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Synthesis and characterization of carbon nanotubes decorated with platinum nanoparticles

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ABSTRACT

Purpose: In presented work results of synthesis of carbon nanotubes decorated with platinum nanoparticles by organic colloidal process as an example of direct formation of nanoparticles onto CNTs are reported.
Design/methodology/approach: CNT were grown by chemical vapour deposition (CVD) by the catalytic decomposition of CO. To improve metal deposition onto CNTs the purification procedure with a mixture of concentrated HNO_3–H_2SO_4 and H_2O_2 reduction reagent was applied. CNT–nanocrystal composite was fabricated by direct deposition of nanoparticles onto the surface of CNTs. Chemical composition and crystallographic structure of the obtained Pt/CNT composites were confirmed by energy dispersive X-ray spectroscopy (EDS) and by X-ray diffraction (XRD) measurements, while transmission (TEM) and scanning electron microscopy (SEM) were used for characterization of the morphology of composite as well as the distribution of nanocrystals on the CNTs surfaces.
Findings: High efficiency of proposed method was confirmed as well as possibility of the coating of Pt nanoparticles onto CNTs, without aggregation of these particles.
Research limitations/implications: Many others noble metals such as palladium, platinum, gold and iridium can be used for deposition on the CNTs using described procedure.
Originality/value: Obtained material can be employed in constructing various electrochemical sensors. As a result of increasing of the surface area of Pt caused by the reduction of the size of used particles, fabricated sensor may be characterized by higher sensitivity.
Keywords: Nanomaterials; Carbon nanotubes; Platinum nanoparticles; Nanocomposites; Sensors

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1. Introduction

Platinum has been widely used in many applications, especially as a catalyst for CO oxidation in catalytic converters and for fuel cell technology [1]. It can also be used as a stable electrode material. Since Pt is particularly expensive material, there is a real incentive to reduce the amount of Pt required in applied processes. With this end of view a lot of effort was put to reduce the size of used Pt particles what additionally can significantly increase surface area of this material. Nanomaterials are characterized by properties different to conventional materials and they are fabricated for various applications [2-6]. Carbon nanotubes (CNTs) have become the one of the mostly researched materials in the last decades because of their promising applications in any aspect of nanotechnology [7]. Potential applications of carbon nanotubes including as catalyst supports in heterogeneous catalysis, components of composites, high-strength engineering fibers, and sensors, result mainly from theirs high surface area, mechanical strength, chemical and thermal stability. Due to the possibility to combine the unique physical and chemical properties of carbon nanotubes with innovative properties of noble (including Pt) metal nanoparticles in one discrete structure there is a great deal of interest in attaching nanoparticles to nanotube surface, leading to novel and prospective applications [8]. The controlled coating of metal nanoparticles onto CNTs, without aggregation of these particles would be crucial for this issue and should be researched. Several method have been successfully developed and practically applied, for example nanocomposites based on depositing platinum nanocrystals onto carbon nanotubes play an important role in fuel cell application [9-11], for fabricating electrochemical sensors [12-17] and in many others.

Among all the enzyme-based biosensors, an important example is glucose biosensors, necessary for an accurate monitoring of blood glucose levels. Recently, Wang et al. [18] demonstrated the promising applications of CNTs in constructing such devices. Considerably larger expectations are connected with the hybrids of CNTs and platinum nanoparticles, as well as with other noble metal such as palladium, gold and iridium. Compared with the conventional scale materials, carbon nanotubes decorated with platinum nanoparticles have some fundamental advantages. Due to the large specific area of CNTs and supported platinum nanoparticles, fabricated sensor will be characterized by high sensitivity. Size of designed devices can be incredibly decreased. Ultrasensitive nanoarrays can be constructed as well as ultrasensitive sensors consisting of only one nanotube. Sensors will be characterized by good biocompatibility.

