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Features of platinum as the carbon nanocomposites component

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ABSTRACT

Purpose: The primary aim of the article is to present the methodology of selection of a noble metal for a constituent component of a Carbon NanoTubes-NanoParticles (CNT-NPs) nanocomposite. The platinum group elements, i.e. Pt, Rh, Rd, Pd, were characterised as part of the works in terms of their suitability for the planned experiments with the weighted scores method.

Design/methodology/approach: A dendrological matrix was used for selection of a noble metal, thus employing a procedural benchmarking method.

Findings: The heuristic investigations conducted have revealed that, considering the criteria used for the assessment of the potential and attractiveness of the analysed metals, platinum was awarded the highest weighted score for the analysed materials.

Practical implications: The CNT-NPs nanocomposites fabricated by deposition of nanoparticles of noble metals onto carbon nanotubes are characterised by subtle electrical properties and a highly developed specific surface, which makes its particularly suitable as active elements of industrial gas sensors such as: H_2, CO, CO_2, NH_3, NO_2, CH_4, H_2S. Moreover, applications are expected of such nanocomposites in biomedicine as glucose and cholesterol sensors.

Originality/value: The selection of a platinum group metal as a constituent component of a nanocomposite consisting of carbon nanotubes and nanoparticles, using the procedural benchmarking technique.

Keywords: Nanomaterials; Platinum; CNT-NPs nanocomposites; Heuristic analysis

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MATERIALS

1. Introduction

The interest in nanostructural materials of Carbon NanoTubes-NanoParticles (CNT-NPs) type manufactured through the deposition of nanoparticles of noble metals onto the surface of carbon nanotubes stems from a synergy of unique physiochemical properties of their constituent components, namely: large specific surface area, high electrical conductivity and high thermal and chemical resistance. The materials, due to their good biocompatibility with enzymes, proteins and DNA, can act as biosensors of such substances [1,2]. Examples are currently known of the fabrication of glucose [3] and cholesterol [4] biosensors in which modified nanotubes act as an active element. Industrial applications of nanotubes coated with other nanoparticles are also expected 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, and in farming for evaluation of conditions in greenhouses [5].

The scientific and business circles are especially interested in the applicability of CNT-NPs nanocomposites with subtle electrical properties and a highly developed specific surface as an active surface of industrial gas sensors [6,7,8,9]. The detection of very low concentrations of such gases as O_2, CO, CO_2, NH_3, NO_2, CH_4, H_2S [6,7,9,10,11] is a very important task in the aspect of chemical safety, environmental objectives and evaluation of leak-tightness and detection of hazardous substances in industrial and home gas installations.

Unmodified carbon nanotubes are already highly sensitive to a chemical character of an environment in which they are located [10,12,13,14,15], and the presence of gases has a significant effect on the change of their electrical properties such as: electrical resistance, thermoelectric force and density of electron states [16]. An ability of gas adsorption and transportation of charges by nanotubes depends on their topological properties such as interaction areas between nanotubes, nanopores and areas of individual nanotubes, but also on the type of gas molecules. The adsorption of gas molecules by carbon nanotubes has a direct impact on their electron properties by changing the Fermi level and density of states, therefore the conductivity of nanotubes is changing in contact with gas molecules [17,18]. The chemical modification of nanotubes' surface, e.g. by deposition of noble metal nanoparticles onto them, such as Pt, Pd, Rh, Au, Ag, Re [6,7,9,19], additionally strengthens this effect and is increasing the sensitivity threshold, selectivity and operating speed of sensors. The selection of the appropriate type of nanoparticles is a fundamental aspect determining the properties of the CNT-NPs nanocomposites fabricated. Therefore, from a scientific and technological viewpoint, new scientific research is important and appropriate, enabling - adequately to the objectives intended – to select the nanoparticles representing a constituent component of a nanocomposite containing also carbon nanotubes. In the group of noble metal elements, platinum draws greatest attention of scientific circles due to its unique catalysing properties [20].

The aim of the article is to present a methodology of selection of noble metal nanoparticles for a constituent component of a CNT-NPs nanocomposite, with special emphasis on the criteria of attractiveness and potential of the considered metals. A dendrological matrix, utilising a procedural benchmarking method of implementing the existing, proven procedures for another thematic area or field of knowledge, was applied for selection of a noble metal.

