



Electro-oxidation of anthracene on polyanilino-graphene composite electrode



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ABSTRACT

A novel graphenated-polyaniline (GR-PANI) nanocomposite sensor was constructed and used for the determination of anthracene. The direct electro-oxidation behavior of anthracene on the GR-PANI modified glassy carbon electrode (GCE) was used as the sensing principle. The results indicate that the response profile of the oxidation of anthracene on GR-PANI-modified GCE provides for the construction of sensor systems based on amperometric and voltammetric signal transductions. A dynamic linear range of 0.012–1000 μM anthracene and a detection limit of 0.0044 μM anthracene were established for the sensor system.

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1. Introduction

The growing concern about the environment and human health has resulted in the search for effective methods for detecting and analysing environmental contaminants. Polyaromatic hydrocarbons (PAHs) are among the persistent organic pollutants (POPs) that have deleterious health effects on both aquatic organisms and humans [1,2]. PAHs are a class of chemical compounds that have more than one fused aromatic rings. They are products of incomplete combustion of petroleum, coal, tar and other forms of organic materials [3]. Anthracene, phenanthrene, fluoranthene, benz[a]anthracene and benz[a]pyrene are some examples of PAHs [4] that have been detected at all levels of the food chain [5]. Consequently, the European Union, World Health Organization (WHO) and several countries have regulations for PAHs in food and environment [6,7].

Sensors are necessary for real time checking of adherence to the set limits of PAHs. Intrinsically conducting polymers (ICPs) and their composites are known to be very effective materials for the construction of sensors [8]. In particular, graphene-based polymeric nanomaterials are expected to possess properties that make them very efficient platforms for the development of

electrochemical sensors [9]. Due to the excellent electronics of its two-dimensional sp^2 -hybridized carbons, electrocatalysis readily occurs on graphene film [10,11]. This property of graphene can be modified by the incorporation of functional nanomaterials to produce required electrochemical sensing performance [12]. Doped form of ICPs, such as polyaniline (PANI), have been recognized as cost effective electrocatalytic sensor materials due to their improved redox activity and conductivity [13,14].

Doped PANI has been reported [15,16] to be characterized by enhanced mechanical, electrical, thermal and electrochemical properties [17]. In the form of nanosheets, graphene can provide active nucleation sites for PANI as well as excellent electron transfer pathways [18]. Graphenated polyaniline (GR-PANI) nanocomposite-based sensor for anthracene is being presented for the first time in this report.

2. Experimental

2.1. Reagents

Natural graphite powder (microcrystal grade, 99.9995%) (Metal base) UCP1-M grade, Ultra "F" purity was purchased from Alfa Aesar and used for the preparation of graphene oxide (GO) by a modified Hummers method [19]. Analytical grade aniline (99%) was obtained from Aldrich Chemical, Gillingham, England and purified by distillation under reduced pressure prior to use. Ammonium

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persulphate ((NH₄)₂S₂O₈), anthracene (99%), lithium perchlorate (LiClO₄, 99.99%), acetonitrile (HPLC grade), hydrochloric acid (HCl, 37%), hydrogen peroxide (H₂O₂, 35 wt% water solution), sulphuric acid (H₂SO₄), sodium nitrite (NaNO₂) and potassium permanganate (KMnO₄) were obtained from Sigma–Aldrich. 0.1 M LiClO₄ in acetonitrile was used as the supporting electrolyte. Ultra-pure water (Millipore) was used for all preparations.

2.2. Apparatus

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed with a BAS 100W electrochemical workstation from BioAnalytical Systems (BAS) Technical Ltd., Stockport, UK. A conventional three-electrode system was used for electrochemical studies and it consisted of a glassy carbon electrode (GCE), Ag/AgCl (with 3 M NaCl salt bridge) and platinum wire as the working, reference and counter electrodes, respectively. The infrared spectra of PANI, graphite, graphite oxide and graphene were recorded on a Fourier Transform Infra-Red (FTIR) spectrometer (Perkin Elmer Spectrum 100) and their structural details were evaluated by X-ray diffraction studies performed with a Phillips X-ray diffractometer that has Cu-K α radiation. A tapping-mode atomic force microscope (Veeco Nanoman V) was used to evaluate the morphology of graphene and its film thickness. Antimony-doped silicon tip (with a curvature radius of 2.5–3.5 μ m, a force constant of 1–5 N m⁻¹ and a resonance frequency of 60–100 kHz) was used for atomic force microscopy (AFM) experiments. The samples for AFM were prepared by drop-coating a silicon wafer with 5 μ L graphene/water dispersion. Transmission electron microscopy (TEM) images of the materials were obtained with a Tecnai G₂ F20X-Twin MAT 200KV high resolution (HR) TEM from FEI (Eindhoven, Netherlands). Scanning electron microscopy (SEM) studies were performed with a LEO 1450 SEM 30KV instrument equipped with energy dispersive X-ray (EDX) and wavelength-dispersive spectrometry (WDS) capabilities. VoltaLab PGL 402 from Radiometer Analytical (Lyon, France) was used for electrochemical impedance spectroscopy (EIS) measurements in 1 M HCl.

