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Obtaining and description of the MWCNTs-Pd nanocomposite

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ABSTRACT

Purpose: The main aim of the research was to produce nanocomposites consisting of carbon nanotubes coated with palladium nanoparticles and the characterisation of the obtained materials.

Design/methodology/approach: High quality multiwalled carbon nanotubes (MWCNTs) with the length of 100-400 nm and the diameter of 6-25 nm obtained in advance with Catalytic Chemical Vapour Deposition (CCVD) were employed in the investigations. Carbon nanotubes–palladium nanoparticles system was fabricated by direct deposition of palladium nanoparticles, produced earlier, onto the surface of multiwall carbon nanotubes.

Findings: The investigations using transmission electron microscopy together with an EDS and XPS analysis have confirmed the fact of producing an MWCNTs-Pd nanocomposite. Examinations with Raman spectroscopy have allowed to determine the difference between the degree of defects of carbon nanotubes before and after modification with palladium nanoparticles.

Research limitations/implications: The presence of palladium has influence on the electrical properties of the nanocomposite, enhances sensitivity and selectivity of the CNTs-NPs system in contact with the chosen chemical substance, and the result is the changing of the conductivity of nanotubes. It is a basis for the application of the studied material as an active substance of sensors of chemical/biological compounds.

Originality/value: The paper presents the results of investigations relating to the synthesis of a nanocomposite material consisting of multiwalled carbon nanotubes and Pd nanoparticles and the characteristics of the material produced in terms of its structure, morphology and the distribution of Pd nanoparticles on the external surface of multiwalled carbon nanotubes and chemical composition.

Keywords: Nanomaterials; Carbon nanotubes; Palladium nanoparticle; Nanocomposites MWCNTs-Pd

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MATERIALS

1. Introduction

Carbon CNT-NPs (Carbon NanoTube-NanoParticles) nanocomposites are a valuable material due to their unique properties, in particular electrical properties resulting from the synergy effect consisting of interaction of two types of materials, i.e. carbon and metal. A possibility of using nanocomposites in the sensors of chemical and biological substances is especially important. The literature describes nanocomposites consisting of carbon nanotubes together with nanoparticles of different metals deposited onto their surface (Au, Ag, Pt, Pd, Rh, Re, Ru, Ni) [1,2] fabricated with various methods and their practical applications in sensors. Several interesting technologies of deposition of palladium nanoparticles onto the surface of carbon nanotubes have been developed to date, in particular electroless deposition methods [1], chemical and physical deposition methods [3,4], electrochemical methods [5], chemical methods with reduction of colloidal solutions [6,7] and methods employing gamma irradiation [8]. A process of placing palladium nanoparticles inside carbon nanotubes has also been carried out [9]. The following is decorated most often with the precursors of palladium particles in different processes: $PdAc_2$ [10], $(NH_4)_2[PdCl_4]$ [5], K_2PdCl_4 [10], $PdCl_2$ [8], Na_2PdCl_4 [11], H_2PdCl_4 [12]. Nanocomposites containing Pd nanoparticles, apart from sensoric applications, exhibit a high hydrogen storage potential [12]. In order to be able to apply CNT-NPs nanocomposites practically, it is essential to develop an effective and affordable technology enabling to control the uniform deposition of nanoparticles of a given metal onto the surface of carbon nanotubes. An indirect method consisting of fabrication of CNT-NPs nanocomposites in two separate processes conducted independently is used in this work. Oxidised nanotubes with function groups on their surface are obtained in a separate process and Pd nanoparticles are obtained in a separate process. A reduction agent must also be added.

The article presents the results of investigations relating to the synthesis of a nanocomposite material consisting of carbon nanotubes and palladium nanoparticles and the characteristics of the material produced in terms of its structure, morphology and the distribution of palladium nanoparticles on the surface of carbon nanotubes and chemical composition. 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 Spectrometer (EDS), Raman spectroscopy and X-ray Photoelectron Spectroscopy (XPS).

