areas, and also in plants, enterprises, and other sources. Therefore, the implementation of regular monitoring to ensure faster and precise detection of H_2S concentrations and to enabling the reduction of H_2S quantity in the ambient air is one of the most prominent of the present day.

There are a number of methods aimed at monitoring and reducing the H_2S emissions in the environment. These approaches can be based on laboratory analyses of air samples or remote sensing measurements.

In recent years, composite nanomaterials have attracted great attention worldwide, as they have many advantages that single-component nanomaterials lack. Nanocomposites are new materials with superior properties, prepared by combining two or more nanomaterials.

Being efficient adsorbents, carbon nanotubes (CNTs) are used for detecting pollutants with the aim of their consequent removal from air. Different types of CNTs have been synthesized and applied for this purpose [7–10].

For example, the electrical and mechanical properties of polypropylene (PP) and polystyrene (PS) are improved by filling them with Ag-decorated MWCNTs, when compared to pristine MWCNTs [11].

The existing methods for the preparation of nanocomposites are mainly based on the use of metals, metal oxides, polymers, and carbon nanotubes [12]. One such method is the decoration of CNTs with nanoparticles of various metals and metal oxides (MO). New materials developed by this method have excellent properties for multifunctional applications, including sensors [13–19]. Multiple types of sensors have been developed to date based on different materials, such as metal oxides, carbon-based nanomaterials, and their composites [20–23].

Thin films or powders of some MOs have been studied for this purpose. A series of studies has been carried out to identify the role of metal (Au, Cu, Pt, Pd, Ag etc.) modification in improving the H_2S gas sensing properties of Fe_2O_3 and ZnO. It should be noted that the highest response (~500%) was achieved for Fe_2O_3 modification with Au thin films at 250 °C temperature [24–26]. However, this temperature is too high to apply them in sensor devices, especially in mobile devices. The number of sensors operating at room temperature is insignificant, and they are mainly based on carbon nanostructures.

Various sensor materials demonstrate different sensitivity mechanisms to selective gases or vapors. For example, the sensitivity of most metal oxides is determined by the trapping of electrons at adsorbed molecules followed by band bending induced by these charged molecules, which are responsible for the change in conductivity, while the identification of the exact fundamental mechanisms that causes a gas response is still controversial [27,28].

Resistive sensors based on MWCNTs have already been prepared and tested to detect nitroaromatic explosives through interaction with their vapors. The outer walls of MWCNTs were covalently functionalized with electron rich amino groups. When the

electron-deficient molecules of trinitrotoluene (TNT) interact with the electron-rich amino groups, sharp changes in the conductance of the electrical-sensing nanoelements due to charge-transfer process can be detected [29].

Pristine CNTs are known as inert materials to environmental influences. Environmental effects activate the outer walls of CNTs, enhancing their adsorption properties. Functionalized CNTs formed by carboxyl groups change their resistance when exposed to the majority of gases and vapors, but do not show higher sensitivity.

An additional functionalization of MWCNTs by metal nanoparticles results in enhancing their sensitivity and selectivity [30].

A number of H_2S gas sensors based on CNTs already have been fabricated and tested. Authors used the magnetic sputtering method for the decoration of MWCNTs by CuO and Cu_2O, which have high sensitive and selective properties for H_2S detection. However, like the majority of sensors working at high temperatures, the optimal H_2S sensing temperature of this sensor is 150 °C [31].

CuO-SWCNTs composition is prepared and tested in the 100 ppb–50 ppm range of H_2S gas concentration, and 150 °C is found as the optimal working temperature. Such sensors have demonstrated a 65% response at 50 ppm H_2S gas concentration. Cu decoration of the functionalized SWCNT via the chemical reduction process shows a 70% response rate at 150 ppm (27% at 20 ppm) to H_2S gas at room temperature [32,33].

The development of simple technologies to produce cost-effective sensors working in open air at room temperature remains as an urgent problem to date. This work presents the results of research and comparative analyses of the sensing capabilities of nanocomposites in air at room temperature, obtained by physical and simple electrochemical deposition methods.

