



Pulsed electrodeposition of palladium nano-particles on coated multi-walled carbon nanotubes/nafion composite substrates: Electrocatalytic oxidation of hydrazine and propranolol in acid conditions

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ABSTRACT

The palladium species were deposited on the multi-walled carbon nanotubes dispersed in nafion membrane by pulsed electrodeposition technique. The resulting modified electrode was defined CNT-Pd. The Pd electrodeposition was carried out in 50 mM H₂SO₄ solution containing 4.0 mM Pd(NO₃)₂ using a double pulse sequence of potentials: E₁ = -0.4 V vs SCE (t₁ = 0.03 s) and E₂ = 0.4 V vs SCE (t₂ = 3 s). SEM analysis showed a well-efficient distribution of Pd nanoparticles dispersed along the nanotubes randomly oriented in the nafion matrix. A surface loading of electrodeposited Pd species comprised between 2.0 nmol and 2.5 nmol was generally observed. The prepared electrode is useful to catalyze the electrooxidation of hydrazine and propranolol. The electroanalytical properties of the electrode were evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Under optimized DPV conditions, the CNT-Pd electrode exhibits interesting analytical performance in terms of linear range of concentrations, low detection limits (i.e., 8 μM and 2 μM for hydrazine and propranolol, respectively) and good temporal stability of the responses (i.e., 4%–5%).

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1. Introduction

The properties of palladium group metals have made them an invaluable source of active materials with a wide range of both scientific and technological applications such as electronics industries, corrosion protective coatings, energy storage and conversion devices, magnetic recording supports, water electrolysis, electrocatalytic and electrosynthesis systems, etc. [1–6]. Due to their important size-dependent electrical, magnetic, optical, chemical and electrocatalytic properties, the Pd metal species have been intensively pursued for their interesting characteristics, very useful in many technological applications [5–9]. As consequence, the definition of adequate preparation procedures and characterization of modulated-size nanoparticles materials is of key importance in many fundamental scientific and technological contexts.

Carbon nanotubes (CNTs) have captured a great attention and interest in the scientific contexts due to their useful electrical and mechanical properties. In fact, the unique one-dimensional geo-

metric structure, high electrical conductivity, large surface areas accompanied with a good chemical and thermal stability of CNTs, makes these materials as excellent candidates as basic substrates for the preparation of electroodic devices with improved electrochemical properties. Thus, in recent years, considerable efforts have been devoted to anchor metal catalysts, and in particular Pd particles, onto the framework of CNTs in the area of the heterogeneous catalysts [10–18]. However, simple metal adsorption on the defect sites of the CNTs surfaces, leads to poor dispersion degree of the catalyst and bad stability of the electroodic active materials. In order to obtain stable electrode configuration, often the metal catalysts species and CNTs must be linked together via covalent bonds and dispersed in stable polymer matrices, such as nafion, polypyrroles, etc. [11–14,19,20].

Electrochemical deposition represents an interesting technique for the preparation of nanoscaled metals or their alloys on various conductive traditional materials. The final composition, morphology and texture of the deposits can be easily modulated by means of several experimental parameters such as: potential, current density, deposition time, solution composition, electrode substrate, etc. Thus, electrochemical methods for the deposition of palladium particles have been proposed in order to prepare various

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types of modified electrodes [11,21–23]. Very recently we have characterized composite electrodes based on Au [24] and Rh [25] dispersed particles into multi-walled carbon nanotubes (MWCNTs) as electrocatalysts for the oxidation of carbohydrates and reduction of nitrate/nitrite, respectively. The studied composite electrode, based on the efficient distribution of the active metal catalysts onto MWCNTs structures have showed interesting electrocatalytic performance.

An interesting electrodeposition strategy is to apply a pulsed electrolysis technique in which a very high current density can be instantaneously applied near the cathode or anode surface. Thus, a pulsed electrodeposition refers to deposition process where a current density or an applied potential is rapidly alternated between two or more values. The potential advantage of the pulsed electrodeposition techniques is that nucleation and growth of the crystallites can be controlled by varying the potential pulse amplitude and duration. In this respect, pulsed electrodeposition was employed to produce nanomaterial structures such as metal nanowires, thin homogeneous magnetic films or nanostructures with excellent size monodispersity [26–29]. However, according to our knowledge, the approach regarding the surface modification of CNTs with palladium nanoparticles by pulsed electrodeposition techniques has not been sufficiently reported yet.

In this study, we have extended the idea of exploring the electrocatalyst potentialities of the combined MWCNTs and nafion polymeric film with active nanoparticles of Pd (CNT-Pd) prepared by pulsed electrochemical deposition technique. In particular, herein we investigate the electrocatalytic performance of the composite electrode in acid medium toward the oxidation of some molecules of pharmaceutical interest such as hydrazine and propranolol.

