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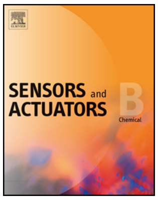

Graphene and ionic liquids new gel paste electrodes for caffeic acid quantification

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ABSTRACT

Graphene/ionic liquids nanocomposite gels were synthesized by an electrochemical etching approach and fully characterized under a morphological and structural point of view. For this purpose, several analytical techniques were applied, as HR-TEM/EDX (High Resolution-Transmission Electron Microscopy/Energy Dispersive X-Ray Analysis); FE-SEM/EDX (Field Emission-Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis); XPS (X-Ray Photoelectron Spectroscopy); FT-IR (Fourier Transform-Infrared Spectroscopy) and electrochemical techniques. After the characterization study, nanocomposite-gel paste electrodes were assembled, exhibiting a selective and specific detection toward the caffeic acid oxidation. Better performances in terms of linear range of concentration (from 0.025 to 2.00 M), reproducibility (intra-; 1.40% and inter-electrode reproducibility-3.20%), sensitivity (3389/μA mM^{-1} cm^{-2}), fast response time (2 s) and detection limit (0.005 mM) were obtained, in comparison with other chemically modified electrodes, described in literature for the caffeic acid detection. This nanocoposite-gel could represent a new prototype of miniaturized nanostructured sensors useful for the "*in situ*" quantification of an important molecule, having pharmacological properties, anti-inflammatory, antibacterial, antiviral, immunomodulatory and antioxidant effects.

1. Introduction

The Single Layer of Graphene (SLG) and Few Layer Graphene (FLGs) derivatives represent new interesting nanostructured materials for their countless chemical–physical and mechanical features [1]. The properties of the new nanomaterials are strictly related to the surface chemistry and therefore to the oxygen containing functionalities [2,3]. The surface modification and the selective functionalization/engineering of graphene sheets depend on the synthesis route [3] used for nanographene production. Recently, the exfoliation process of a graphite anode into graphene nanosheets, triggered by anodic oxidation of water in presence of Ionic Liquids (ILs) has been reported [4]. It is very well known in the literature [4] that water is one of the key factors that significantly affect several properties of ILs, such as viscosity, electrochemical potential window and conductivity [4]. Especially the electrochemical conductivity is proportional to the specific double layer capacitance (CDL) of the electrodic materials, their specific surface area (SSA), and to the accessible surface portion (the electrochemical area, related to the roughness of the working electrode surfaces) for electrolytes and electro-active molecular targets [5]. In this communication, two different nanocomposite gels were electrochemically synthesized as G/bmim$^+$Br$^-$ and G/bmim$^+$Cl$^-$. Among several kind of ILs described in literature, bmim$^+$Cl$^-$ and bmim$^+$Br$^-$ have been selected because they exhibits superior chemical-physical and electrochemical properties (Table S1A and B in ESI), especially in terms of higher electrochemical and electronic conductivity, wider potential window and lower viscosity (this latter related to the mobility of the charged ions, during the electron transfer processes that occur in the solution during the CV and DPV measurements). The second reason concerning the choice of these two kinds of ILs is related to our previous work, [5b]

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where we studied the influences of different cations in ILs composition (maintaining constant the same anion component) on the electrochemical signals and here, we are interested to investigate the influence of different anions on the sensor responses. Finally we selected the two ILs for their biocompatibility [5a,b] if compared with that exhibited from other ILs, reported in Table S1B, ESI. The resulting new nanocomposite materials show an exceptionally high SSA (2700 m^2/g, evaluated in this work) and also a high electrochemical conductivity (reported in ESI). These data suggest that G/ILs nanocomposite gels represent eligible new nanomaterials for the assembly of electrodes and electrochemical devices. Accordingly, in the present communication we describe the use of G/ILs based paste electrodes for a selective amperometric detection of caffeic acid; an important target molecule that exhibits (as flavonoids and phenolic compounds [6]) several pharmacological properties, such as antiproliferative activity in human tumor cells [7], or anti-inflammatory [8], antibacterial [9], antiviral [10], immunomodulatory [11] and antioxidant [12] effects. A morphological/topographic investigation (performed by HR-TEM/EDAX: High Resolution-Transmission Electron Microscopy/Energy Dispersive X-Ray Analysis) and a structural study (carried out by the XPS: X-Ray Photoelectron Spectroscopy and FT-IR: Fourier Transform-Infrared spectroscopy) were performed, prior to examining the analytical performance of the resulting sensor in caffeic acid oxidation.

2. Experimental

All the materials and reagents were reported in ESI.

2.1. Apparatus and procedures

2.1.1. HR-TEM/SAED

HR-TEM analyses was performed on $G/bmim^+Cl^-$ nanocompoite gel. A JEM-2100 (JEOL, Japan) microscope was used, operating at 200 kV accelerating voltage and equipped with an energy dispersive X-ray spectrometer (EDS) (Oxford Instruments, UK) suited for element identification. The acquired high-resolution micrographs were obtained by the Inverse Fast Fourier Transformer (IFFT), equipped by the Digital-Micrograph GATAN software. The samples were prepared by placing a drop of $G/bmim^+Cl^-$ nanocompoite gel on a copper grid and letting it dry.