2. Material and Methods

2.1. CNTs Synthesis and Functionalization

The Aerosol-CVD (chemical vapor deposition) system (SCIDRE inc., Dresden (Germany) was used to synthesize the MWCNTs. One of the advantages of this system is the use of different liquid precursors, which can be transformed into vapor (aerosol) during ultrasonication at high frequency. MWCNTs were deposited in the inner surface of a quartz tube, situated inside a horizontal quartz reactor. Ferrocene ($Fe(C_5H_5)_2$) from Sigma–Aldrich, Co. (St-Louis, MO, USA) was used as a catalyst precursor, which was dissolved in heptane (a carbon source) before starting the growth process. A high frequency (800 kHz) ultrasonic device (Meinhardt Ultrasonics, Leibzig, Germany) was used for the aerosol formation.

The optimal temperature for the growth of these samples was found to be 900 °C. Other details of the growth method are reported in the author's previous work [34].

The purification of the synthesized MWCNTs from clusters containing iron, or non-tubular carbon structures and amorphous carbon, was performed by treating the samples with diluted xylene at 80 °C for two hours. The solution was then cooled to room temperature, and the purified MWCNTs were filtered and washed with deionized water. The purification process was finished by drying the MWCNTs in an oven at 125 °C for 1.5 h.

After purification from amorphous carbon and hydrocarbon residues, the outer walls of the MWCNTs are functionalized by oxygen-containing carboxyl (COOH) and hydroxyl (OH) groups. The MWCNTs were subjected to ultrasonic waves at room temperature for 5 h in a mixture of H_2SO_4 and HNO_3 acids in a 3:1 ratio, respectively. The MWCNTs were then washed several times with deionized water until becoming completely acid-free, filtered, and finally, dried at 100 °C for one hour.

2.2. Metal Deposition

Both pristine and functionalized MWCNTs (f-MWCNTs) were dispersed homogeneously on the dielectric (pyroceramic glass) substrate, and a very thin (1–5 nm) layer of metallic copper (Cu) was deposited on it.

The deposition process was carried out by the two methods described below:

(1) Physical method—electron beam evaporation (EBE): the sample is placed in the vacuum (10^{-2} Torr) chamber of the Angstrom Engineering Equipment and very thin (5 nm) pure Cu (99.99%) was deposited on its surface using the e-beam evaporation method. The thickness of the deposited Cu layer was controlled by a special sensor placed in the chamber.

(2) Chemical method—electrochemical deposition: 4 g of $CuSO_4$ salt was dissolved in 16 mL of distilled water and added to electrolyte. A graphite or copper electrode was used for the cathode, and a structure consisting of a network of closely spaced MWCNTs on the substrate was used for the anode. When the required voltage was applied to the electrodes, the current generated between the electrodes carried the Cu^{2+} ions onto the MWCNTs. This process resulted in the deposition of Cu atoms on MWCNTs. The process was repeated a number of different times and the optimal condition was chosen for the deposition of a very thin metal layer.

2.3. Scanning Electron Microscopy

Scanning electron microscopy (SEM) analysis was performed in a Zeiss Auriga Compact system equipped with a Schottky field-emission gun. The morphological analysis was carried out with a 5 keV accelerated electron beam; the produced secondary electrons were collected with an Everhart-Thornley detector in case of low magnitude images, and with an Inlens detector for high resolution images.

2.4. Raman Spectroscopy

The Raman EnSpecter R532 spectroscope setup (Enhanced Spectrometry Inc., San Jose, CA, USA) was used for optical analysis of MWCNT samples. Green laser line 532 nm was used to excite the samples. All the measurements were performed at room temperature. The Raman signal was collected by a back-thinned charge-coupled device (CCD).

2.5. Gas Sensing Test

In order to study the sensor properties, silver (Ag) contacts are deposited on both sides of the f-MWCNTs/Cu nanocomposite placed on a pyroceramic substrate. The structure prepared by this method is shown in Figure 1. In all samples, the contact area was 1.85×3 mm^2 and the distance between contacts was 6 mm. The stability of the sample contacts was tested and the I-V characteristics were studied. The resistances of the samples prepared by both chemical and physical methods were measured as 62 and 27 Ohms, respectively (Figure 1).