2. Experimental

2.1. Reagents

The stock solutions were prepared by using ultrapure water supplied by a Millipore Direct-Q UV unit (Bedford, MA, USA). The used chemicals: K_2SO_4 , $Pd(NO_3)_2$, H_2SO_4 , hydrazine, propranolol, nafion 117 solution (5% in a mixture of lower aliphatic alcohols and water) and MWCNTs (>99%) were purchased from Aldrich-Chemie. The MWCNTs used in this study were synthesized by an electrical arc discharge method, having approximately 5–20 graphitic layers with an outer diameter of 7–15 nm and a length comprised between 0.5 and 10 μm . All chemicals employed were of ACS grade and were used without further purification. Stock solutions of hydrazine and propranolol were prepared daily in ultrapure water and stored at ambient temperature.

2.2. Apparatus

The voltammetric experiments were performed with an μ Autolab Type III Potentiostat/Galvanostat (Eco Chemie, Utrecht, The Netherlands) and the data were acquired using an Autolab GPES software package version 4.9. Cyclic voltammetry (CV) was done in a three-electrode cell using the CNT-Pd as working electrode, a SCE reference electrode and a platinum foil counter electrode (Amel, Italy). The glassy carbon (GC) substrates (3 mm diameter), used in all experiments, were also purchased from Amel (Milan, Italy). All current densities in this paper were quoted in terms of $mA\ cm^{-2}$ of apparent geometric area of substrate electrode. The experiments were carried out at ambient temperature (20–22 °C). When necessary, the solutions were deoxygenated by bubbling with nitrogen prior to the electrochemical experiments.

SEM micrographs were obtained from an environmental scanning electron microscope Philips ESEM XL 30. X-ray photoelectron spectra were collected using a Leybold LH X1 spectrometer using unmonochromatized Al K α radiation (1486.6 eV). All modified electrodes, after the preparation or the electrochemical treatment in acid solutions were washed thoroughly with ultrapure water and dried before executing the morphological or spectroscopic analysis.

2.3. Electrode preparation

MWCNTs (10 mg) were dispersed in 5 mL of ultrapure water and sonicated for 60 min at room temperature. The casting solution (9:1) was prepared by mixing 900 μL of MWCNTs emulsion with 100 μL of nafion (5% wt). The polished glassy carbon substrate was modified with 10 μL of the casting dispersion (9:1). The modified electrode surface was dried in an oven at about 70 °C for 15 min and then rinsed with ultrapure water. The resulting electrode was cycled between $-0.3 V$ and $1.2 V$ vs SCE (40 cycles) in 0.5 M K_2SO_4 solution in order to produce surface oxide functional groups such as carbonyl, hydroxyl, carboxyl, etc. [30–32]. The palladium electrodeposition on the activated electrode was performed using an optimized double pulse sequence of potentials based on the following waveform: $E_1 = -0.4 V$ vs SCE and $E_2 = 0.4 V$ vs SCE for the relevant pulse duration of $t_1 = 0.03 s$ and $t_2 = 3 s$, respectively, for 100 s of total deposition time. The deposition process was carried out by using a not de-aerated 50 mM H_2SO_4 solution containing 4.0 mM $Pd(NO_3)_2$. The electrodeposited Pd particles on the MWCNT-Nafion activated substrate was simply defined as CNT-Pd modified electrode. Before modification the glassy carbon surfaces were polished with 0.05 μm α -alumina suspension on a micro-cloth polishing pad, washed with HCl (15%) and finally with ultrapure water to remove traces of surface impurities. As comparison, glassy carbon electrodes modified with Pd species without MWCNTs, were obtained directly by placing 10 μL of the casting dispersion of nafion (0.5% wt) onto the GC surface and dried in an oven at about 70 °C. The surface electrode activation and Pd deposition were carried out in the same way as the preparation of the CNT-Pd modified electrode. The resulting electrode not containing MWCNTs, was defined Nafion-Pd electrode. Similarly, glassy carbon electrodes modified with electrodeposited Pd species without MWCNTs and nafion film, were defined GC-Pd electrodes.

The apparent active surface loading (Γ_{Pd} , nmol) of electrodeposited Pd species was evaluated under cyclic voltammetry (CV) by integrating the cathodic wave I_c , corresponding to the reduction of the Pd oxide species. Assuming that under wave I_c is operative only the Pd^{2+}/Pd^0 redox transition couple and considering that all Pd surface particles are electroactive on the voltammetric time scale considered, a nominal surface loading of Pd species (Γ_{Pd}) comprised between 2.0 nmol and 2.5 nmol, was evaluated. The deposition efficiency or the rate of palladium electrodeposition was expressed as a function of the Γ_{Pd} on the electrode substrate.

3. Result and discussion

3.1. Electrochemical deposition and characterization of Pd particles

The pulsed electrochemical procedure adopted for the Pd deposition on the MWCNT-Nafion electrode substrate employs a sequence of two potentials ranging continuously between the anodic and cathodic values. In order to define the best operative conditions, the influence of pulse amplitude and frequency of potential pulsation (pulse duration) on the palladium growth are considered. The sequence of pulse potentials adopted here, induces a cathodic electrodeposition process of Pd species (E_1) alternate to a

Table 1
Effect of the electrodeposition parameters on the Pd formation (rate of deposition) on the electrode substrate.

