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Comparative analysis of the structure of nanocomposites consisting of MWCNTs and Pt or Re nanoparticles

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Introduction

The principal task lying ahead of the present and future generations of engineers is to design and fabricate new materials with unique properties. The requirements that engineering materials must satisfy these days quickly become out of date due to efforts to achieve better and better functional characteristics of products fabricated with them. A new era in carbon materials begun when Professor Iijima discovered carbon nanotubes in 1991 [1]. This spectacular discovery initiated an entire field of academic enquiry into this new carbon allotrope type of carbon with unique properties. Theoretical considerations backed up with experimental results confirm the electrical, mechanical, thermal, optical and magnetic properties of carbon nanotubes unprecedented to date in other material groups in opinion of many scientists [2-19]. A versatile array of unique properties of carbon nanotubes indicates their broad pool of potential applications. A prerequisite for the practical exploitation of carbon nanotubes' potential application opportunities on a wide scale is an ability to build larger structures and to combine them with other materials in a planned and controlled manner. Interesting chemical phenomena concerning carbon nanotubes include molecular surface sorption, attachment of functional groups to their surface and endings, improved wettability, and also additions of other elements outside, inside and within a graphene nanotube plane. The modification of carbon nanotubes' structure is possible through their chemical functionalisation leading to the creation of completely new nanotube hybrids combining unique properties of carbon nanotubes with other materials. By enriching nanotubes chemically, it is possible to control their electrical, mechanical, thermal, optical and magnetic properties [20-24]. Carbon nanotubes deposition methods using various types of nanoparticles, in particular SiO₂, TiO₂, Ti, Pd, Ag, Pt, Au, Cu, CdS, CdSe, CdTe, are described in the literature [25-34]. The outcomes of the research pursued by research institutions and own research point out that deposition of noble metals nanoparticles of Pd, Pt, Rh, Au type onto the surface of carbon nanotubes may contribute to a substantially higher density of carriers of free loads, hence to nanotubes' enhanced thermal and electrical conductivity [32-34]. A material produced in a deposition process may be characterised as carbon nanotubes-nanoparticles (CNTs-NPs). The popularisation of effective deposition methods of noble metals' nanoparticles onto carbon nanotubes' surface is also of high utilitarian importance, as research progress can be achieved in areas related to optoelectronics, medicine, energy conversion and storage, where a number of promising applications of the materials discussed can be differentiated. An example of a practical application of CNT-NPs nanocomposites are sensors of selected chemical substances (NH₃, CH₄, H₂, CO₂, CO, O₂, NO₂, NO, N₂, H₂O₂) [35-37] existing in negligible or trace concentrations, where carbon nanotubes coated with noble metal nanoparticles are an important active element. High sensitivity, selectivity, a fast response rate and an ability to work in the environment conditions, which is a great benefit compared to the conventionally used sensors, are the advantages of employing sensors containing a CNT-NP nanocomposite. In addition, the miniaturisation of sensors contributes to their reduced weight, lower energy consumption and diminished manufacturing costs. As regards CNT-NP nanocomposites manufacturing methods, two main groups can be differentiated, comprising direct methods consisting of direct formation of nanoparticles on the surface of carbon nanotubes, and indirect methods where nanoparticles are deposited at two separate stages, i.e. nanoparticles are synthesised and bonded to the surface of the previously functionalised nanotubes [23,32,33].

CNTs-NPs-type nanocomposites fabrication methods

Numerous research institutes have been searching methods of carbon nanotubes' modification since discovering them in 1991. Such activities are aimed at ensuring their newer and better properties and also at broadening the applicability of CNTs. CNTs-NPs nanocomposites fabrication methods can be grouped into physical, chemical and electrochemical methods [38,39,40]. Another classification of such methods also exists, which considers the type of interaction between a nanotube surface and nanoparticles of metals, according to which direct and indirect methods are distinguished (Fig.2.1) [38,39].

The direct CNTs-NPs nanocomposites fabrication methods are characterised by the fact that metal nanoparticles are formed directly on carbon nanotubes. The *in situ* creation of nanotubes, reduction reactions and electrolytic deposition can be classified as indirect methods allowing to deposit metal nanoparticles onto nanotubes. The principal disadvantage of this group of methods is their harmful impact on the natural environment resulting from the necessity to use toxic reagents, and also disadvantageous changes in electrical properties of modified nanotubes being a consequence of changes to their electron structure due to chemical reactions [38,39].

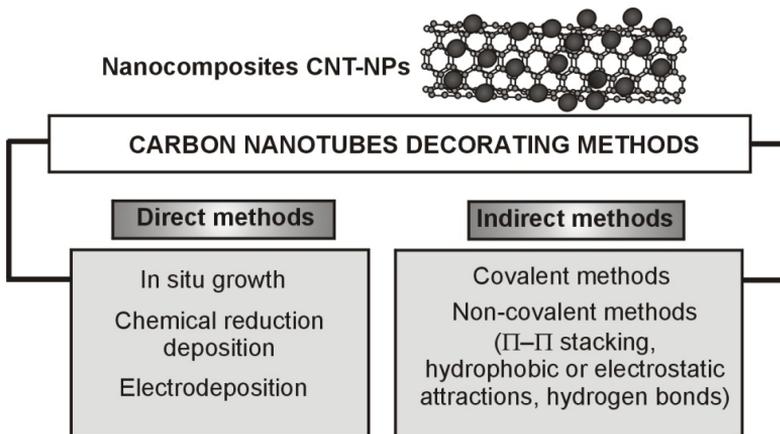


FIGURE 2.1.
Carbon nanotubes decorating methods [based on 38,39]

The deposition of Pt and Au nanoparticles onto single-walled carbon nanotubes is an interesting and unprecedented example of a direct reduction reaction presented by a research team headed by Choi [41]. No reducing agent was applied in this process due to a redox reaction occurring between metal ions and single-walled carbon nanotubes [41]. The similar result was achieved by Kong et al. [42], who created an SWCNTs-Pt nanocomposite. The examples provided belong to *in situ* methods, for the application of which an additional reducing agent or other reduction methods are required. The functional groups occurring on the surface of CNTs during functionalisation not only increase the solubility of nanotubes, but also represent the nucleus places of nanocrystals [39].

The commonly known reduction reactions are usually carried out using various reducing agents, mainly: ethylene glycol (EG) [43], sodium borohydride [44] and sodium citrate [45]. Reduction

reactions are also additionally assisted frequently by such factors as: light [46], temperature [47], microwaves [48].

Raghuvveret al. [49] has presented an interesting example of an effective CNTs-Au nanocomposites fabrication process, in which microwave irradiation is applied for nanotubes functionalisation and for the deposition of gold nanoparticles onto them in a single, simple process. Ethylene glycol was employed in this process as a reducing agent and assistance with microwaves has ensured the uniform distribution of Au nanoparticles on the surface of multi-walled nanotubes. A good result was also attained by resorting to a sonochemical method (Xing, 2004; Chen et al., 2012). The so obtained CNTs-Pt nanocomposites are homogenous and are characterised by the uniform dispersion of Pt particles on the surface of CNTs [50,51]. The method of direct growth of metal nanoparticles on the surface of carbon nanotubes using chemical reduction has many advantages. The application of this method enables, most of all, to control the size and distribution of metal particles by controlling process parameters such as solution concentration [38,39,52].