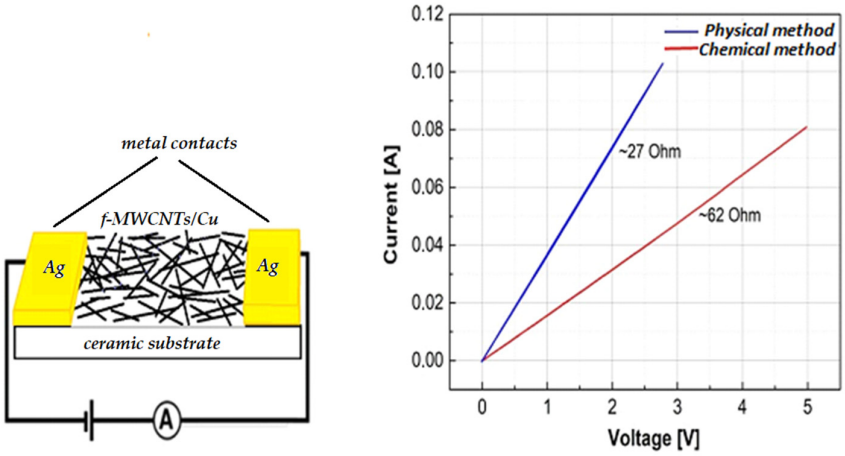

Figure 1. Sensor structure (**left**) and I-V characteristics of the Ag-f-MWCNTs/Cu-Ag structures (**right**).

A special hermetic test box was prepared to test the sensitivity of the samples (Figure 2). As H_2S is a toxic gas, the test box was specially sealed and placed in a fume hood. To

carry out the sensor testing process, the pure H_2S gas was obtained through a chemical reaction in the flask: $ZnS+2HCl = ZnCl_2+H_2S(g)$, at which point then H_2S immediately passed into the measure chamber of test system through a flexible polymer tube (Figure 2). The calculated amounts of chemicals were used to obtain 10 ppm H_2S gas.

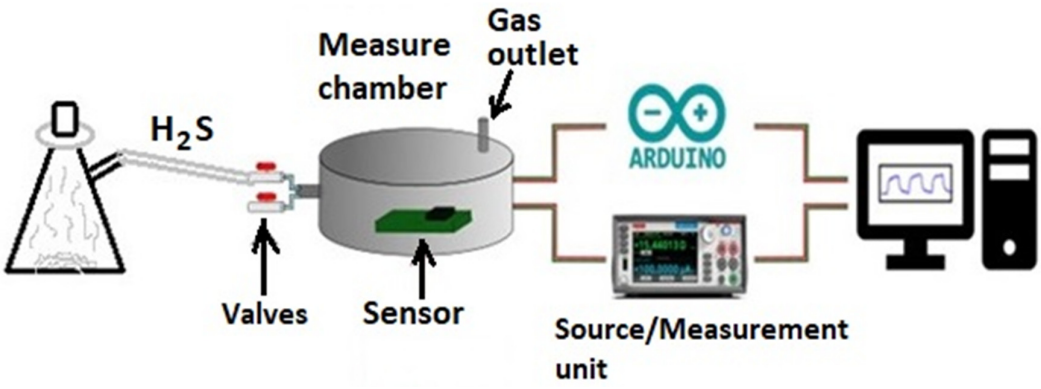

Figure 2. Sensor testing system.

The nanocomposite sample was placed in a box in advance. The gas enters the box through a special pipe and an air pump is used to remove it.

3. Results

3.1. Material Characterization

The morphology of the samples was observed at each stage after the synthesis of the MWCNTs (Figure 3). As reported earlier, the diameter of the 200–600 µm-long MWCNTs was determined to be between 30–85 nm [35]. SEM observations showed that the purification and functionalization processes did not damage the MWCNTs (the smooth structure or the length), while the purification reduced the quantity of amorphous carbon and clusters (see the red circles in Figure 3, left panel). The presence of functional groups was confirmed by the IR spectroscopy method reported in the previous work [34].

