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Manufacturing and structure of nanocomposites consisting of MWCNTs decorated respectively with Rh, Re and Pt nanocristals

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ABSTRACT

Purpose: The primary aim of the paper is to compare fabrication methods and present newly fabricated nanocomposites whose structural components are multi-walled carbon nanotubes (MWCNTs) and respectively Rh, Re and Pt nanocrystals.

Design/methodology/approach: The newly fabricated nanocomposites underwent Transmission Electron Microscopy (TEM) examinations in the bright to show their structure. Spectroscopy examinations were carried out, as well, to determine chemical composition of the material.

Findings: It was found based on a comparative analysis of the structure of selected nanocomposites that functionalisation methods and a reduction method of precursors of selected noble elements have a significant effect on the structure and morphology of the compared carbon nanocomposites.

Research limitations/implications: Nanocomposites consisting of carbon nanotubes decorated with metal nanoparticles possess special electrical properties and a developed specific area, which makes them particularly suitable as active elements of industrial gas sensors. The materials can also be used as biosensors and catalysts in the future.

Originality/value: The paper presents the results of investigations relating to the synthesis of nanocomposites consisting of multiwalled carbon nanotubes and respectively Rh, Re and Pt nanocrystals and their structure and chemical composition.

Keywords: Nanomaterials; Nanocomposites; MWCNTs; Noble nanocrystals; TEM; EDS

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MANUFACTURING AND PROCESSING

1. Introduction

Researchers have been interested in carbon nanomaterials, including Single- and Multiwalled Carbon Nanotubes (MWCNTs) since they have been discovered reportedly by a Japanese, Iijima, in 1991 [1]. Depending on the manufacturing method, Carbon Nanotubes (CNTs) may be arranged perpendicular to the substrate, forming a so-called forest, occurring as entangled carbon deposits, or create thin or thick deposit on the substrate [2]. Carbon nanotubes have been subject to intensive research, mainly due to their extensive applications, notably in electronics, optoelectronics, medicine, textile and sports industry. Carbon nanotubes are also used as reinforcement in composites intended for constructional parts, principally due to the small mass as compared to their excellent strength properties. CNTs may be modified differently to enhance their application possibilities [3 - 5]. Currently there is high demand for materials used in chemical and biochemical sensors. It was proved that carbon nanotubes, especially those modified with nanoparticles of other compounds, work very well as sensors [6, 7]. The biggest advantages connected with the activity of modern sensors, the active elements of which are nanostructural materials, include chiefly: sensitivity, selectivity, and stability. X.J. Huang and Y.K. Choi have defined the properties as 3 ‘S’ [8]. One of possible modifications of carbon nanotubes is permanent deposition of nanoparticles (NPs) on their surface, including nanoparticles of noble metals. The structure of this type of nanocomposites depends mainly on the type of carbon nanotubes applied and their method of functionalisation, the type of the applied precursor of the selected metal being the nanocomposite component and on the manufacturing process parameters [9,10].

2. Materials and methodology

The article presents nanocomposites whose components are carbon nanotubes and nanoparticles of, respectively: Rh, Re and Pt. The overriding aim of microscope examinations of the nanocomposites produced is to determine the presence of nanocrystals of selected noble metals on the surface of carbon nanotubes, and also to describe their shape and arrangement on MWCNTs’ surface and to determine chemical composition of the material obtained. The manufacturing methods of MWCNTs-Rh and MWCNTs-Re nanocomposites have been submitted for patent protection [11, 12].

Rhodium, rhenium and platinum are in the group of transition metals. The atomic number of those elements is, respectively: 45 (Rh), 75 (Re), 78 (Pt), while the density is, respectively: 12.41 g/cm^3, 21.02 g/cm^3, 21.45 g/cm^3. Rhodium is a chemical element belonging to the light platinum group, and is in the 9th group and in the 5th period of the periodic table of elements, rhenium is in the 7th group and in the 6th period, while platinum in the 10th group and in the 6th period [13]. The elements listed were used as components of nanocomposites consisting of carbon nanotubes and nanoparticles of noble metals. The following was used as a metal precursor: for rhodium-$RhCl_3$, for rhenium-$HReO_4$, and for platinum-H_2PtCl_6. Multiwalled carbon nanotubes with the diameter of 10-20 nm and length of 10-30 μm fabricated with the Chemical Catalytic Vapour Deposition (CCVD) method were used to fabricate MWCNTs-M nanocomposites (where M = Rh, Re, Pt). The MWCNTs intended for further studies contain small impurities in the form of amorphous carbon and few metallic catalyst nanoparticles, which was identified in preliminary microscope examinations. MWCNTs-Rh and MWCNTs-Re nanocomposites were fabricated as a result of a high-temperature reduction reaction of precursors of Rh and Re metals in a heating oven, while the MWCNTs-Pt nanocomposite was manufactured with the chemical synthesis method.

The custom manufacturing method of MWCNTs-Rh [11] nanocomposites embraces two stages: (i) the functionalisation of carbon nanotubes for 2 hours with ultrasounds at the temperature of 60°C in an oxidising medium being the mixture of HNO_3 and H_2SO_4 at a rate of 1:3; (ii) leaving CNTs in acids for 24 hours without any interference; (iii) mixing the pre-filtered carbon nanotubes with an $RhCl_3$ metal precursor for 2 hours with ultrasounds; (iv) leaving the mixture without interference for 24 hours; (v) high-temperature processing of the wet carbon-metal material for 45 minutes at the temperature of 850°C in the shield of inert gas - Ar.

The production of MWCNTs-Re nanocomposites according to the custom method [12] comprises the following steps: (i) the functionalisation of carbon nanotubes for 3 hours with ultrasounds in an oxidising medium (HNO_3); (ii) leaving in acid for 24 hours without any interference; (iii) mixing the pre-filtered carbon nanotubes with an $HReO_4$ metal precursor for 3 hours with ultrasounds; (iv) leaving the mixture without any interference for 24 hours; (v) high-temperature processing of the wet carbon-metal material for 45 minutes at the temperature of 800°C in the shield of inert gas Ar and in the presence of H_2 whose flow rate after 15 minutes of the process is gradually decreased.

The fabrication method of MWCNTs-Pt nanocomposites detailed in [14] does not require the interaction of high temperature and consists of the following steps, as appropriate: (i) the functionalisation of carbon nanotubes by 0.5h using ultrasounds at the room temperature in an oxidising medium being the mixture of HNO_3 and H_2SO_4 at a rate of 1:3 or 30% of H_2O_2 solution; (ii) leaving CNTs in acids for 24 hours without any interference; (iii) dispergating the material in an ultrasound washer for 30 minutes, with adding (after 5 minutes of preliminary mixing) chloroplatinic acid H_2PtCl_6 and sodium borohydride $NaBH_4$; (iv) stirring the material for 8 hours at the temperature of 140°C with a reflux condenser; (v) dispergating the material in ethylene with ultrasounds and drying it with free air.

Microscope observations of the fabricated MWCNTs-M nanocomposites (where M = Rh, Re, Pt) were pursued by means of an S/TEM TITAN 80-300 high-resolution transmission electron microscope by FEI Company. The microscope applied is fitted with an electron gun with XFEG field emission, a Cs condenser spherical aberration corrector, a STEM scanning system, and also Bright Field (BF) and Dark Field (DF) detectors and High Angle Annular Dark Field (HAADF), and also an EDS spectrometer for chemical composition analysis. Imaging in the transmission mode with a parallel beam was used during the examinations. Nanoparticles of the particular metals, due to large differences in the atomic number of platinum (Z = 78), rhenium (Z = 75) and rhodium (Z = 45) than carbon (Z = 6), are clearly discernible as dark precipitates on the surface of grey carbon nanotubes.

3. Results and discussion

The outcomes of the undertaken microscope examinations clearly indicate that the applied synthesis methods of carbon-metal nanocomposites are effective and allow to permanently connect carbon nanotubes with nanocrystals of different noble metals, i.e., respectively: rhodium (Fig. 1), rhenium (Fig. 2) and platinum (Fig. 3). The morphology of carbon nanotubes decorated with nanoparticles of various metals is different. The size of oval rhodium nanoparticles deposited on the surface of carbon nanotubes is quite differentiated within the entire volume of the observed nanocomposites and their diameter is within the range of 2-10 nm. Minor single rhodium nanoparticles with diameter over 10nm and locally occurring agglomerates were also observed. It was found during the microscope observations of the MWCNTs-Re nanocomposite that rhenium nanoparticles are usually oval shaped, but some of them are irregularly shaped.

Generally, rhenium nanoparticles occur as individual precipitates with diameter about 3-10 nm, but the presence of agglomerates concentrated on the area of about 100 nm^2 was also noticed during microscope observations. MWCNTs-Pt nanocomposites possess uniformly arranged platinum nanoparticles on the surface of carbon nanotubes and no tendency of such nanoparticles to agglomerate. The diameter of oval platinum nanoparticles deposited on the surface of carbon nanotubes is approx. 3-5 nm.

