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## THE MWCNTs-Rh NANOCOMPOSITE OBTAINED BY THE NEW HIGH-TEMPERATURE METHOD

### NANOKOMPOZYT MWCNTs-Rh OTRZYMANY NOWĄ WYSOKOTEMPERATUROWĄ METODĄ

A nanocomposite was fabricated during the research undertaken, consisting of multiwalled carbon nanotubes coated with rhodium nanoparticles by the new high-temperature method being the subject of the patent claim. High quality multiwalled carbon nanotubes (MWCNTs) with the length of 100÷500 nm and the diameter of 8÷20 nm obtained in advance with Catalytic Chemical Vapour Deposition (CVD) were employed in the investigations. The nanotubes manufactured under the own research contain small amounts of metallic impurities and amorphous carbon deposits. Multiwalled carbon nanotubes functionalisation in acids was applied to deposit rhodium nanoparticles onto the surface of carbon nanotubes, and then the material was placed in a solution being a precursor of rhodium nanoparticles. The material prepared was next placed in a quartz vessel and subjected to high-temperature reduction in the atmosphere of argon to deposit rhodium nanoparticles onto the surface of multiwalled carbon nanotubes. The following examinations were performed, respectively: MWCNTs fabrication, fabrication of a CNT-NPs (Carbon NanoTube-NanoParticles) nanocomposite material; the characterisation of the materials produced including examination of the structure and morphology, and the assessment of rhodium nanoparticles distribution on the surface of carbon nanotubes. Micro- and spectroscopy techniques were employed to characterise the structure of the nanocomposites obtained.

*Keywords:* carbon nanotubes, nanocomposite materials, rhodium nanoparticles, transmission electron microscopy

W ramach wykonanych badań wytworzono nanokompozyt składający się z wielościennych nanorurek węglowych pokrytych nanocząsteczkami rodu nową wysokotemperaturową metodą, będącą przedmiotem zgłoszenia patentowego. W badaniach wykorzystano wysokiej jakości wielościenne nanorurki węglowe MWCNTs o długości 100÷500 nm i średnicy 8÷20 nm uprzednio otrzymane w procesie katalityczno-chemicznego osadzania z fazy gazowej (CCVD). Wytworzone w ramach prac własnych nanorurki zawierają nieznaczne ilości zanieczyszczeń metalicznych i amorficznych depozytów węglowych. W celu osadzenia nanocząsteczek rodu na powierzchni nanorurek węglowych zastosowano funkcjonalizację wielościennych nanorurek węglowych w kwasach, następnie materiał umieszczono w roztworze będącym prekursorem nanocząsteczek rodu. Przygotowany materiał umieszczono w dalszej kolejności w kwarcowym naczyniu i poddano redukcji wysokotemperaturowej w atmosferze argonu w celu osadzenia nanocząsteczek rodu na powierzchni wielościennych nanorurek węglowych. Wykonane badania obejmują kolejno: wytworzenie MWCNTs, wytworzenie materiału nanokompozytowego typu nanorurki węglowe – nanocząsteczki (CNT-NPs), scharakteryzowanie wytworzonego materiału obejmujące badanie jego struktury i morfologii oraz ocenę rozmieszczenia nanocząsteczek rodu na powierzchni nanorurek węglowych. Dla scharakteryzowania struktury otrzymanych nanokompozytów zastosowano techniki mikro- i spektroskopowe.

### 1. Introduction

The globally pursued scientific and research works reassert that carbon nanomaterials possess so far unprecedented electrical, mechanical, thermal, optical and magnetic properties [1-7]. Moreover, nanocomposite materials, in this case CNT-NPs (Carbon NanoTube-NanoParticles) nanocomposites achieve, due to synergy, improved properties, in particular electrical properties by integrating two types of materials: carbon and metal, therefore can be applied in sensors of chemical and biological substances, in which nanocomposites are a chemically active element [1,3,4]. The currently known nanocomposites consisting of carbon nanotubes together with nanoparticles of one (Au, Ag, Pt, Pd, Rh, Re) [5,6,8-10] or

more (Pd and Rh, Pt and Ru, Pt-Ru-Mo) [11-13] metals deposited on their surface are manufactured with diverse methods. In order to be able to apply CNT-NPs nanocomposites more effectively, a technology must be devised in modern industry enabling to control the uniform deposition of nanoparticles of a given metal onto the surface of carbon nanotubes.