2.1.2. FE-SEM/EDAX

(Field Effect-Scanning electron Microscopy/Energy Dispersive X-Ray Analysis). The topographic characterization of the modified SPE (Screen Printed Electrodes) surfaces was performed by using a field emission-scanning electron microscope/energy dispersive X-ray analyzer (FE-SEM/EDX, LEO 1550) equipped with a sputter coater (Edwards Scan Coat K550X). A volume of 5 μL of the dispersions has been directly deposited on the SPE surface, leaving the solvent to evaporate at room temperature (RT). The modified SPEs were fixed on the aluminum stub, with carbon tape. The samples were then coated by a thin Au layer (with a thickness of 20 nm), deposited by sputtering for 2 min at $I = 25$ mA.

2.1.3. XPS. (X-ray photoelectron spectroscopy)

The surface characterization of ionic liquids and graphene modified gels was performed by using a Thermo VG Theta Probe spectrometer equipped with a microspot monochromatised AlKα source (spot = 300 μm). Survey spectra were recorded in constant analyzer energy mode (CAE) at a pass energy of 150 eV, while high-resolution regions (C1s, O1s, N1s) were acquired in CAE mode at a pass energy of 100 eV. When charging compensation was required a flood gun operating at −1 eV was used. Calibration of the Binding Energy (BE) scale was performed by fixing the C—C component at BE values of 284.8 ± 0.1 eV. The samples were spin coated on glass substrates and directly fixed on the XPS sample holder with carbon tape. The base pressure during the analyses was in the range 10^{-9} mbar.

2.1.4. FT-IR (Fourier transform-infra red spectroscopy)

The spectrophotometer that was used in this study is a Shimadzu Prestige-21, as equipment model, having these set-up experimental parameters: the resolution of 4 cm^{-1} and the wavenumber range of 4000–400 cm^{-1}. The liquid samples have been sandwiched between NaCl disks.

2.1.5. Pore surface area measurements (BET method)

Nitrogen adsorption was measured at 77 K with an automatic adsorptiometer (Micrometrics ASAP2000). The samples were pretreated at 573 K for 2 h under vacuum. The surface areas were determined from adsorption values for five relative pressures (P/P_0) ranging from 0.05 to 0.2 using the BET method [13]. The pore volumes were determined from the total amount of N_2 adsorbed between $P/P_0 = 0.05$ and $P/P_0 = 0.98$.

2.1.6. Electrochemical measurements

The electrochemical cell was assembled with a conventional three-electrode system: a $G/bmim^+Cl^-$; $G/bmim^+Br^-$ based paste electrodes (PEs) working electrode (1-mm diameter), a Ag/AgCl/KCl (3M) reference electrode, and a Pt counter electrode. All experiments were carried out at room temperature. Cyclic voltammetry experiments were carried out at a scan rate of 100 mV/s over the relevant potential range using 0.1 M phosphate buffer (pH 7.4). The value of 100 mV/s represents the best compromise to achieve a higher Signal/to Noise Ratio, during measurements. It was selected during the scan rate study, performed by CV, ranging from 5 mV/s to 500 mV/s, as scan rate. DPV were performed with a pulse amplitude of 50 mV, a pulse width of 60 ms, a scan rate of 10 mV/s, a pulse interval of 200 ms, and a sampling time of 20 ms; $E_i = -0.2$ V and $E_f = +0.8$ V for the caffeic acid calibration curves. Only for the AA, 0.1 M acetate buffer (pH = 5.4) and a scan rate 100 mV/s have been used as additional working conditions, according to the literature [14a]. The electrochemical and physiochemical properties of carbon based materials used for the paste electrodes assembly, such as: the specific double layer capacitance (CDL) of the electrode materials, their specific surface area (SSA) and the electrical resistivity were evaluated according to the literature, and reported in Table S1-A, in ESI section. For a comprehensive discussion see Ref. [14b, and references cited therein]. The permeability (P%) test and the perm-selectivity assay were described in ESI, in details.

2.2. Synthesis of materials and paste electrodes assembly

2.2.1. Ionic liquids synthesis & NMR characterization

The syntheses were performed in water, slightly modifying a literature method [15]. 1-Butyl-3-methylimidazolium bromide, $bmim^+Br^-$. 70 ml distilled H_2O and 60 ml 1-methylimidazole were mixed under a gentle stream of Ar. 1-Bromobutane (162 ml, 2 equivalents) was added dropwise, under argon atmosphere, and the resulting mixture was stirred ad 70 °C in a thermostatted oil bath. After 24 h, the $CuCl_2$ test for the presence of 1-methylimidazole was negative and therefore the reaction was stopped, cooled and transferred into a separatory funnel. After removing the organic phase (alkyl bromide excess), the aqueous layer was repeatedly extracted with diethyl ether, to remove 1-bromobutane completely. After treatment with active carbon, to remove yellow impurities, the solution was poured into a 250 ml Erlenmeyer flask and diluted with more water. The title was determined lyophilizing a 5 ml sample and weighing the white solid $bmim^+Br^-$. Yield, 93.5%. ^1H NMR spectrum of $bmim^+Br^-$ in $CDCl_3$: