MWCNT-Pt nanocomposite as the active element of harmful gas sensors

A.D. Dobrzańska-Danikiewicz a,*, D. Łukowiec a, W. Wolany a, M. Procek b, A. Sękala a

a Faculty of Mechanical Engineering, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
b Department of Optoelectronics, Silesian University of Technology, ul. Akademicka 2, 44-100 Gliwice, Poland
* Corresponding e-mail address: anna.dobrzanska-danikiewicz@polsl.pl

ABSTRACT

Purpose: The goal of this paper is presentation of the variations in MWCNTs-Pt nanocomposite resistance which were examined in the presence of hydrogen with a rising concentration of, respectively, 1, 2, 3 and 4% H₂ as well as nitrogen dioxide with a rising concentration of, respectively, 20, 100, 200, 400 ppm of NO₂.

Design/methodology/approach: Variations in electrical conductivity for the MWCNTs-Pt composite placed, alternately, in the atmosphere of gas and in the atmosphere of selected gases, were measured with a measuring station equipped with precision and inert gas reducers, mass flow meters, filtration systems of gas mixture and the studied mixture's humidity and temperature control. An active layer of the transducer consisted of MWCNTs-Pt nanocomposite deposited thereon. All the measurements were carried out in the atmosphere of synthetic air (20% of O₂ and 80% of N₂) at 22.5°C.

Findings: It was found based on the results obtained that system resistance is rising as hydrogen concentration is rising in the atmospheric air. The results of analogous examinations of variations in MWCNTs-Pt nanocomposite resistance carried out for a varying concentration of nitrogen dioxide in the atmosphere of synthetic air are opposite, because lowering system resistance was noted along with a heightening concentration of NO₂. The best results were achieved for the nanocomposite presented in the article having a 5% mass concentration of platinum and with uniformly dispersed Pt particles on the surface of carbon nanoparticles.

Practical implications: The outcomes presented signify the selectiveness of the applied system consisting of carbon nanotubes decorated with platinum nanoparticles. It means that this material can be used as the active element of harmful gas sensors.

Originality/value: A carbon-metal MWCNTs-Pt nanocomposite with special electrical properties was fabricated in the course of research works, whose originality is based on the appropriately selected composition and the specific morphology.

Keywords: Gas sensors; Carbon nanotubes; Nanocomposites; Platinum

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1. Introduction

Sensors of chemical substances are used wherever the investigated signal cannot be recorded directly with human senses or when they represent parts of devices responding automatically to signal occurrence. The role and application ranges are constantly broadening and are encompassing new fields of science [1] and industrial plants managed in a modern way [2-4] representing various industries [5-11].

The sensors are operating by using the phenomena taking place at the boundary of solid-gas or solid-liquid phases. Chemical bonds are formed between the molecules of substances and the sensor’s active material as a result of contact between the analysed substance with the sensor surface. The concentration of current carriers of the sensor’s active material is changing as a result, leading to changes in its surface conductivity. This contact relates only to the near-the-surface layer of the sensor material. The sensor activity can therefore be measured with the ratio of its area to volume. The higher the ratio, the more sensitive to gas or liquid the sensor is. It hence seems substantiated to use materials with strongly developed specific surface for the construction of sensors, and the carbon nanotubes and nanoparticles of some metals are clearly such materials. The modern sensors of chemical substances are expected to feature, apart from a high sensitivity threshold, also selectiveness and durability allowing the sensor to work in difficult conditions.