CNT–nanocrystal nanocomposites can be obtained by two different strategies. First approach involves the prior synthesis of nanoparticles that are then subsequently connected to functionalized CNTs by covalent or noncovalent interactions. The second approach involves direct deposition of nanoparticles onto the surface of CNTs. In such a case final result can be obtained through formation of nanoparticles in situ during a reduction reaction, or through an electrodeposition process using CNTs as templates [19]. There are several advantages and disadvantages of each particular method. The main gain of covalent approaches is possibility to form well-defined, structurally characterizable chemical bonds between the nanotubes and nanocrystals. Non-covalent approaches allows for the preservation of the intrinsically interesting optoelectronic properties of used nanostructures. Using that method CNTs can be uniformly coated with a relatively high density of nanocrystals. Direct formation of nanoparticles onto CNTs has two important advantages: it is highly effective method as well as the inherent properties of the nanocrystals and nanotubes are preserved. Each of these methods can be applied to obtain Pt/CNT nanocomposites.

Because of diverse set of applications, different kinds of electrochemical, chemical and physical methods have been developed to effectively synthesize Pt/CNTs composites, for example [20, 21]. In presented work we report results of synthesis of carbon nanotubes decorated with platinum nanoparticles by organic colloidal process as an example of direct formation of nanoparticles onto CNTs [22]. High efficiency of proposed method is expected, but like for any methods involving direct deposition of nanoparticles onto the surface of CNTs resulting morphology and composition can't be predicted and it is worthy of testing. The purpose of our work is to obtain Pt/CNT composites, expected to be applied for preparation glucose sensor. For this reason fabricated material have to be homogenous and contains CNTs evenly decorated with Pt nanocrystals. The density of attached nanocrystals should be enough high as well as their size not larger than a few nanometers, since finer Pt nanoparticles are expected to be more efficient catalysts. Chemical composition and crystallographic structure of the obtained Pt/CNT composites will be confirmed by energy dispersive X-ray spectroscopy (EDS) and by X-ray diffraction (XRD) measurements, while transmission (TEM) and scanning electron microscopy (SEM) will be used for characterization of the morphology of composite as well as the distribution of nanocrystals on the CNTs surfaces.

2. Experimental

2.1. Synthesis of CNTs

These days commonly two ways are used for preparation CNTs: the carbon-arc process and the catalytic decomposition of some hydrocarbons or other organics in the presence of various metal catalysts, like Ni or Co. The first method make possible to obtain relatively thin and straight carbon nanotubes, characterized by high crystallinity. The catalytic decomposition is more effective method and has been widely studied in recent years, even if obtained CNTs are worse quality. For that reason the second strategy give better possibility to obtain sufficient amount of materials for fabricating and testing electrochemical sensors. In this end of view in our work carbon nanotubes were grown by chemical vapour deposition (CVD) by the catalytic decomposition of CO. A quartz boat with nickel catalysts was placed in a CVD reactor. The nickel catalyst was prepared according to the method reported by Chen et al. [23] and calcinated at 989 K in air for 5 hours and reduced in hydrogen atmosphere for 2 hours [24]. The reactor temperature was increased under an argon flow to 900K and then kept for 15 minutes in hydrogen atmosphere (5% in argon balance). Then the feed gas (20% CO and 5% H_2 in ratio 1:1) was initiated with flow rate at 45 ml/min. The process was terminated after 3 hours, and the furnace was turned off and allowed to cool to room

temperature. The raw product was purified from the catalysts by diluted solution of hydrochloric acid to dissolve the catalyst particles, followed by washing by de-ionized water and drying. As a result homogenous material containing multiwalled carbon nanotubes with the outer diameter of 40-100 nm, and the tube length up to 10 μm, was obtained (Fig. 1).

