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Carbon nanotubes decorating methods

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ABSTRACT

Purpose: The work is to present and characterise various methods of depositing carbon nanotubes with nanoparticles of precious metals, and also to present the results of own works concerning carbon nanotubes coated with platinum nanoparticles.

Design/methodology/approach: Electron transmission and scanning microscopy has been used for imaging the structure and morphology of the nanocomposites obtained and the distribution of nanoparticles on the surface of carbon nanotubes.

Findings: The studies carried out with the HRTEM and SEM techniques have confirmed differences in morphology, homogeneity and density of depositing platinum nanoparticles on the surface of carbon nanotubes and its structure.

Research limitations/implications: The studies conducted pertained to the process of decorating carbon nanotubes with platinum nanoparticles. Further works are planned aimed at extending the application scope of the newly developed methodology to include the methods of nanotubes decorating with the nanoparticles of other precious metals (mainly palladium and rhodium).

Practical implications: CNTs-NPs (Carbon NanoTube-NanoParticles) composites can be used as the active elements of sensors featuring high sensitivity, fast action, high selectivity and accuracy, in particular in medicine as cholesterol and glucoses sensors; in the automotive industry for the precision monitoring of working parameters in individual engine components; in environmental conservation to examine CO_2, NO_x, and CH_4 concentrations and for checking leak-tightness and detecting hazardous substances in household and industrial gas installations.

Originality/value: The comprehensive characterisation of the methods employed for fabricating nanocomposites consisting of carbon nanotubes deposited with Pt, Pd, Rh, Au, Ag nanoparticles with special consideration to the colloidal process.

Keywords: Nanomaterials; Carbon nanotubes; Precious metals nanoparticles; Nanocomposites

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MATERIALS

1. Introduction

Carbon, together with its allotropic variants, is one of the most important engineering materials. Nanostructural materials, including graphene and carbon nanotubes (CNTs), have become especially significant these days. The above-mentioned nanostructured materials can be modified by adding to the structure atoms of other elements. For example a two-dimensional crystal graphane, which, unlike graphene, is an insulator, is obtained by combining hydrogen with graphene. The existence of additional double and triple bonds between the atoms of carbon leads to the formation of graphyne. Single Walled Carbon NanoTubes (SWCNTs) as well as Multi Walled Carbon

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NanoTubes (MWCNTs) have interesting electrical, mechanical, optical and chemical properties, therefore can be applied in numerous fields - from electronics to medicine [1,2]. The decoration of CNTs with the nanoparticles of precious metals is a surface treatment method and may improve some of nanotubes' properties. The most promising results concern the following precious metals: Ag, Au, Pt, Pd, Rh for the nanoparticles deposited. A new composite material, CNT-NPs (Carbon NanoTube-NanoParticles), is created by attaching nanoparticles to the surface of external carbon nanotubes. A composite CNT-NPs material can be obtained by the functionalisation of carbon nanotubes. Covalent or noncovalent bonds may be created between the surface of a carbon nanotube and a covering nanoparticle. The efficiency and reasonableness of applying the relevant methods is dependent on the type of nanotubes used and on the deposited nanoparticles of precious metals, as well as on the area of potential applications of the nanocomposites formed.

The purpose of the article is to present and characterise the physiochemical basis of the carbon nanotubes decoration method and various methods of depositing nanoparticles of precious metals onto the surface of carbon nanotubes, and also to present the results of own works concerning carbon nanotubes coated with platinum nanoparticles with the indirect covalent method.

2. The essence of the physiochemical phenomenon of carbon nanotubes' functionalisation

Carbon nanotubes are structures with a strongly hydrophobic character exhibiting small reactivity and not dissolving in polar and non-polar solvents [2]. After a synthesis process, carbon nanotubes often contain numerous contaminants such as relatively large amounts of amorphous carbon and catalyst particles [3], which is a barrier in utilising them without further modification. Procedures are hence purposeful leading to their initial purification and introducing changes in their structure, causing for example better dispersion in water. The practical application areas of such nanostructures are broadened through carbon nanotubes' functionalisation [2,3,4]. The aim of this chapter is to present different CNTs functionalisation methods The methods of changing the structure of carbon nanotubes fall into the following groups [2,3,5]:

- *noncovalent functionalisation* - Van der Waals interactions or π-π interactions are used to attach different substances to the external walls of CNTs (Fig. 1 presents the examples of noncovalent functionalisation of carbon nanotubes);
- *endohedral functionalisation* - a process of filling the free cores of nanotubes with different chemical compounds;
- *covalent functionalisation* - is based on linkage of ligands to CNTs' walls as a result of chemical reactions.

The research conducted with the electron microscopy technique has allowed to observe that carbon nanotubes possess various defects in their structure. SWCNT, as compared to MWCNT structures, are more homogenous and characterised by fewer defects, however, the process of fabricating them is much more difficult in practise. The occurrence of structural defects in the spatial lattices of carbon nanotubes influences their physiochemical properties, hence they become more chemically reactive and their electrical and magnetic properties change [2]. The following types of defects can be distinguished [2]: topological defects related to the presence of rings consisting of five- and seven-membered rings in a hexagonal spatial lattice; hybridisation defects related to the formation of bonds with an indirect degree of hybridisation, and also defects consisting of the presence of voids in form of missing carbon atoms in the structure.