Carbon nanotubes [12] are one of the most interesting carbon nanomaterials due to their unique electrical, chemical and mechanical properties [13-16]. They have a small diameter of one to several dozens of nm, and the length of usually from a fraction to several microns and their specific surface area is between 50 to over 1000 m²/g [17]. For this reason, owing to their high electrical conductivity and durability in the liquid and gas environment, they are suitable for applications as, e.g. electrode modifiers. It has been proven that unmodified carbon nanotubes are sensitive to the chemical character of the environment in which they are placed [18-20], and the presence of gases has significant impact on changes in their electrical properties, such as: electrical resistance, thermoelectric force and density of electron states [21]. The electrical properties of single-walled and multi-walled nanotubes depend on their diameter and chirality. Nanotubes’ ability to adsorb gas and transport charges depends on their topological properties, i.e. the area of interactions between nanotubes, nanopores and the specific area of individual nanotubes, but also on the type of gas molecules. The adsorption of gas molecules by carbon nanotubes has a direct effect on their electron properties. The varying Fermi level and the density of electron states automatically changes the conductivity of nanotubes [22,23]. The chemical modification of nanotubes’ surface, e.g. by deposition of noble metal nanoparticles onto them, such as Pt, Pd, Rh, Au [24-26], is additionally strengthening this effect and is increasing the sensitivity threshold, selectivity and operating speed of sensors.

Platinum (Pt), apart from such elements as, in particular, Ru, Rh, Pd, Os, Ir, belongs to the platinum group metals and has found a wide group of uses due to its unique properties. It has high melting point and boiling point, is ductile, exhibits high chemical resistance and very good catalytic properties (best for platinum group metals), which are exploited in numerous industrial processes. High biocompatibility and good mechanical strength enable to use Pt for producing surgical instruments and biomedical appliances (mainly heart pacers, defibrillators, stents). Platinum also has good electrical conductivity, hence it is employed in the electrical and electronic branch as an element of electric contacts, resistors, thermocouples, heating elements and hybrid integrated circuits [8-10]. The physiochemical and electrical properties of platinum at a nanometric scale significantly differ from platinum properties in the macroscopic dimension. The occurrence of platinum as platinum nanoparticles is directly reflected in their larger specific surface, and also higher transport velocity of electrons and high catalytic activity [11]. The interesting examples of using nanometric platinum include, among others: a nanocomposite consisting of monodisperse Pt nanoparticles on glassy carbon electrode used for methanol detection [27], platinum nanoparticles/graphene-oxide hybrid as a cysteine sensor [28], carbon nanotubes decorated with Pt nanoparticles being the sensors of such gases as CO, NO [29], H₂ [30], as well as platinum nanoparticles as elements of CO₂ [31], Hg(II) [32] and As(III) [33] sensor systems. Moreover, platinum nanoparticles’ ability to oxidise and reduce hydrogen peroxide (H₂O₂) shows they can be used as the active elements of electrochemical biosensors, among others, glucose, cholesterol and dopamine [34-36]. The economic aspect, well visible in electrochemistry where costs of producing electrodes containing platinum nanoparticles are much lower than for electrodes fully made of platinum, is favouring platinum nanoparticles [26].

The applicability of nanocomposites with interesting electrical properties, structure and, most of all, a highly developed specific surface, created by combining carbon nanotubes with Pt nanocrystals as an active surface of sensors of industrial gases, is an interesting research aspect for the authors [37-39]. This publication presents
a methodology of fabricating newly developed nanocomposite CNT-Pt materials, having a 5% mass concentration of platinum and uniform dispersion of Pt particles on the surface of carbon nanoparticles, and the results of examinations of electric properties of such materials in the presence of hydrogen and nitrogen dioxide in the atmosphere of synthetic air.