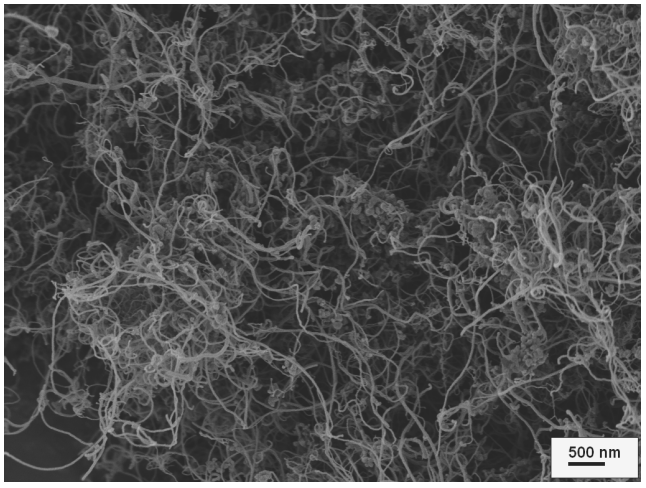

Fig. 1. SEM image of pure CNT

2.2. Functionalization of CNTs

Because of hydrophobic properties CNTs cannot be successfully wetted by liquids and most metal nanoparticles not adhere to them. To improve metal deposition onto CNTs the purification procedure with a mixture of concentrated HNO_3–H_2SO_4 (1:3 in volume) at room temperature was applied. After 12 h pretreated CNTs were dispersed by ultrasonic vibration for 0.5 h. The same treatment was repeated using H_2O_2 (30%) as reduction reagent. It is worthy to underline that used treatment process not contain heating, so we can expect that the structure of the CNTs is not heavily damaged and the good conductivity of the CNTs is retained. Simultaneously carboxylic acid, hydroxide and other functional groups, attached to the exterior surface of the CNTs during used procedure, can act as the anchor seeds for metal nanopartices deposition [25].

2.3. Deposition of Pt nanoparticles on the functionalized CNTs

Deposition of Pt nanoparticles was performed according to the procedure described at [22]. To deposit Pt nanoparticles on the functionalized CNTs, 148 mg pretreated CNTs were dispersed into 15 mL ethylene glycol by ultrasonic vibration for 0.5 h. The obtained suspension was mixed with 5 mL of acetone with continuous stirring. Afterwards 5 mL H_2PtCl_{l6} solution (0.0386 M) and 0.114 g sodium citrate were added and the pH value of the obtained suspension was adjusted to 8 by addition of 5% NaOH solution. After stirring for half an hour and heating in oil bath at 150 °C for 8 h the obtained material was washed with water for 3 times and finally dried at 70 °C.

2.4. Characterization of obtained Pt/CNT composites

SEM images in SE mode were obtained using a Zeiss Supra 35 field emission SEM equipped with energy dispersive X-ray (EDX) analyzer. Ultra high resolution and precise imaging can be obtained using high efficiency In-lens SE detector working at low beam energy and at very short working distances. Samples for scanning electron microscopy were imaged without coating. Samples for transmission electron microscopy were prepared by dispersing powder in ethanol, placing in an ultrasonic bath, then putting droplets onto 3 mm copper grids coated with amorphous carbon film and drying in air at room temperature. TEM images were recorded using a JEOL JEM-3010 transmission electron microscope operated at 300 kV. The crystal structure of the Pt nanoparticles supported on CNTs was determined by powder XRD diffractometer (Panalytical X'Pert Pro, Co K_α radiation, $\lambda = 0.1789$ nm). For the determination of the position of the diffraction peaks in XRD pattern curve fitting was performed with the software program Fityk (www.unipress.waw.pl/fityk/; Levenberg–Marquardt algorithm). The goodness-of-fit was indicated by the residuals between the calculated fit curve and the observed spectrum. Determined positions of the diffraction peaks in XRD pattern were compared with JCPDS data sets to obtain crystallographic parameters (Table 1).