2. Experimental

2.1. Materials

Multiwalled carbon nanotubes were fabricated by Catalytic-Chemical Vapour Deposition (CCVD). The material was synthesised on a silicon substrate containing a catalyst in the form of a thin film of 2 nm Fe. The growth of the nanotubes was controlled in an oven at a temperature of 750°C for 30 minutes using the mixture of the following gases: C_2H_4, H_2, Ar. Details concerning the synthesis process of carbon nanotubes and its optimisation are described in the author's another work [13]. Figure 1 presents an SEM image of parallely oriented multiwalled carbon nanotubes directly after a synthesis process with the CCVD method. Figure 2 presents a TEM image of pristine multiwalled carbon nanotubes before the process of decoration with palladium nanoparticles.

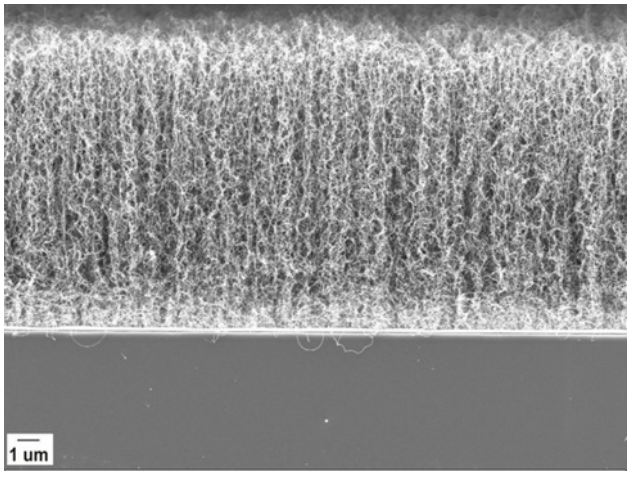

Fig. 1. SEM image made directly after MWCNTs synthesis with the CCVD method

The multiwalled carbon nanotubes were subjected to functionalisation with a mixture of HNO_3 (65%) and H_2SO_4 (95%) concentrated at a rate of 1:3 in order to obtain function groups on the outer surface of the carbon nanotubes which are used for bonding the palladium nanoparticles. Functionalisation lasted 2 hours and was

carried out in an ultrasound washer at an elevated temperature of 60°C. The mixture was then put aside under cover without any interference for 24 hours, and the mixture was further filtered and the acid mixture was collected.

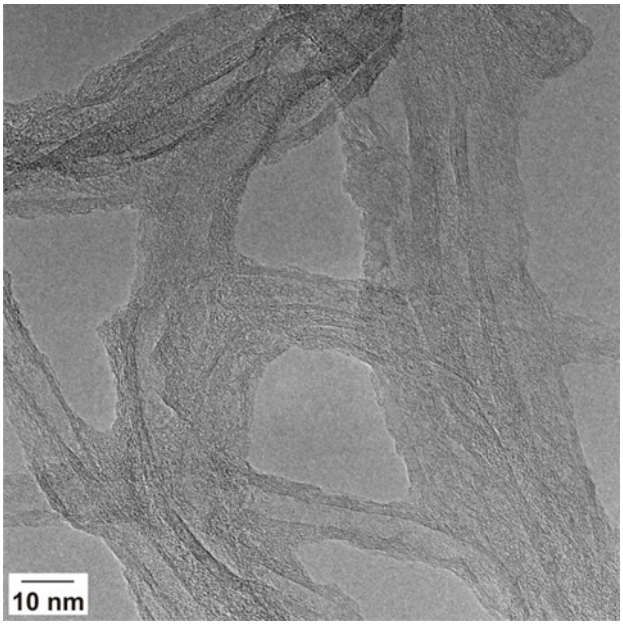

Fig. 2. TEM image of pristine MWCNTs being the input material for MWCNTs-Pd nanocomposite synthesis

A synthesis of palladium nanoparticles was carried out as a result of the reduction reaction of palladium chloride mixture (II) $PdCl_2$ with ethylene glycol and sodium citrate. The functionalised multiwalled carbon nanotubes, with 15 ml of ethylene glycol added, were dispergated in an ultra-sound washer for 30 minutes. 5 ml of acetone was added to the suspension obtained during constant mixing with a magnetic stirrer. Then, after 5 minutes, the appropriate amount of palladium chloride (II) PdCl2 and sodium citrate was added to the suspension. All this was heated under a reflux condenser for 2.5 hours at a temperature of 130°C. The material achieved was then filtered and washed in deionised water, and then the sample was dried for 12 hours at 120°C.