2. Research methodology

2.1. Pt-decorated carbon nanotubes fabrication method

Carbon nanotubes with the length of 100-200 µm and the diameter of 10-20 nm, fabricated by the Chemical Vapour Deposition (CVD) method, were used in the experiment. The synthesis of MWCNTs was performed using EasyTube® 2000 system on a silicon substrate containing a catalyst in the form of thin film (2 nm Fe) and two nanometric buffer layers Al₂O₃ and SiO₂. The growth of the nanotubes took place at the temperature of 750°C for 45 minutes and with the constant flow of process gases of, respectively, 300 SCCM for H₂ and C₂H₄, and 1 SLPM for Ar [40,41]. The so-called indirect method was selected for MWCNTs-Pt nanocomposite fabrication. In this method, a carbon-metal material is produced in two processes, and the purpose of the first process is to modify the surface of carbon nanotubes with function groups due to covalent functionalisation, and the other to fabricate and cover nanotubes with Pt nanoparticles by chemical synthesis. A mixture of HNO₃ and H₂SO₄ acids concentrated at a rate of 1:3 was in the first place used to produce carbon function groups (-COOH, -COH, =CO) on the surface of carbon nanotubes, and then a 30% H₂O₂ solution was used. Following a functionalisation process, carbon nanotubes were filtered and washed in deionised water and dried and underwent further experiments. Platinum is precipitated as a result of a reduction reaction of a chloroplatinic acid mixture H₂PtCl₆ with a popular reducer, i.e. sodium borohydride NaBH₄ and ethylene glycol. A suspension of carbon nanotubes placed in a mixture is stirred and heated with a reflux condenser for approx. 8 hours at 140°C. The suspension obtained is filtered, the material is washed in deionised water and then dried. Figures 1 and 2 present a nanocomposite consisting of carbon nanotubes decorated with platinum nanoparticles. The image was achieved using an STEM TITAN 80-300 high-resolution microscope by FEI, with the dark field (HAADF) (Fig. 1) and bright field (Fig. 2). The described fabrication technique is relatively simple and effective. The process parameters and a concentration of reagents can be modified in order to control the chemical composition of MWCNTs-Pt nanocomposites and to achieve materials with diverse morphology.

Fig. 1. MWCNTs-Pt nanocomposite observed in dark field [42]

Fig. 2. MWCNTs-Pt nanocomposite observed in bright field [42]
2.2. Measurement of electrical properties of the fabricated CNT-Pt nanocomposites

The investigations of electrical properties of MWCNTs-Pt nanocomposites were performed using an appropriately designed system. The manufacture of a transducer with an active layer made of MWCNTs-Pt comprises the following stages: (i) disposition of an Au layer onto an Si substrate with the dimensions of 10 x 10 mm by Reactive Magnetron Sputtering (RMS), (ii) a photolithography process, (iii) deposition of a suspension droplet of the nanotubes decorated with Pt dispersed in anhydrous ethyl alcohol onto the transducer surface, (iv) drying in an oven for 30 minutes at the temperature of 70°C, (v) removal of a neodymium mask for protecting transducer electrodes against contamination when depositing a nanotube material, (vi) cleaning with compressed air. The distance between the individual electrodes of a single transducer was 5 µm. Figure 3 presents a photo of a transducer with the deposited material prepared for the research.

![Fig. 3. Photo of a transducer with CNT-Pt material deposited](image)

Fig. 4. Layout of station for measurement of electrical properties (based on [41])

Investigations into resistance variations of carbon nanotubes coated with platinum nanoparticles under the influence of H2 and NO2 were performed at a measuring station presented in Figure 4.

All the measurements were taken in the atmosphere of synthetic air (20% of O2 and 80% of N2) with a constant flow rate of gas of 500 ml per min. Transducer resistance with the materials deposited was measured with an AGILENT 39470 switch unit with the accuracy of ± 0.5·10⁻⁴ within the range of 10-100 Ω and ± 0.5·10⁻³ within the range of 100-999 Ω. The measurements were made at a stabilised sensor temperature of 22.5°C with the constant relative gas humidity of RH = 5.25% at room temperature (22.5°C). Investigations into resistance variations were carried out with a varying concentration of hydrogen (1, 2, 3, 4% of H2) and nitrogen dioxide (20, 100, 200, 400 ppm of NO2) in the atmosphere of synthetic air. 5-minute periods of dosing the synthetic air alternately with a gas
A mixture of H\textsubscript{2} hydrogen with synthetic air were used in the first measuring variant. A concentration of hydrogen in the atmosphere of synthetic air increased, respectively, from 1% to 4%, by 1 per cent. 30-minute periods of dosing the synthetic air alternately with a gas mixture of NO\textsubscript{2} nitrogen dioxide with synthetic air were used in the second measuring variant. An NO\textsubscript{2} concentration in the synthetic air atmosphere was increased, respectively, from 20 through 100, 200 up to 400 ppm.