Table 1.
The crystallographic parameters of the chemical components (the Bragg angle 2θ for for Co K_α radiation)

Chemical name	2θ, degrees	d_{hkl}, A	hkl
Platinum JCPDS 87-0647	47.1095	2.2389	(111)
	54.944	1.9390	(200)
	81.445	1.3710	(220)
	99.814	1.1692	(311)
Graphite JCPDS 75-1621	30.552	3.3950	(002)

3. Results and discussion

As a result of catalytic decomposition of CO black, fluffy and porous material including CNTs was obtained (Fig. 1). Fabricated material is homogenous and contained mainly carbon nanotubes, although some amount of not dissolved catalysts is visible. The typical CNTs produced by CVD in this work are roughly up a few μm in length and between 10 to 50 nm in diameter, though diameters as large as 100 nm are also observed. Outward appearance of the material obtained after deposition of Pt nanoparticles on the functionalized CNTs remain invariable. Figs. 2 (a)-(d) show morphology of the received Pt/CNT composite. Two important facts can be noted:

- obtained Pt/CNT composite is homogenous what is confirmed by SEM images performed with different magnifications,
- morphology of the obtained Pt/CNT composite, observed with higher magnifications, is distinctly different from pure CNTs.

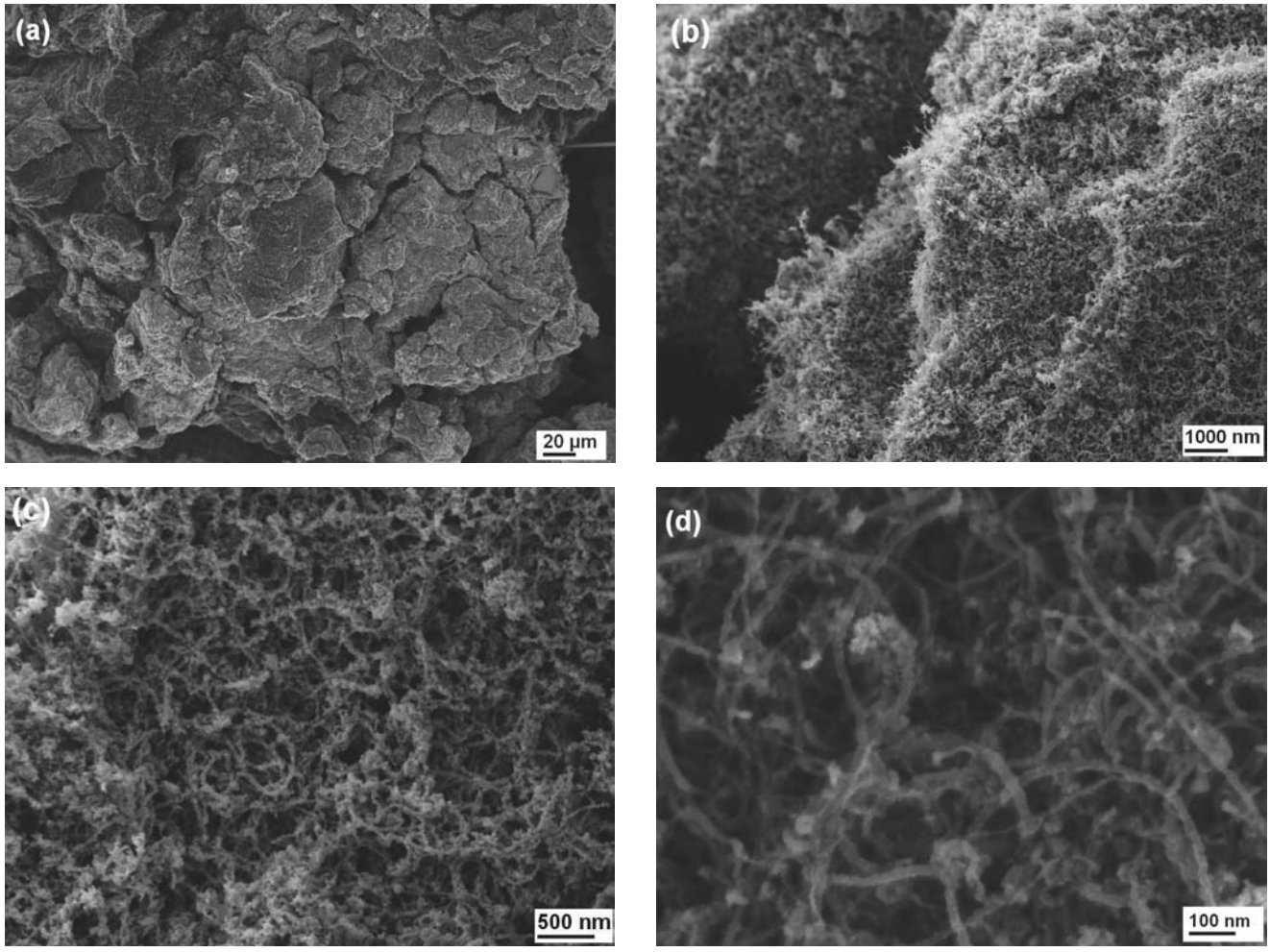

Fig. 2. (a)-(d) SEM images of Pt/CNTs composite with different magnifications. Light spots on walls of the carbon nanotubes correspond to Pt nanoparticles

