



The study of adenine and guanine electrochemical oxidation using electrodes modified with graphene-platinum nanoparticles composites



Stela Pruneanu^{a,*}, Alexandru R. Biris^a, Florina Pogacean^a, Maria Coroș^a,
Ganesh K. Kannarpady^b, Fumiya Watanabe^b, Alexandru S. Biris^b

^a National Institute for Research and Development of Isotopic and Molecular Technologies, Donath Street, No. 65-103, RO-400293 Cluj-Napoca, Romania

^b Center for Integrative Nanotechnology Sciences, University of Arkansas at Little Rock, 2801 S. University Ave., Little Rock, AR 72204, United States

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ABSTRACT

Composite materials based on graphene and platinum nanoparticles (Gr-Pt-2 and Gr-Pt-3) were synthesized over two catalysts (Pt_x/MgO, where x = 2 or 3 wt.%) using radio-frequency catalytic chemical vapor deposition (RF-CCVD), with methane as carbon source. After morphological (TEM/HRTEM) and structural characterization (XRD, XPS, FTIR and UV-Vis) they were used to modify two gold electrodes and subsequently employed for the investigation of adenine and guanine electrochemical oxidation. For the Au/Gr-Pt-2 electrode, the oxidation peak potential of adenine was observed at +1.19 V vs. Ag/AgCl, while, for Au/Gr-Pt-3 electrode, this was negatively shifted to +1.09 V vs. Ag/AgCl. In addition, the oxidation current densities were approximately 2.7×10^{-4} and 6.9×10^{-4} A·cm⁻² (for Au/Gr-Pt-2 and Au/Gr-Pt-3, respectively) demonstrating that the Gr-Pt-3 composite had a better electro-catalytic activity towards the oxidation of adenine. A similar behavior was observed for guanine oxidation. The excellent electro-catalytic properties of the Gr-Pt-3 sample were correlated with the fact that the composite material had a higher amount of platinum nanoparticles which were not fully covered by graphene layers (about 50%). In addition, it has a larger surface area ($335 \text{ m}^2 \cdot \text{g}^{-1}$) compared with that of the Gr-Pt-2 sample ($271 \text{ m}^2 \cdot \text{g}^{-1}$), which also greatly improved the electron kinetics.

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1. Introduction

Adenine and guanine play a fundamental role in all living systems, due to their participation in processes such as cellular energy transduction or cell signaling [1]. This has led to the necessity to develop easy and efficient methods for their analysis, in comparison with the classical methods: chemiluminescence [2], high performance liquid chromatography [3], or isotope dilution mass spectrometry [4]. The accurate determination of purine bases in DNA is extremely important, since their abnormal change may indicate the initiation of some diseases (e.g., cancer). The electrochemical methods offer many advantages over the classical ones, such as low cost, fast response, high sensitivity and real-time detection [5,6]. However, the direct electrochemical oxidation of adenine and guanine cannot be recorded with bare electrodes due to the high over-potential and slow transfer of electrons, which generally

characterize this type of electrodes. In order to overcome these hurdles, various types of modified electrodes have been prepared and used to investigate the electrochemical oxidation of purines, such as carbon nanotubes-modified electrodes [5] or fullerene-C60-modified glassy carbon electrodes [7]. Within the last few years, graphene-modified electrodes have been used extensively to study the oxidation of various biomolecules [8,9] due to the fact that graphene exhibits a huge surface area along with excellent electrical conductivity and electron mobility at room temperature [10,11]. Zhou et al. [11] have used a glassy carbon electrode modified with chemically reduced graphene oxide (CR-GO/GCE) to detect a single-nucleotide polymorphism site in short oligomers, without any hybridization or labeling process. Xie et al. [12] have sequentially modified a gold electrode with a self-assembled monolayer (SAM) of n-octadecyl mercaptan and graphene sheets to obtain a graphene/SAM modified Au electrode. The graphene sheets were randomly distributed on top of the SAM, forming nano- or sub-microarrays. The modified electrode has a wide potential window and excellent electro-catalytic activity for the simultaneous detection of all DNA bases: adenine, guanine, thymine, and cytosine.

* Corresponding author.

E-mail address: stela.pruneanu@itim-cj.ro (S. Pruneanu).

Moreover, the modified electrode prevents the fouling of the gold substrate and considerably improves the electron transfer kinetics.

In this work, we present, for the first time to our best knowledge, a comparative study of the electro-catalytic properties of two electrodes modified with composite materials based on graphene and platinum nanoparticles. They were investigated in the presence of adenine and guanine by using various electrochemical approaches, such as cyclic voltammetry and linear sweep voltammetry. These studies were complemented by the results obtained with other advanced techniques, like TEM/HRTEM, X-Ray powder diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), UV-Vis and FTIR spectroscopy, which gave us information about the morphological and structural characteristics of the two composite materials.

2. Experimental

2.1. Preparation of graphene-platinum nanoparticles composites

Two catalysts (Pt_x/MgO, where x = 2 or 3 wt.%) were prepared by wet impregnation of the MgO support with H₂PtCl₆ (Alfa-Aesar) aqueous solutions which contained the appropriate amounts of platinum [13]. Afterward, the catalysts were dried at room temperature, then calcined in the air at 600 °C for 4 h, and next reduced in H₂ at 500 °C for 3 h. Graphene-platinum nanoparticles composites were synthesized by radio-frequency CCVD (RF-CCVD) using a quartz reactor with double walls, as described in details in ref [13]. After preparation, the samples were purified (removal of the MgO support) by sonication at room temperature in solution of aqueous HCl (1:1) for 30 minutes and then left overnight in similar HCl solution. After this process, the samples were filtered and washed abundantly with distilled water to neutral pH and dried overnight at 120 °C. The composite samples were denoted as Gr-Pt-2 and Gr-Pt-3, respectively, corresponding to each catalyst.

2.2. Equipment for morphological and structural characterization of graphene-platinum nanoparticle composites

The morphological characteristics of the purified samples were investigated by **Transmission Electron Microscopy (JEOL JEM-2100F)** equipped with EDAX Genesis X-ray Energy Dispersive Spectroscopy (EDS) system for elemental analysis. Specimens were dissolved in ethanol and sonicated, before a few drops of these suspensions were dried on holey carbon grids. After drying for 1–15 minutes, the grids were inserted in our TEM for observation at 80 kV.

X-Ray Diffraction (XRD) measurements were performed at room temperature and were collected in the $5 < 2\theta < 85^\circ$ angular domain with a **Bruker D8 Advance** diffractometer, using CuK α_1 radiation ($\lambda = 1.5406 \text{ \AA}$). In order to increase the resolution, a Ge (111) monochromator in the incident beam was used to filter out the K α_2 radiation.

The chemical status of Pt in the graphene composite was studied using **X-ray Photoelectron Spectroscopy (XPS)** (K Alpha, Thermo Scientific). The data were collected at a background pressure of 10^{-9} torr, using a monochromated Al K α ($h\nu = 1436.6 \text{ eV}$) X-ray source. The X-ray beam used was 36 W and 400 μm in diameter. Survey scans (0 – 1350 eV) were taken at a pass energy (CAE) of 200 eV and 1 eV step size. The collected data were referenced to the C1s peak to 284.5 eV based on the data obtained for adventitious carbon grown on a glass slide. Narrow scans (25 – 40 eV width) of the peaks of interest (C1s, Pt4f) were taken at pass energy of 50 eV and 0.1 eV step size to provide higher resolution analysis of the peaks. Curve fitting was performed using Powell and Simplex algorithms after Shirley type backgrounds were subtracted on narrow scans using the Avantage V. 5.38 software.

Fourier Transform Infrared Spectroscopy (FTIR) measurements were recorded with a JASCO 6100 instrument, within 4500–1000 cm^{-1} spectral domain with a resolution of 4 cm^{-1} using KBr pellet technique.

UV-Vis spectroscopy (JASCO V-570 spectrophotometer) was used to investigate the optical properties of Gr-Pt-2 and Gr-Pt-3 suspensions (0.05 $\text{mg}\cdot\text{mL}^{-1}$ in acetate buffer pH 5).

2.3. Electrochemical measurements

Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LCV) were performed with a Potentiostat/Galvanostat Autolab-302 N (Metrohm Autolab B.V., Utrecht, The Netherlands) connected to a three electrode cell and controlled by Nova1.8 software. A gold substrate (0.07 cm^2) was used as working electrode while a large area (approx. 2 cm^2) Pt electrode was employed as counter-electrode. An Ag/AgCl electrode was used as reference. CV and LCV were typically recorded between +0.2 and +1.35 V vs Ag/AgCl at a scan rate of 50 mVs^{-1} .

2.4. Preparation of gold electrodes modified with graphene-platinum nanoparticles composites

Prior to any modification, two gold electrodes having the same surface area (0.07 cm^2) were electrochemically cleaned in 0.5 M H₂SO₄ solution by cyclic voltammetry (from –0.25 to +1.6 V vs Ag/AgCl; 50 cycles with a scan rate of 50 $\text{mV}\cdot\text{s}^{-1}$). Next, they were ultrasonically cleaned in both ethanol and double-distilled water several times (3 minutes). Afterward, the same volume (20 μL) of colloidal suspension (0.5 $\text{mg}\cdot\text{mL}^{-1}$) of Gr-Pt-2 or Gr-Pt-3 in N,N-dimethyl formamide (DMF) was deposited onto each gold substrate and dried at room temperature for at least 5 hours. The modified electrodes were subsequently denoted as Au/Gr-Pt-2 and Au/Gr-Pt-3, respectively.

2.5. Reagents and Solutions

The chemicals used for the electrochemical experiments were of analytical grade. Guanine was purchased from Alfa-Aesar (SUA-Germany) while adenine was purchased from Tokyo Chemical Industry Co, Ltd (Tokyo, Japan). A 0.2 M acetate buffer pH 5 was prepared from 0.2 M acid acetic and 0.2 M sodium acetate by mixing the appropriate volumes. Stock solutions (10^{-4} M guanine and 10^{-3} M adenine) were prepared in this buffer and then diluted to lower concentrations, down to 10^{-6} M. N,N-dimethyl formamide was purchased from Fluka-Germany and used for the dispersion of the Gr-Pt-2 and Gr-Pt-3 composites (0.5 $\text{mg}\cdot\text{mL}^{-1}$).

3. Results and discussion

3.1. Morphological and structural characterization of graphene-platinum nanoparticle composites

Fig. 1(a,b) presents typical TEM images of the two composite materials (Gr-Pt-2 and Gr-Pt-3, respectively) which clearly reveal the graphene morphology. The edges of graphene layers are seen as dark lines, while the black spots represent the platinum nanoparticles, as indicated by X-ray Energy Dispersive Spectroscopy (XEDS) analysis (data not shown). In both cases, one can see the presence of rectangular graphene flakes with variable dimensions (e.g., 42 × 44 nm; 74 × 79 nm) and a variable number of layers. The HRTEM images in Fig. 1(c,d) present graphene flakes with 2, 5, or 6 layers, indicated by the blue arrows. Moreover, Fig. 1(d) shows two metallic nanoparticles (8 and 12 nm in size) surrounded by several graphene layers.

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