A review of the literature points out that fabrication methods are known and described of a nanocomposite based on carbon nanotubes and rhodium nanoparticles using a plasma generator [14], chemical reduction using NaBH<sub>4</sub> of relevant compounds, mainly salt, being the precursors of selected metals [15], i.e. electrodesposition of metallic nanoparticles onto carbon nanotubes [16]. This paper presents the unpublished to date optional method of fabricating a nanocomposite con-

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sisting of carbon nanotubes joined permanently with rhodium occurring in the form of nanocrystals. The new developed method is based on high-temperature reduction of a substance containing rhodium nanoparticles [17].

This paper discusses the following detailed examinations: fabrication of a CNT-NPs nanocomposite material using MW-CNTs produced earlier as part of own works; the characterisation of the material produced including examination of its structure and morphology, and the assessment of rhodium nanoparticles distribution on the surface of carbon nanotubes. The following research techniques were employed to characterise the structure of the nanotubes and nanocomposites obtained: Scanning Electron Microscopy (SEM), Scanning Transmission Electron Microscopy (STEM), Transmission Electron Microscopy (TEM), Energy Dispersion Spectroscopy (EDS) and Raman spectroscopy.

## 2. Experimental studies

### 2.1. Materials

Multiwalled carbon nanotubes, being an input material used further in the research to fabricate an MWCNTs-Rh nanocomposite, were produced with Catalytic-Chemical Vapour Deposition (CCVD) using an EasyTube@2000 device. The nanotubes were manufactured on a silicon substrate containing a catalyst in the form of a thin film and two buffer layers (2 nm Fe, 15 nm Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>). The growth of the nanotubes was controlled in an oven at a temperature of 750°C for 45 minutes using ethylene (C<sub>2</sub>H<sub>4</sub>) as a source of carbon. Details concerning the synthesis process of carbon nanotubes are described in the author's another work [18]. Fig. 1 presents an SEM image of parallelly oriented multiwalled carbon nanotubes directly after a synthesis process

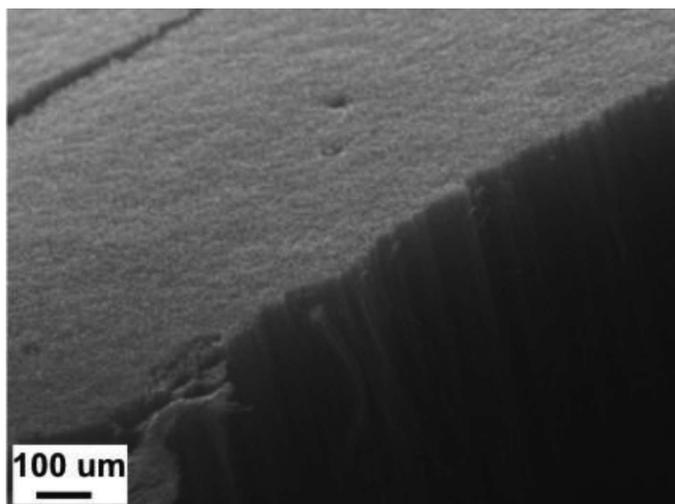


Fig. 1. SEM image showing “forest” of MWCNTs produced with CCVD method

with the CCVD method forming a so-called “forest” of nanotubes. Fig. 2 presents a TEM image of pure multiwalled carbon nanotubes before the process of decoration with rhodium nanoparticles. Rhodium chloride (III), i.e. RhCl<sub>3</sub>, was used

in the decoration process of multiwalled carbon nanotubes of rhodium nanoparticles as a precursor.