2. Platinum characteristics and applications

Platinum (Pt) is a greyish-white, ductile metal crystallising in the A1 lattice (Fig. 1) belonging to the platinum group. The group also comprises palladium (Pd), ruthenium (Ru), rhodium (Rh), osmium (Os) and iridium (Ir). Platinum group metals, due to their unique physio-chemical properties, presented in Table 1, are classified as noble metals together with gold and silver. Platinum plays the most crucial technical role for the noble metals listed. Platinum had already been used by Colombian Indians for producing small everyday objects, hence its name (*plata* in Spanish means silver). The global platinum resources are estimated at about 31,000 tonnes, and the greatest deposits of this material are situated in South Africa, Canada, Russia and Zimbabwe. Platinum may occur in its virgin form, in virgin alloys with other platinum group metals or as chemical compounds. Poland's platinum resources are situated in Lower Silesia Province near Lubin and Polkowice, where it is extracted from copper with platinum content of up to do 1 gram per tonne [20,21,22].

Platinum has widespread applications owing to its unique chemical and physical properties such as high melting temperature and boiling point, ductility, high chemical resistance, very good catalytic properties (best for platinum group metals) and good electrical conductivity. Platinum is used in particular in the chemical, automotive, petroleum, electrical and glass industry, jewellery, medicine, dentistry and for capital investments (Fig. 2) [23]. Platinum's excellent catalytic properties are used in numerous industrial processes, notably in oxidisation and reduction reactions when producing sulphuric acid (VI), nitric acid from ammonia and hydrocyanic acid. Platinum is also used as a catalyst for hydrogenation of organic substances. The physiochemical properties of platinum are used in the petroleum industry for producing high-octane fuel, mainly lead-free fuel and for catalytic cracking and isomerisation. Raw materials having worse and worse quality are supplied due to diminishing resources of crude oil deposits, hence the role of such processes and importance of platinum will continue to grow [20,21,22,24].

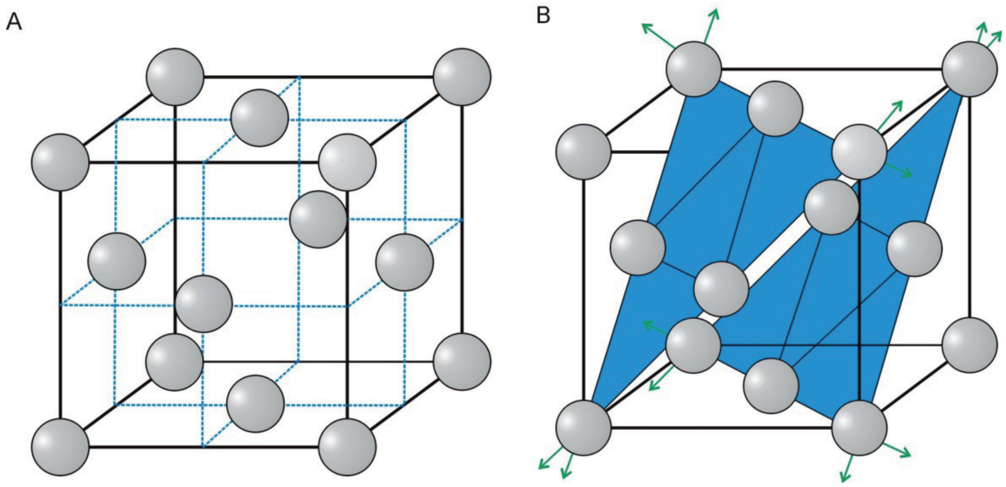


Fig. 1. Lattice structure of A1- regular and wall-centred: (A) distribution of atoms, (B) planes {111} and directions <110> with dense arrangement of atoms [24]

Table 1.
Physical and chemical properties of platinum versus other platinum group metals [20,24]

