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Graphenated polyaniline-doped tungsten oxide nanocomposite sensor for real time determination of phenanthrene

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ABSTRACT

A graphenated polyaniline/tungsten oxide (PANI/WO_3/GR) nanocomposite sensor was prepared by electropolymerisation of a mixture of aniline monomer and tungsten oxide on a graphene-modified glassy carbon electrode (GCE). The PANI/WO_3/GR/GCE nanocomposite electrode was tested as a sensor for the determination of phenanthrene. The direct electro-oxidation behaviour of phenanthrene on the PANI/WO_3/GR modified GCE was carefully investigated by cyclic voltammetry. The results indicated that the PANI/WO_3/GR/GCE sensor was more sensitive to phenanthrene (with a dynamic linear range of 1.0 - 6.0 pM and a detection limit of 0.123 pM.) than GCE, PANI/GCE or PANI/WO_3/GCE. The sensor exhibited excellent reproducibility and long-term stability. The sensor exhibits lower detection sensitivity than the WHO permissible level of 1.12 nM phenanthrene in wastewater.

1. Introduction

The growing concern about the environment and the health of every individual has resulted in the search for an effective method of determination and quantification of contaminants in order for pollution free environment. Polyaromatic hydrocarbons (PAHs) are among the persistent organic pollutants (POPs) that has been recognized as teratogenic, mutagenic and carcinogenic in nature [1], and to have deleterious effect on both aquatic organisms and humans, through natural and anthropogenic activities, via industrial, agricultural and domestic waste [2]. PAHs are a class of several individual chemical compounds defined to be composed of more than one fused aromatic rings, commonly found in petroleum fuels, incomplete combustion of coal, tar products and other forms of organic materials [3]. Anthracene, phenanthrene, fluoranthene, benz[a]anthracene and benz[a]pyrene to mention a few, are some examples of PAH [4]. Because of their profusion, it is not astonishing that they are able to have their way into the food chain in every level [5]. They are potentially serious health risk and therefore become attention for greater focus of research. In recent times the regulations for PAHs have been enacted and anticipated in Europe as well as by the world health organization (WHO) for monitoring [6,7]. Presently, instrumental methods of analysis involving chromatographic (TLC, GC, HPLC spectroscopic [8], (UV-Vis, IR, MS) or coupled techniques (GC-MS) [9] are heavily relied upon for environmental analysis. These instrumental techniques are usually expensive, not easily amenable to on-site applications, require extensive pre-treatment stages before analyte quantification and they fail to indicate whether the compounds are accessible for assimilation by living organisms. Herein, a simple, less time consuming, low cost and reliable electrochemical sensor is being proposed for real time determination of PAHs.

Intrinsically conducting polymers (ICPs) are useful materials for applications in electronics, electrochemistry and sensors [10]. Among the ICPs, polyaniline (PANI) has attracted great attention due to a good combination of properties; reasonable stability, low cost, eases of synthesis, environmental and thermal stability as well as adequate electrical conductivity. There have been numerous attempts to apply high conductivity, electrochromic, catalytic, sensor, redox and other properties of this PANI to different practical needs. Direct [11] application is, however, greatly limited because of processibility limitations and its intractable nature. Of recent,

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the application of PANI has been widened through the formation of composites or blends with common polymers [12,13] and other particulate dispersants like WO_3, SiO_2 and SnO_2 to form PANI nanocomposites with better processibility [14].

Considering inorganic materials for the fabrication of sensor, semiconductive metal oxides are of great attention owing to their interesting properties e.g. ZnO_2 [15,16], TiO_2 [17]. Among the known transition metals oxide that has been widely studied, tungsten oxide (WO_3) has gained a lot of recognition due to its intrinsic properties. It can exhibit different oxidation states which results in its different forms of oxides, e.g., WO_2 and WO_3. Tungsten oxide (WO_3), with a high percentage of oxide and as an n-type semiconductor, that has been reported to have a band gap of 2.8 eV, is economically stable and its band gap has the ability to absorb within the solar spectrum. WO_3 semiconductor is a promising candidate for a sensor, and because of the high surface-to-volume ratio as well as advantage of its high sensitivity performance, it has also found suitable applications in devices such as photochromic [18], gas sensors [19], optochromic, optical devices, electrochromic [20], energy-saving devices e.g. smart windows in cars and buildings [21].

Recently, graphene-based nanomaterials have shown fascinating applications in electrochemical sensors and biosensors, which provide an effective sensing platform for small biomolecules [22]. Owing to the extraordinary electronic transport property and high electrocatalytic activity of graphene, a single atom of two-dimensional sp^2-hybridized carbon, the electrochemical reactions of analyte are greatly promoted on graphene film, resulting in enhanced voltammetric response [23]. In addition, graphene has a high quality alternative to carbon nanotubes (CNTs) and carbon nanofibers in composite applications. An outstanding electrical and thermal conductivity is exhibited compared to CNTs, and the specific surface area is twice that of CNTs [24]. The electrochemical properties of graphene can be well modified by incorporation with other functional nanomaterials such as catalyst nanoparticle or polymer to produce resourceful electrochemical sensing performance [11]. Doped form of polyaniline has been recognised as a promising and cost effective electrocatalytic sensor due to the improved redox activity and conductivity [25–29].