The small Pt nanoparticles are poorly seen as bright spots on the CNT surfaces, evenly distributed. Their size may be estimated to about a few nm. The density of deposited particles is very high and no agglomerates were observed. The Pt phase appearance is convincingly confirmed by energy dispersive X-ray spectrometry (Fig. 3). Beside C and Pt signals, EDX spectrum includes also signals connected with O and Ni elements. The peak of O element is connected with the process of functionalization of CNTs, while the peak of Ni element is connected with presence of remained catalysts impurities.

Two representative TEM images of the Pt/CNT composite are presented in Fig. 4. Dark spots corresponds to Pt nanoparticles and light tubes corresponds to CNTs. The side walls of CNTs with diameter of 10-50 nm are evenly decorated with Pt nanoparticles. The density of attached nanocrystals are high. Observed platinum particles appear to have a narrow size distribution, and no free particles are observed in the background of the TEM images, which confirms all formed Pt nanoparticles are durably attached to the nanotubes. The size of Pt nanoparticles are significantly smaller than diameter of carbon nanotubes and could be estimated about a few up to a few dozen nm.

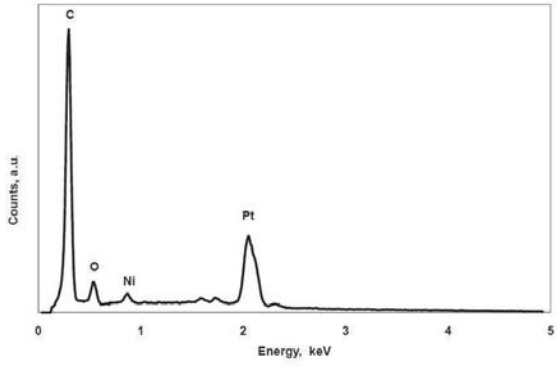

Fig. 3. EDX spectrum of Pt/CNT composites imaged in Fig. 2c

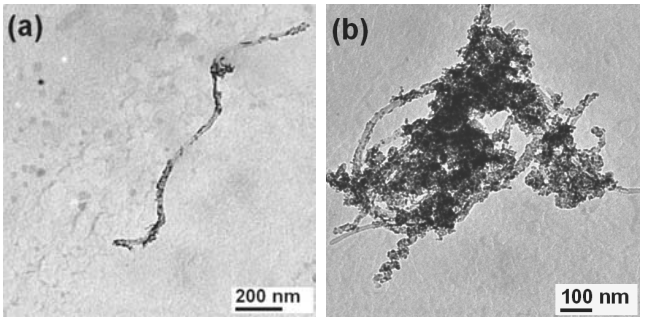

Fig. 4. TEM image (BF) of Pt/CNTs composite with dark spots corresponding to Pt nanoparticles

Fig. 5. shows the XRD pattern for the Pt nanoparticles supported on CNTs. As expected for nanomaterials obtained spectrum is noisy and difficult to interpret so for the determination of the position of the diffraction peaks curve fitting was performed, what enable to explain shape of the noisy XRD patterns correctly.

