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Electrochemical behavior of reduced graphene oxide and multi-walled carbon nanotubes composites for catechol and dopamine oxidation

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A B S T R A C T

Glassy carbon electrodes were modified by drop casting carbon nanomaterials, graphene oxide, GO, and multi-walled carbon nanotubes, MWCNTs, alone, mixed together (Composite) or in the form of bi-layers. The reduction of GO was carried out by means of a green approach using cyclic voltammetry (CV). Two model compounds, catechol and dopamine, which can be considered representative of the polyphenols class, were taken into account to determine the modifying system giving the highest oxidation current. Furthermore, the fouling effects of the electrode surface were also taken into account. The electrochemically active areas of the tested configurations were estimated by two approaches, to highlight the various phenomena that may affect the redox processes of the two analytes at the different chemically modified electrodes (CMEs). All the CMEs were characterized by SEM, FT-IR and UV–vis spectroscopies. In addition, zeta potential and heterogeneous electron transfer constant were determined. The most performing configuration was found to be the Composite, as it is the best compromise in terms of sensitivity and resistance to fouling.

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1. Introduction

The determination of dopamine (DA) and catechol (CA) is still a subject of significant interest. DA, which is a catecholamine, plays a key role as neurotransmitter in the central nervous system and alterations of its levels are related to important neurological diseases [1]. The presence of phenol and its derivatives, like CA, in the environment results from their extensive use as raw materials or synthetic intermediates in many industrial sectors such as chemicals, cosmetics, pharmaceuticals and textile industries. Phenols are hazardous to both environment and human and hardly degraded in the ecological environment and therefore, they are considered as major environmental pollutants [2].

Electroanalytical methods are suitable for the determination of phenolic compounds as they are sensitive, fast and inexpensive. Besides, they can easily be miniaturized both to achieve portable sensors and to develop on-site analytical methods for fast and real-time analyses when a test of detection for pollution is required.

The glassy carbon electrode (GCE) is popular in electroanalysis for its wide potential range, low cost, availability, and chemical inertness in most electrolytes [3]. However, the main problem in the use of GCE for phenols detection is the sensitivity of the response, due to the fouling of its surface during the oxidation of these analytes. This effect is either related to the adsorbed oxidized products and/or to polymerization processes [2,4]. Different modifiers have been proposed to overcome this problem and/or to decrease the oxidation potential of phenolic compounds so to improve the selectivity of the determination [2]. In recent years, many composite materials based on carbon nanomaterials [5,6], metal oxides and metal nanoparticles [6–8] and conducting polymers [9,10] have been proposed to produce modified GCEs for the electrochemical determination of di-hydroxybenzene derivatives.

Carbon nanotubes (CNTs) have been very popular in electrochemical applications through the years [11–13], especially in the field of chemically modified electrodes (CMEs) due to their reported ability to promote electron-transfer processes. More recently, graphene has attracted a great deal of attention owing to its highly accessible surface area, good electrical conductivity, chemical and thermal stability, and mechanical strength [11,14,15]. Moreover, it also shows fascinating electrochemical properties, including wide electrochemical potential windows, low charge-transfer resistance, and excellent electrochemical activity. The major problem related to the use of graphene has been its high cost if produced by mechanical exfoliation. The chemical synthesis has overcome this issue, especially when carried out first oxidizing

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graphite to graphene oxide (GO) and then performing a reduction. GO is an electrically insulating material but its conductivity can be partially restored by the reduction, which can be conducted by both traditional chemical and electrochemical methods [16–18].

In the literature, the electrochemical reduction of graphene oxide has been performed on different electrode materials such as GC, gold, indium tin oxide (ITO) or Pt [19–21].

Coupling CNTs with reduced GO yields composites that have the characteristics of both nanomaterials, and, thanks to a synergetic effect, even display more outstanding features [22], which have been also exploited in the field of the electrochemical sensing [23,24]. On the basis of the above considerations, it seemed interesting to investigate the electroactivity of CA and DA on a GCE modified with a composite made of multi-walled carbon nanotubes (MWCNTs) and reduced GO so to check if this modification induces an improvement of the analytical signal of the two phenols and/or a minor occurrence of the passivation phenomena.

In this work we study the modification by drop casting of the electrode with GO and MWCNTs. The procedure is rapid and simple to perform since the only preliminary treatment has consisted of a sonication of MWCNTs in DMF. Three configurations have been investigated, namely, a composite obtained by mixing the two nanomaterials and two bi-layers composed of the single components. In the former the GO was deposited directly on the GC support with MWCNTs on the top, while the latter was obtained by swapping the order of the nanomaterials. The resulting modified electrodes have been submitted to an electrochemical reduction treatment to convert GO to ERGO, i.e, a green approach has been followed to restore the conductivity. Then they have been employed in the oxidation of CA and DA in aqueous solutions at different pHs. The aim was to find out the best configuration which allows for the maximum contact of the two nanomaterials, optimizing the electron transfer processes of the two analytes. The main parameters which can affect the sensing performance of the CMEs have been investigated. In particular, the electrochemically active area has been estimated by means of two approaches and related to the morphology of the carbon nanomaterials casted on GCE and the fouling effects occurring during the electrochemical processes have been taken in consideration. To the best of our knowledge, this kind of study has not been performed yet for the electro-oxidation of catechol and dopamine.