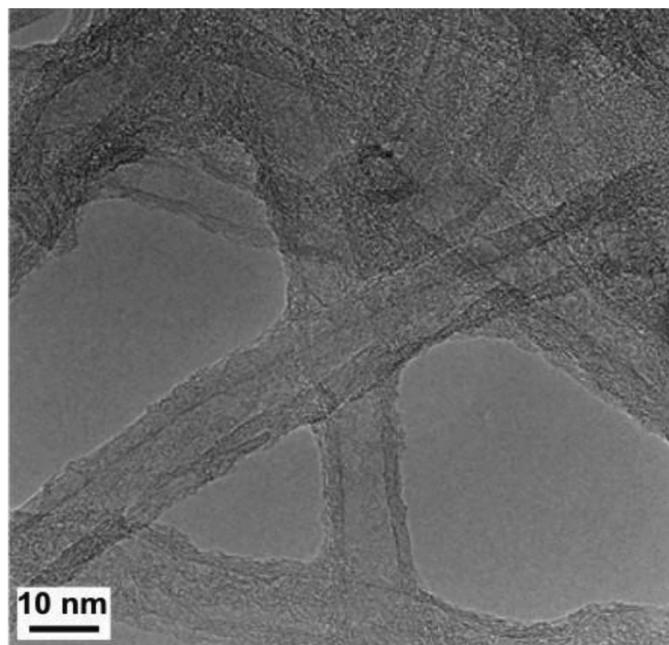


Fig. 2. TEM image of pristine MWCNTs being the input material for MWCNTs-Rh nanocomposite fabrication

### 2.2. Synthesis of MWCNT-Rh nanocomposite

In order to produce function groups on the surface of carbon nanotubes to which rhodium nanoparticles were attached at the next stage, the multiwalled carbon nanotubes were subjected to functionalisation with a mixture of HNO<sub>3</sub> acids with the concentration of 65% and with H<sub>2</sub>SO<sub>4</sub> the concentration of 95% at a rate of 1:3. Functionalisation lasting 2 hours was carried out in an ultrasound washer at an elevated temperature of 60°C, and the mixture was then put aside under cover without any interference for 24 hours. The mixture was further filtered and the acid mixture was collected.

The process of carbon nanotubes decoration with rhodium nanoparticles was carried out in a high-temperature furnace with a high-temperature reduction reaction of rhodium chloride solution (RhCl<sub>3</sub>). The functionalised carbon nanotubes were placed in RhCl<sub>3</sub> solution and then subjected to the activity of ultrasounds for 2 hours and put aside for 24 hours. The wet carbon-metal material deposited onto the surface of a boat-sized quartz vessel was placed in a quartz sample feeder and placed into a heated furnace with a temperature of above 800°C, and then the material was subjected to heating at 850°C for 45 minutes in the argon atmosphere with the flow rate of 2 SLPM. After finishing heating, the sample was cooled to room temperature, removed from the oven and quartz vessel, and then was subjected to microscopic and spectrometric investigations. The described method of MWCNTs-Rh nanocomposite high-temperature fabrication is new and is subject to a patent claim [17].

### 2.3. Methodology

The carbon nanotubes and carbon-metal nanocomposites obtained were observed using electron scanning and transmission microscopes. SEM images were made using a Scanning Electron Microscope SEM Supra 35 by Carl Zeiss equipped with the X radiation spectrometers: an energy dispersion EDS and wavelength WDS spectrometer and a system for analysing diffraction of back scattered electrons EBSD by EDAX. The high resolution and the precision imaging of the preparations viewed was achieved by applying a high-performance In-lens SE detector working at low beam voltage and very small distance of the preparation examined to the electron gun. TEM images were made using a Transmission Electron Microscope STEM TITAN 80-300 by FEI fitted with an electron gun with FEG field emission, a condenser spherical aberration corrector, STEM scanning system, bright and dark field detectors, High Angle Annular Dark Field (HAADF), and EFTEM energy image filter and an EDS used for determining the chemical composition of the nanocomposite obtained. The exact imaging of the materials examined was possible by applying an HAADF detector (Z contrast). Atomic numbers in the case of an MWCNTs-Rh nanocomposite differ largely and are, respectively: for carbon  $Z=6$ , and for rhodium  $Z=45$ . Preparations for transmission electron microscopy investigations are prepared by dispersing the nanocomposites obtained in ethanol using an ultrasound washer, and then by depositing them using a pipette with droplets onto a copper mesh. The material deposited as a droplet is dried with free air at room temperature.

The degree of defects of the obtained carbon nanotubes and carbon-metal nanocomposites' structure was examined using a in Via Reflex Raman Spectrometer by Renishaw fitted with a confocal Research Grade microscope by Leica where specimens can be observed in the reflected and transiting light. Excitations were carried out with a line with the wavelength of  $\lambda = 514$  nm of an ion-argon laser with the capacity of 50 mW, with

a plasma filter for 514 nm. Laser capacity adjustment range is between 0.00005% to 100% inclusive. The measurements were recorded using a Long Working Distance (LWD) lens with magnification of twenty times. Materials for the investigations using a Raman spectroscope were prepared by depositing a material onto a glass substrate. The so prepared preparations were examined over the entire range of spectrum registration, i.e. 50-4100  $\text{cm}^{-1}$ .