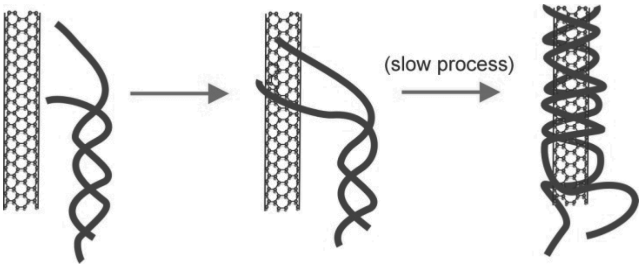

Fig. 1. Noncovalent functionalisation of carbon nanotubes, according to [3]

2.1. Noncovalent functionalisation of CNTs

CNTs have in their graphene structure delocalised π electrons may be subject to noncovalent functionalisation. The π-type interaction occurs between π electrons coming from CNTs and the electrons of molecules attached to them. An example can be attaching pyrene derivatives to the surface of CNTs [6]. As four conjugated benzene rings occur in them, permanent noncovalent attachment with the surface of nanotubes is obtained. Pyrene derivatives are substantially increasing the solubility of CNTs in water. Owing to the interaction of π-π, there are many possibilities of carbon nanotubes modification, including with the use of different polymers. In case on noncovalent functionalisation of carbon nanotubes, surfactants, aromatic compounds, polymers with long chains, polypeptides and biomolecules, including DNA chains, can be used for modification [3,4].

2.2. Endohedral functionalisation of CNTs

Diverse chemical compounds can be used for filling the interior of nanotubes. In the case of endohedral functionalisation, the durability of the structures created is ensured by hydrophobic bonds, electrostatic interactions or Van der Waals interactions [2]. The electron structure of carbon nanotubes, especially of SWCNTs, is not disturbed in such case [2]. The void cores of carbon nanotubes can be filled with atoms of particles of other chemical compounds (Fig. 2). Carbon nanotubes inside assume the form of separate particles or create continuous metallic nanowires, metal oxide and other nanowires. The filling techniques of the nanotubes filled earlier can be distinguished as well as processes of filling nanotubes' core occurring at the same time as their in situ synthesis [2].

2.3. Covalent functionalisation of CNTs

Covalent functionalisation leads to a change in the surface properties of carbon nanotubes as a result attaching permanently the of particles of specific chemical compounds. For this reason, this type of functionalisation is referred to as chemical functionalisation [3].

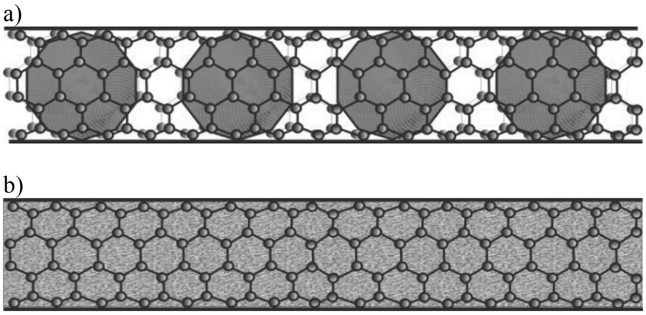

Fig. 2. Endohedral functionalisation: a) a piece of carbon nanotube with the particles of other chemical compounds, b) the core of carbon nanotube filled completely

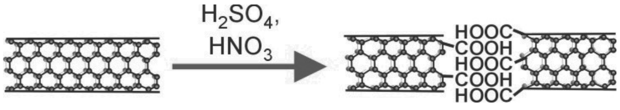

Fig. 3. Functionalisation of CNTs by oxidisation, according to [7]

A change in the hybridisation of carbon atoms in nanotubes from sp^2 to sp^3 takes place during such processes, which, in turn, changes the electrical conductivity of CNTs and affects mechanical properties negatively. There are many ways of covalent functionalisation of carbon nanotubes, and the most popular of them will be characterised in this subchapter [3,5,7].

The oxidisation of carbon nanotubes using acids or their mixtures (Fig. 3) is an effective method of CNTs' purification. When nanotubes are subjected to the activity of acids, the hemispheres are split located at the termini of nanotubes and occurs destruction of the external surface of carbon nanotubes. Carboxyl (-COOH), hydroxyl (-OH) and/or carbonyl (=CO) groups are created in the place of intersection. The most common chemical compounds used in this process include: concentrated nitric acid (HNO_3), perchloric acid ($HClO_4$), sulphuric acid (H_2SO_4), a mixture of concentrated nitric and hydrochloric acid or perhydrol (30% H_2O_2). The functionalisation degree of nanotubes' walls due to oxidisation depends on such parameters as: process temperature, type of oxidiser used and nanotube curvature causing stresses between sp^2 bonds. Walls with a larger radius of curvature exhibit higher reactivity, thus they have higher susceptibility to oxidisation [3,7].

Oxidised carbon nanotubes can be subjected to further reactions in order to attach other groups to their walls, and the example is amidation [8] or esterification [9]. It is a popular method of CNTs' functionalisation as a result of which nanotubes soluble in water and organic solvents are obtained. The carboxyl groups created during oxidisation are in the first place transformed to acid chlorides, for example using thionyl chloride, and reactions with amines or esters (Fig. 4) are performed in the next step.