2.2. Research methodology

The carbon nanotubes and carbon-metallic nanocomposites achieved were observed using scanning and transmission electron microscopes. SEM images were made using a scanning electron microscope SEM Supra 35 by Carl Zeiss. TEM images were made using an STEM TITAN 80-300 transmission electron microscope by FEI. The exact imaging of the materials examined was possible by applying an HAADF detector (Z contrast). The preparations for transmission electron microscopy investigations are prepared by dispergating the nanocomposites obtained in ethanol using an ultrasound washer, and then by depositing them using a pipette with droplets onto a copper mesh covered with a carbon film. The preparation is dried with free air at room temperature. The carbon-metallic material was subjected to a local quality analysis of chemical composition with Energy Dispersive Spectroscopy (EDS) by EDAX. The degree of defects of the newly fabricated carbon-metal CNTs-NP nanocomposites' structure compared to pristine carbon nanotubes being the input material for further fabrication of nanocomposites was examined using a Raman 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 beam with the wave-length of λ = 514 nm of an ion-argon laser with the power of 50 mW, with a plasma filter for 514 nm. The laser power adjustment range is between 0.00005% to 100% inclusive. Measurements were recorded using a Long Working Distance (LWD) lens with magnification of x20. A chemical composition analysis by X-ray Photoelectron Spectroscopy (XPS) was carried out with an X-ray photoelectron spectroscope by Physical Electronics PHI 5700/660. Monochromatic X-ray radiation coming from an Al Kα aluminium anode with radiation energy of hν = 1486.6 eV was utilised for the measurements. The material intended for the tests was deposited directly onto the surface of the standard specimen carrier and placed in an XPS measuring chamber. Survey spectra within a wide range of binding energy of 0-1400 eV were measured under the investigations.

3. Results

3.1. Microscopic research results

The microscopic examinations of the MWCNTs-Pd nanocomposite were carried out in the bright and dark field using a transmission electron microscope (TEM). Figure 3 presents carbon nanotubes together with palladium nanoparticles permanently deposited on their surface occurring individually and in small agglomerated

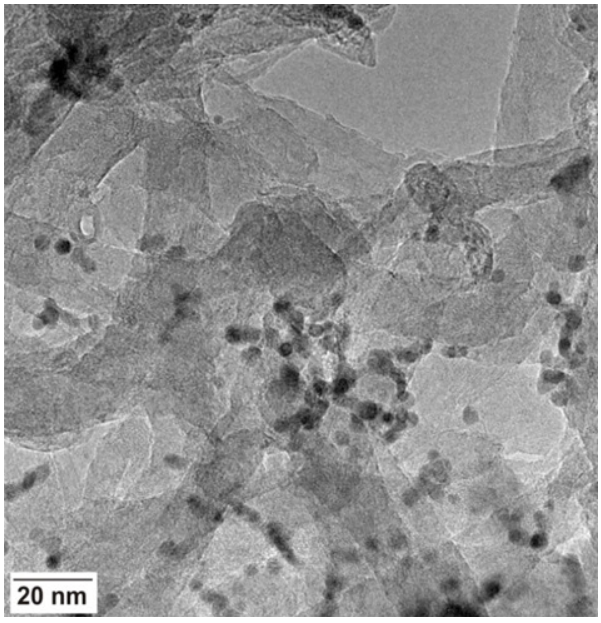

Fig. 3. TEM image of MWCNTs-Pd nanocomposite

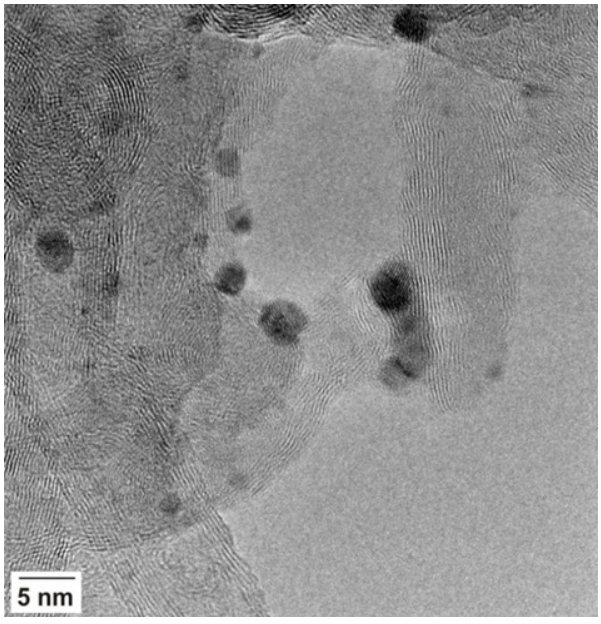

Fig. 4. HRTEM image of Pd nanocrystals permanently deposited on surface of multiwalled carbon nanotube

groups. The particles are spherically shaped and their diameter is between 2 and 8 nm. Figure 4 presents a high-resolution TEM (HRTEM) image of palladium nanocrystals permanently deposited on the surface of a multiwalled carbon nanotube with clearly visible crystalline planes. Palladium nanoparticles are visible during observations in the dark field as lightly illuminating

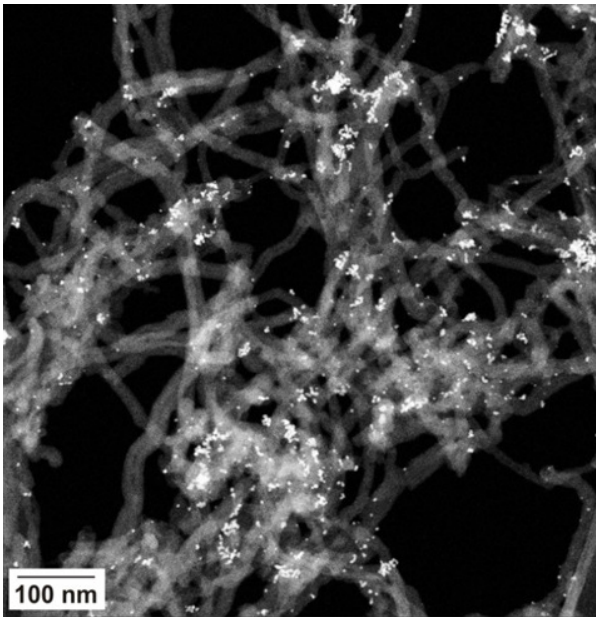

Fig. 5. STEM image of MWCNTs-Pd nanocomposite made using HAADF detector

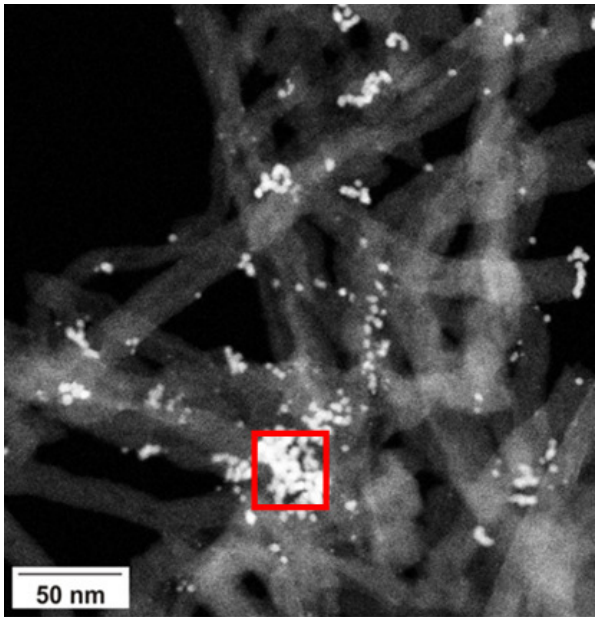

Fig. 6. STEM image made using HAADF detector presenting MWCNTs-Pd nanocomposite with a large number of agglomerates marked with red rectangle

precipitates on the surface of grey carbon nanotubes (Figs 5-6). This results from a large difference between the value of atomic numbers of elements forming part of the nanocomposite, i.e., respectively, 6 for carbon and 46 for

palladium. Observations with an HAADF detector confirm that the distribution and size of palladium nanoparticles on the surface of carbon nanotubes is quite differentiated within the whole volume of the observed nanocomposites (Fig. 5). Spots with large agglomeration of synthesised palladium nanoparticles were also observed, and one of such spots is marked with a red square in Fig. 6.

The preliminary experiments performed indicate that the agglomeration, shape and size of palladium nanoparticles is dependent on the following factors: the number of function groups created on the surface of nanotubes in the functionalisation process [14], the mass fraction and type of the metal nanoparticles precursor and the time and temperature of heating the suspension. The authors of the article are planning further experiments to identify precisely the influence of the particular listed factors on the agglomeration of palladium nanoparticles on the surface of carbon nanotubes.

3.2. Spectroscopic research results

A qualitative analysis of chemical composition from the microarea (Fig. 7) and a local analysis were made as part of the experiments conducted, the results of which are shown in Figure 8. A spectral qualitative analysis of chemical composition has revealed that the composition of the investigated preparation contains palladium, carbon related to the presence of carbon nanotubes, and copper, the presence of which is explained by a copper mesh used at the stage of preparation, onto which the studied nanocomposite was deposited.

Figure 9 presents Raman spectra recorded for pristine carbon nanotubes and MWCNTs-Pd nanocomposites. Table 1 presents a summary of numerical values of the characteristic bands recorded for the studied materials. A spectrum of pristine carbon nanotubes is characterised by the occurrence of the following bands: D (~1344 cm^{-1}), G (~1572 cm^{-1}) and 2D (~2683 cm^{-1}). A Raman spectrum recorded for the MWCNTs-Pd nanocomposite has the following peaks: D (~1348 cm^{-1}), G (~1577 cm^{-1}) and 2D (~2690 cm^{-1}). The intensity of band D corresponding to the MWCNTs-Pd nanocomposite is higher than intensity corresponding to pristine carbon nanotubes, and also a shift of the bands D,G and 2D is seen by, respectively, about 4 cm^{-1}, 5 cm^{-1} and 7 cm^{-1} in relation to pristine nanotubes. The ratio ID/IG for a sample of pristine nanotubes is 1.08, while it is 1.00 for the MWCNTs-Pd nanocomposite. A comparative analysis of variations in the ratio of the intensity of 2D band and the D band (I_{2D}/I_D) was also undertaken due to the fact that the 2D band is independent of the impurities present in the sample. The value of the quotient I_{2D}/I_D for pristine nanotubes is 0.53, and for MWCNTs-Pd nanocomposites - 0.37. The results presented confirm that chemical changes have taken place in the studied material caused by the functionalisation of carbon nanotubes and the further attachment of palladium nanoparticles to their surface.

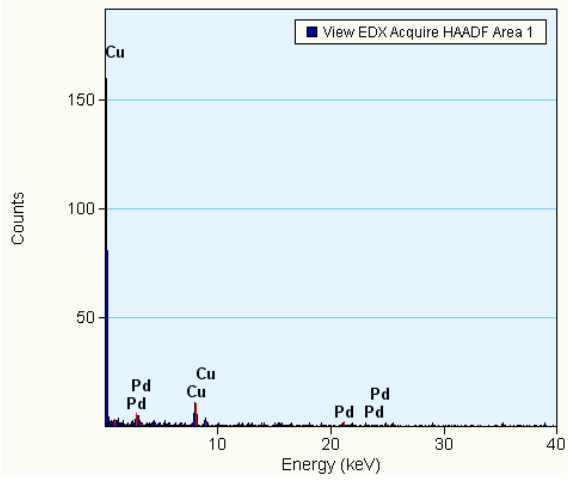

Fig. 7. A qualitative analysis of chemical composition from a microregion was made with the EDS method

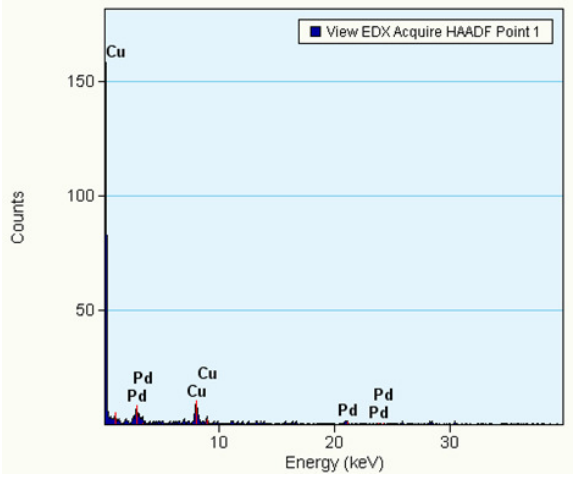

Fig. 8. Point qualitative analysis of chemical composition performed with the EDS method

X-ray Photoelectron Spectroscopy (XPS) methods have been used in order to analyse more accurately the quality and quantity of chemical composition of nanocomposites created in the Pd nanoparticles deposition process on the surface of carbon nanotubes as compared to

pristine MWCNTs. Figure 10 shows a review spectrum created as a result of examining unmodified carbon nanotubes with X-ray Photoelectron Spectroscopy (XPS). Two main photoemission lines are shown on the spectrum corresponding, respectively, to electron states of carbon marked as C1s (maximum counts for the binding energy of 285 eV) and oxygen marked as O1s (maximum counts for the binding energy of 533 eV). Carbon content in the material was identified at the level of 97.22% in atomic terms, while oxygen contents – 2.78% in atomic terms. A small amount of the adsorbed oxygen as compared to the amount of carbon signifies a very good quality of the studied material. The presence of the Auger line for carbon C KLL (above 1200 eV) and oxygen O KLL (about 980 eV) was also observed on the analysed spectrum.

Table 1.
The results of comparative spectroscopy examinations of pristine carbon nanotubes and MWCNTs-Pd nano-composites

Materials	Raman shift (cm^{-1})	I_D/I_G
Pristine MWCNT	(D) 1344, (G) 1572, (2D) 2683	1.08
MWCNTs-Pd	(D) 1348, (G) 1577, (2D) 2690	1.00
Materials	Intensity (a.u)	I_{2D}/I_D
Pristine MWCNTs	(D) 2315, (G) 2141, (2D) 1224	0.53
MWCNTs-Pd	(D) 2967, (G) 2957, (2D) 1086	0.37

The recorded photoemission measurements for MWCNTs-Pd nanocomposites were obtained in a wide range of binding energy and presented in Figure 11. Photoemission lines are visible on the spectrum coming from the states of core lines of carbon C1s (about 284 eV), oxygen O1s (about 531 eV), Auger lines C KLL (approx. 1200 eV) and O KLL (about 980 eV). Photoemission lines coming from palladium were also recorded: connected with the state of fluorine F1s, F KLL and nitrogen N1s. The presence of the mentioned elements in the spectrum indicates that the nanocomposites produced are contaminated with, respectively, fluorine and nitrogen, however, the contamination level is low and is in total, for both elements, below 0.4% in atomic terms. The concentration of the basic elements making up the nanocomposite MWCNTs-Pd is at the following level: carbon C = 86.89% at., oxygen O_2 = 12,03% at. and palladium Pd = 0.67% at. Table 2 compares a chemical composition analysis of pristine carbon nanotubes and nanocomposites consisting of carbon nanotubes and palladium nanoparticles.

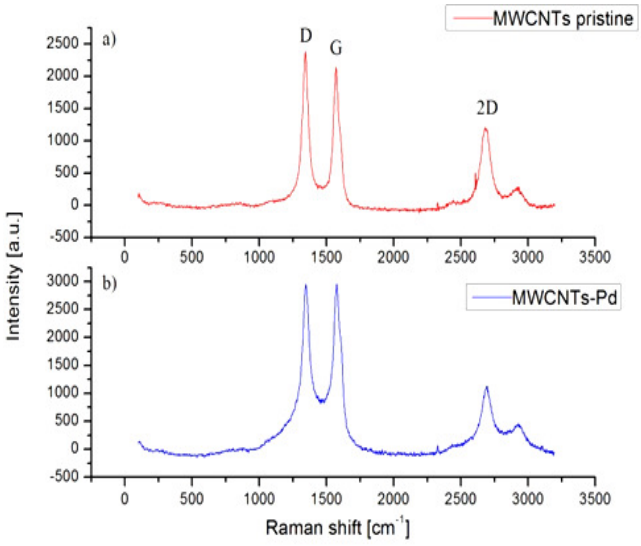

Fig. 9. Raman spectra: a) for pristine multi-walled carbon nanotubes, b) of multi-walled carbon nanotubes with palladium nanoparticles

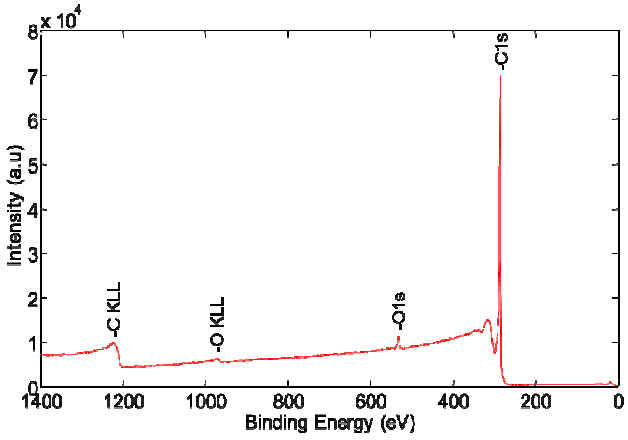

Fig. 10. XPS spectrum for pristine carbon nanotubes

Table 2.
Qualitative analysis of chemical composition of pristine carbon nanotubes and nanocomposites MWCNT-Pd

Materials	Fraction (in atomic terms) of constituent elements				
	C	O_2	Pd	F	N
Pristine MWCNTs	97.22	2.78	-	-	-
MWCNTs-Pd	86.89	12.03	0.67	rest	

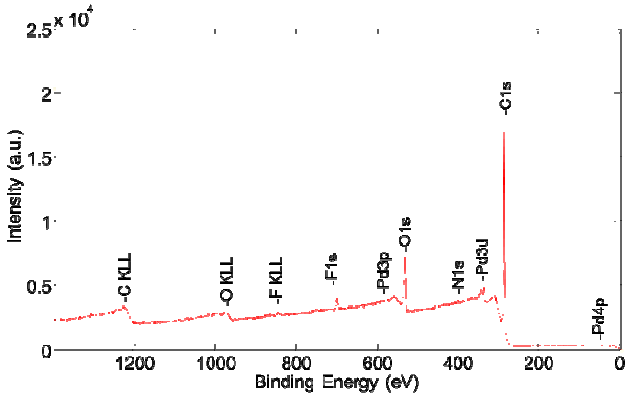

Fig. 11. XPS spectrum of carbon nanotubes decorated with palladium - MWCNTs-Pd

4. Conclusions

This work presents the results of investigations concerning the fabrication and characteristics of CNTs-NPs nanocomposites. The investigations using transmission electron microscopy together with an EDS and XPS analysis have confirmed the fact of producing an MWCNTs-Pd nanocomposite with the fraction of Pd = 0.67% at. The manufactured palladium nanoparticles are spherically shaped and their diameter is usually between 2 and 8 nm. Examinations with Raman spectroscopy have allowed to determine the difference between the degree of defects of carbon nanotubes before and after modification with palladium nanoparticles. The presence of palladium has influence on the electrical properties of the nanocomposite, enhances sensitivity and selectivity of the CNTs-NPs system in contact with the chosen chemical substance, and the result is the changing of the conductivity of nanotubes. This phenomenon is a basis for the application of the studied material as an active substance of sensors of chemical/biological compounds and provides the next step of the research works being implemented. In the opinion of the authors, it will be possible in the future to use the nanocomposite obtained in order to store hydrogen.

The authors are planning to optimise the MWCNTs-Pd synthesis process and also to broaden the current research to include Fourier transform infrared spectroscopy (FTIR), in order to determine and confirm the type of function groups achieved on the surface of nanotubes after the functionalisation process; electrochemical examinations as well as thermogravimetric measurements (TGA) in order to compare the quality and homogeneity of the series of nanocomposites produced.

Acknowledgements

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Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME’2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

References

[1] V. Georgakilas, D. Gournis, V. Tzitzios, L. Pasquato, D.M. Guldie, M. Prato, Decorating carbon nanotubes with metal or semiconductor nanoparticles, Journal of Materials Chemistry 17 (2007) 2679-2694.
[2] A.D. Dobrzańska-Danikiewicz, W. Wolany, G. Benke, Z. Rdzawski, The new MWCNTs rhenium nanocomposite, Physica Status Solidi B 251/12 (2014) 2485-2490.
[3] I. Stępińska, J. Radomska, M. Kozłowski, E. Czerwosz, W. Kowalski, K. Sobczak, Nanostructural films of CNTs covered with nanocrystals of palladium, Nanocontainers 1 (2014) 1–6.
[4] N. Karousis, G.E. Tsotsou, F. Evangelista, P. Rudolf, N. Ragoussis, N. Tagmatarchis, Carbon nanotubes decorated with palladium nanoparticles: synthesis, characterization, and catalytic activity, The Journal of Physical Chemistry C 112 (2008) 13463-13469.
[5] B. Wu, Y. Kuang, X. Zhang, J. Chen, Noble metal nanoparticles/carbon nanotubes nanohybrids: Synthesis and applications, Nano Today 6 (2011) 75-90.

[6] A.D. Dobrzańska-Danikiewicz, D. Łukowiec, Synthesis and characterisation of Pt/MWCNTs nanocomposites, Physica Status Solidi (b) 250/12 (2013) 2569-2574.
[7] J.V. Rojas, C.H. Castano, Production of palladium nanoparticles supported on multiwalled carbon nanotubes by gamma irradiation, Radiation Physics and Chemistry 81 (2012) 16–21.
[8] H. Liu, L. Zhang, N. Wang, D. Sheng Su, Palladium Nanoparticles Embedded in the Inner Surfaces of Carbon Nanotubes: Synthesis, Catalytic Activity, and Sinter Resistance, Angewandte Chemie International Edition 53 (2014) 12634 -12638.
[9] F.P. Zamborini, S.M. Gross, R.W. Murray, Synthesis, Characterization, Reactivity, and Electrochemistry of Palladium Monolayer Protected Clusters, Langmuir 17 (2001) 481-488.
[10] M. Han, D. Jung, G.S. Lee, Palladium-nanoparticle-coated carbon nanotube gas sensor, Chemical Physics Letters 610–611 (2014) 261-266.
[11] R. Campesi, F. Cuevas, R. Gadiou, E. Leroy, M. Hirscher, C. Vix-Guterl, M. Latroche, Hydrogen storage properties of Pd nanoparticle/carbon template composites, Carbon 46 (2008) 206-214.
[12] A.D. Dobrzańska-Danikiewicz, D. Cichocki, M. Pawlyta, D. Łukowiec, W. Wolany, Synthesis conditions of carbon nanotubes with the chemical vapour deposition method, Physica Status Solidi (b) 251 (12) (2014) 2420-2425.
[13] X. Gu, W. Qi, X. Xu, Z. Sun, L. Zhang, W. Liu, X. Pan, D. Su. Covalently functionalized carbon nanotube supported Pd nanoparticles for catalytic reduction of 4-nitrophenol, Nanoscale 12 (2014) 6609-6616.