## 3. Results and discussion

### 3.1. Microscope research

As part of the microscope investigations carried out of the MWCNTs-Rh nanocomposite, observations were made in bright field using a Transmission Electron Microscope (TEM). Fig. 3 presents carbon nanotubes together with rhodium nanoparticles permanently deposited on their surface, which are spherically shaped, and their diameter is between 2 and 10 nm. Fig. 4 presents a High-Resolution TEM (HRTEM) image of rhodium nanocrystal permanently deposited on the surface of a multiwalled carbon nanotube with clearly visible crystalline planes.

An HAADF detector working in the STEM mode, i.e. with a concentrated beam of electrons, and not as is the case in the TEM mode, with a parallel beam, was utilised to obtain more accurate information about the arrangement of rhodium nanoparticles on the surface of carbon nanotubes. Considering a large difference between the value of atomic numbers of elements forming part of a nanocomposite, i.e., respectively, 6 for carbon and 45 for rhodium, high Z contrast is present as a result of which rhodium nanoparticles are seen as lightly illuminating precipitates on the surface of dark grey or nearly black carbon nanotubes. Observations in the dark field reaffirm that the size of rhodium nanoparticles on the surface

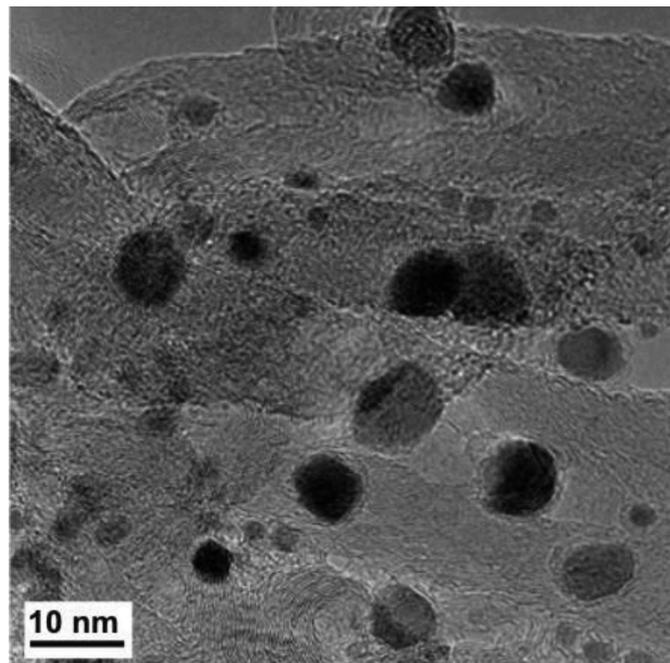


Fig. 3. TEM image of MWCNTs-Rh nanocomposite

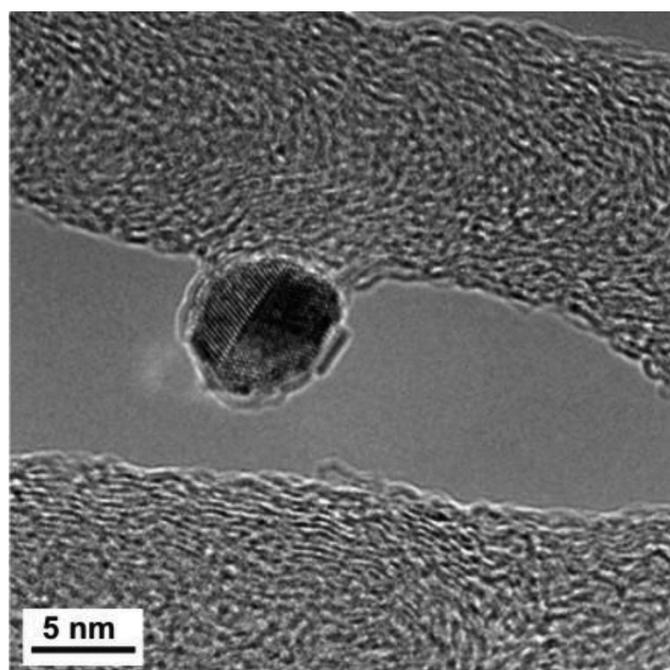


Fig. 4. HRTEM image of single Rh nanocrystal permanently deposited on surface of multiwalled carbon nanotube

of carbon nanotubes is quite differentiated within the whole volume of the observed nanocomposites and their diameter is usually within the range of  $2\div 10$  nm (Fig. 5). Few single rhodium nanoparticles with the diameter of above 10 nm were observed, however, which was marked with a red rectangle in Fig. 6. Both, a crystalline structure of rhodium nanoparticles as well as crystallographic planes characteristic for it, similar as in the bright field, can be observed also in the dark field (Fig. 7).