### 3. Research results and discussion

Figure 5 shows the results of investigations into the resistance of carbon nanotubes decorated with platinum nanoparticles with a varying 1, 2, 3, 4% H\textsubscript{2} concentration of hydrogen in the atmosphere of synthetic air. It was found in the course of the experiment that as a hydrogen concentration is rising in the measuring system (1-4%) so is growing transducer resistance. The values of the recorded transducer resistance with the deposited CNT-Pt material are proportional to the subsequently dosed concentrations of hydrogen (1-4%), which renders the sensors scalable. The sensors’ response time to the occurrence of hydrogen in a measuring system is below 5 seconds. Similarly, the sensor are quickly, i.e. in less than 15 seconds, returning to the initial resistance values during breaks in hydrogen dosing, which signifies their high sensitivity to the varying research environment.

Identical investigations of variations in CNT-Pt nanocomposite resistance were carried out for a varying concentration of nitrogen dioxide of, respectively, 20, 100, 200, 400 ppm in the atmosphere of synthetic air, the results of which are presented in Figure 6. The investigations performed have confirmed a response of the system to the varying concentration of nitrogen dioxide. As a concentration of NO\textsubscript{2} (20-400 ppm) is heightening in a measuring system, a sensor based on nanotubes coated with platinum nanoparticles shows resistance drops. The values of the recorded resistance of the sensor system for various concentrations of nitrogen dioxide NO\textsubscript{2} (20-400 ppm) are proportional to the concentration of the supplied NO\textsubscript{2}, signifying their scalability. Similar as in the case of hydrogen, a fast response of the sensor system to the nitrogen dioxide supplied to the working chamber (below 10 seconds) and to breaks in hydrogen dosing (about 20 seconds) was recorded.

Variations in the resistance of sensors based on CNT-Pt materials, i.e. growth in case of hydrogen dosing and decline when dosing nitrogen dioxide, are the result of interactions occurring among molecules of the gas supplied

**Fig. 5.** Variations in the resistance of CNT-Pt nanocomposite with a varying 1, 2, 3, 4% H\textsubscript{2} concentration of hydrogen in the atmosphere of synthetic air (T=22°C; RH = 5.25% in 22°C)

**Fig. 6.** Variations in the resistance of CNT-Pt nanocomposite with a varying (20, 100, 200, 400 pm) concentration of nitrogen dioxide in the atmosphere of synthetic air (T=22°C; RH = 5.25% in 22°C)
platinum nanoparticles system. This phenomenon is lengthening the average free path of electrons, which translates directly into the decreased resistance of the fabricated nanocomposites.

4. Summary

Carbon nanotubes currently represent a precious material for electronic engineering. Investigations into the application of the nanotubes in an industrial scale have been conducted since discovering them, starting with modern and innovative manufacturing technologies of cables using the nanotubes [45], which are likely to replace conventional conductors, through carbon nanotube fibers connection technologies [44,46], ending with ultrasensitive selective electro-sensors which have a chance to revolutionise the market. The outcomes of the investigations presented in this article are highly utilitarian and can be applied directly in industrial conditions. A practical application of the CNT-Pt nanocomposites obtained as a result of the experiments carried out include sensors of selected chemical substances, e.g. hydrogen and/or nitrogen dioxide. The advantages of using sensors containing a CNT-Pt nanocomposite: (1) small size thus low mass and reduced production costs; (2) high chemical and thermal resistance; (3) no requirement to work at elevated temperature, as in the majority of optional solutions, which provides energy savings; (4) operating sensitivity; (5) fast reaction and (6) selectivity translating directly into detectability of several gases simultaneously. Further investigations are planned in the future into the electrical properties of nanomaterials manufactured in the presence of industrial gases such as: methane, carbon oxide or ammonia. The application of the developed materials as glucose biosensors seems to be an interesting issue. Preliminary studies have confirmed a reaction of a CNT-Pt system to the presence of glucoses in a study environment. It therefore seems that it is only a matter of time to construct a versatile sensor of chemical gases (H₂, NO₂) and biological materials (H₂O₂), the active surface of which will be made up of CNT-Pt-type nanocomposites.

References