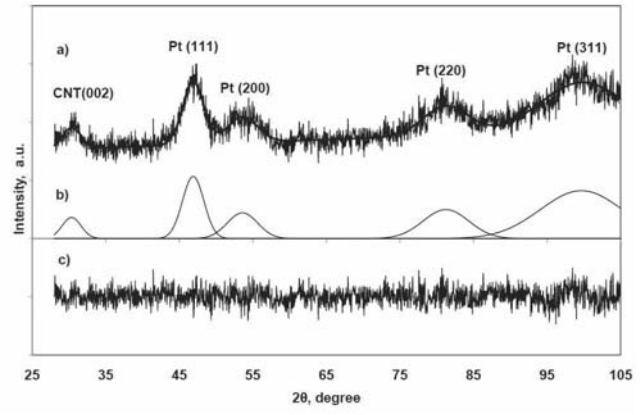

Fig. 5. a) XRD patterns of Pt/CNTs composite; b) Gaussian functions used for modeling XRD patterns by Levenberg-Marquardt algorithm; c) residuals between the calculated fit curve and the observed spectrum

The combination of one linear and five Gaussian functions were used for modeling XRD patterns. The best fit (described by the weighted sum of squared residuals value) by Levenberg-Marquardt algorithm was obtained for Gaussian functions presented in Table 2. The diffraction peaks in XRD pattern at 46.9, 53.6, 81.3 and 99.7° can be assigned to reflections from the (111), (200), (220) and (311) planes of the face-centered-cubic Pt, indicating a good crystallinity of the supported nanoparticles. The broad peaks in the XRD pattern indicate that the platinium nanoparticles are small. The average crystallite size of Pt was calculated using the Debye–Scherrer formula:

$$d = \frac{K\lambda}{\beta\cos(\theta)} \quad (1)$$

in which d is the crystallite size, λ the wavelength of the X-ray radiation, K is usually taken as 0.89, 2θ is the Bragg angle of the Pt (111) peak, and β is the line width at half-maximum height, after subtraction of equipment broadening. The average crystallite size of platinum nanoparticles was determined as about 4 nm, consistent with SEM and TEM observations. The diffraction peak at $2\theta=30.4^{o}$ is related to the presence of carbon nanotubes with graphite structure.

Table 2.
Calculated parameters of Gaussian functions used for modeling XRD patterns by Levenberg-Marquardt algorithm

Function type	Center, degrees	Area, a.u.	Height, a.u.
Gaussian	30.36	116.8	36.3
Gaussian	46.90	389.0	106.8
Gaussian	53.59	228.6	44.2
Gaussian	81.25	387.1	49.8
Gaussian	99.65	1149.9	82.3

4. Conclusions and perspectives

Results of synthesis of carbon nanotubes decorated with platinum nanoparticles by organic colloidal process were demonstrated in this work. High efficiency of proposed method was confirmed as well as possibility of the coating of Pt nanoparticles onto CNTs, without aggregation of these particles. As a result black, fluffy and porous material including CNTs was obtained. The side walls of CNTs with diameter of 10-50 nm are evenly decorated with Pt nanoparticles. The Pt phase appearance is convincingly confirmed by energy dispersive X-ray spectrometry. Observed platinum particles appear to have a narrow size distribution and they are durably attached to the nanotubes. The diffraction peaks in XRD pattern indicating a good crystallinity of the supported nanoparticles. The average crystallite size of Pt calculated using the Debye–Scherrer formula was determined as about 4 nm, consistent with SEM and TEM observations. Obtained material can be employed in constructing various electrochemical sensors.

As a result of increasing of the surface area of Pt caused by the reduction of the size of used particles, fabricated sensor are expected to be more sensitive. Promising prospective is to repeat described procedure with others noble metals such as palladium, platinum, gold and iridium.

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