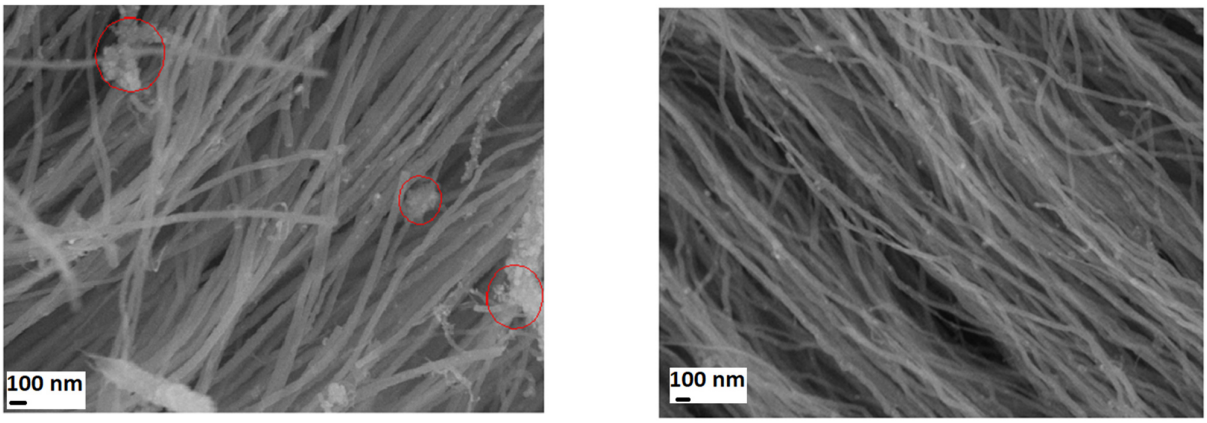

Figure 3. SEM images of pristine (**left**) and functionalized (**right**) MWCNTs.

Significant changes were observed in the morphology of the f-MWCNTs/Cu obtained by both physical and chemical methods. The deposition of a very thin metal layer (5–6 nm) on f-MWCNTs by the EBE method results in the formation of a set of densely located plots (not a solid layer) adhering to the outer walls (Figure 4a). As can be seen in Figure 4b, the Cu deposited through the electrochemical deposition procedure is accumulated on the MWCNTs' wall, forming separately located islands (parts in lighter color) of different sizes (within 18–33 nm) (Figure 4c). Herein, these islands will be called nanoclusters.

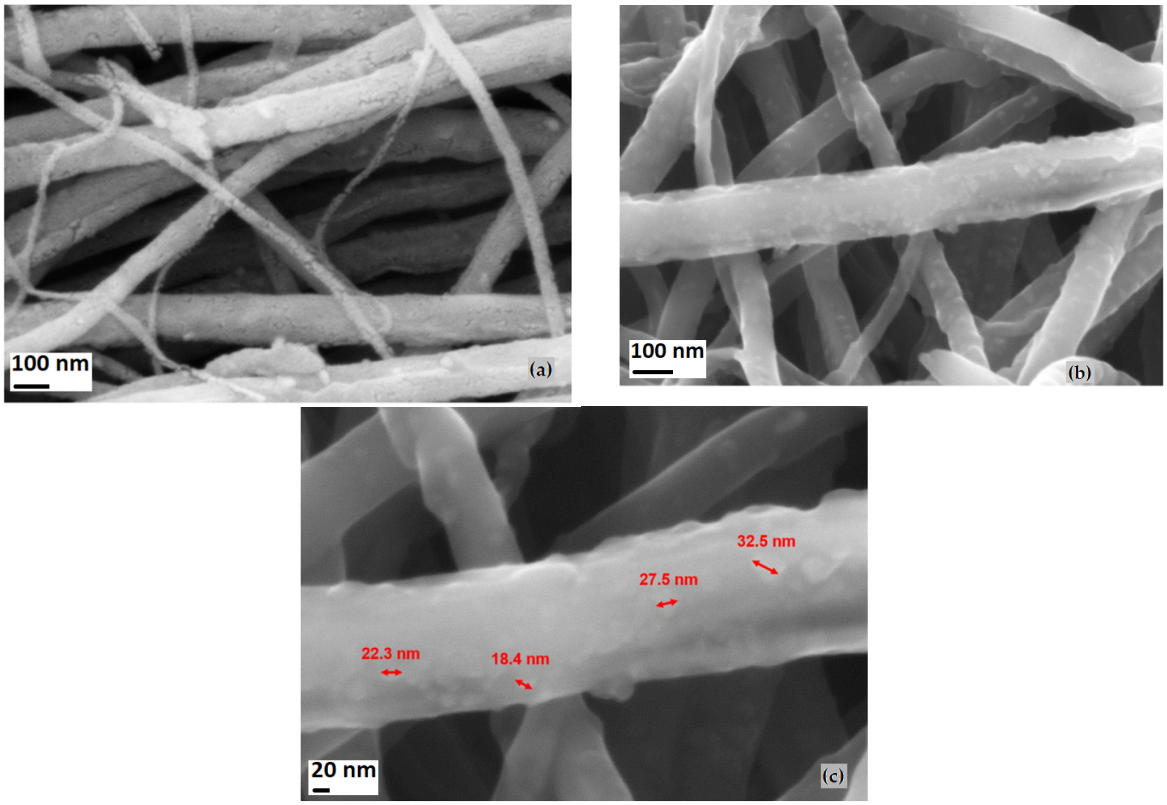

Figure 4. SEM images of f-MWCNTs/Cu nanocomposite obtained by (**a**) physical and (**b**) chemical methods; (**c**) higher magnification of (**b**).