Electrodeposition represents an effective CNTs-NPs nanocomposites fabrication method [53,54]. Nanotubes decorated with more than one element can be achieved this way [55-56]. The side walls of carbon nanotubes are used as an electrodeposition template in this process. Nanotubes are also defined as a wire connecting electrically the metallic nanoparticles being deposited onto them [57]. In this process, CNTs are placed in a solution containing a precursor of the selected metal, most often in the form of salts of metals, and then ions of metals are reduced with the activity of current. K_2PtCl_4 and $HAuCl_4$ are used most often, respectively, to obtain a CNTs-Pt and CNTs-Au nanocomposite. Cation surfactants such as CTAC, CTAB, DTAB [54] can be used to deposit Ag, Al or Cu nanoparticles onto CNTs to ensure an additional charge for nanotubes. Two electrodes are then submerged in the solution and current is passed through them. Metal cations together with positively charged nanotubes are deposited onto a cathode as a thin film. A concept of a research group led by Son et al. [54] provides that nanotubes decorated with such metals as Au, Ag, Rh, Cu, Ni, Cr, Zn, Cd, Sn can be successfully obtained using an electroplating method. A decoration process lasts usually between several seconds to several minutes, hence the method is effectively and commonly used. The external walls of CNTs may be deposited completely with metal nanoparticles in some cases, thus creating a coating.

The indirect methods, unlike the direct methods, consist of the fabrication of CNT-NPs nanocomposites in two separate processes conducted independently. Covalent or noncovalent bonds may exist optionally between the surface of nanotubes and the nanoparticles deposited onto them. Metal nanoparticles can be obtained in chemical reduction reactions. In accordance with the idea described by Jana et al. [58], gold nanocrystals are obtained as a result of a reduction reaction of tetrachloroauric acid (III) $HAuCl_4$ with sodium borohydride $NaBH_4$ in the presence of another acid, namely trisodium citrate $C_6H_5Na_3O_7$. A suspension containing nanoparticles of noble metals is subjected to the interaction of ultrasounds, washing and centrifuging. In parallel, the surface of carbon nanotubes must be functionalised in an oxidation process with a mixture of HNO_3/H_2SO_4 acids at appropriate proportions. Jiang et al. [59] and Lee et al. [60] have observed, when performing the experiments, that the surfaces of the nanotubes subjected to oxidation are characterised by the high density of functional groups such as $-COOH$, $-CO$ and $=OH$, and the noble metal nanocrystals formed in a separate process may be easily bonded to them. Following the introduction of functionalised carbon nanotubes, containing numerous carboxyl, carbonyl and/or hydroxyl groups, into a suspension containing nanocrystals of the given noble metal, nanocrystals of Au or another noble metal are finally deposited onto the surface of carbon nanotubes.

The indirect covalent method allows to attach permanently the nanoparticles of a noble metal to the surface of carbon nanotubes and, as a result, when purifying a ready nanocomposite, the

nanoparticles attached to carbon nanotubes are not separated. The covalent method involves the reconstruction of the surface structure of carbon nanotubes as a result of attaching the necessary functional groups to their surface, i.e. carboxyl – COOH, hydroxyl – OH and carbonyl = CO groups. This is usually done using the following concentrated acids: nitric acid HNO₃, sulphuric acid H₂SO₄ and their mixtures, i.e. HNO₃/H₂SO₄ [38,39,61,62,63,64]. As a consequence of attaching functional groups to the surface of nanotubes, their chemical activity is increasing, manifested by increased solubility in aqueous solutions and connectivity of a large group of chemical compounds to their surface. The strong treatment of nanotubes' surface leads, however, to chemical transformation of structural defects and to the rehybridisation of carbon atoms from sp² to sp³. The deformation of the sp² network has clear impact on the deterioration of nanotubes' physical and chemical properties [39,65,66,67].

The indirect noncovalent method consists of the chemical modification of carbon nanotubes' surface using active surfactants such as: peptides, nucleic acids, polymers and oligomers [39,68,69,70,71]. The π-π stacking, hydrophobic and van der Waals interactions are responsible for the noncovalent character of functionalisation. A significant advantage of the noncovalent method is the lack of a destructive effect on the structure of nanotubes and the related unchanged electron properties [65,72,73,74,75,76,77,78,79].

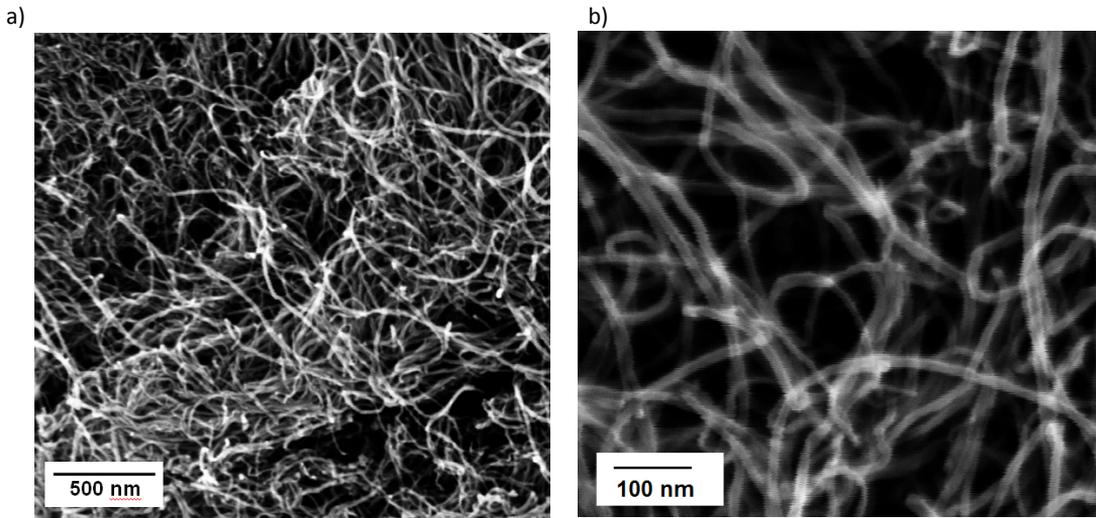
The both groups of the indirect methods allow, without using costly devices, to control the shape and size of the nanoparticles applied and to distribute them carefully on the surface of carbon nanotubes, thus creating nanocomposites with a wide spectrum of current and future applications.