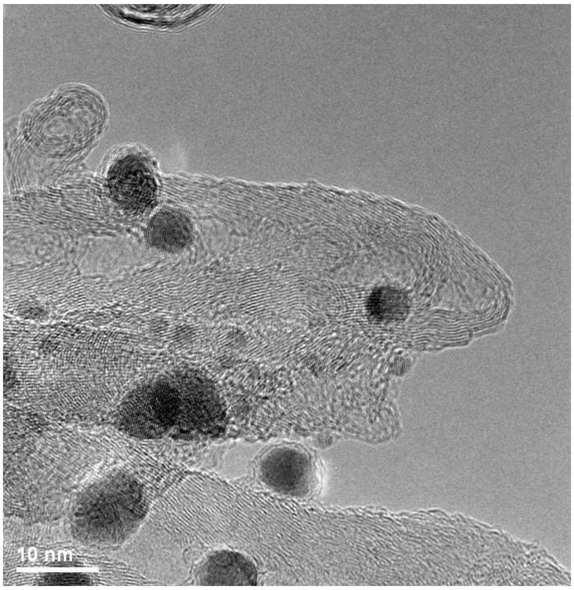

Fig. 1. TEM image of MWCNTs-Rh nanocomposite

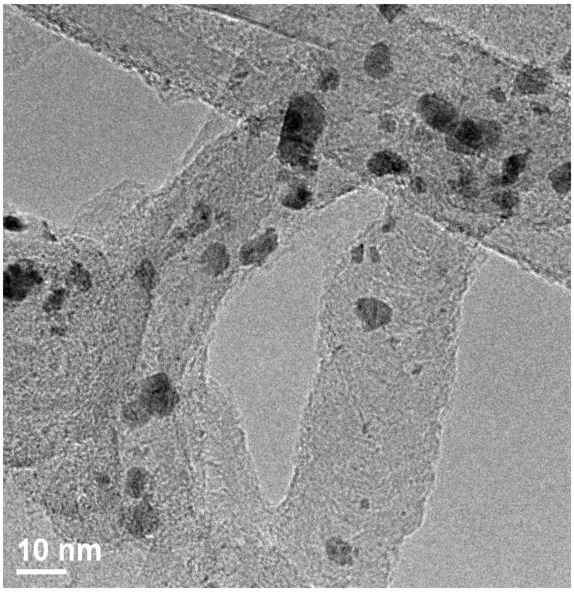

Fig. 2. TEM image of MWCNTs-Re nanocomposite

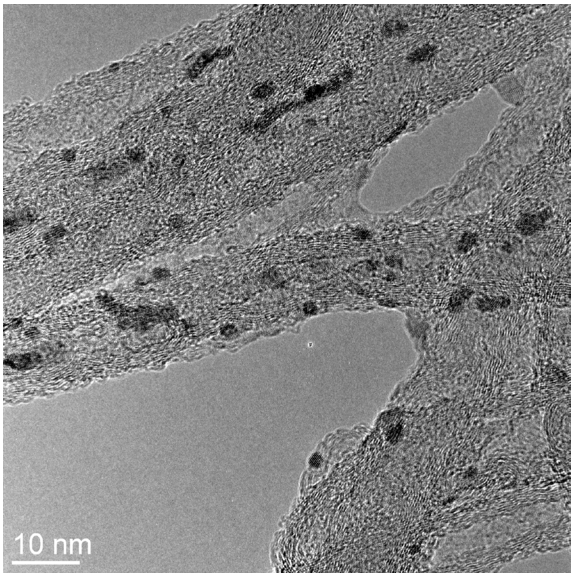

Fig. 3. TEM image of MWCNTs-Pt nanocomposite

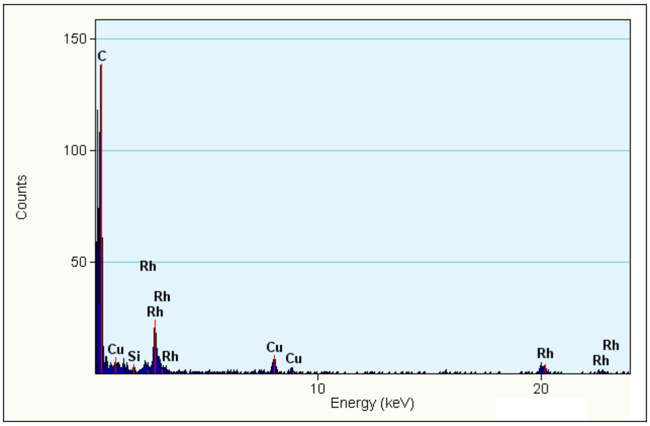

Fig. 4. Result of qualitative analysis of chemical composition made with EDS for MWCNTs-Rh