Properties	Platinum	Palladium	Rhodium	Ruthenium	Iridium	Osmium
Atomic number	**78**	46	45	44	77	76
Atomic mass, u	**195.08**	106.42	102.91	101.07	192.22	190.23
Electron configuration	**$4f^{14}5d^{9}6s^{2}$**	$4d^{10}$	$4d^{8}5s^{1}$	$4d^{7}5s^{1}$	$4f^{14}5d^{7}6s^{2}$	$4f^{14}5d^{6}6s^{2}$
Oxidisation level	**II, IV**	II, IV	II, III, IV, VI	I, II, III, IV, V, VI, VII, VIII	I, II, III, IV	III, IV, VI, VIII
Crystalline structure	**A1**	A1	A1	A3	A1	A3
Atomic radius, Pm	**138**	137.6	134.5	134	135.7	135
Density, g/cm^3	**21.45**	12.02	12.41	12.45	22.65	22.61
Melting point, °C	**1772**	1552	1966	2310	2410	3045
Boiling point, °C	**3800**	2900	3700	4150	4500	5020±50
Ionisation energy, kJ/mol	**870**	805	720	711	880	840
Ionisation potential, eV	**8.9-21.4**	8.3-12.0	7.7-12.4	7.7-12.4	8.7-22.4	8.7-22.5
Resistivity in 0°C, μΩ·cm	**9.85**	9.93	4.33	6.8	4.71	8.12

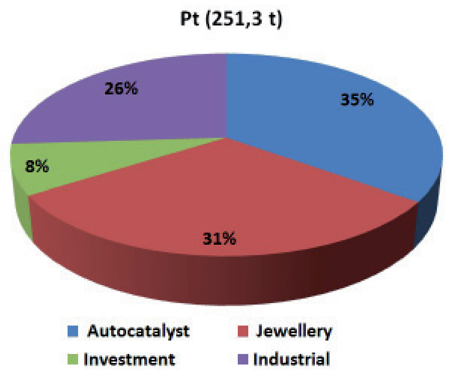


Fig. 2. Global platinum consumption in 2012 [23]

At room temperature, platinum is resistant to the activity of the most of chemical reagents, and only dissolves in aqua regia. High corrosion resistance and high melting temperature make it suitable for producing chemical apparatuses, melting pots, electrodes, thermo-elements. In addition, high biocompatibility and good mechanical strength allow to use platinum for manufacture of surgical instruments and biomedical appliances such as: pacemakers, defibrillators, stents and cochlear implants. Another unique property of platinum applied in the field of medicine is its ability to inhibit division into living cells, hence it is applied in treatment of tumor diseases. One of platinum's most important applications in the automotive field is production of catalytic converters of flue gases. Platinum-based catalysts reduce the emission of flue gases to the environment by converting at the same time the three toxic substances: CO into CO_2, hydrocarbons into water and CO_2 and NO_x into nitrogen and oxygen. The electric and electronic industry is using platinum for production of electrical contacts, resistors, thermocouples, heating elements and hybrid integrated circuits. High platinum prices at international exchanges are a reason why capital is invested in bars, coins, medals and stocks made of this material. Moreover, a rising demand for platinum is seen in the jewellery sector where it is used for making jewellery, especially rings and for decoration of noble stones [20,21].

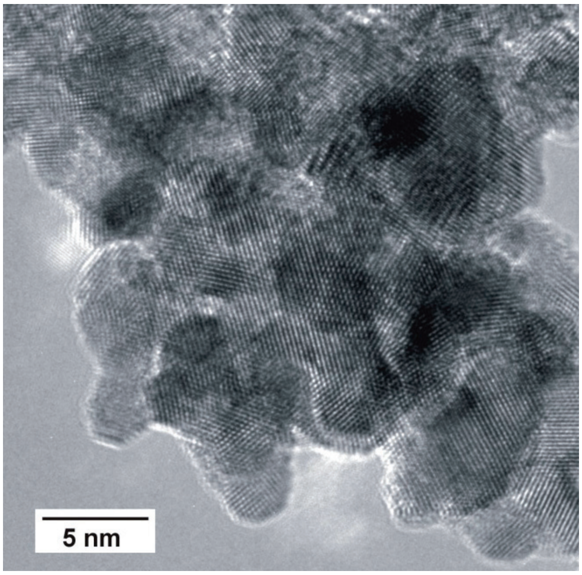
The durability of platinum compounds depends on several factors, namely: solution acidity, presence of chloride ions and a concentration of metal ions, while platinum creates strongest compounds in its 2nd and 4th level of oxidisation (electron configuration d^8 and d^6). Nitrosyl complexes $[(NO)_2(PtCl_6)]$ are formed due to dissolution of platinum in aqua regia. The complexes achieved are further processed through evaporation several times with sulphur acid to decompose to hexachloroplatinic acid (IV) – H_2PtCl_6 according to the reaction (1) [20]. Hexachloroplatinic acid (IV) is the most important platinum compound in the 4th level of oxidisation, and also an input substance for achieving various platinum compounds (tetrachloroplatic acid (II), $PtCl_4$, PtS_2) and their nanoparticles.