CNTs can be classified as related to polyolefins that can be functionalised using fluorine. The degree of fluoridation can be adjusted by selecting the appropriate fluoriding reagent such as, e.g. iodine pentafluoride or xenon difluoride and a process temperature within the range of 20-600°C. The experiments performed prove that the fluoridation process is best progressing between 150 and 400 °C. A lattice of nanotubes may be subjected to considerable damage at higher temperatures. Fluorine can be easily replaced by other functional groups obtainable using Grignard reagents (RMgBr), alkylolite (RLi) or alkyl peroxides. A fluoridation process chart is shown in Fig. 5. Gaseous halogens are highly poisoning and reactive, high safety standards are therefore required when carrying out chemical reactions with fluorine [7,5].

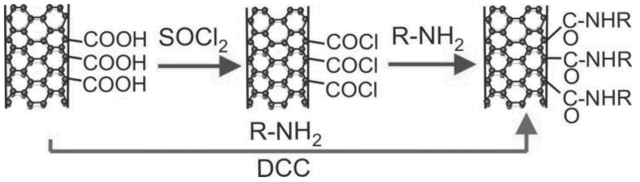

Fig. 4. CNTs amidation process, according to [3]

CNTs' functionalisation can also be carried out during a reaction with nitrenes or during thiolation the oxidised nanotubes. Other methods include addition of radicals or carbons and the Bingel or Prato reaction that are commonly used for the functionalisation of fullerenes [3].

The nanotubes functionalisation techniques listed serving to change their properties represent only an outline of modification possibilities of such structures' surface. Modern chemistry offers huge possibilities in selection of appropriate chemical substances and CNTs functionalisation methods. For this reason, studies in this area are substantiated so that nanotubes' optimum functionalisation method can be picked allowing to shapen their properties according to their potential users' expectations.

3. Carbon nanotubes decoration methods

3.1. Types of CNT-NPs fabrication methods

The first attempts of decorating carbon nanotubes were carried out in 1994 by Professor Ajayan and his collaborators [10].

The initial aim of depositing the surface of CNTs with nanoparticles was to determine the location and density of nanotubes' structural defects. The research was focussed on singlewalled carbon nanotubes covered with ruthenium clusters. It turned out that the composite material obtained showed promising results as a catalyst in the heterogenic catalysis process. Experiments were thus commenced aimed at searching other interesting applications of carbon nanotubes decorated with nanoparticles. The main aim of manufacturing CNT-NPs nanocomposites is to synthesise new materials having good electrical, chemical and/or mechanical properties. Many different decoration methods of carbon nanotubes with nanoparticles exist these days, most of all for precious metals. Several classification methods of the CNT-NPs nanocomposites manufactured can be differentiated.

One of the approaches is classification to direct and indirect methods. Metal nanoparticles are formed in a single stage on the surface of CNTs in the first case. The process is efficient, but disturbs the electron structure. The indirect (chemical, sonochemical, colloid process) method takes place in two independent processes. Functionalised nanotubes are obtained in the first process, and nanoparticles of precious metals in the second process [11].

A suspension is mixed at the last stage of works, as a result of which NPs are deposited on the surface of CNTs, which is equivalent to the formation of CNT-NPs nanocomposite.

Nanotubes decoration methods can also be classified according to the type of bonds existing between nanotubes' surfaces and the nanostructures deposited onto them. The bonds fall into covalent and noncovalent bonds.

One more grouping for CNT-NPs manufacturing methods is also available in the references [10,12,13]: electrochemical deposition, electroless deposition, dispersion of precious metals' nanoparticles on functionalised carbon nanotubes and physical methods including deposition by: sputtering deposition, irradiation with a beam of electrons and evaporation.

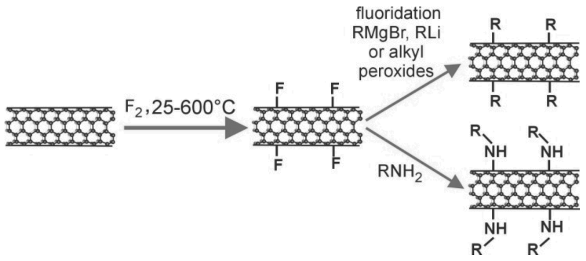

Fig. 5. Functionalisation of CNTs by fluoridation, according to [7]

This classification of carbon nanotubes' decoration methods together with the areas of their current and future applications is shown in Fig. 6.