Procedure	E_2/E_1 (V)	t_2/t_1 (ms)	Charge (Ic, mC)	Pd loading (Γ_{Pd} , nmol)
Pulsed	0.4/−0.8	30/30	390	2.0
Pulsed	0.4/−0.4	300/300	490	2.5
Pulsed	0.4/−0.4	3000/30	470	2.4
Pulsed	0.4/−0.4	3000/300	270	1.4
Pulsed	0.4/−0.4	3000/3000	250	1.3
Pulsed	0.8/−0.4	300/30	480	2.5
Pulsed	0.1/−0.4	300/30	450	2.3
Pulsed	0.4/−0.1	300/30	340	1.8
Potentiost.	−0.4	−/−	150	0.8
Potentiost.	−0.2	−/−	170	0.9

The electrodeposition process was carried out by using a not de-aerated 50 mM H_2SO_4 solution containing 4.0 mM $Pd(NO_3)_2$ for 100 s of total deposition time. The Pd loading was evaluated by integrating the cathodic wave Ic, obtained under CV conditions (50 mV s^{-1} in 50 mM H_2SO_4).

The CNT-Pd was prepared as reported in the experimental section.

second potential (E_2) which oxidizes the surface electrode cleaning it of eventual extraneous deposited/adsorbed species. The relevant experimental results are summarized in Table 1. As can be seen, the rate of deposition process of palladium species decreased by increasing the time of the cathodic pulse (t_1), while it appears to be rather independent from the value of the applied cathodic potential (E_1) in the investigated region comprised between -0.1 V and -0.8 V vs SCE. The effect of the anodic potential (E_2), valuated in the range comprised between 0.1 V and 0.8 V (SCE), seems to play a secondary role on the kinetics of the palladium electrodeposition. On the contrary, the rate of palladium electrodeposition is related to the pulse duration; in fact it increases with increasing the frequency of pulsation. In particular, the pulse duration of the cathodic potential (E_1) markedly influences the rate of palladium deposition; the surface Pd loading changes from ca 1.3 nmol to 2.4 nmol if the t_1 changes from 3 s to 0.03 s (an increases of about 85%). In agreement with this trend, after a massive electrodeposition process (i.e., 100 s), carried out at -0.2 V or -0.4 V vs SCE, a Γ_{Pd} of 0.8–0.9 nmol was observed. This result suggests that the electrodeposition process of Pd requires both cathodic and anodic excursion of the applied potentials and the hydrogen reduction/absorption process markedly inhibits the palladium reduction/nucleation phenomenon. Thus, an optimized sequence of two applied potential pulse at -0.4 V (E_1) and 0.4 V (E_2) with pulse duration of 0.03 s (t_1) and 3 s (t_2), respectively, was used in this study for the preparation of CNT-Pd electrodes.

In order to rationalize the effect of the absence of the nanotubes on the rate of Pd deposition, glassy carbon electrode modified with nafion films without MWCNTs substrate were used as electrode material during the electroplating process of Pd species (Nafion-Pd). As expected, the Pd particles can be easily electrodeposited onto nafion electrode substrates. In fact, using the optimized pulsed electrodeposition procedure, a Γ_{Pd} average value of 0.9₆ nmol, was obtained. Thus, the Pd surface concentration changes from ca 2.4 nmol for CNT-Pd to 0.9₆ nmol for Nafion-Pd electrode. In this respect, in presence of nanotubes an increase of about 150% in Γ_{Pd} , was observed. This result can be attributed to the favorable distribution of the Pd particles on the MWCNTs structure. It is reasonable to expect that carbon nanotube bundles induces a significant increase of the surface electrode roughness.

A typical wide scan XP spectra of the prepared CNT-Pd modified electrode is shown in Fig. 1. In first instance, the well resolved signals of the fluoride, sulfur and palladium species, indicates the success of incorporating the MWCNTs fibers and palladium particles in the nafion matrix. The relevant detailed XP spectra of the Pd 3d, C 1s and O 1s signals can be seen in Figs. S1, S2 and S3, in the Supplementary information file. Based on the XPS surface

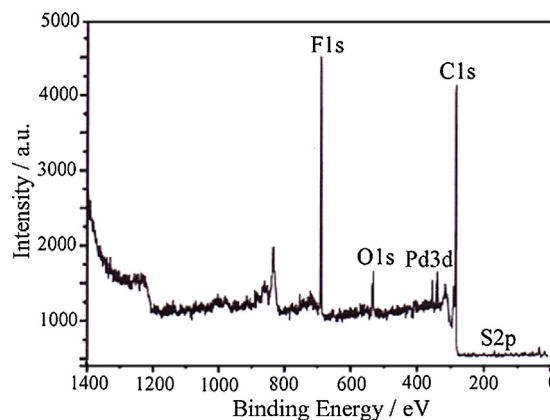
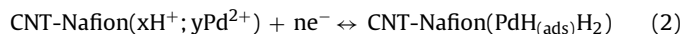
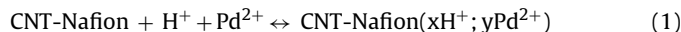


Fig. 1. XPS wide scan spectra acquired for freshly prepared CNT-Pd composite electrode.

characterization, the Pd 3d signal gives three contribution, which can be assigned to Pd, $PdOH_{ads}$, PdO species, although other PdO_x species can not be excluded. The C1s region shows the presence of two C-F signals at 292.4 eV and 295.1 eV corresponding at C-F + C-F₂ and C-F₃ groups, respectively. This result confirms the presence of the nafion polymer backbone on the electrode surface. The virtual identical shape of the Pd 3d signal obtained before and after electrochemical cycling in solutions, reveals an interesting and useful chemical stability of the redox mediator in the modified CNT-Pd film. The binding energies (BEs) of the detailed XPS regions can be seen in Table S1 and the XPS characterization is reported in the supplementary information file.