The Raman spectroscopy results of all the samples used during the research were comparatively analyzed. Both the functionalization of MWCNTs by oxygen-containing groups and by Cu decoration mainly influences the intensities of the D band (1343 cm^{-1}) that relates to sp^3 hybridized carbon. Such hybridized carbon does not have the same plane symmetry as grapheme, which is associated with both defectiveness and with the amorphous carbon G graphite band (1573 cm^{-1}) corresponding to the stretching mode of sp^2 carbon atoms of graphitic materials [36].

Figure 5 shows that the ratio between the intensities of D band and G band I(D)/I(G) increases when MWCNTs are oxidized and decorated with Cu nanoparticles by both physical and chemical methods. Thus, an increase of I(D)/I(G) value after oxidation by acid testifies to the creation of carboxyl and hydroxyl groups on the MWCNTs surface, which are extra covalent bonding-like defects that result in the carbon hybridization changes from C-C sp^2 to C-C sp^3 [36]. An increase in the I(D)/I(G) ratio of the Cu deposited-nanocomposites—f-MWCNTs/Cu obtained by both physical and chemical methods can be attributed to the setting of Cu nanoclusters on the f-MWCNTs' surface. This weakens the signals scattered from the C-C bonds, which leads to the decrease of the graphite's G band intensity [37]. A similar process is observed with MWCNTs/Cu nanocomposites.

3.2. H_2S Sensing Characteristics

The curves in Figure 6 show the comparative responses of f-MWCNTs/Cu nanocomposites obtained by physical and chemical deposition methods to H_2S gas. The resistance of both samples increases under H_2S gas influence. However, the response of the sample prepared by the chemical method is about 5 times higher than that of the sample prepared by the physical method.

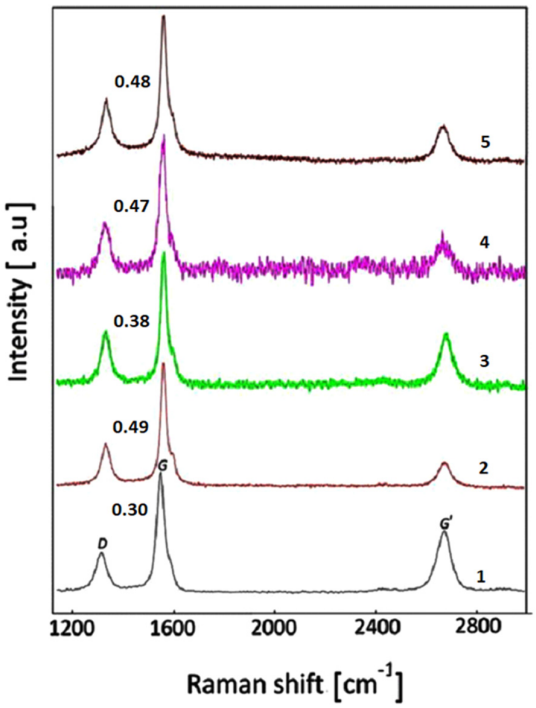

Figure 5. Raman spectra of the samples: 1—pristine MWCNTs, 2—MWCNTs/Cu (physical method), 3—f-MWCNTs, 4—f-MWCNTs/Cu (physical method), and 5—f-MWCNTs (chemical method) with calculated I(D)/I(G) relation.

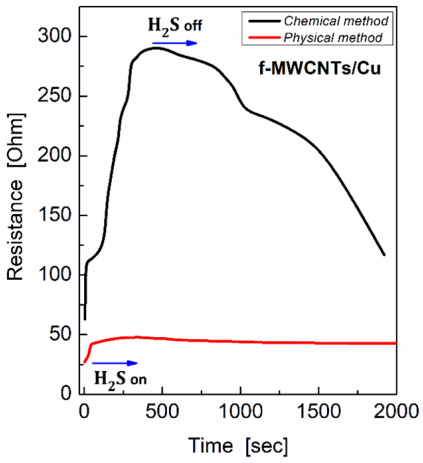

Figure 6. Sensitivity of the f-MWCNTs/Cu nanocomposites prepared by physical and chemical deposition methods.

In order to assess the selectivity of the sensors, several gaseous media (ammonia, ethanol, methanol, and several common organic solvents) were tested under the same conditions. Although the concentration of these gases and vapors in the test box was 10–15 times higher (100–150 ppm) than the concentration of H_2S, both sensors demonstrated lower sensitivity (physically prepared: 5 times lower; chemically prepared: 10 times lower) to these gases compared to H_2S (Figure 7a,b). At the same time, both sensors appear to be more sensitive to ammonia (NH_3) than to the other gaseous compounds (with the exception of H_2S).

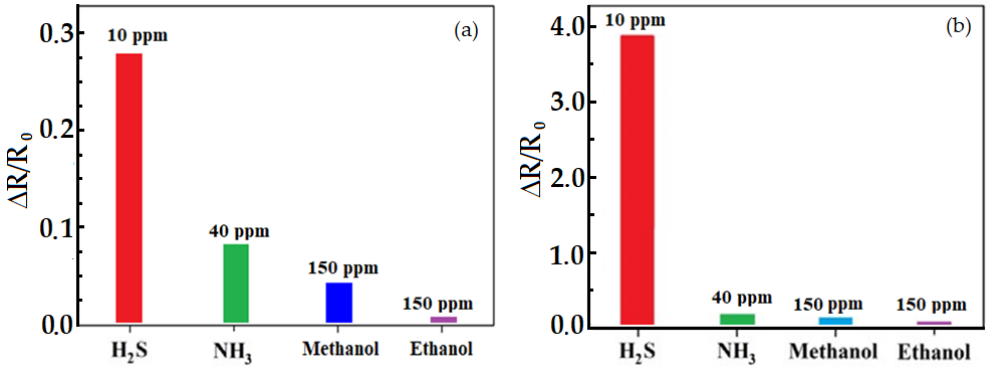

Figure 7. Selectivity of the sensors, prepared by (**a**) physical and (**b**) chemical methods.

The recovering capability and the time spent recovering are among the most important requirements for sensors. This parameter determines their lifetime (repeated use) and durability.

The results of the tests have shown that f-MWCNTs/Cu-based sensors may recover within a few seconds after the influence of volatile and low-impact gases and vapors (ethanol, methanol, methane, etc.). However, under the influence of H_2S and ammonia, both the reaction time and the recovery time of the sensing elements increase. It should be noted that the self-recovery time of the chemically obtained sample is smaller compared to the sample obtained by EBE method (Figure 6).

Various methods are used to reduce the recovery time and promote the self-recovery of the sensors, including UV light, heating, fans, etc. [38]. For example, most of the metal oxide-based sensors operate at high temperatures and recover within several seconds when separated from the gaseous medium by heating.

It has been experimentally revealed that the sensitivity of the sensors based on f-MWCNTs/Cu structure at room temperature was two times higher than at 50 °C (Figure 8). But in this case, the self-recovery time is reduced by several times when the sensor is heated up to 50 °C. Therefore, it is possible to conduct the process at room temperature and then rise the temperature up to 50 °C to recover the sensor after the H_2S vapors are removed from the test box. This was tested also in the author's previous work [30].

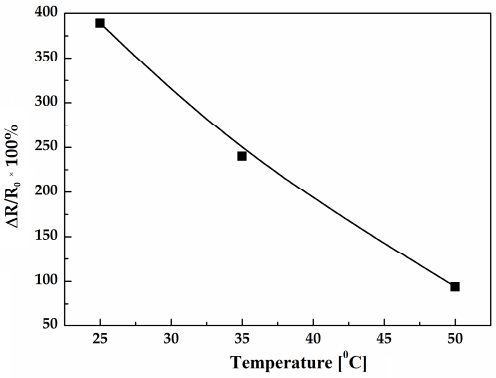

Figure 8. Temperature dependence of the sensitivity of f-MWCNTs/Cu structure.