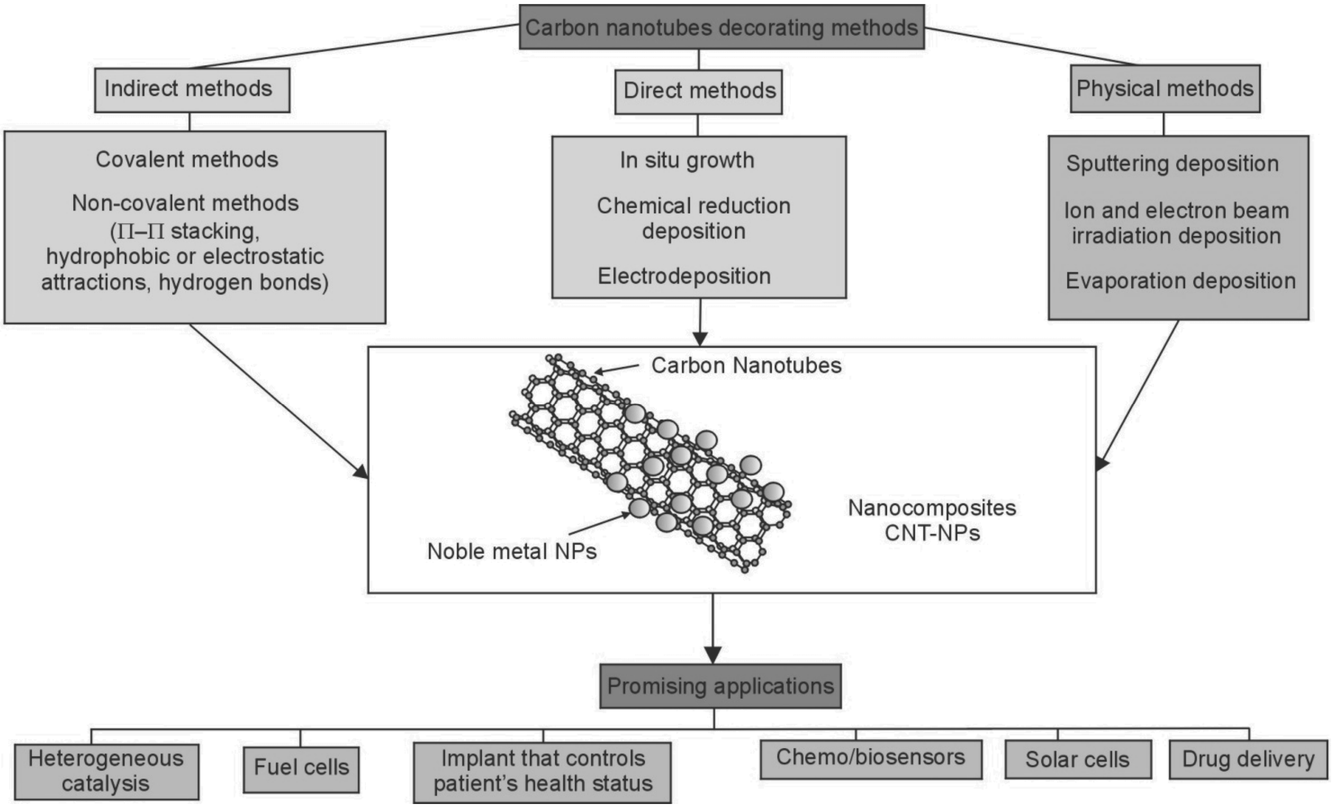

Fig. 6. Classification of carbon nanotubes' decoration methods together with their potential applications, according to [12,13]

3.2. Direct methods

Nanoparticles of precious metals can be formed in a single stage directly on carbon nanotubes. The following groups can be distinguished for the most popular, currently used, direct methods of CNT-NPs nanocomposites production [13,14]: in situ, electroless deposition, deposition as a result of chemical reduction and electrolytic deposition.

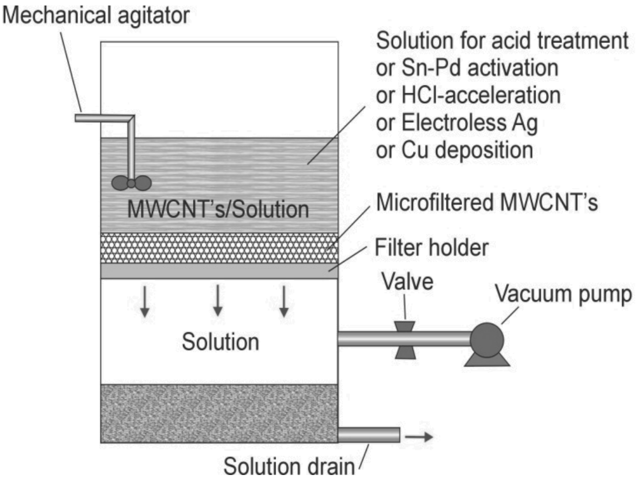

Fig. 7. Diagram of experimental device used in electroless deposition in situ process [15]

The in situ method does not require a reducing agent or additional radiation. Carboxyl function groups are created on the surface of carbon nanotubes due to oxidising chemical processing. This increases carbon nanotubes' solubility. In addition, the ions of metals also start to interact with the surface of CNTs which is leading to local propagation of nanoparticles on the surface of nanotubes [14,15]. A diagram of a device enabling the deposition of nanoparticles in situ is shown in Fig. 7. The entire process, including HNO_3 processing, activation and acceleration is carried out in an experimental device and monitored by setting a vacuum pump's parameters.