In this work, WO_3 was prepared from a solution of an inexpensive tungstic acid (WO_3 precursor) and peroxide. The problem of precipitation usually encountered in WO_3, is eliminated and a homogenous solution of WO_3 is prepared to achieve a high surface-volume-ratio and thin film of tungsten oxide, this is then incorporated with PANI and graphene nanosheets to improve the performance of the nanocomposite. Therefore, a polyaniline/tungsten oxide/graphene (PANI/WO_3/GR) nanocomposite has been prepared by electrochemical deposition of a mixture of WO_3 and PANI on a graphene modified glassy carbon electrode. The electrochemical sensor fabricated has exhibited an excellent performance in the detection of polyaromatic hydrocarbon in aqueous medium which serves as the working electrolyte, and which may stand as a challenge because of the hydrophobic nature of polyaromatic hydrocarbons instead of the general detection in organic medium e.g. acetonitrile.

2. Experimental

2.1. Reagents

Natural graphite powder (microcrystal grade, 99.9995%) (Metal base) UCP -1–M grade, ultra "F" purity purchased from Alfa Aesar was used for graphite oxide preparation using Hummers method with some modification [30,31]. Analytical grade aniline (99%) was obtained from Aldrich Chemical, Gillingham, England and purified by distillation under reduced pressure prior to use for chemical synthesis. Phenanthrene (99%), hydrochloric acid (HCl, 37%), hydrogen peroxide (H_2O_2, 30% wt water solution), sulphuric acid (H_2SO_4), sodium nitrite ($NaNO_3$), potassium permanganate ($KmNO_4$), tungstic acid were obtained from Sigma-Aldrich. All chemicals used in this study were analytical reagent grade and were used without further purification. 1 M HCl was used as the supporting electrolyte. Ultra pure water (Millipore) was used for all preparations.

2.2. Apparatus

Cyclic voltammetric (CVs) and square wave voltammetric (SWVs) measurements were carried out using a BAS 100 W integrated, automated electrochemical workstation from BioAnalytical Systems (BAS) Technicol, Stockport, UK. A conventional three-electrode cell system was used, which consisted of a glassy carbon (GCE), an Ag/AgCl (saturated NaCl) and a platinum wire as working, reference and counter electrodes, respectively. Aqueous hydrochloric acid was used as the supporting electrolyte. All experimental solutions were purged with high purity argon gas during measurements and experiments were carried out at controlled room temperature (25 °C). The detailed structural properties of the prepared materials was evaluated using Fourier transform infrared spectrometer (FT-IR, Perkin Elmer Spectrum 100), X-ray diffraction (XRD) measurement (Phillips X-ray diffractometer with Cu-Kα radiation). A tapping-mode atomic force microscope (AFM) (Veeco Nanoman V) was employed to evaluate the morphology of graphene, with special emphasis on estimating its thickness. The silicon tip [antimony (n) doped] had a curvature radius of 2.5–3.5 μM, a force constant of 1–5 N m^{-1} and a resonance frequency of 60–100 kHz. The samples for AFM were prepared by drop coating the graphene/water (5 μL) dispersion onto a silicon wafer. High resolution transmission electron microscopy images were taken on a Tecnai G_2 F20X-Twin MAT 200KV HRTEM from FEI (Eindhoven, Netherlands) and the high resolution scanning electron microscopy images were taken using LEO 1450 HRSEM 3OKV instrument equipped with EDX and WDS. Raman spectra were recorded on a Dilor XY Raman spectrometer with a Coherent Innova 300 Argon laser with a 532 nm laser excitation. Electrochemical impedance spectra (EIS) measurements were performed using Volta Lab PGL 402 from Radiometer Analytical (Lyon, France) in a solution containing 1 M HCl. UV-Vis spectra and measurements were recorded over a range of 350-700 nm using 3 cm^3 quartz cuvettes with Nicolette Evolution 100 Spectrometer (Thermo Electron Corporation, UK). Polishing pads obtained from Buehler, IL, USA and Alumina micro powder (1.0, 0.3 and 0.05 μm alumina slurries) were used for polishing the GCE.

2.3. Material synthesis

Graphene oxide was synthesized from graphite powder by the modified Hummers method [31,32]. Concentrated sulphuric acid (50 mL) was gradually added to a 500 mL volumetric flask containing mixture of powdered graphite flakes (2.0 g) and sodium nitrate (1.0 g) at room temperature. The solution was then cooled to 0 °C in an ice bath, while vigorous agitation was maintained; potassium permanganate (7.0 g) was added to the suspension for duration of about 30 min. 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 suspension was brought to room temperature, where it was maintained for 30 min. The temperature was then raised to 35 °C in a water bath, and then stirred with a Teflon coated magnetic stirring bar for 12 h. As the reaction progressed, the slurry gradually thickened with diminishing effervescence. The mixture was then cooled in ice bath, followed