2.3. Material synthesis

Graphene oxide (GO) was synthesized from graphite powder by a modified Hummers method [19]. Accordingly, 2.0 g powdered graphite flakes and 1.0 g NaNO₂ were gently added to 50 mL concentrated H₂SO₄ at room temperature. The solution was then cooled to 0 °C in an ice bath while stirring vigorously. 7.0 g KMnO₄ was added to the suspension and the rate of addition was carefully controlled to prevent the temperature of the suspension from exceeding 20 °C. The ice bath was then removed and the temperature of the suspension was raised to room temperature and maintained for 30 min. The temperature was then raised to 35 °C in a water bath and then stirred for 2 h. As the reaction progressed, the slurry gradually thickened with diminishing effervescence. The mixture was cooled in ice bath and excess deionized water was added to it. The reaction mixture was treated with 35% H₂O₂ until gas evolution ceased, in order to reduce the residual KMnO₄ and MnO₂ to colorless and soluble MnSO₄. The precipitate was filtered off, washed several times with warm deionized water/concentrated HCl mixed solvent (9/1 volume ratio) and then dried under reduced pressure at 60 °C for 24 h to obtain graphene oxide. The GO was then exfoliated in distilled water through ultrasonication to form thin GO sheets for subsequent use.

GR-PANI was prepared by *in situ* polymerization of aniline in a suspension of GO, by chemical oxidation of aniline with (NH₄)₂S₂O₈ in an acidic medium [17], followed by the reduction of the solution with NaBH₄ [20]. The reaction product was then dispersed in 1 M HCl containing (NH₄)₂S₂O₈ and stirred overnight at room

temperature to allow the reoxidation and reprotonation of PANI to occur and form crystalline GR-PANI. The resultant GR-PANI nanocomposite was collected by filtration and dried in vacuum. For comparison, polyaniline film was prepared by the same procedure under the same condition but without adding graphene oxide. Graphene nanosheets were also synthesized by the NaBH₄ reduction method. Typically 100 mg GO powder was dispersed in 100 mL deionized water and exfoliated into GO sheets by ultrasonication for 1 h to form a stable aqueous dispersion. 200 mg NaBH₄ was then added to the dispersion while stirring the mixture continuously at 125 °C for 3 h. Finally a black precipitate was obtained and isolated by filtration and dried under vacuum at 60 °C to obtain graphene [20] (Scheme 1).

2.4. Preparation of modified electrodes

A 0.071 cm² GCE was polished with slurries of 0.05, 0.3 and 1.0 μ m alumina powder (Buehler, IL, USA), rinsed with distilled water, ultrasonicated in ethanol and deionized water, and then dried at room temperature. 1 mg GR-PANI nanocomposite was dispersed in 1 mL ethanol and ultrasonicated for 30 min to form a homogenous suspension. The surface of the polished GCE was coated with 5 μ L of the suspension and dried at room temperature to form GR-PANI|GCE sensor. PANI|GCE and GR|GCE systems were also prepared by drop-coating GCE with 5 μ L of their respective suspensions.

3. Results and discussion

3.1. Characterization of GR-PANI nanocomposite

The CV of GR-PANI|GCE was run in 1 M HCl within a potential window of -0.2 to +1.2 V vs. Ag/AgCl. The electrochemical reactivities of the different electrodes are depicted in the CVs presented in Fig. 1(a)–(d). As shown by the innermost voltammogram (unlabeled) in Fig. 1(a), no peak was observed for unmodified GCE, but after modification with graphene, i.e. CVs (*i* – *v*), a pair of redox peaks was observed. The peaks increased as scan rate increased, accompanied by an anodic and cathodic shifts in oxidation and reduction peak potentials, respectively. This behavior is typical of carbon materials because of the transition between quinone and hydroquinone electrochemistry [15]. The PANI|GCE system depicted in Fig. 1(b) has two redox couples, labeled $I_{p,c1}/I_{p,c1}$ and $I_{p,a2}/I_{p,c2}$, as is typical with polyaniline redox transitions of the semiconductive leucomeraldine form ($I_{p,c1}$) to the conductive polaronic–leucomeraldine form ($I_{p,a1}$); and the Faradaic transformation of emeraldine ($I_{p,c2}$) to penigraniline ($I_{p,a2}$) [21]. The CV of GR-PANI-modified GCE is characterized by well-defined redox peaks and an enhancement of the peak currents relative to those of PANI-modified and unmodified GCE. The current density and the anodic to cathodic peak separation (ΔE_p) analyses of the CVs drawn in Fig. 1(b) gave $\Delta E_{p(1)}$ and $\Delta E_{p(2)}$ values of 184 and 137 mV, respectively, for PANI|GCE. The corresponding values for GR-PANI|GCE were 83 and 51 mV. The results demonstrate a graphene-induced reduction in the ΔE_p values of PANI by a factor of 2.2 for the leucomeraldine/polaronic–leucomeraldine transition, and 2.7 for the emeraldine/penigraniline process. The reduction in the ΔE_p value means that the electrochemistry of the graphenated system is faster and the material is more conducting.

In addition to the good conductivity of graphene, its excellent catalytic properties as a result of its higher surface-to-volume ratio, provides greater surface accessibility of the polymer matrix [22,23]. The anodic peak currents ($I_{p,a1}$ and $I_{p,a2}$) of GR-PANI|GCE (Fig. 1(c)) were found to be linearly dependent on scan rates, in accordance with the equations: $I_{p,a1} = 2.0461 \times 10^{-4} + 2.7413 \times 10^{-5} \nu$

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