Taking into account our experimental results, a schematic mechanism of electrodeposition process of Pd species can be hypothesized:



The term (PdO_n) represents the various palladium oxide-hydroxide species formed on the electrode surface such as: $Pd(OH)$, $Pd(OH)_{ads}$, PdO_{ads} , PdO , etc.

The probable mechanism of palladium deposition involves several consecutive steps related to applied electrode potential: (1) a strong exchange affinity between the nafion film and inorganic cation species induces an important preconcentration phenomenon on the electrode surface of these ions (i.e., H^+ and Pd^{2+}) [33]; (2) a consequent reduction reaction of the exchanged ions with simultaneous formation of Pd, H_{ads} and H_2 species; (3) re-oxidation of adsorbed hydrogen species (H_{ads}) during the anodic pulse of the potentials. Although the exchange equilibrium between nafion chain in water is very rapid for small ions such as H^+ , the formation of poorly soluble Pd oxides layers [34] (i.e., $Pd(OH)_2/PdO$) during the anodic pulse, favors significantly the nucleation and growth of the palladium particles. Thus, in agreement with these hypothesis, the continuous sequence of pulses of applied potentials between the anodic and cathodic values plays an important role on the kinetics of electrodeposition process (efficiency of deposition) of the palladium oxides on the MWCNTs-Nafion substrate.

A morphological investigation of the CNT-Pd modified electrode was carried out by scanning electron microscopy (SEM). Fig. 2 show the relevant investigation. Fig. 2A reports a low magnification picture of a typical surface of the CNT-Pd electrode. Using a casting dispersion of MWCNTs-Nafion with ratios equal to 9:1, nanotubes tend to form large agglomerates of dimensions comprised between

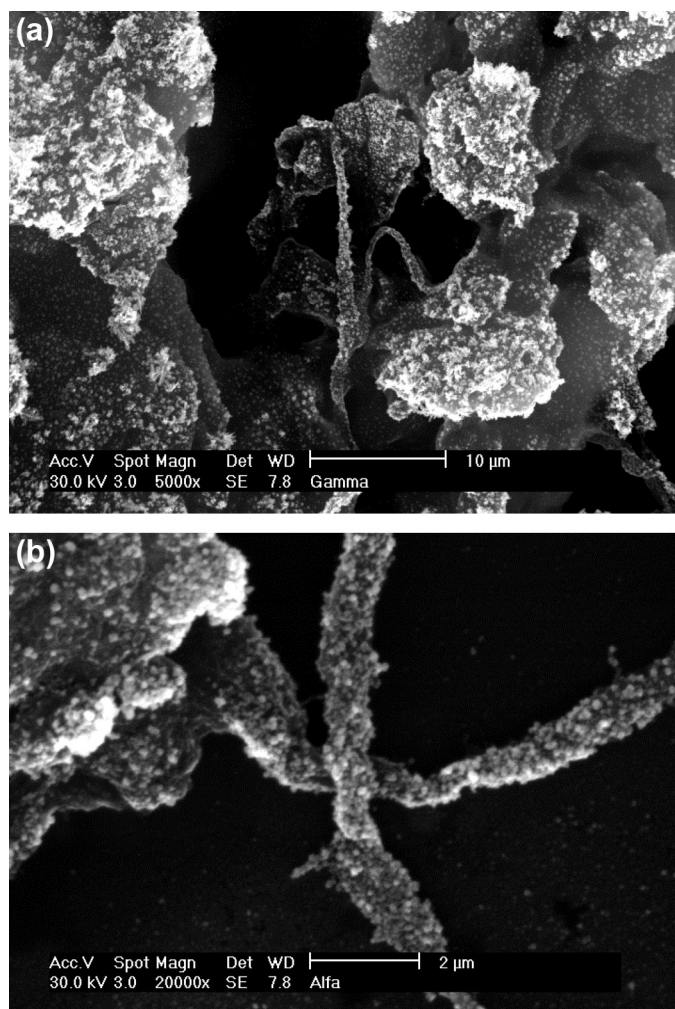


Fig. 2. A) A low magnification (5000x) SEM picture and B) high magnification picture (20000x) of the CNT-Pd electrode obtained as reported in the experimental section.

1 μm and 1.5 μm totally covered with well defined globular particles of Pd species. The image shows that the nanotubes are randomly oriented in the nafion matrix and form interconnecting structures. As can be seen, nafion acts as a polymer backbone to give mechanical stability at the MWCNTs fibers and to ensure a good degree of surface adhesion between the graphitic substrate and nanotubes. As expected, we found that the CNT-based electrodes, prepared by confining MWCNTs on GC electrodes with nafion matrix are very stable; the profiles of the CVs obtained in 50 mM H_2SO_4 solution remained essentially unchanged on continuous potential cycling and repetitive uses of the electrodes. Due to the complexity of the nanotubes network, it is virtually impossible to obtain any information about the fiber length since both their ends were not visible simultaneously. The electrodeposited palladium particles appear dispersed uniformly on the MWCNTs agglomerate structures, in aggregate conformations formed by twinned, trimer or poly-globular islands. Fig. 2B shows a detailed scanning electron micrograph where appear some features of single MWCNTs bundles with a diameter comprised between 300 and 400 nm, totally covered by Pd electrodeposited nanoparticles with well defined surface geometry, having diameter comprised between 30 and 50 nm. The comparison between the scanning electron pictures obtained under low (5000x) and high (20000x) magnification of the CNT-Pd (see Fig. 2) suggests an interconnected nature of the MWCNTs with a 3D architecture. We speculated that, Pd deposited particles can assume a three-dimensional distribution

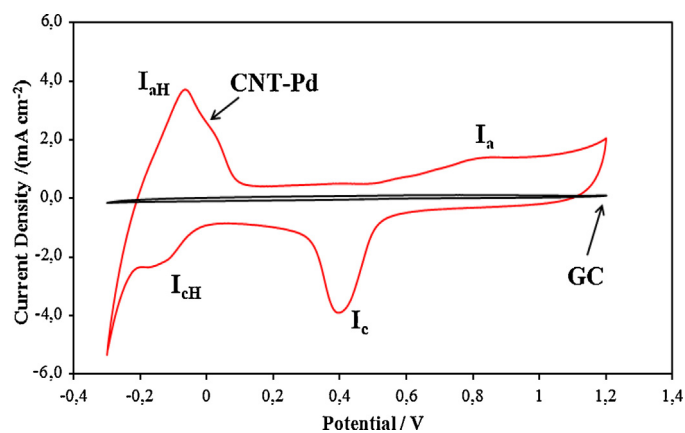


Fig. 3. Comparison between the cyclic voltammogram of a CNT-Pd (red curve) and an unmodified glassy carbon electrode (GC, black curve) obtained in 50 mM H_2SO_4 solution. Scan rate, 50 mV s^{-1} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(3D) on the MWCNT-Nafion-Pd substrate electrode. On the other hand, this hypothesis is clearly supported by literature data, where transmission electron microscopy (TEM) and SEM analysis reveal that a similar CNT-Pd modified electrode possesses a three-dimensional network structure in which the Pd nanoparticles, are uniformly distributed on the surface of the MWCNTs [35]. This surface distribution of the composite material affects significantly the electrode surface area, leading to an increase of the electrochemical active area of the electrode. Consequently, a stronger electrocatalytic activity of these electrodes toward the oxidation and/or reduction of electroactive molecules can be expected.

Fig. 3 shows a comparison between the typical cyclic voltammogram of a CNT-Pd and an unmodified glassy carbon electrode (GC) obtained in 50 mM H_2SO_4 solution. It is immediately observed that, in the entire region of explored potentials, the randomly dispersion of nanotubes in nafion matrix increases significantly the wetted conductive electrode surface with a consequent increase of the capacitive currents. The electrochemical redox processes involving the Pd species deposited on the carbon multiwalled structure are relatively complexes because several palladium oxide species are involved during the redox transition. In general, the NCT-Pd electrode shows a large redox system for applied potentials lower than 0.15 V, related to the redox transition and the adsorption/desorption processes of hydrogen atoms (redox wave I_{aH}/I_{cH}). It is well known that during the cathodic potential scan, hydrogen is strongly adsorbed on the Pd surface and can be also adsorbed to a large extent into the Pd lattice [36,37]. In this respect, two forms (i.e., α -PdH and β -PdH) of hydrogen species on the Pd surface can be considered. Depending on the applied potential and physical distribution of Pd, the diffusion of hydrogen atoms into bulk palladium particles (absorption processes) can result in the formation of either the α or the β phase [38]. In addition, during the anodic sweep, the modified electrode shows a broad peak centred at about 0.8 V (I_a) corresponding to the formation of Pd oxide species (i.e., $\text{Pd}(\text{OH})_2$, PdO, etc.); during the cathodic sweep there is a well resolved peak (I_c) observed at about 0.4 V, corresponding to the reduction of Pd oxide species produced during the previous anodic sweep.

3.2. Electrocatalytic detection of hydrazine and propranolol

In order to ascertain the electrocatalytic capabilities and analytical performance of the NCT-Pd electrode, hydrazine and propranolol were investigated as model compounds. Hydrazine compounds represent an important family of organic species with a wide use in industrial and pharmacological contexts. Moreover,

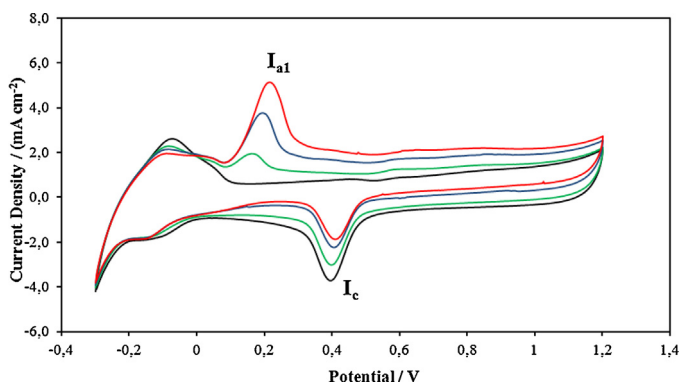


Fig. 4. Cyclic voltammograms obtained on the CNT-Pd electrode in presence of increasing hydrazine concentration. Black curve: 50 mM H₂SO₄ solution; green curve: plus 0.8 mM hydrazine; blue curve: plus 2.0 mM; red curve: plus 3.0 mM. Scan rate, 50 mV s⁻¹. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

these compounds are considered to be hazardous air pollutant by the Environmental Protection Agency (EPA).

Due to the absence of chromophore or fluorophore groups on the hydrazine structure, the detection by spectrophotometric UV–vis or fluorimetric techniques is hindered, thus electroanalytical approaches based on the use of palladium chemically modified electrodes have been successfully proposed [10,35,39–44]. The I–E profile of hydrazine on the CNT-Pd electrode is shown in Fig. 4. As can be seen, in presence of hydrazine a well defined anodic wave (I_{a1}) at about 0.2 V vs SCE was observed. It is interesting to observe that, the wave I_{a1} is centered between the hydrogen region and the oxide region of the potentials. As consequence, the oxidation wave I_{a1} avoids the high background discharge currents observable in the hydrogen and oxide regions of the potentials. The peak current I_{a1} increases linearly with analyte concentration up to 16 mM (correlation coefficient > 0.99) and the relevant peak potential ($E_{p_{a1}}$) increases with increased analyte concentration. This last result indicates that the oxidation of hydrazine presents an electrochemical irreversible character. Moreover, the intensity of the redox transition I_{aH}/I_{cH} allocated within the hydrogen region and the reduction peak I_c , decreased with increasing analyte concentration. The original peak intensities of these signals were partially restored when the CNT-Pd electrode was cycled in free hydrazine solutions, indicating a strong and irreversible adsorption process of analyte on the electrode surface. On the other hand, hydrazine having a pK_a of 8.1, exists in 50 mM H₂SO₄ as a protonated form (N₂H₅⁺) and may be subject to an intense electrostatic interaction with the negatively charged sulfonic acid groups of the nafion film. At an unmodified glassy carbon electrode, in the same experimental conditions and in presence of hydrazine no significant oxidation currents were observed, confirming the electrocatalytic character of the CNT-Pd electrode.

The propranolol (1-(isopropylamino)-3-(1-naphthoxy)-2-propanol), is considered the prototype drug of β -adrenergic blockers and particularly useful for therapy of cardiovascular diseases and infantile haemangiomas in pediatric patients. Moreover, propranolol could also be used in some sports as a doping agent and has included in the list of forbidden substances. Similarly at the hydrazine, the propranolol having a pK_a value of 9.4, under acid conditions should be charged as a cationic form. Thus, favorable electrostatic interactions between the analyte and the nafion film can be easily hypothesized. Several studies regarding the electrochemical behaviour of propranolol (Pp) are often based on the use of nanostructured modified electrodes [45–50], nevertheless on the basis our knowledge, there are no studies on the use of palladium based electrodes as redox catalyst toward the Pp electrooxidation.

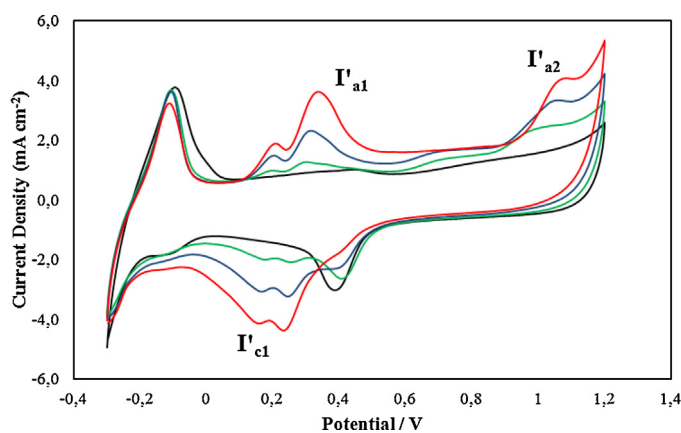


Fig. 5. Cyclic voltammograms obtained on the CNT-Pd electrode in presence of increasing propranolol concentration. Black curve: 50 mM H₂SO₄ solution; green curve: plus 0.5 mM hydrazine; blue curve: plus 1.5 mM; red curve: plus 3.0 mM. Other experimental conditions as in Fig. 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5 shows a family of cyclic voltammograms obtained on the CNT-Pd electrode in presence of increasing concentration of Pp. As can be seen, in presence of Pp a well defined complex redox system of waves (I'_{a1}/I'_{c1}) in the double region layer (between 0.0 and 0.5 V vs SCE) was observed. Moreover, in presence of Pp a second oxidation wave (I'_{a2}) at about 1.0 V is observed during the anodic sweep of the potentials. All peak currents $I'_{p_{a1}}$, $I'_{p_{a2}}$ and I'_{p_c} increase linearly with analyte concentration up to about 20 mM (correlation coefficient > 0.98₆). On increasing the analyte concentration, the peak potentials $E_{p_{a1}}$ and $E_{p_{a2}}$ increase, while the E_{p_c} shows the opposite pattern. Similarly with the hydrazine behavior, the redox couple related to the adsorption/desorption processes of hydrogen atoms (I_{aH}/I_{cH}) and the cathodic peak (I_c) corresponding to the reduction of Pd oxide species, decrease with increasing propranolol concentration. These findings suggested that the redox transition of the propranolol presents an electrochemical irreversible character and the surface reaction involves a competitive adsorption/desorption process of propranolol species in both the hydrogen and double layer region of the potentials. Generally, the overall oxidation reaction of propranolol, involves multi-step processes, where the oxidation of imino and hydroxyl groups of the molecule produce two well-defined irreversible oxidation peaks (see, peaks I'_{a1} and I'_{a2}) [45–51]. At an unmodified glassy carbon electrode the propranolol shows no electrochemical transitions up to 1 V of applied potentials (not shown). Thus, the nanostructured Pd dispersed species on the MWCNTs, act as useful electrocatalyst toward the propranolol electrooxidation process.

In order to check the analytical performance of the CNT-Pd electrode for the electrochemical determination of hydrazine and propranolol, the high-resolution and high sensitivity technique such as the differential pulse voltammetry (DPV) was tested and optimized for the detection of these molecules. Fig. 6A and B show typical families of DPV obtained on the CNT-Pd electrode in presence of increasing concentration of hydrazine and propranolol, respectively. As shown in these figures, the addition of analytes leads to a fast and well-resolved increase of the peak currents at about 0.1 V and 0.25 V for hydrazine and propranolol, respectively. It is interesting to observe the DPV wave of the propranolol electrooxidation shows a well defined and symmetrical profile where the peak potential remains unchanged under analyte addition. On the contrary, the DPV wave of the hydrazine oxidation, presents a pronounced asymmetric character showing a peak potential markedly dependent on the analyte concentration. The Fig. 7 shows the relevant calibration graphs corresponding to

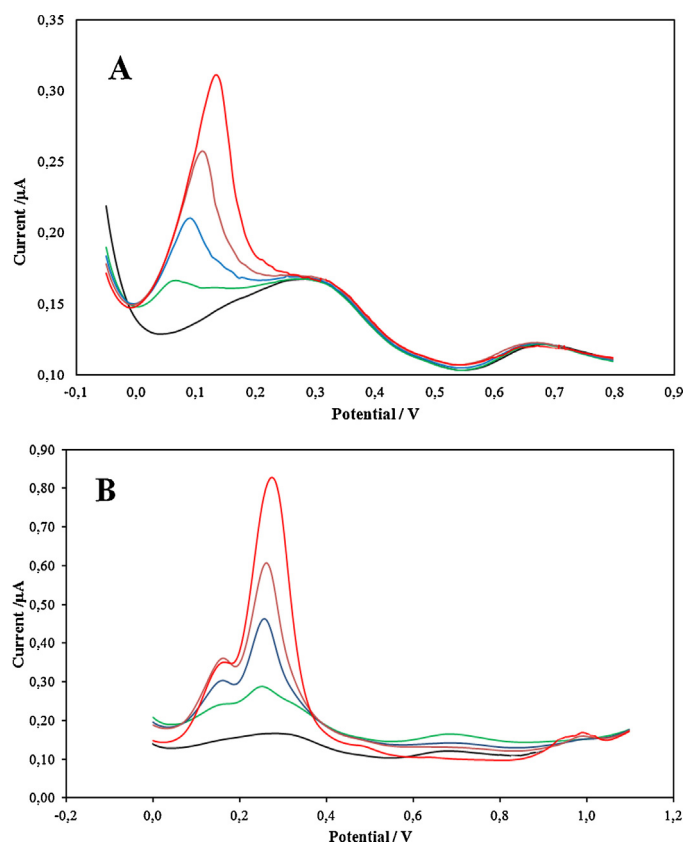


Fig. 6. (A) A series of differential pulse voltammograms (DPVs) obtained on the CNT-Pd electrode in presence of increasing hydrazine concentration. Black curve: 50 mM H_2SO_4 solution; green curve: plus 0.4 mM hydrazine; blue curve: plus 0.8 mM; brown curve: plus 1.6 mM; red curve: plus 3.2 mM. DPV conditions: modulation time, 0.1 s; modulation amplitude, 55 mV; interval time, 0.8 s; step potential, 5 mV. (B) DPVs obtained on the CNT-Pd electrode in presence of increasing propranolol concentration. Black curve: 50 mM H_2SO_4 solution; green curve: plus 0.1 mM propranolol; blue curve: plus 0.3 mM; brown curve: plus 0.5 mM; red curve: plus 1.2 mM. DPV conditions as in Fig. 5A. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

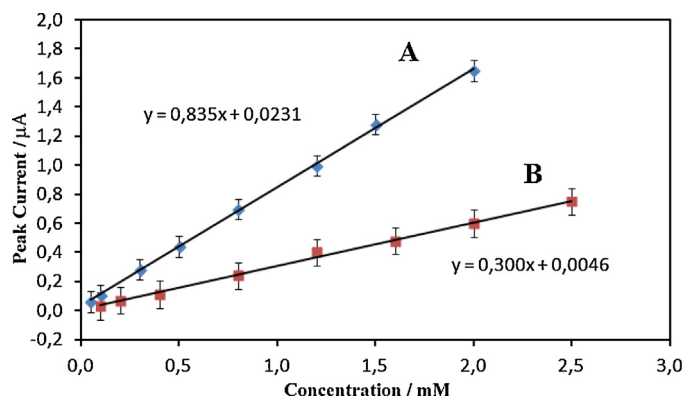


Fig. 7. Calibration graphs of: Ip vs concentration for (A) propranolol; (B) hydrazine. The graphs were obtained using the DPV experiments as reported in Fig. 6A and B.

the analyzed molecules under DPV conditions. The best fit linear calibrations show a correlation of 0.99₅ in the range of concentration of 0.2–2.5 mM and 0.05–2.0 mM (with each data point generated from three experiments) for hydrazine and propranolol, respectively. The analytical results including the detection limits (LODs), linear ranges, coefficients of correlations, sensitivities, precision and temporal stability are summarized in Table 2. As can be seen, the performance of the CNT-Pd electrode evaluated

Table 2

Electroanalytical performance of the CNT-Pd electrode toward the electrooxidation of hydrazine and propranolol in acid medium by DPV.

	Ep(V)	Linearity (mM)	Sens. ($\mu\text{A}/\text{mM}$)	LOD (μM)	RSD(%)
Hydrazine	0.1	0.2–2.5	0.3	8	4
Propranolol	0.25	0.05–2.0	0.8	2	3.5

The sensitivities were evaluated in the relevant linear range of the hydrazine and propranolol calibration. The reproducibility was estimated as temporal electrode stability expressed as percent standard deviation RSD (%) and was calculated from ten consecutive analysis of standard solutions containing 0.2 mM of each investigated analyte. Experimental conditions such as in Fig. 6.

DPV conditions: modulation time, 0.1 s; modulation amplitude, 55 mV; interval time, 0.8 s; step potential, 5 mV.

under DPV conditions, in the double region of potentials (i.e. about 0.1 V) for the detection of hydrazine, can be considered similar to those obtained with other Pd nanostructured electrode systems [10,39–44]. It is interesting to underline that, propranolol was successfully determined at μM level using the CNT-Pd electrode at an applied potential of about 0.25 V vs SCE, while other electrochemical sensing probes show similar analytical performance at applied potentials greater than 1.0 V vs SCE [45–50,52], where the background currents and/or competitive redox processes may compromise the analytical determinations.

The encouraging electrochemical and analytical performance of the proposed CNT-Pd electrode as a sensing probe for the electrooxidation of these molecules can be attributed to the combination of the following factors: (a) the favorable enrichment of ionized hydrazine and propranolol species at the nafion structure due to the electrostatic attraction between the positively protonated analytes and the negatively charged sulfonic acid groups on the nafion membrane; (b) the efficient electrocatalytic character of the Pd dispersed particles; (c) a well-efficient distribution of Pd catalyst on the MWCNT fibers and within the MWCNTs-Nafion substrate.

4. Conclusions

A chemically modified glassy carbon electrode based on multi-walled carbon nanotubes and nafion membrane with electrodeposited palladium nanoparticles was successfully characterized in 50 mM H_2SO_4 solution. An optimized pulsed electrochemical procedure for the Pd deposition on the MWCNT-Nafion electrode substrate was employed. The well resolved signals S 2p, F 1s, C 1s, O 1s and Pd 3p on the wide scan XPS spectra, indicates the success of incorporating the MWCNTs fibers and palladium particles in the nafion matrix. The SEM analysis shows the presence on the electrode surface of large agglomerates structures of MWCNTs with an average diameter comprised between 1 μm and 1.5 μm . In addition, the comparison between the scanning electron pictures obtained under low and high magnification of the CNT-Pd composite suggests an interconnected nature of the MWCNTs with electrodeposited Pd particles. The palladium particles appear dispersed uniformly on the MWCNT-nafion structure having a diameter comprised between 30 and 50 nm. The CNT-Pd electrode tested as a sensing probe toward hydrazine and propranolol oxidation shows interesting and useful electrocatalytic currents in the double region layer of the potentials (i.e., 0.0 and 0.5 V vs SCE). An optimized form of DPV technique, operating in the double region of potential, was successfully tested in order to check the analytical performance of the CNT-Pd electrode in 50 mM H_2SO_4 and the selected molecules were determined at μM level with good sensitivity and precision.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2016.06.109>.

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