2. Experimental

2.1. Reagents and apparatus

Aqueous GO solution ($4 \, mg \, ml^{-1}$), MWCNTs (O.D. $\times$ wall thickness $\times$ L = 20–30 nm $\times$ 1–2 nm $\times$ 0.5–2 μm), anhydrous sodium acetate (99% pure), dopamine hydrochloride (98% pure), N,N-dimethyl formamide (DMF), $LiClO_4$, and acetic acid were obtained from Sigma-Aldrich. H_3PO_4 and KOH were obtained from Farmitalia Carlo Erba S.p.A., $K_3[Fe(CN)_6]$ (>99% purity) from Riedel-de Haën and catechol (>99% purity) from ACROS Organics. Phosphate buffer solution (PBS) was prepared from a 0.1 M solution of H_3PO_4 with the pH being set to the chosen value by addition of KOH. Acetate buffer solution was prepared from a 0.1 M solution of CH_3COONa with the pH being set to the chosen value by addition of acetic acid. All chemicals were of analytical reagent grade and were used as received, without further purification. All aqueous solutions were prepared with doubly distilled (DD) water with the exception of the MWCNTs which were suspended in DMF ($2 \, mg \, ml^{-1}$). The suspension was submitted to ultrasonic treatment for 20 min at 40% maximum power using a Bandelin Sonorex Super Sonicator (RK 103 H). The DMF solution was kept in ice bath duration sonication to prevent loss of the solvent by evaporation.

The electrochemical experiments were performed with a potentiostat/galvanostat electrochemical workstation CHI 660C (CH Instruments Inc, Austin, TX, USA) interfaced with a personal computer. A three-electrode conventional electrochemical cell was employed, with a 3 mm diameter GCE from BASi as the working, a saturated calomel electrode (SCE) as the reference and a Pt wire as the counter electrode, respectively. No normalization was performed on the current data.

2.2. Preparation of the chemically modified electrode

Prior to the electrochemical measurements, the GC surface was gently polished on a wet (4000 grit) SiC sand paper until a mirror finish was obtained. Then it was thoroughly rinsed with DD water and left for drying at room temperature. The CMEs were prepared by drop casting the carbon nanomaterials (GO or MWCNTs) directly on the GC surface. Various amounts of GO and MWCNTs in DMF were tried to prepare the CMEs. Three different configurations were tested as shown below, indicating the carbon nanomaterial(s) used, and the deposition order in the case of the bilayers:

1-Bilayer MWCNTs/ERGO (Bil-1)
2-Bilayer ERGO/MWCNTs (Bil-2)
3-Composite ERGO-MWCNTs (Composite)

In addition, two other CMEs were fabricated employing only GO or MWCNTs (named as GO and MWCNTs) to compare the electrochemical performances of the mixed systems and to check if a synergism between the two nanomaterials occurs. Each kind of CME was prepared using the same total mass of carbon nanomaterials (0.4 mg, corresponding to 0.2 mg + 0.2 mg of GO and MWCNTs). To obtain the Composite, equal volumes of the two nanomaterials suspensions were mixed and casted on the electrode surface. In any case, after casting a material the electrodes were dried at 60 °C in an oven for 15 min.

2.3. Nanomaterials characterization

The morphologies of the films made of carbon nanomaterials were investigated by SEM analysis, using an EVO 50 Series Instrument (LEO ZEISS). The accelerating voltage was 20 or 15 kV, the beam current up to 6 pA and the spectra collection time 100 s. SEM images were acquired for GO, ERGO, the two bilayers and the Composite. For the last configuration the morphology was investigated before and after the electrochemical reduction treatment. Samples for SEM analysis were prepared by dropcasting the aqueous suspensions onto graphite sheets (Grafoil grade GTJ, purchased by VED S.r.l). After drying, the samples were coated by sputtering a thin layer of gold to enhance the conductivity of the films.

The UV/Vis spectra of GO and ERGO coatings on ITO electrodes (Delta Tech, R_s = 4–8 Ω cm^{-1}) were recorded in reflectance, using an OceanView spectrophotometer at room temperature. For these measurements, GO was electrochemically reduced in acetate buffer 0.1 M at pH 4.5, performing 10 voltammetric cycles from 0 to −1.5 V vs SCE, at the scan rate of 0.05 V s^{-1}.

Infrared spectra were recorded on a Perkin Elmer Spectrum 2000 FT-IR spectrophotometer. Samples for FT-IR spectra were prepared in the same way as for SEM analysis and were analyzed as such and after the electrochemical reduction. The signal due to the graphite sheet used to support the nanomaterials was subtracted to each spectrum.

Z potential was estimated with a Zetasizer nano series Malvern. 0.1 mg mL^{-1} of GO or MWCNTs were suspended in 0.1 M LiClO$_4$ solution, and reduced at −1.3 V for 7200 s. The suspensions of reduced nanomaterials were diluted 1:10 with water in order to