Limitations of the electroless in situ deposition method consists in applying metal nanoparticles only the ions of that only the ions of a redox potential larger than a reducing agent or carbon nanotubes. As a consequence, it is not possible to use Cu and Ag nanoparticles for deposition, and this has contributed to developing the Substrate-Enhanced Electroless Deposition (SEED) method enabling to deposit effectively diverse nanoparticles (Au, Pt, Pd) on the surface of CNTs [14,15]. A schematic diagram of the SEED method is shown in Fig. 8.

Another variant of the electroless deposition method based on redox reactions between the ions of metals and nanotubes consists of maintaining negatively charged carbon nanotubes CNTs and then adding them to the solution of metal cations and creating nanoparticles (NPs) along the surface of CNTs [16]. With this method, the decoration process was performed of singlewalled and multiwalled nanotubes with the nanoparticles of Au, Ag, Ru, Rh, Pd, Pt, without functionalization of CNTs in prior and use active surfactants [12,17].

A widely used method of decorating nanotubes with nanoparticles is also electrolytic deposition where CNTs are submerged in the relevant solution (e.g. $HAuCl_4$,K_2PtCl_4), being a source of the desired coating nanoparticles and of controlling the potential and concentration of precursors. The nanoparticles of precious metals deposited on the side surface and on the ends of carbon nanotubes are characterised by high purity. Usually, the entire decoration process lasts from several seconds to several minutes, and in some cases the external surface of nanotubes is completely coated with NPs [10,12,14]. An example of an electrolytic deposition process is shown in Fig 9.

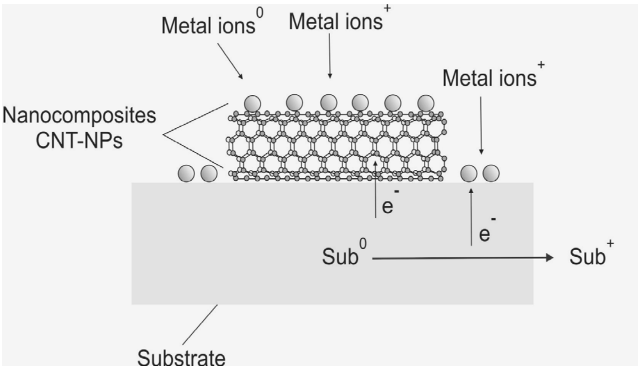

Fig. 8. Scheme of electroless deposition of nanoparticles of precious metals of NPs on carbon nanotubes CNTs with the SEED method, according to [10,14].

The direct methods of producing CNT-NPs nanocomposites are characterised by high efficiency and controllability of nanoparticles' size and deposition density of carbon nanotubes, and the thus obtained nanocomposites are often used as semi-conductors and catalysts [12,14,16-17].

The production of nanocomposites with direct methods is accompanied by numerous difficulties related to the formation of large agglomerations of nanoparticles and controlling their location, and also to the planned shape of morphology, dispersion and properties of newly formed nanostructures.

An important disadvantage of such methods is the fact that a manufacturing process takes place in the presence of toxic reagents. Moreover, specialised and costly equipment needs to be used for such methods, and still barriers exist with the large-scale industrial manufacturing of nanocomposites with such methods [12-14,17].

3.3. Indirect methods

Indirect methods, unlike direct methods, consist of fabricating CNT-NPs nanocomposites in two separate processes conducted independently. Covalent or noncovalent bonds may exist between the surface of a nanotube and the nanoparticle deposited onto them. Metal nanoparticles can be obtained in chemical reduction reactions. A suspension containing nanoparticles of precious metals is subjected to the interaction of ultrasounds, washing and centrifuging. Oxidised nanotubes with carboxyl (-COOH), carbonyl (=CO) and/or hydroxyl function groups (-OH) are obtained on the surface. The so prepared nanotubes are placed in a mixture containing metal nanoparticles. A reduction agent (e.g. $C_4H_{12}BNO$, $NaBH_4$ - according to the coating nanoparticles applied) must be added causing the attachment of nanoparticle ions to the function group, and hence uniform deposition of NPs on the surface of CNTs [12-15,16-17]

In the direct covalent method and its different variants, carboxyl groups can be used for other modifications consisting of attaching subsequent molecules by means of ester or amidic bonds. The direct covalent method allows to attach permanently the nanoparticles of precious metal to the surface of carbon nanotubes and as a result, when purifying a ready nanocomposite, the attached nanoparticles are not detached from carbon nanotubes. Unfortunately, it is also possible that structure defects occur of nanotubes due to a change in the hybridisation of carbon atoms from sp^2 to sp^3. If the other type of the indirect method is used, i.e. noncovalent method, the electron structure of carbon nanotubes is not disturbed, and contributes to preserving optoelectronic properties and an advantageous change of the formed nanostructures' magnetic properties [12-15,17].