$$(NO)_2[PtCl_6] + 12\ HCl \leftrightarrow H_2[PtCl_6] + 2NOCl\uparrow \qquad (1)$$

Platinum nanoparticles, due to their dimensions (1-100 nm), possess unique chemical, physical or electrical properties which vary completely from platinum properties in macroscopic terms [25]. Figure 3 shows images of a high resolution transmission electron microscope in bright field (Fig. 3a) and dark field (Fig. 3b) obtained in the HRTEM mode, presenting platinum nanoparticles with a visible system of atom orders. Small dimensions of nanoparticles are directly associated with their large specific area, higher speed of transporting electrons and a high catalytic activity [25].

A higher detection ability of platinum nanoparticles is also a consequence of their large specific surface, but also ability of electron interaction with the molecules of reacting substances. The ability of platinum nanoparticles of oxidisation and reduction of hydrogen peroxide (H_2O_2) indicates their potential application as a sensitive sensor of this compound. The successful attempts of using platinum for building an H_2O_2 senor consisted of modification, using platinum nanoparticles, a carbon layer of electrodes and surface of carbon nanotubes [26]. It is worth highlighting that hydrogen peroxide is a product of many enzymatic reactions, which may support the use of platinum nanoparticles as active elements of electrochemical biosensors, e.g.: glucose, cholesterol and dopamine [4,26,27]. In addition, much lower production costs in relation to electrodes made fully of platinum are also a significant economic factor crucial for the use of platinum nanoparticles in electrochemistry [25]. Composites containing platinum nanoparticles may also react to the presence of other gases obnoxious for the environment.

a)



b)

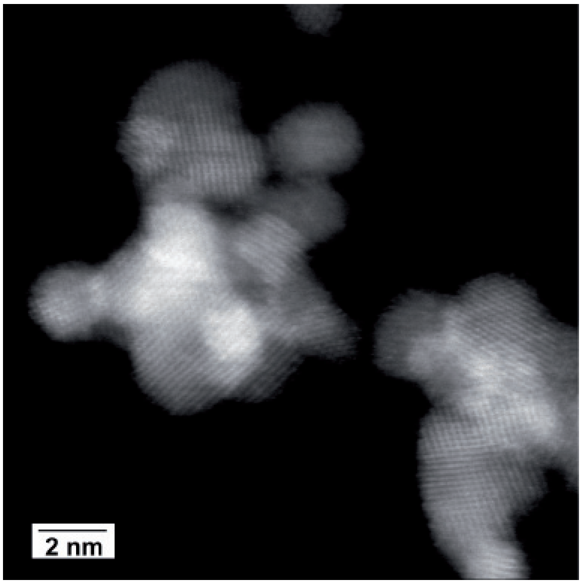


Fig. 3. HRTEM images showing platinum nanoparticles: a) bright field [28], b) dark field