Characteristic of carbon nanotubes and noble metal nanoparticles

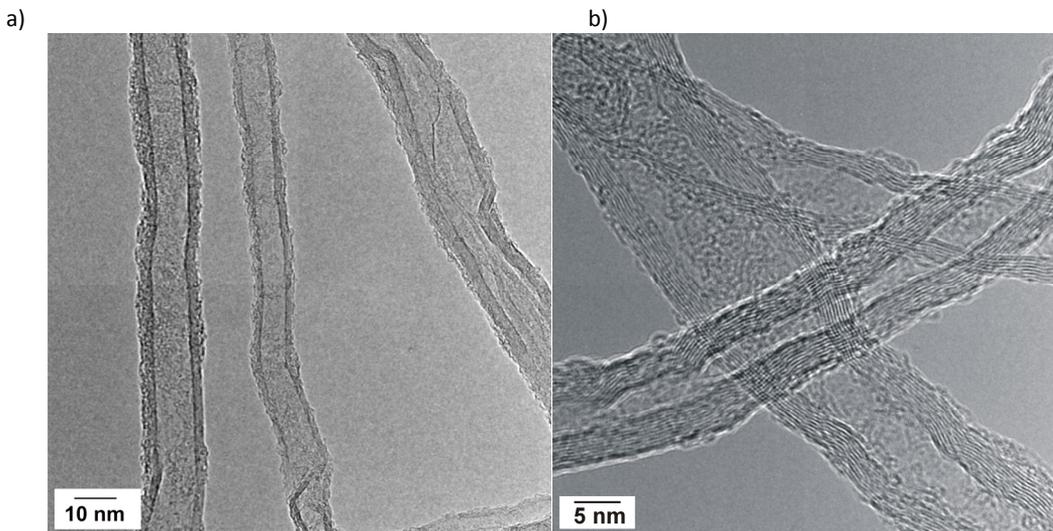
Carbon nanotubes, since releasing the first publications concerning this topic, have been subject to intensive research, mainly due to their extensive applications, notably: in electronics, optoelectronics, medicine, textile and sports industry, as a reinforcement in composites for constructional parts [80-83]. They also work very well as chemical and biochemical sensors detecting selected chemical substances in a gas and liquid environment. Such cylindrical rolled layers of graphene, ended theoretically with halves of fullerenes, may be modified differently to enhance their application alternatives. The diameter of nanotubes is from a fraction of nanometre to several dozen nanometres with their length reaching up to several micrometers, and even centimetres (nanotubes manufactured by CVD), and for this reason they are classified as one-dimensional nanomaterials.

A Single-Walled Carbon Nanotube (SWCNT) consists of a single rolled graphene layer, while a Multi-Walled Carbon Nanotube (MWCNT) features multiple co-axially arranged graphene sheets [84,85]. A structure of the carbon nanotubes used in the investigations aimed at developing own methods of manufacturing MWCNT-Pt and MWCNT-Re nanocomposites is shown in Fig. 2.2. and 2.3.

Platinum (Pt) is a greyish-white, ductile metal crystallising in the A1 lattice belonging to the platinum group, in which the following also exist: palladium (Pd), ruthenium (Ru), rhodium (Rh), osmium (Os) and iridium (Ir). Platinum group metals are classified as noble metals together with gold and silver. Platinum has widespread applications owing to its unique chemical and physical properties such as high melting temperature and high boiling point, impressive ductility, high chemical resistance, very good catalytic properties (best for platinum group metals) and good

**FIGURE 2.2**

SEM image of pristine MWCNT dedicated to the further experiments (a,b) [86]

**FIGURE 2.3**

TEM image of pristine MWCNT dedicated to the further experiments (a,b) [86]

electrical conductivity. Platinum is used in particular in the chemical, automotive, petroleum, electrical and glass industry, jewellery, medicine and dentistry [86]. Platinum's excellent catalytic properties are used in numerous industrial processes, notably in oxidation and reduction reactions for producing sulphuric acid (VI), nitric acid from ammonia and hydrocyanic acid. High corrosion resistance and high melting temperature make it suitable as a component for producing chemical apparatuses, melting pots, electrodes, thermoelements. In addition, high biocompatibility and good mechanical strength allow to use platinum for the manufacture of surgical instruments and biomedical appliances such as: pacemakers, defibrillators, stents and cochlear implants. The

automotive sector is using platinum for production of catalytic converters of flue gases; it is utilised in the electrical and electronic branch as a component of electrical contacts, resistors, thermocouples, heating elements and hybrid integrated circuits [87,88].

Rhenium (Re) [89] belongs to the group of transition metals, the atomic number of this element is 75, it crystallises in a hexagonal lattice, and its density is 21.02 g/cm^3 . It is therefore a chemical element belonging to the group of heavy metals, and is in the 7th group and in the 6th period of the periodic table of elements. It has silver-greyish colour, and its name derives from one of the longest rivers in Europe - the Rhenium. It is an element resistant to high temperatures with its melting point of $3,182^\circ\text{C}$, possesses good electrical and thermal properties, and is used, in particular, in electrical devices such as: electrodes, electromagnets, thermocouples, including such operating at high temperatures. Rhenium is used also as a component of superalloys applied in the space and aviation industry, for production of components of jet engines, combustion chambers and outlet nozzles of rockets, as its small addition significantly improves hardness, corrosion resistance and strength of alloys. A very extensive range of rhenium' chemistry of complex compounds has allowed to create a large number of catalysts on their basis. It is also employed notably as a catalyst for producing high-octane fuels. Re contents in the earth crust is estimated at approx. $10^{-7}\%$, hence it is a highly valued and very rare element [88-90].

Similarities and differences between methods of MWCNTs-Pt and MWCNTs-Re nanocomposites manufacturing

Carbon nanotubes possess hydrophobic properties associated directly with their low wettability by fluids [20,91]. Considering the above, preliminary functionalisation prior to a deposition process is necessary to bond platinum nanoparticles to the surface of carbon nanotubes. The stage of carbon nanotubes functionalisation consists of producing functional groups (-COOH, -COH, -CO) on their surface by applying processing with a mixture of acids. Carbon nanotubes are immersed in a mixture of concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4$ acids for this purpose. The carbon nanotubes are dispersed in the mixture of acids in a beaker placed in an ultrasound washer and left covered for about a day. The same nanotubes treatment procedure with, respectively, submerging, ultrasound dispergation and leaving under cover, is then applied using a 30% H_2O_2 solution. Following a functionalisation process, carbon nanotubes are filtered and washed in deionised water and dried. Platinum is precipitated as a result of a reduction reaction of a chloroplatinic acid mixture H_2PtCl_6 with sodium borohydride NaBH_4 and ethylene glycol. An MWCNT-Pt nanocomposite manufacturing schematic is shown in Fig. 2.4.

The functionalisation of carbon nanotubes in an oxidising medium is performed in the first place when fabricating an MWCNT nanocomposite, as a result of which functional groups are formed on their surface representing the nucleus place of Rhenium nanoparticles. The functionalised carbon nanotubes are separated from a medium in which they were functionalised, filtered or centrifuged, and then they are placed in a medium containing a rhenium precursor - in HReO_4 acid and next the carbon nanotubes are separated from the suspension, placed as a wet material in a heat-resistant vessel, and then it undergoes a high-temperature reduction reaction in an atmosphere of H_2 in the shield of inert gas. An MWCNT-Pt nanocomposite manufacturing schematic is shown in Fig. 2.5.