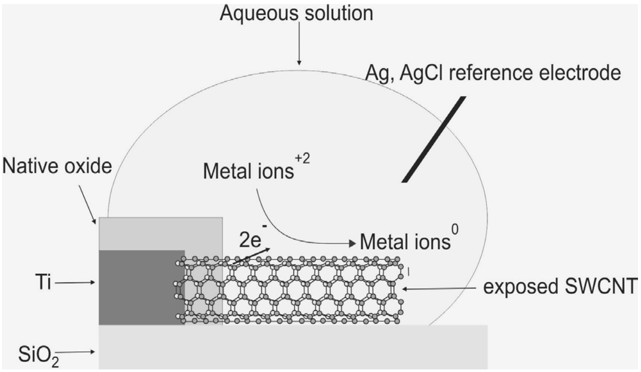

Fig. 9. The scheme of an electrolytic deposition process of precious metals' nanoparticles onto SWCNT [10]

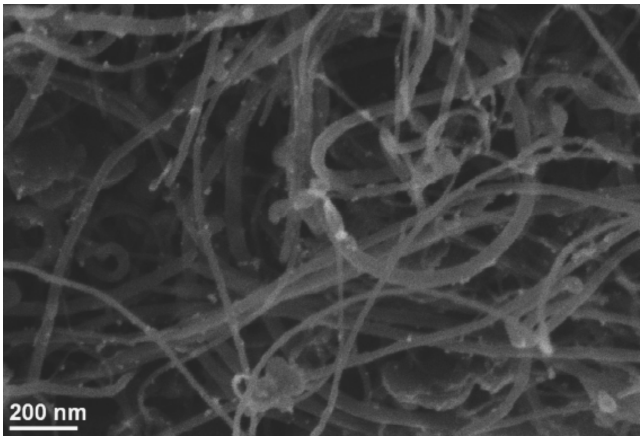

Fig. 10. SEM image showing CNT-NPs nanocomposite consisting of carbon nanotubes coated with nanoparticles of gold [17]

The both groups of the indirect methods allow, without using costly devices, to control the shape and size of nanoparticles applied and to arrange them carefully on the surface of carbon nanotubes, thus creating nanocomposites with a wide spectrum of current and future applications. A difficulty in employing this group is the necessity to recognise thoroughly the synthesis mechanisms of CNT-NPs nanocomposites and not always satisfactory repeatability of the experiments carried out. An example of a CNT-NPs nanocomposite produced with the indirect covalent method is shown in Fig. 10.

4. Experimental

4.1. Materials

An indirect covalent method of attaching the earlier produced nanoparticles to the surface of functionalised carbon nanotubes was employed to deposit platinum nanoparticles onto the surface of carbon nanotubes. Pt nanoparticles were precipitated as a result of the reduction reaction of a chloroplatinic acid mixture H_2PtCl_6 with sodium borohydride $NaBH_4$ and ethylene glycol. A material for the investigations was prepared according to a procedure consisting of several stages. Pre-processed carbon nanotubes, with 15 ml of ethylene glycol added, were dispergated in an ultrasound washer in a process lasting 30 minutes. 5 ml of acetone was added to thesuspension obtained during constant mixing with a magnetic stirrer. A suitable amount of chloroplatinic acid H_2PtCl_6 and sodium borohydride $NaBH_4$ was added to the suspension using a pipette after preliminary mixing for 5 minutes. All this was heated under a reflux condenser for 8 hours at a temperature of 140°C. The nanotubes fabricated were then filtered and washed 5 times in deionised water. The nanotubes were dried for 12 hours at 120°C following decoration.

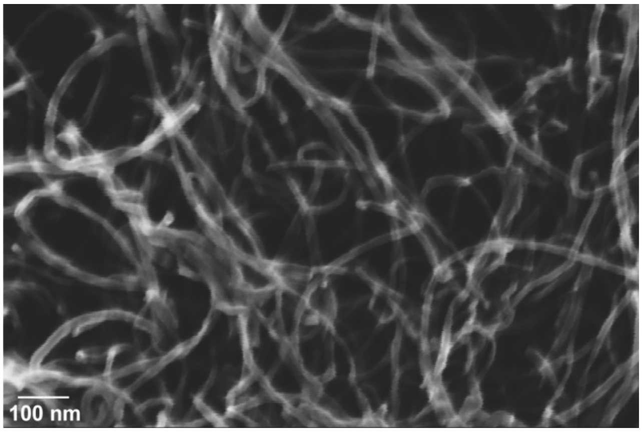

Fig. 11. SEM images of unmodified multiwalled carbon nanotubes

4.2. Research methodology

The Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) techniques were used for viewing the nanocomposite materials obtained. SEM images were made using a scanning electron microscope SEM Supra 35 by Carl Zeiss equipped with an X radiation spectrometers of energy dispersion EDS by EDAX. The high resolution of the samples viewed was achieved by applying a high-performance In-lens SE detector working with low beam voltage and with a very small distance of the sample examined to the electron gun. No conductive layers were applied for imaging the samples of nanocomposite materials. TEM and STEM images were performed using a transmission electron microscope STEM TITAN 80-300 by FEI fitted with FEG field emission, a condenser spherical aberration corrector, STEM scanning system, light and dark field detectors, HAADF (High Angle Annular Dark Field), and EFTEM energy image filter and an EDS spectrometer. The exact imaging of the structure and morphology of the materials examined was possible by applying an HAADF detector (Z contrast). Platinum nanoparticles, due to the different numbers of carbon and platinum atoms: C (Z=6), Pt (Z=78), were seen as lightly illuminating precipitates on the surface of carbon nanotubes. The samples for the transmission electron microscopy investigations were prepared by dispergating the carbon nanotubes coated with platinum nanoparticles in ethanol using an ultrasound washer, and then by depositing them using a pipette with beads onto a TEM mesh. A copper grid coated with a carbon film was used for the investigations. The material deposited as beads was dried in free air at room temperature.

