



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

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