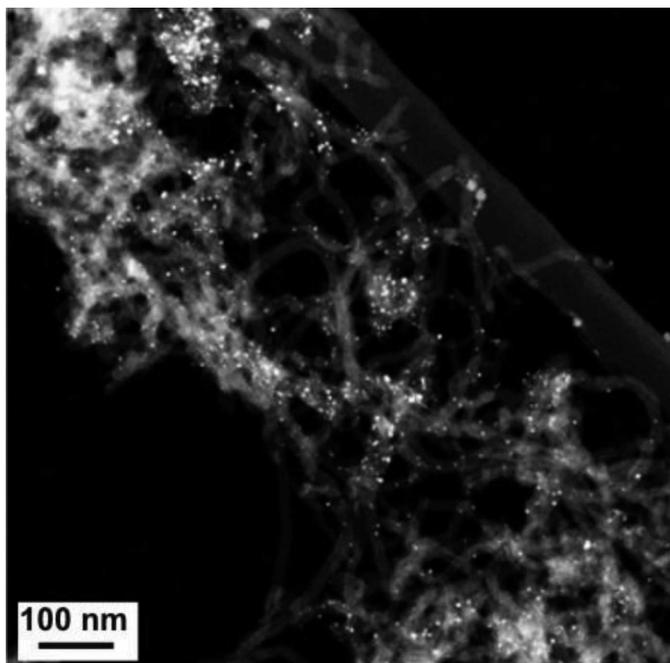


Fig. 5. STEM image of MWCNTs-Rh nanocomposite made using HAADF detector

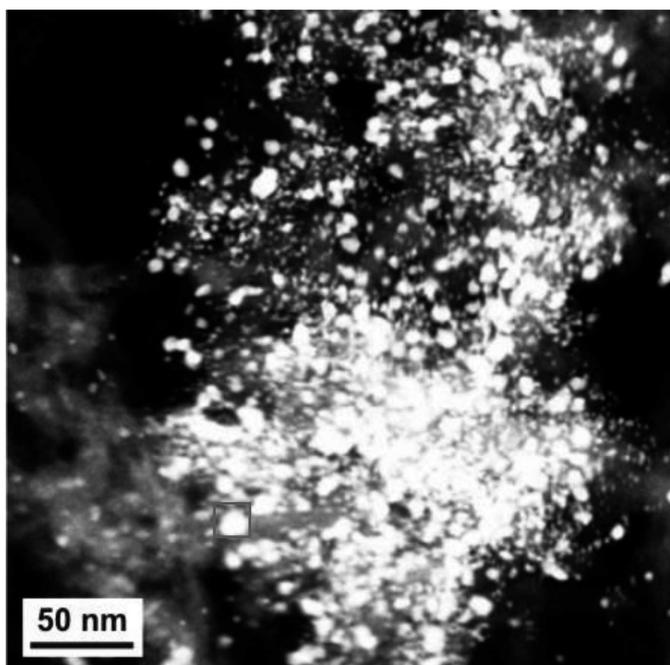


Fig. 6. STEM image made using HAADF detector presenting MWCNTs-Rh nanocomposite with a large number of agglomerates and an example of a large Rh nanoparticle ( $\varphi > 10$  nm) marked with red rectangle