4.3. Results and discussion

Fig. 11 shows the results of observations of the carbon nanotubes used in the decoration process. The nanotubes observed are homogenous, and their diameter is approx. 10 nm, which is well visible in an HRTEM image (Fig. 12). The outcomes also confirm that the material analysed is pure, i.e. deprived of metallic impurities and amorphous carbon deposits.

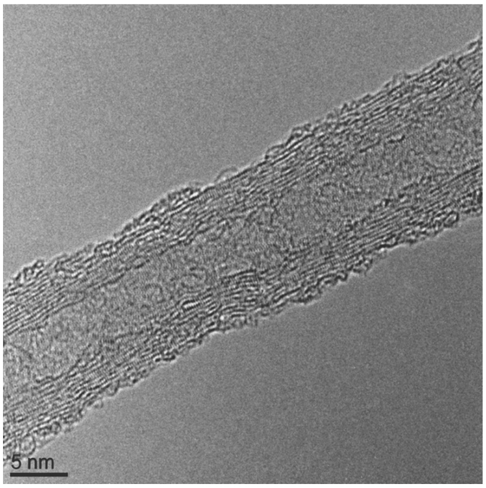

Fig. 12. TEM image of unmodified multiwalled carbon nanotube

The images of nanocomposites consisting of carbon nanotubes decorated with platinum nanoparticles made in the transmission electron microscope are presented in Fig. 13. It can be seen based on the images made with the HAADF detector in the STEM mode that the nanocomposite material obtained in the decoration process is characterised by platinum nanoparticles arranged on the surface of carbon nanotubes. Platinum nanoparticles are discernible on the images as clearly light precipitates. No tendency to agglomerate platinum nanoparticles and their constant size within the entire volume of the nanocomposites observed point out that the decoration process has been performed correctly. The platinum nanoparticles deposited on the surface of nanotubes are spherically shaped and have a diameter of approx. 3-4 nm. In addition, platinum nanoparticles have a crystalline structure, as confirmed by crystalline planes discernible on the images (Fig. 14). Further experiments are planned to decorate carbon nanotubes using Pd, Rh or Re nanoparticles with varied mass fractions.

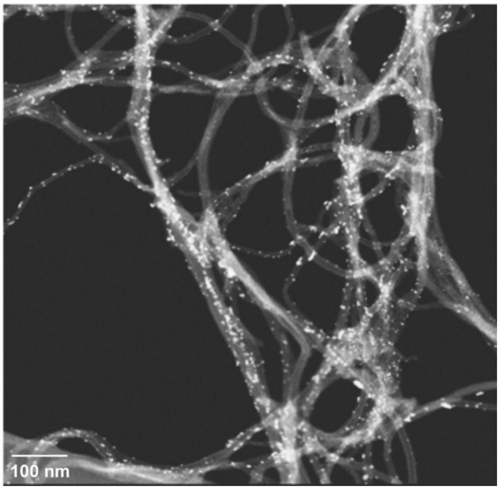

Fig. 13. STEM image using the HAADF detector of carbon nanotubes decorated with platinum nanoparticles.

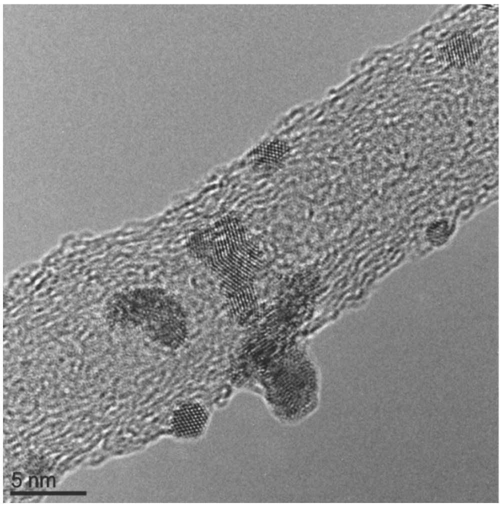

Fig. 14. HRTEM image of carbon nanotube with deposited platinum nanocrystals

5. Conclusions

The review of the literature reveals the existence of numerous optional methods of manufacturing nanocomposites consisting of carbon nanotubes on the surface of which naoparticles are deposited, including nanoparticles of precious metals. Direct and indirect methods of fabricating such nanostructures are known, and the efficiency and reasonableness of applying such methods is dependent on the type of the constituent components of the composite and its properties expected by the user. It is becoming an obligatory design practise these days that materials on demand are delivered with the desired structure and physiochemical properties, meeting functional requirements conforming to the client's demands and products' usable function. Physicochemical phenomena conditioning the potential modification of CNTs' surface have to be identified thoroughly each time in order to make the correct decisions. The own research performed confirm that the indirect covalent method is effective and efficient in relation to the production of nanocomposites consisting of MWCNTs coated with platinum nanoparticles [18,19].