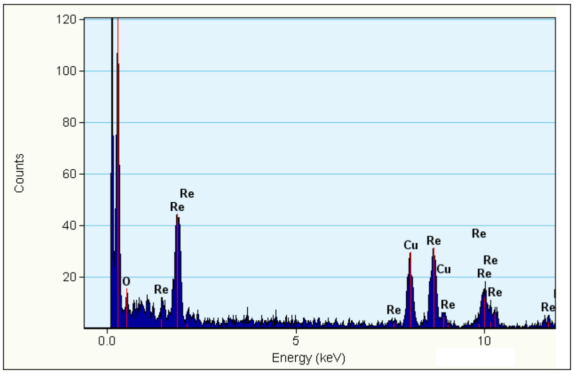

Fig. 5. Result of qualitative analysis of chemical composition made with EDS for MWCNTs-Re

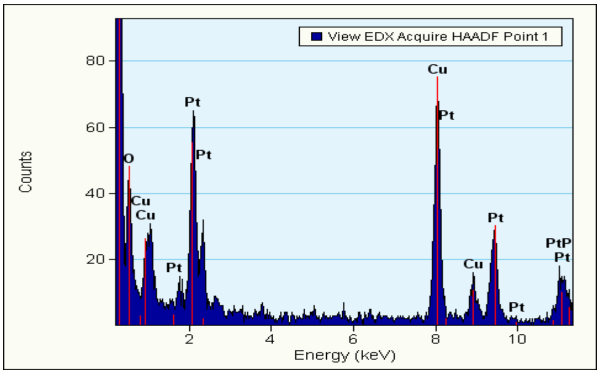

Fig. 6. Result of qualitative analysis of chemical composition made with EDS for MWCNTs-Pt

A qualitative chemical composition analysis of the MWCNTs-M carbon-metal nanocomposites presented in the article, where M=(where M = Rh, Re, Pt), was undertaken with the Energy Dispersive Spectroscope (EDS). The results of EDS examinations confirm each time the occurrence of carbon in the investigated material being a building block of carbon nanotubes and copper, which results from employing a copper mesh to prepare the microscope preparation, onto which the nanocomposite material subject to examination was deposited. Peaks are also visible on the presented diagrams deriving from nanoparticles of metals being in the composition of the studied nanocomposites, which are, respectively, Rh (Fig. 4), Re (Fig. 5) and Pt (Fig. 6).

4. Conclusion

The article presents a structure of the selected CNTs-NPs nanocomposites observed with a transmission electron microscope (TEM). The work characterises, in particular, three types of nanocomposites consisting of multiwalled carbon nanotubes, to the surface of which single nanoparticles of rhodium, rhenium and platinum were permanently attached. The functionalisation method of carbon nanotubes and the fabrication method of the presented carbon-metal materials are fundamental for the morphology of such nanocomposites. It was found that nanocomposites fabricated with the chemical synthesis method are more homogenous within their entire volume, as compared to nanocomposites formed by adding metal precursors to functionalised carbon nanotubes and subjecting the so prepared wet preparation to a high-temperature reduction reaction. The nanocomposites, whose last stage of manufacturing is high-temperature treatment (800ºC and more), exhibit a tendency to create the clusters of metal nanoparticles, which hinders to achieve nanocrystals with narrow size distribution. The nanocomposites produced were synthesised in view of the ever growing demand for materials being active elements of chemical and biochemical sensors, and the materials described, having special electrical properties, are very suitable for this. The article presents only some results of the investigations associated with the deposition of various nanoparticles onto the surface of carbon nanotubes. Other articles [15-18] contain, in particular, the results of microscope observations of the nanomaterials manufactured in the dark field, carried out with a concentrated beam in the STEM mode. The directions of the further research pursuits of the Authors of this publication include, in particular, the modification and optimisation of fabrication conditions of various CNTs-NPs nanocomposites in order to obtain high repeatability of processes serving to synthesis materials with the highest possible quality.

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Additional information

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