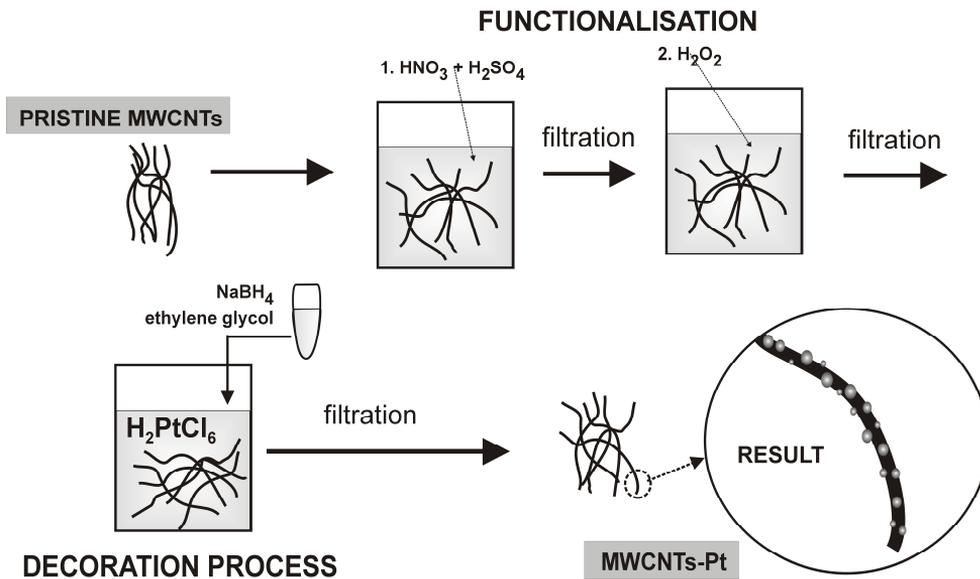


FIGURE 2.4
Schematic of MWCNT-Pt nanocomposite fabrication process [30]

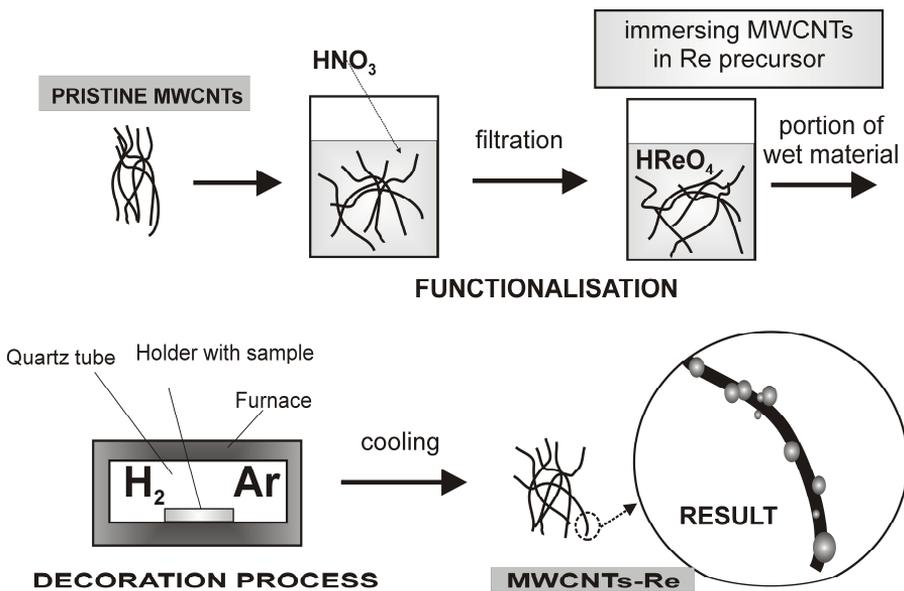


FIGURE 2.5
Schematic of MWCNT-Re nanocomposite fabrication process [30]

TABLE 2.1

Comparative analysis of the functionalisation method and conditions of MWCNTs-Pt and MWCNTs-Re

Analysis factors	MWCNTs-Pt	MWCNTs-Re
Functionalisation type	Covalent functionalisation	Covalent functionalisation
Oxidising reagent used	HNO ₃ /H ₂ SO ₄ at a rate of 1:3 (1) 30% of H ₂ O ₂ solution (2)	HNO ₃
Duration of mechanically-assisted functionalisation	30 min (1) 30 min (2)	3 hrs
Functionalisation aiding method	Ultrasounds	Ultrasounds
Functionalisation time without interference	24 hrs (1) 24 hrs (1)	24 hrs

The exemplary results of the investigations presented by the authors concern an MWCNT-Pt nanocomposite in which carbon nanotubes are functionalised as presented in Table 2.1. The functionalised carbon nanotubes were then dispersed in an ultrasound washer for 30 minutes with an addition of 15 ml of ethylene glycol. 5 ml of acetone was added to the suspension obtained during constant mixing with a magnetic stirrer. Chloroplatinic acid H₂PtCl₆ and sodium borohydride NaBH₄ 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 140°C, while stirred all the time. The nanotubes achieved were then filtered and washed 5 times in deionised water. The nanotubes were dried for 12 hours at 120°C following decoration, and then the samples were subjected to microscopic and spectrometric investigations.

Due to the specificity of Re precursors, the presented manufacturing method of carbon nanotubes decorated with rhenium takes place as a result of a reduction reaction. At the same time, the material containing CNTs and HReO₄ are subject to the heating in a presence of H₂. The reduced metal is attached automatically in the place of nanotube functional groups as nanocrystals. The presented method of CNTs-Re nanocomposites fabrication is new and is pending patent protection [92]. An MWCNT-Re nanocomposite manufacturing process comprises the following phases: the exemplary functionalisation of MWCNTs functionalised as presented in Table 2.1; one-off filtering; placing in rhenium acid (VII) aided with ultrasounds for 3 hours; putting aside the mixture for 24 hours again. The actual decoration process of CNTs with Re nanoparticles is taking place in a heating oven as a result of reduction of rhenium acid with hydrogen. Wet carbon nanotubes are placed in a quartz tube-shaped vessel with the cross section of 7 mm and with openings at the both sides, placed with its inlet towards the gas flow direction. The carbon material was then subjected to preheating at the temperature of 800°C in the atmosphere of hydrogen, the flow rate of which is 400 SCCM and in the shield of inert gas - Ar. A flow rate of hydrogen after 15 minutes of heating is decreased to 250 SCCM and the process was continued for 30 minutes to harmonise the composition of the so obtained material. The sample is then cooled down to the room temperature, and it is subjected to further specialised materials science investigations. Table 2.1

shows a comparative characteristic of carbon nanotubes functionalisation processes intended for fabrication of MWCNT-Pt and MWCNT-Re nanocomposites.