Investigations into the materials described, consisting of carbon nanotubes and nanoparticles of precious metals deposited on their surface, are vital due to numerous current and potential applications. The nanostructures manufactured, having their unique electrical, mechanical and heat properties, will be applied as an active element of sensors featuring high sensitivity, fast action, high selectivity and accuracy, and also in biomedicine as implants controlling a patient's health condition; and in medicine as cholesterol and glucoses sensors [20]. They can also be implemented in the automotive industry for the precise monitoring of working parameters in individual engine components, in the food industry for monitoring food storage conditions and detection of toxic substances, in farming for evaluating conditions in greenhouses, in nature conservation for concentration tests of CO_2, NO_x, and CH_4 emissions and for checking leak-tightness and detecting hazardous substances in household and industrial gas installations. It is especially interesting to use the newly designed components for constructing sensors for gases obnoxious for the environment. This concept is based on changing the conductivity of carbon nanotubes by moving a charge between the nanotube surface and the substance analysed. A chemical compound was formed here between the particles of the examined substance and the absorbent. The authors of this publication are very interested in this field and the field will be further researched experimentally by them with the support of world literature.

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References

[1] L.A. Dobrzański, Fundamentals of material science, Silesian University of Technology Press, Gliwice, 2012 (in Polish).

[2] J. Mielcarek, P. Skupin, Functionalization of carbon nanotubes for multimodal drug delivery, Overview of Medicine 68/3 (2011) 167-170 (in Polish).

[3] G. Schroeder (ed.), Chemical functionalization of surfaces for nanotechnology, CURSIVA, 2011 (in Polish).

[4] A. Bianco, K. Kostarelos, C. Partidos, Biomedical applications of functionalised carbon nanotubes, Chemical Commmunication 5 (2005) 571.

[5] D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, Chemistry of Carbon Nanotubes, Chemical Review 106 (2006) 1105-1136.

[6] J. Liu, O. Bibari, P. Mailley, J. Dijon, E. Rouvie`re, F. Sauter-Starace, P. Caillat, F. Vineta, G. Marchand, Stable non-covalent functionalisation of multi-walled carbon nanotubes by pyrene-polyethylene glycol through π-π stacking, New Journal of Chemistry 33 (2008) 1017-1024.

[7] L. Cademartiri, G.A. Ozin, Nanochemistry - basic concepts, PWN, Warsaw, 2011 (in Polish).

[8] M.G. Afshar, M. Soleimani, M. Bazrpach, Amidation of purified carbon nanotubes for selective solid phase extraction of mercury (II) ions from aqueous solution, World Academy of Science, Engineering and Technology 51 (2011) 388-389.

[9] X.F. Xie, L. Gao, J. Sun, Esterification of chemical functional single-wall carbon nanotubes, Materials Science Forum 695 (2011) 373-376.

[10] 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.

[11] M. Pawlyta, D. Łukowiec, A.D. Dobrzańska-Danikiewicz, Characterisation of carbon nanotubes decorated with platinum nanoparticles, Journal of Achievements in Materials and Manufacturing Engineering 53/2 (2012) 67-75.

[12] B. Wu, Y. Kuang, X. Zhang, J. Chen, Noble metal nanoparticles/carbon nanotubes nanohybrids: synthesis and applications, Nano Today 6 (2011) 75-90.

[13] L.A. Dobrzański, A.D. Dobrzańska-Danikiewicz, Engineering materials surface treatment, Open Access Library 5, 2011, International OCSCO World Press, Gliwice (in Polish).

[14] X. Peng, J. Chen, J.A. Misewich, S.S. Wong, Carbon nanotube-nanocrystal heterostructures, Chemical Society Reviews 38 (2009) 1076-1098.

[15] J.H. Byeon, J. Hwang, Morphology of metallic nanoparticles as a function of deposition time in electroless deposition of metal on multi-walled carbon nanotubes, Surface & Coatings Technology 203 (2008) 357-363.

[16] E. Lorencon, A.S. Ferlauto, S. de Oliveira, D.R. Miquita, R.R. Resende, R.G. Lacerda, L.O. Ladeira, Direct production of carbon nanotubes/metal nanoparticles hybrids from a redox reaction between metal ions and

reduced carbon nanotubes, ACS Applied Materials & Interfaces 1/10 (2009) 2104-2106.

[17] L.A. Dobrzański, M. Pawlyta, A. Krztoń, B. Liszka, C.W. Tai, W. Kwaśny, Synthesis and Characterization of Carbon Nanotubes Decorated with Gold Nanoparticles, Acta Physica Polonica A 118 (2010) 483-486.

[18] A.D. Dobrzańska-Danikiewicz, Foresight methods for technology validation, roadmapping and development in the surface engineering area, Archives of Materials Science and Engineering 44/2 (2010) 69-86.

[19] L.A. Dobrzański, M. Pawlyta, A. Hudecki, Conceptual study on a new generation of the high-innovative advanced porous and composite nanostructural functional materials with nanofibers, Journal of Achievements in Materials and Manufacturing Engineering 49/2 (2011) 550-565.

[20] L.A. Dobrzański, M. Pawlyta, A. Krztoń, B. Liszka, K. Labisz, Synthesis and characterization of carbon nanotubes decorated with platinum nanoparticles, Journal of Achievements in Materials and Manufacturing Engineering 39/2 (2010) 184-189.