In order to understand the role of functionalization, thin Cu nanolayers were deposited on both pristine and carboxyl group-functionalized MWCNTs, dispersed on a dielectric substrate. As can be seen from SEM images (Figure 9), the metal atoms are gathered on the CNTs agglomerates, because the MWCNTs are closely intertwined with each other. When comparing Figure 9 (high resolution picture) with Figure 4b, it can be seen that they are very similar. However, they form structures with different resistances. The comparison of the pristine MWCNTs with the MWCNTs functionalized by oxygen-containing groups during has revealed that the main advantages of the CNTs' functionalization are in both

their good dispersion on the substrate and improved adhesion properties. Due to the poor adhesion of the pristine MWCNTs on the substrate, which caused some difficulties during electrochemical deposition, the samples prepared by physical deposition were used to compare the sensing properties of the pristine and f-MWCNTs.

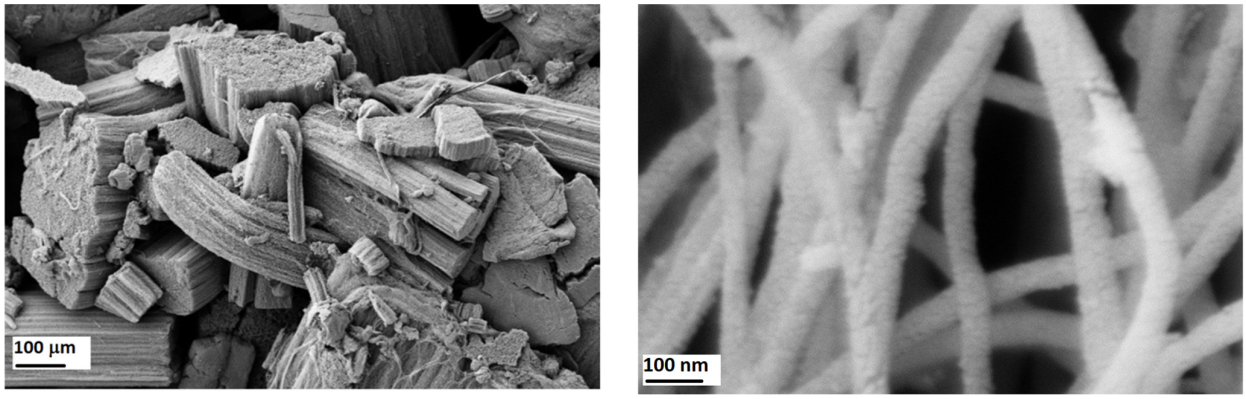

Figure 9. SEM image of MWCNT/Cu (**left**); high resolution SEM image (**right**).

The sensing properties of the MWCNTs/Cu and f-MWCNTs/Cu structures obtained by the physical method were comparatively analyzed (Figure 10). It was established that the sensitivity significantly increases after functionalization of MWCNTs by oxygen-containing groups.

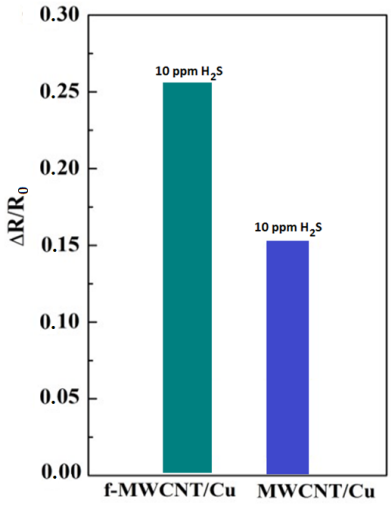

Figure 10. Sensitivity diagram of the MWCNTs/Cu and f-MWCNTs/Cu structures obtained by the physical method (in the H_2S medium).

4. Discussion

H_2S Sensing Mechanism

As mentioned above, the functionalization of CNTs by oxygen-containing groups activates their surface, making them sensitive to environmental effects. However, this fact does not justify the use of such a functionalized CNT (f-CNT) structure as a sensor element, since its response to the acting gases is weak and not selective [30]. The sensitivity and selectivity of f-CNTs to different gases and vapors can be improved through their composition with metals, metal oxides, polymers, and many other materials. These materials can react with the detected gases or vapors, which will eventually result in the change of CNTs resistance.

In case of metal decoration, the metal atoms located on a CNT's outer wall as nanoclusters (or nanoparticles) increases the surface size of the matrix (CNTs) and influences their electronic properties during gas detection. In this work was developed a new method

for the preparation of a metal (Cu)-MWCNT composite through decoration of f-MWCNT surface by Cu using electrochemical deposition.

The highly improved sensitivity and selectivity of the f-MWCNTs/Cu structure (due to decoration of f-MWCNTs by Cu) can be explained by the catalytic role of Cu in some reactions that occur during H_2S gas sensing [39,40].