Obtained nanocomposites observed in nanoscale

The achieved MWCNT-Pt and MWCNT-Re nanocomposites were subject to microscopic observations in the bright field and dark field using the transmission electron microscope STEM TITAN 80-300 by FEI with the point resolution of ≤ 0.200 nm. 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 EDS. Imaging in the transmission mode (parallel beam) and scanning-transmission mode (concentrated beam) was used during the examinations using BF and HAADF detectors. An HAADF detector in the STEM mode was used to assess a morphology and structure of the examined nanocomposite. This type of examinations is adequate for materials the components of which are strongly differing in their ordinal number (so-called Z contrast). Platinum and rhenium nanoparticles, due to their much higher atomic number of platinum ($Z=78$) and rhenium ($Z=75$) than carbon ($Z=6$), are strongly scattering electrons from an electron beam and are thus discernible as lightly illuminating precipitates on the surface of carbon nanotubes. Materials for transmission electron microscopy investigations are prepared by dispersing the MWCNT-Pt or MWCNT-Re nanocomposites achieved in ethanol with an ultrasound washer, and then by depositing them as droplets using a pipette onto a copper mesh covered with carbon film. The material deposited as a droplet is dried with free air at the room temperature. The photographs of the carbon nanotubes decorated with platinum and rhenium nanoparticles, being the outcome of own observations made with a transmission electron microscope, are presented in Figures 2.6-2.9.

An MWCNT-Pt nanocomposite is characterised by highly dispersed Pt particles on the surface of carbon nanotubes and no tendency to agglomerate nanoparticles pointing out that a decoration process has been done correctly. It was found, however, as a result of further investigations that if a larger amount of H_2PtCl_6 is used in the decoration process, this diminishes the homogeneity of loading nanoparticles on the surface of nanotubes and heightens the probability of their agglomeration [27]. A structure of an MWCNTs-Pt nanocomposite features a morphology similar to other such nanocomposites produced with chemical methods, which are presented in a literature review [44,50,51]. The results of studies confirm that the application of chemical reduction using sodium borohydride is an effective method and leads to the creation of a homogenous nanocomposite structure. The method is worth recommending in case of mass fraction of platinum of below 15%. The own studies have revealed that in the situation where the mass fraction of Pt in an MWCNTs-Pt-type nanocomposite is equal to or higher than 20%, Pt nanoparticles are deposited non-uniformly, thus creating agglomerates.

An MWCNT-Re nanocomposite possesses non-uniformly arranged rhenium nanoparticles on the external walls of carbon nanotubes. As compared to an MWCNT-Pt nanocomposite, the shape of Re nanoparticles covering carbon nanotubes is diverse, and also numerous irregularly shaped nanoparticles occur. The diameter of the majority of rhenium nanoparticles does not exceed 10 nm (usually 3-7 nm), the presence of Re agglomerates was however seen during microscopic studies. An HAADF detector was used in the STEM imaging mode (Fig. 2.7 and 2.8) in order to obtain more exact information about the arrangement of platinum and rhenium nanoparticles on the surface of MWCNTs. Both, platinum nanoparticles and rhenium nanoparticles are visible as light precipitates in microscope images. The size of the platinum nanoparticles manufactured on the surface of carbon nanotubes is uniform in the whole volume of the observed nanocomposites and is about 3-

5nm. An average diameter of a single rhenium nanoparticle varies between 3 and 7 nm in presented results. A large number of rhenium nanoparticles with their diameter exceeding 10 nm was also noted during the examinations. The agglomerates occur in samples especially when

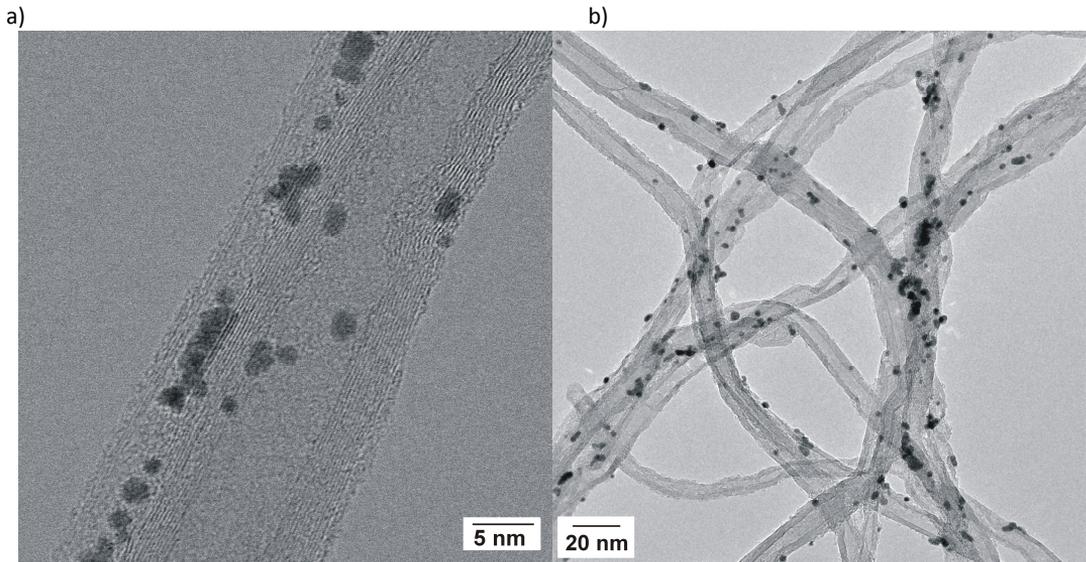


FIGURE 2.6

MWCNTs-Pt nanocomposites observed in bright field (a,b) [30, 86]

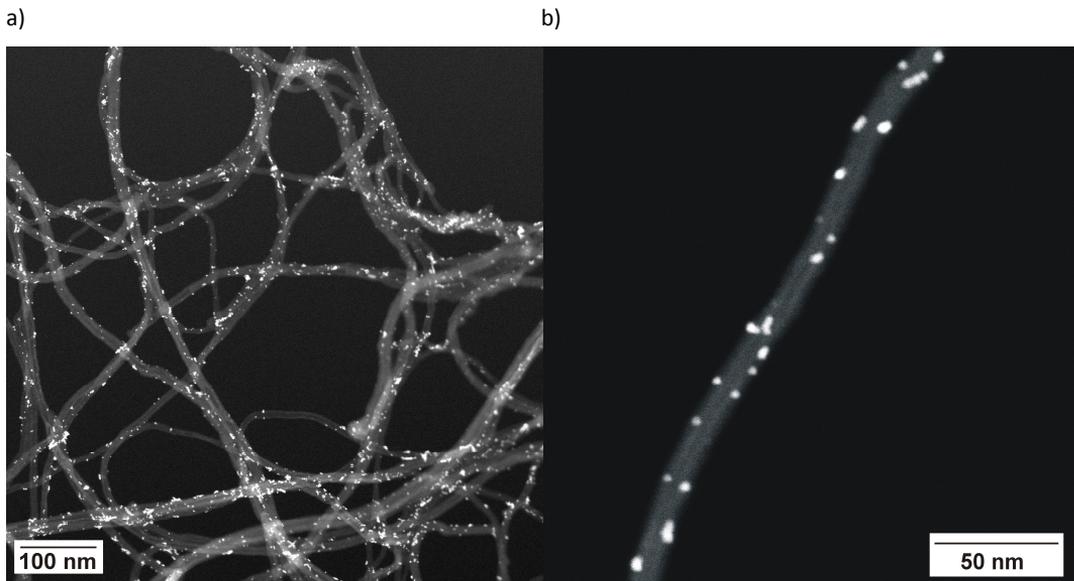


FIGURE 2.7

MWCNTs-Pt nanocomposites observed in dark field (a,b) [30, 86]