3. Methodology and background

An heuristic analysis [29] undertaken under a technology foresight of materials surface engineering [30] for critical technologies classified as technologies of nanostructural surface layers has revealed that prototype technologies consisting of surface treatment of materials, including decoration of carbon nanotubes with platinum nanoparticles, possess very high development prospects corresponding to 9 points in a 10-degree universal scale of relative states. The development prospects of ten groups of critical technologies of nanometric surface layers marked as A_{M6}-J_{M6}, expressed quantitatively, are presented graphically using a matrix of strategies for technologies (Fig. 4) [29]. The matrix is a result of individual variants being a combination of four values of technologies with four types of environment interaction [30]. The value of a technology expressed with a value of its potential and attractiveness is presented using a four-field dendrological matrix in which the following fields are distinguished: a wide-stretching oak (high technology potential and high attractiveness), a soaring cypress (low technology potential and high attractiveness), a rooted dwarf mountain pine (high technology potential and low attractiveness) and a quaking aspen (low technology potential and low attractiveness). The environment influence intensity, both positive (opportunity), and negative (difficulty), is presented graphically with a four-field meteorological matrix consisting of the following fields: sunny spring (many opportunities and few difficulties from the environment), hot summer (many opportunities and many difficulties from the environment), rainy autumn (few opportunities and few difficulties from the environment) and frosty winter (few opportunities and many difficulties from the environment).

The technology strategy matrix (Fig. 4) allows to establish a strategy which is recommended for use in relation to individual groups of critical technologies of nanostructural surface layers, to which the following was classified based on the foresight investigation pursued [29,30]: A_{M6}: Reactive Ion Etching (RIE); B_{M6}: Electron Beam Lithography (EBL); C_{M6}: Chemical Vapour Deposition of nanometric surface layers; D_{M6}: Physical Vapour Deposition of surface layers using Ion Beam Assisted Deposition (IBAD); E_{M6}: Physical deposition of nanometric surface layers with Electron Beam Physical Vapour Deposition (EB-PVD); F_{M6}: Atomic Layer Deposition (ALD); G_{M6}: Electrodeposition of nanometric surface layers; H_{M6}: Sol-gel method of fabrication of nanometric surface layers; I_{M6}: Deposition of coatings with nanomaterials on surface layers; J_{M6}: Surface treatment of nanomaterials.

The J_{M6} group of technologies, including deposition of metal nanoparticles onto carbon nanotubes, is in its prototype phase of development and requires the usage of a cypress in spring strategy. The strategy indicates it is necessary to pursue further scientific and research efforts to improve and strengthen the potential of such promising young technologies, numerous opportunities should also be exploited emerging in the closer and farther environment. 60% of the experts surveyed think that in the nearest 20 years the technology group J_{M6} will be growing in relation to other nanostructural technologies of surface layers, which confirms the suitability of conducting further research serving to develop technologies belonging to this group [29,30].

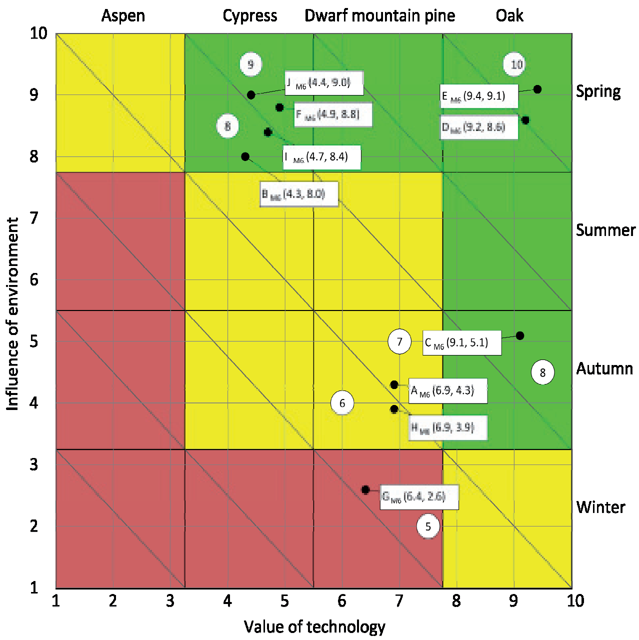


Fig. 4. Strategy matrix for technologies of nanostructural surface layers [29]

Theoretical studies, the outcomes of foresight research and an analysis of the most recent practical applications show that undoubtedly it is necessary to undertake further investigations to optimise the solutions used to date, with special attention to developing more efficient and repeatable technologies for deposition of carbon nanotubes with nanoparticles from a wide spectrum of noble metals. The newly developed solutions should be better adjusted to specific applications and enable to deposit nanocrystals with a complex morphology and dispersion.

4. Noble metal selection

A dendrological matrix of technology value [30] was used for selection of a noble metal planned for deposition onto carbon nanotubes under the own work, hence utilising a procedural benchmarking technique of implementing the existing, proven procedures for another thematic area or field of knowledge. A dendrological matrix allows for graphical presentation of results of an analysis of preferences being a research approach consisting of classifying objects within a specific scale, as expressed by a precedence hierarchy of objects presented in an ordered manner by a preferential series. The dendrological matrix applied, being a universal and original formula, enables to transform hidden qualitative knowledge into open quantitative knowledge possible for presentation using analytical methods and tools.

The method of weighted scores for comparative evaluation aimed at classifying the relevance of specific elements in the context of relations between them was used to determine the value of individual elements from the platinum group (Pt, Rh, Rd, Pd) for their appropriateness for the planned experiments. The method of weighted scores allows for a multi-criteria aggregated evaluation using a universal scale of relative states, being a 10-point single-pole scale without zero, where 1 is a minimum score and 10 is a maximum high score. Detailed criteria for evaluation of attractiveness and potential of the initially considered metals were used to select a noble metal for decoration of carbon nanotubes: Pt, Rh, Rd, Pd (Tab. 2) and their gradation was introduced by assigning specific weights to specific criteria. The values expressed in different units were rescaled to a universal scale of relative states by using 0 as a minimum value and the highest value for each considered criterion as a maximum value (10 points). The values expressed in relation to specific criteria were further calculated and summed up thus producing values being a basis for a comparative analysis (Tab. 3).

Table 2.
Detailed criteria for evaluation of attractiveness and potential of noble metals subjected to heuristic studies; the values rescaled to a universal scale of relative states are presented in grey columns [28]

Evaluation criteria	Noble metals								Mass
	Platinum		Palladium		Rhodium		Ruthenium		
Potential									
1. Melting point, °C	1772	8	1552	7	1966	9	2310	10	0.1
2. Ionisation energy, kJ/mol	870	10	805	9	720	8	711	8	0.5
3. Maximum ionisa-tion potential, eV	21.4	10	12.0	6	12.4	6	12.4	6	0.3
Attractiveness									
1. Global resources, T	31000	10	11000	4	4000	1	6000	2	0.5
2. Global consumption in 2012, T	251.3	10	262.8	10	28.2	1	25.2	1	0.3
3. Price, $/28.3g (as on 2014)	1459	10	836.6	6	1097.4	8	71	5	0.2

Table 3.
Results of multi-criteria analysis of noble metals subjected to heuristic studies for use as a nanocomposite component [28]

Noble metal	Potential				Attractiveness			
	Criterion 1	Criterion 2	Criterion 3	Weighted average	Criterion 1	Criterion 2	Criterion 3	Weighted average
Platinum	0.8	5.0	3.0	8.8	5.0	3.0	2.0	10.0
Palladium	0.7	4.5	1.8	7.0	2.0	3.0	1.2	6.2
Rhodium	0.9	4	1.8	6.7	0.5	0.3	1.6	2.4
Ruthenium	1	4	1.8	6.8	1.0	0.3	1	2.3

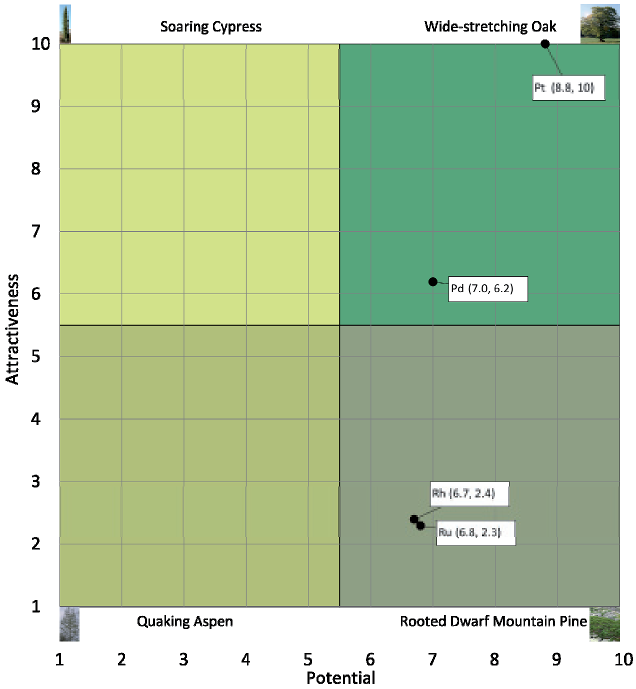


Fig. 5. Strategy matrix for technologies of nanostructural surface layers [28]

The results obtained were then presented graphically using a dendrological matrix (Fig. 5). The heuristic studies carried out point out that the highest weighted score, considering the criteria used for the assessment of the potential and attractiveness of metals, were given to platinum and this was chosen for further materials science experiments detailed in, notably [28,31,32,33]. Fig. 6 presents TEM images in the bright field (Fig. 6a) and dark field (Fig. 6b) of nanocomposites containing platinum nanoparticles in their structure apart from carbon nanotubes.

5. Conclusions

The design and fabrication of new materials with unique properties is the principal task lying ahead of the present and future generations of engineers [34,35]. 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 such materials. The modification of carbon nanotubes' structure through its initial functionalisation is leading to the creation of completely new nanotube hybrids combining unique properties of carbon nanotubes with other materials. Progress in science has made it feasible to conduct research into the development of materials based on carbon nanotubes modified with selected elements or chemical compounds.

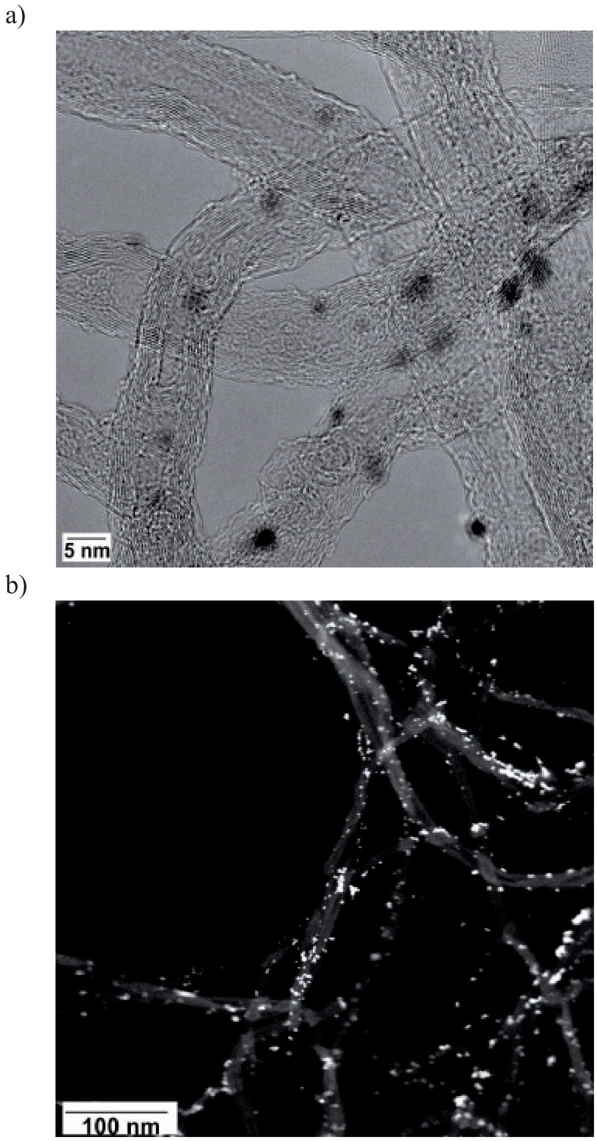


Fig. 6. TEM images of CNT-Pt nanocomposites; observations (a) in the light field; (b) in the dark field

The article presents a methodology of selection of noble metals nanoparticles for a constituent component of a CNT-NPs nanocomposite. A dendrological matrix, utilising a procedural benchmarking method of implementing the existing, proven procedures for another thematic area or field of knowledge, was applied for selection of a noble metal. The heuristic studies carried out point out that the highest weighted score, considering the criteria used for the assessment of the potential and attractiveness of metals, were given to platinum and this was chosen for further materials science experiments.

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