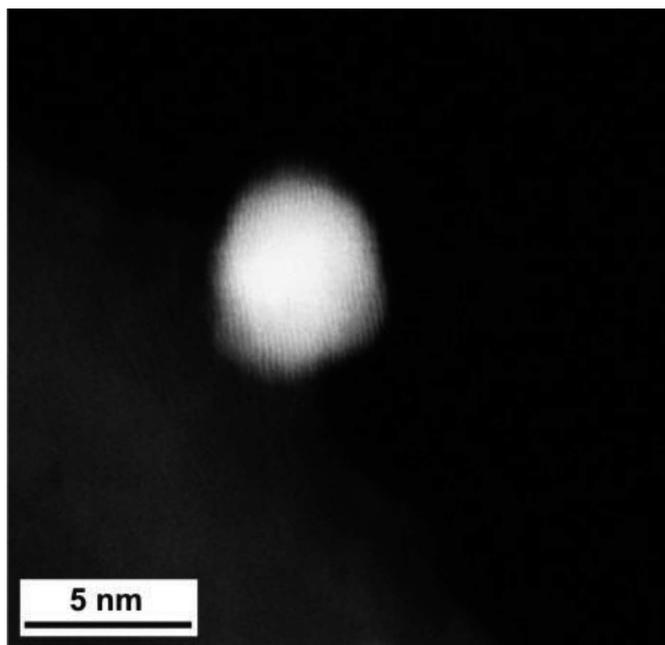


Fig. 7. STEM image of single rhodium nanocrystal made with HAADF detector

The experiments performed indicate that the agglomeration of rhodium nanoparticles is dependent on the following factors: the number of function groups created on the surface of nanotubes in the functionalisation process, a concentration of rhodium chloride solution and the time and temperature of sample heating in the oven. The authors of the article are planning further experiments to identify precisely the influence of the particular listed factors on the agglomeration of rhodium nanoparticles on the surface of carbon nanotubes. Further investigations are planned aimed at, optionally, widening or narrowing the set of the most significant factors, to clearly identify what is determining the uniformity of rhodium nanocrystals' distribution on the surface of carbon nanotubes and what is decisive for the diameter of nanocrystals. The actions are to finally contribute to optimisation of the MWCNTs-Rh nanocomposite fabrication process and the related possibility of designing, at first, both the extent to which carbon nanotubes are loaded with rhodium nanoparticles, as well as the diameter of Rh nanocrystals.

### 3.2. Spectroscopy research

The spectroscopy examinations presented in the article were carried out with two specialist instruments. A qualitative analysis of chemical composition from the microarea and from a specific point of the studied carbon-metal preparation was performed with Energy Dispersive Spectroscopy (EDS) by EDAX. The defects degree of the structure of carbon nanotubes decorated with rhodium against the defects degree of pristine carbon nanotubes and carbon nanotubes after functionalisation was determined using Via Reflex Raman Spectrometer by Renishaw.

Particular elements forming the given material were identified through an EDS analysis based on the radiation energy value recorded by the instrument expressed with [keV], which is individual and specified for each element. A qualitative analysis of chemical composition from the microarea was

made as part of the experiments, the results of which are shown in Fig. 8 and with a point analysis the results of which are presented in Fig. 9. Fig. 10 shows a TEM image with a microarea marked and a point with reference to which a spectral analysis of chemical composition of the newly developed MWCNTs-Rh nanocomposite was made as

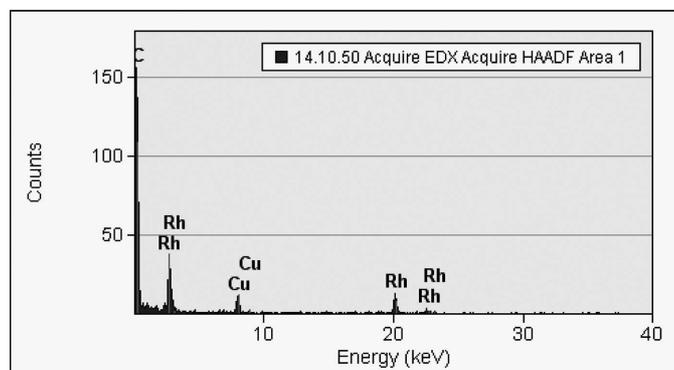


Fig. 8. A qualitative analysis of chemical composition from a microregion performed with the EDS method

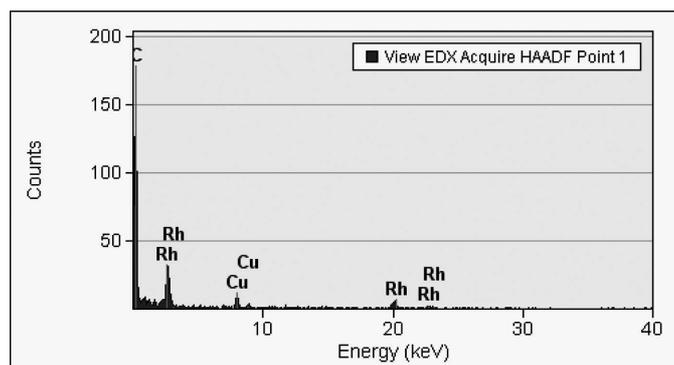


Fig. 9. A point qualitative analysis of chemical composition performed with the EDS method

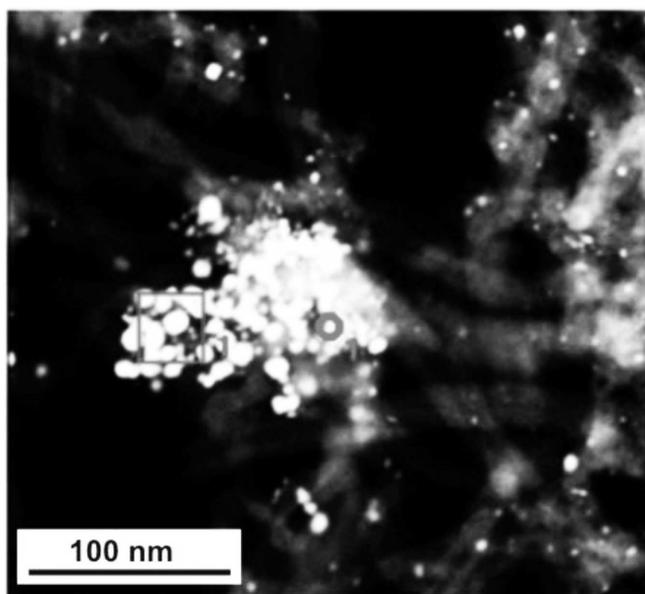


Fig. 10. TEM image made with the HAADF detector with a microarea marked (red rectangle) and point (red circle) in relation to which spectral qualitative analysis of chemical composition was made

presented in, respectively, Fig. 8 and 9. A spectral qualitative (point and microarea) analysis of chemical composition has revealed that the composition of the investigated preparation contains Rh, C related to the presence of carbon nanotubes and Cu, the presence of which is explained by a copper mesh used at the stage of preparation, onto which the studied nanocomposite was deposited.

Investigations with a Raman spectrometer have indicated the occurrence of bands characteristic for multiwalled carbon nanotubes for all the three investigated materials. A spectrum of pristine carbon nanotubes (Fig. 11a) is characterised by the occurrence of the following bands: *D* ( $1344\text{ cm}^{-1}$ ), *G* ( $1571\text{ cm}^{-1}$ ) and *G'* ( $2682\text{ cm}^{-1}$ ). The following bands exist for the spectrum of functionalised nanotubes (Fig. 11b): *D* ( $1346\text{ cm}^{-1}$ ), *G* ( $1581\text{ cm}^{-1}$ ) and *G'* ( $2697\text{ cm}^{-1}$ ). A spectrum of carbon nanotubes decorated with rhodium, being an MWCNTs-Rh nanocomposite (Fig. 11c), is characterised by the occurrence of the following band: *D* ( $1343\text{ cm}^{-1}$ ), *G* ( $1571\text{ cm}^{-1}$ ) and *G'* ( $2680\text{ cm}^{-1}$ ). Table 1 presents a summary list of numerical values of all the characteristic spectrum bands recorded for each of the studied materials.

The intensity of band *D* recorded for pristine MWCNTs is higher than the intensity of band *G*, which may signify the presence of small impurities in the material. Such theory is confirmed by TEM observations which have revealed small amounts of amorphous carbon and/or residual catalyst particles. Functionalised carbon nanotubes are characterised by the

TABLE 1  
Results of Raman spectroscopy research conducted for pristine MWCNTs, functionalized MWCNTs and MWCNTs-Rh nanocomposite

Materials	Raman shift [ $\text{cm}^{-1}$ ]			Intensity			$I_D/I_G$
	<i>D</i>	<i>G</i>	<i>G'</i>	<i>D</i>	<i>G</i>	<i>G'</i>	
Pristine MWCNTs	1344	1571	2682	2389	2144	1198	1,11
Functionalized MWCNTs	1346	1581	2697	5270	5370	1652	0,98
MWCNTs-Rh nanocomposite	1343	1571	2680	2385	2141	1203	1,11

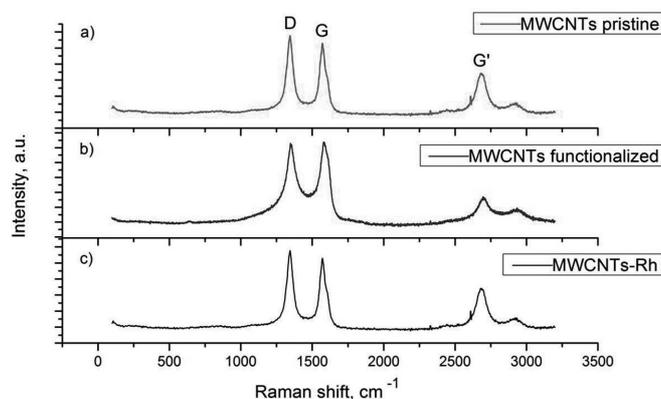


Fig. 11. Raman spectra: a) for multi-walled carbon nanotubes fabricated with the CCVD used for the experiment, b) of functionalized multi-walled carbon nanotubes, c) of multi-walled carbon nanotubes with rhodium nanoparticles

changed shape and increased intensity of band *D*, which signifies the defects of their structure equivalent with the presence of components corresponding to  $sp^3$  hybridisation and/or distortions of  $sp^2$  hybridisation towards  $sp^3$  hybridisation, which is connected with higher reactivity of carbon nanotubes after the functionalisation process [19-21].

The intensity ratio of the bands *D* to *G* ( $I_D/I_G$ ) was also assessed in the course of the works. A variation in the value of this coefficient in the oxidised material results from changes in the geometry of MWCNTs, caused by the formation of function groups. It was revealed by analysing the functionalised MWCNTs in relation to pristine nanotubes that the bands *D* and *G* have shifted by, respectively:  $2\text{ cm}^{-1}$  and  $10\text{ cm}^{-1}$ , which can be caused by doping after treatment of nanotubes with a mixture of acids, as the oxidisation process also significantly influences the structure of carbon nanotubes' walls [22,23]. The defected structure of the material after functionalisation is manifested by small extension of the analysed bands, as shown in Fig.11b.

A Raman spectrum of an MWCNTs-Rh nanocomposite in terms of the shape and intensity of its characteristics bands, i.e. *D*, *G* and *G'*, is very similar to the spectrum of pristine carbon nanotubes, which should be related to the improved quality of the material as a result of interaction of high temperature (over  $800^\circ\text{C}$ ) [24] accompanying the process of nanotube decoration with rhodium nanoparticles in a CVD furnace.

#### 4. Conclusions

The article presents the outcomes of investigations into the new method of CNT-NPs nanocomposites high-temperature fabrication, where rhodium is a nanoparticle deposited onto the surface of multiwalled nanotubes [17]. Investigations using transmission electron microscopy together with an EDS analysis have confirmed the fact of producing an MWCNTs-Rh nanocomposite with a new method. The rhodium nanoparticles obtained are spherically shaped and their diameter is usually between 2 and 10 nm. Minor single rhodium nanoparticles with diameter over 10 nm were also observed. The examinations carried out using a Raman spectrometer have shown a modification of nanotubes' structure on particular stages on the fabrication process. Functionalised carbon nanotubes are distinctive for the highest level of defects which is higher than a defect level of pristine nanotubes as well as those decorated with rhodium nanoparticles, which should be associated with the interacting high temperature accompanying the last stage of MWCNTs-Rh nanocomposite fabrication on the decreased number of defects.

The proposed method of high-temperature fabrication of an MWCNTs-Rh nanocomposite is effective and relatively simple, however it requires further studies into the optimisation of a nanocomposite fabrication process and the related possibility of designing, at first, both the extent to which carbon nanotubes are loaded with rhodium nanoparticles, as well as the diameter of Rh nanocrystals. Rhodium, as a metal from the light platinum group, has influence on electrical properties of a nanocomposite, which is especially interesting for the authors of the article in terms of the future application of the material as active substances of sensors of chemical/biological

compounds and provides the next step of the research works being implemented. Furthermore, the authors are planning to broaden the possibility of characterising the nanocomposite to include examinations with Fourier Transform Infrared (FTIR) to confirm and distinguish function groups achieved on the surface of nanotubes after the functionalisation process, and also an additional chemical composition analysis through X-ray Photoelectron Spectroscopy (XPS). Actions are also being carried out at the same time to produce a nanocomposite consisting of single- or multiwalled nanotubes permanently attached to nanoparticles of at least two precious metals, of which one is Rh, attached as a result of a high-temperature reduction reaction, which is a subject of the patent claim [25].

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