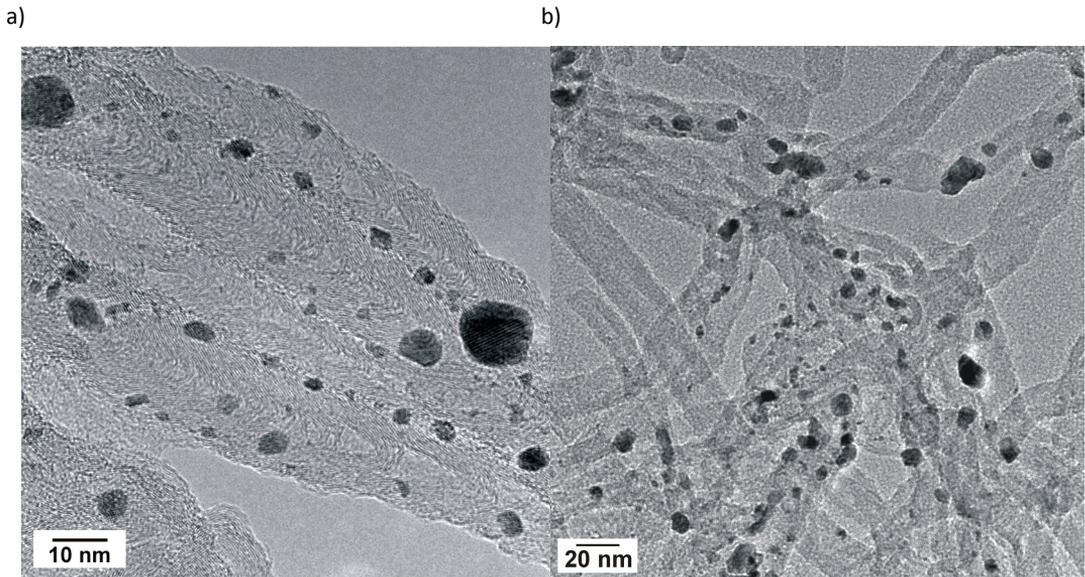


FIGURE 2.8
MWCNTs-Re nanocomposites observed in bright field (a,b) [31]

ultrasound is applied for a short time. Rhenium nanoparticles exhibit a clear agglomeration tendency, noticeable especially during imaging with smaller magnification. The fabrication of and research into the structure of newly created MWCNTs-Re-type nanocomposites is a novelty in the world of science and as such is pending patent protection [92]. It was noticed in the course of the studies that agglomeration and differences in the shape and size of Re nanoparticles are mainly

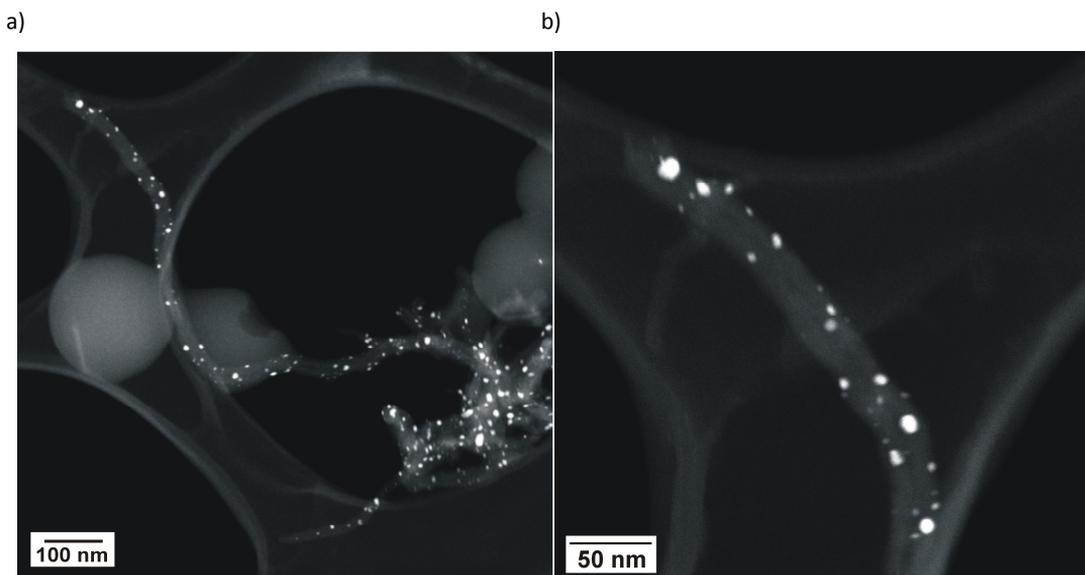


FIGURE 2.9
MWCNTs-Re nanocomposites observed in dark field (a,b) [31]

dependent on the functionalisation method, a concentration of a metal precursor solution and heating parameters. A crystalline character of the platinum and rhenium nanoparticles fabricated is confirmed by STEM observations made with an HAADF detector, allowing to record visible crystalline planes. Table 2.2 compares the structure and morphology of MWCNT-Pt and MWCNT-Re nanocomposites.

TABLE 2.2

Comparative analysis of structure and morphology of MWCNTs-Pt and MWCNTs-Re [30]

Properties	MWCNTs-Pt	MWCNTs-Re
Deposited metal	Platinum	Rhenium
Nanoparticle shape	Spherical nanoparticles discernible in the whole volume of the observed nanocomposites	Irregularly-shaped and spherical nanoparticles was observed
Nanoparticle size	3-5 nm	Nanoparticles with average diameter of 3-7 nm and nanoparticles with diameter over 10 nm
Arrangement of nanoparticles	High level of dispersion, no agglomeration tendency	Non-uniformly arranged, agglomeration tendency

The examinations of MWCNT-Pt and -Re nanocomposites clearly reveal that a functionalisation method of carbon nanotubes and a fabrication method of the presented carbon-metal materials are fundamental importance for the morphology of such materials. It can be concluded that the nanocomposites fabricated with the chemical synthesis method are more homogenous within their entire volume, while the reduction, in an oven, of wet carbon materials previously placed in a precursor of a given metal is contributing to the formation of clusters of nanoparticles, which hinders to achieve nanocrystals with narrow size distribution.

Quality and chemical composition of obtained nanocomposites

The level of defects of the carbon nanotubes' structure before and after a platinum and rhenium nanoparticles deposition process was examined using a Raman Via Reflex spectrometer by Renishaw fitted with a confocal Research Grade microscope by Leica. Excitations were carried out with a beam with the wavelength of $\lambda = 514$ nm of an ion-argon laser with the power of 50 mW, with a plasma filter for 514 nm. Measurements were recorded using a Long Working Distance (LWD) lens with magnification of x 20.