The H_2S molecules adsorbed on the MWCNTs surface decomposes into sulfur and hydrogen due to the catalytic effect of Cu nanoparticles:

$$H_2S\ (g) \rightarrow H_2\ (g) + S \quad (1)$$

Decomposition of H_2S in the vicinity of MWCNTs promotes the breakdown of H_2 molecules into H^+ ions, thus transferring the electrons to the MWCNTs:

$$H_2\ (g) \rightarrow 2H^+ + 2e^-$$

This leads to the increase of resistance of the sensing materials [33].

This process occurs in both physically and chemically decorated samples. Even though pure Cu was deposited by both methods, different processes occur during deposition. In EBE deposition, the evaporated Cu atoms are deposited on the f-MWCNTs surface. However, Cu^{+2} ions are deposited on the MWCNTs surface during the electrochemical deposition process. This means that a van der Waals interaction occurs between the neutral Cu atoms and MWCNTs during physical deposition. We assume that the electron exchange occurring between Cu^{+2} ions and MWCNTs in case of electrochemical deposition leads to strong connection of them, i.e., most probably Cu^{+2} ions are neutralized by extracting 2 electrons from MWCNTs, which results in the formation of closer bonds.

Cu atoms are densely located in the physically structured f-MWCNTs/Cu, which decreases the number of MWCNTs interacting with H_2S molecules. On the contrary, as can be is seen from Figure 11 (see parts in red circles), there is a very thin binding film between the chemically decorated MWCNTs. Most probably, this binding film plays a certain role in the electron transfer between f-MWCNTs and f-MWCNTs–Cu. All the above stated factors result in an 8 times higher response to H_2S gas of the f-MWCNTs/Cu structure prepared by the electrochemical method compared to the same structure prepared by the physical method.

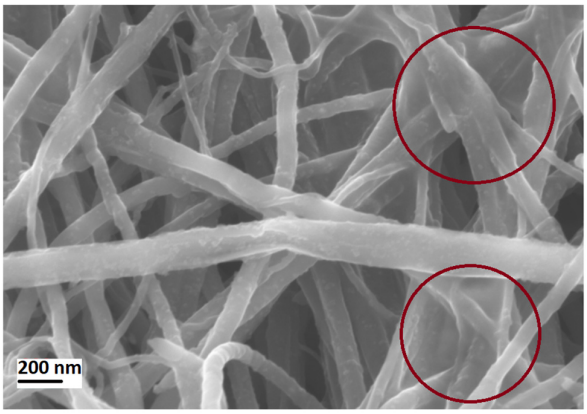

Figure 11. SEM image of f-MWCNTs/Cu nanocomposite obtained by the chemical method.

5. Conclusions

In summary, new nanocomposites of f-MWCNTs/Cu with better sensing properties were prepared by decorating MWCNTs with metallic Cu. Based on the results derived from the research, it can be concluded that:

- The functionalization of CNTs with oxygen-containing groups increases their sensitivity to environmental effects.

- The morphological analyses carried out by SEM have revealed that there are noticeable changes in the morphology of the f-MWCNTs/Cu obtained by both physical and chemical methods.
- The nanocomposites prepared by both the physical and chemical methods have good sensing properties for H_2S gas detection.
- The sensor structure of f-MWCNTs/Cu demonstrated high sensitivity to H_2S gas at room temperature.
- It was established that the sensor element based on f-MWCNTs/Cu obtained by the chemical method is more highly sensitive to H_2S gas than to methanol, ethanol, and ammonia.
- The tests carried out to study the selectivity of the developed new sensors to other gases and vapors, including ammonia, ethanol, methanol and several organic solvents have demonstrated their lower sensitivity to the mentioned gases compared to H_2S (physically prepared: 5 times lower; chemically prepared: 10 times lower), with the exception of their insignificant response to ammonia.
- The f-MWCNTs/Cu prepared by the chemical method demonstrates about 5 times (~400%) higher sensitivity to H_2S gas at room temperature in comparison with the same structure prepared by physical deposition method.
- It is possible to reduce the recovery time of the f-MWCNTs/Cu structure by heating it up to 50 °C after the H_2S gas sensing process.

Hence, it is concluded that the f-MWCNTs/Cu nanocomposite material can be successfully applied as a highly sensitive, selective, and cost effective H_2S gas sensor working at room temperature.

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