Figure 2.10 shows the Raman spectra of unmodified carbon nanotubes and carbon nanotubes decorated with platinum nanoparticles. A spectrum of the input nanotubes is characterised by the occurrence of the following bands: D at ~ 1344 cm^{-1} , G at ~ 1574 cm^{-1} and G' at ~ 2685 cm^{-1} . The bands mentioned also exist on the spectrum of nanotubes modified with platinum, however, D and

G peaks are shifted slightly to the right relative to the location of such peaks corresponding to pristine nanotubes. The presence of D ($\sim 1345 \text{ cm}^{-1}$), G ($\sim 1582 \text{ cm}^{-1}$) and G' ($\sim 2685 \text{ cm}^{-1}$) band can be observed. The intensity of the G band coming from structural defects or impurities is the most important difference between the two recorded spectra. The chemical modification of carbon nanotubes' structure due to the attachment of functional groups (-COOH, =CO, -OH) onto their surface and then the attachment of Pt nanoparticles, causes a disruption to MWCNTs' structure, and is manifested by a higher intensity of the D band. The average intensity of the D band in a Raman spectrum, as compared to the intensity of the G band (I_D/I_G), for a sample of pristine MWCNTs, is 0.97, while the I_D/I_G ratio grows to, respectively, 1.26 for samples modified with Pt nanoparticles (table 2.3). A comparative analysis of variations in the ratio of the G' band and the D band intensity ($I_{G'}/I_D$) was also undertaken due to the fact that the G' band is independent of the impurities present in the sample. The results in table 2.3 confirm that the input carbon nanotubes are chemically modified, moreover, a higher value of the $I_{G'}/I_D$ ratio for an MWCNT-Pt nanocomposite (0.66) was recorded as compared to unmodified nanotubes (0.51). The change of G band location of about 8 cm^{-1} (1582 cm^{-1}) in relation to pristine MWCNTs is another considerable difference observed for the analysed spectra. All those changes confirm that functionalisation has been carried out effectively.

Figure 2.11 compares Raman spectra registered for MWCNTs intended for further experiments and MWCNTs modified with rhenium nanoparticles. A Raman spectrum of the input carbon nanotubes is characterised by the occurrence of the D band at $\sim 1343 \text{ cm}^{-1}$, G at $\sim 1571 \text{ cm}^{-1}$ and G' at $\sim 2686 \text{ cm}^{-1}$, while the presence of the D band at $\sim 1345 \text{ cm}^{-1}$, G band at 1574 cm^{-1} and G' band at $\sim 2693 \text{ cm}^{-1}$ was recorded for a spectrum of carbon nanotubes decorated with Re. It was pointed out based on the comparative analysis of the recorded spectra that a considerably higher intensity of the G band (threefold) and D band (twofold), as compared to the input material, is noticed on a spectrum for an MWCNT-Re nanocomposite. The experiments performed to date confirm that

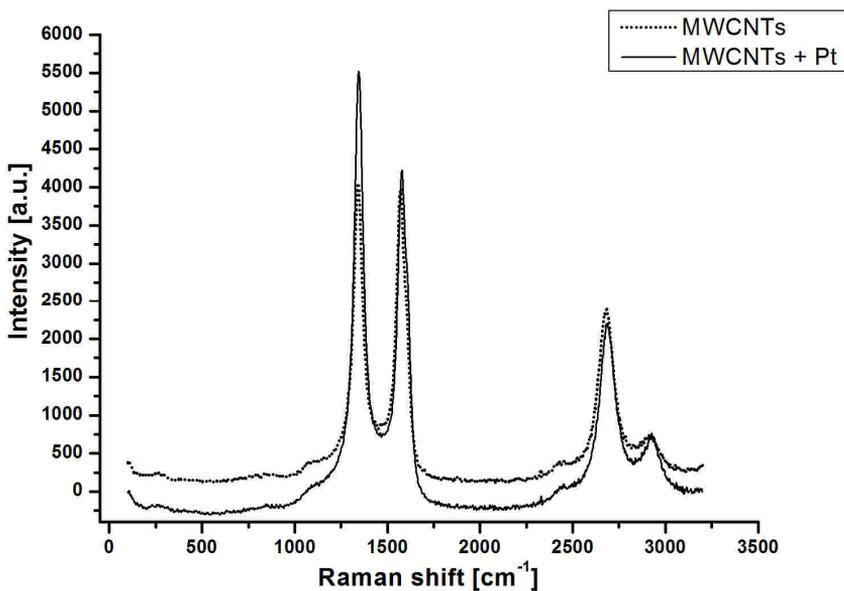
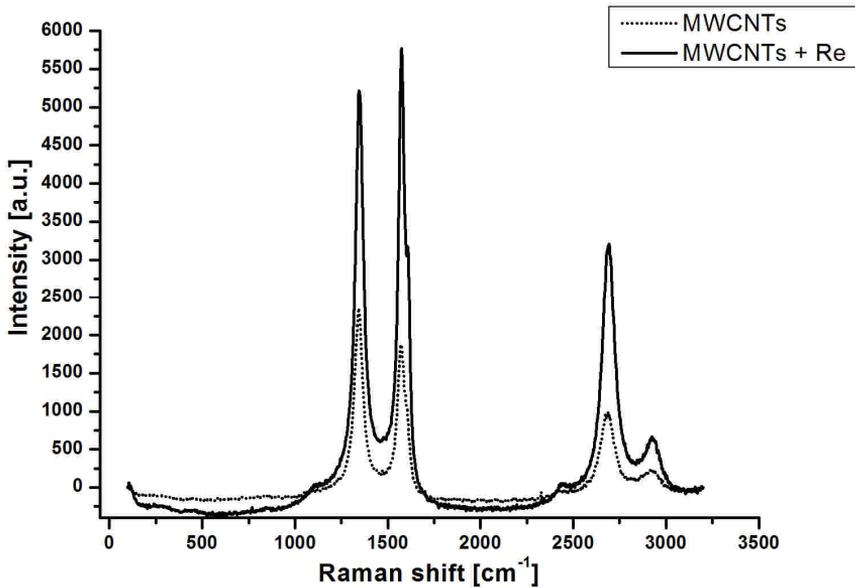


FIGURE 2.10

Raman spectra of pure carbon nanotubes and exemplary MWCNTs-Pt nanocomposites formed on their basis [30]

**FIGURE 2.11**

Raman spectra of pure carbon nanotubes and exemplary MWCNTs-Re nanocomposites formed on their basis [30]

usually, after a decoration process, the I_D/I_G ratio calculated for MWCNT-Re nanocomposites is smaller for pristine MWCNTs prior to an experiment. This fact is accounted for by the specificity of the fabrication process, as one of the stages of the decoration process of carbon nanotubes with

TABLE 2.3

Comparative analysis of results of spectroscopy examinations carried out for unmodified carbon nanotubes and MWCNTs-Pt, MWCNTs-Re nanocomposites formed on their basis [30]

Material	I_D/I_G	I_G/I_D	D band location[cm^{-1}]	G band location[cm^{-1}]
Unmodified MWCNT being future component of MWCNTs-Pt nanocomposite	0.97	0.66	1344	1574
MWCNT-Pt nanocomposite	1.26	0.51	1345	1582
Unmodified MWCNT nanocomposite being a future component of MWCNTs-Re nanocomposite	1.25	0.42	1343	1571
MWCNT-Re nanocomposite	0.9	0.62	1345	1574

rhodium nanoparticles is that they are heated at a high temperature in the atmosphere of H_2 . A high temperature (800-1600°C) is conducive to the improved order of graphene nanotubes' structure and removes carbon contaminants formed at the stage of synthesis or functionalisation.

The ratio of the D band to G band intensity (I_D/I_G) for nanotubes decorated with Re nanoparticles is 0.9 and is smaller by about 30% relative to the input nanotubes (1.25). This result signifies that

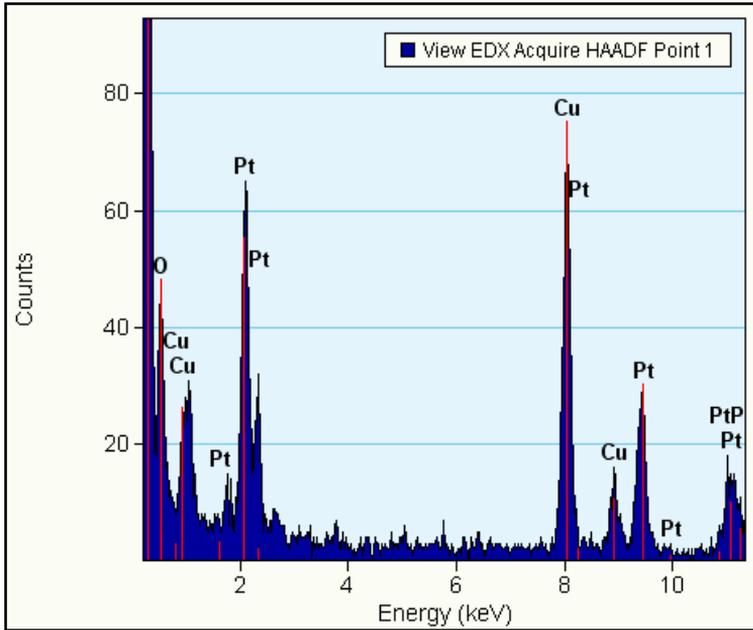


FIGURE 2.12

Result of analysis of chemical composition made with EDS for MWCNTs-Pt [93]

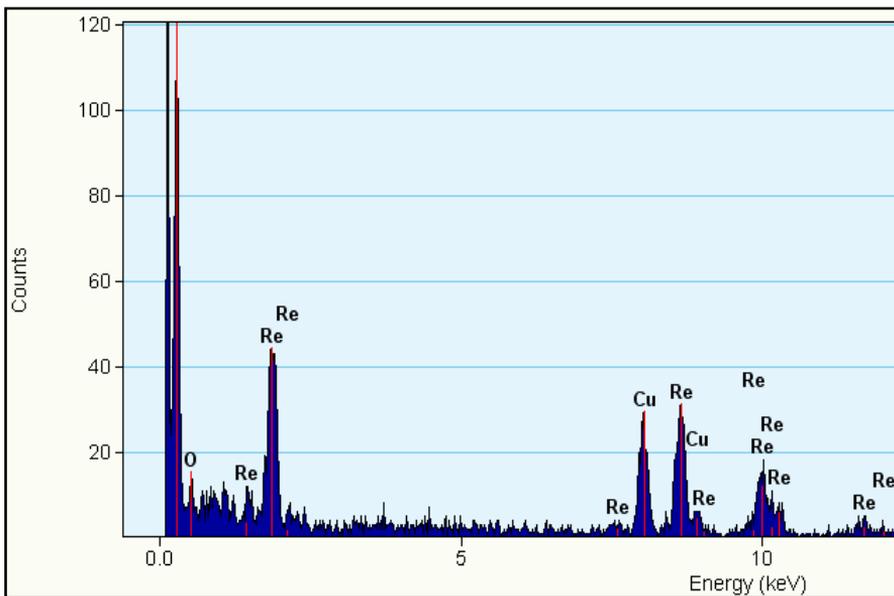


FIGURE 2.13

Result of analysis of chemical composition made with EDS for MWCNTs-Re [93,94]

a material with better quality is achieved. This is also reaffirmed by microscopic examinations. In addition, the intensity ratio of G' mode to D mode ($I_{G'}/I_D$) calculated for unmodified nanotubes and those decorated with Re has also changed and is, respectively: 0.42 (MWCNTs-raw) and 0.62 (for MWCNTs-Re). Another difference observed on the analysed spectrum recorded for an MWCNT-Re nanocomposite is a shifted location of the D and G band relative to pristine MWCNTs. The shift of the band D by 2 cm^{-1} and G by 3 cm^{-1} was found. The presented comparative analysis of Raman spectra clearly shows that a synthesis method of CNT-NP nanocomposites has a significant effect on the morphology of the materials and also has an effect on the formation of possible structural defects or, on the contrary, it improves the quality of the carbon as is the case for nanocomposites heated at high temperatures.

The chemical composition of the presented carbon-metal nanocomposites, including the presence of, respectively, Pt and Re in a sample, was confirmed with an Energy Dispersive Spectroscopy (EDS) fitted with a Supra 35 scanning electron microscope (SEM) by Carl Zeiss. The results of the tests are presented in Fig. 2.12 and 2.13.

Conclusions

Much attention in materials engineering is devoted to usable functions of materials. The designing of new materials at a nanometric scale with the desired structure and expected physiochemical properties is currently an objective of numerous research teams. Very rapid advancements have been seen in research and development works associated with nanomaterials, including nanocomposites consisting of carbon nanotubes and nanoparticles permanently deposited on their surface. High demand for new materials with unique and excellent properties has been witnessed. New applications for such materials are still being sought. It is therefore reasonable to develop and optimise fabrication methods of CNT-NPs nanocomposites. It is important that their quality is as good as possible and the manufacturing process uncomplicated and efficient. The two carbon-metal nanocomposites presented, differing in the metal deposited on MWCNTs as nanoparticles, feature an interesting structure and properties. The specificity of the two elements, i.e. platinum and rhenium, and a reduction method of such metals' precursors is decisive when designing a method of manufacturing the presented nanocomposites. It is concluded based on a comparative analysis of the structure of MWCNT-Pt and MWCNT-Re nanocomposites that the progress of a decoration process has a significant effect on the morphology of the compared carbon-metallic nanocomposites. Nanocomposites with a definitely different structure have been achieved as a result, despite applying the same input material. A process, in which platinum nanoparticles are precipitated and then attached permanently to external walls of MWCNTs, takes place in a liquid environment with a magnetic stirrer. The permanent movement of nanotubes in a medium is therefore ensured, as a result of which uniform dispersion of Pt nanoparticles on MWCNTs is attained. The last step of the manufacturing process for MWCNTs-Re nanocomposites is the reduction of a wet carbon material placed in a specially designed vessel. A process of HReO_4 reduction with hydrogen takes place in a furnace then and is not assisted mechanically in any way. This is leading to the formation of large Re agglomerations and hinders the homogenous distribution of nanoparticles on the surface of carbon nanotubes. An MWCNT-Re nanocomposite has been established and submitted for patent protection recently [92] and further research efforts are pursued to find the optimum process parameters which will consequently allow to achieve high-quality nanocomposite materials.

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