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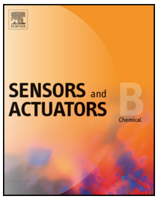

Fabrication of platinum nitrogen-doped graphene nanocomposite modified electrode for the electrochemical detection of acetaminophen

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ABSTRACT

An electrochemical sensor for the determination of acetaminophen (AC) was fabricated on glassy carbon electrode (GCE) modified with platinum nitrogen-doped graphene (Pt/NGr) nanocomposite. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and square-wave voltammetry (SWV) were performed to investigate the electrochemical behaviour of AC. From the electrochemical results, the synergy between platinum nanoparticles and nitrogen-doped graphene improved the interfacial electron transfer process, thus exhibited a higher catalytic performance towards the electrochemical oxidation of AC. A linear range between 0.05–90 μmol L^{-1} for the determination of AC was achieved with a limit of detection of 0.008 μmol L^{-1}. The prepared sensor demonstrated acceptable reproducibility, stability and good selectivity in the presence of interferences such as ascorbic acid, *p*-aminophenol and dopamine. In addition, this method showed satisfactory results in commercial tablets.

1. Introduction

Acetaminophen (AC) or paracetamol has been an alternative to aspirin since introduced by Sterling-Winthrop Co. in 1953 [1]. AC is a useful analgesic and antipyretic drug which is utilized extensively for relieving fever, cold, cough and pain such as headache, toothache and backache [2,3]. In general, AC is considered safe and does not exhibit any serious side effects when consumed in prescribed doses [4,5]. However, the excessive consumption of AC leads to accumulation of toxic metabolites that could cause hepatotoxicity and nephrotoxicity, which is related to liver and kidney damage [6,7]. Therefore, the development of an easy, facile, sensitive and accurate method for the determination of AC is crucial for quality control in pharmaceutical and overdose diagnosis [3,8]. Numerous methods have been utilized for the detection of AC such as chromatography [9], chemiluminescence [10], capillary electrophoresis [11], spectrophotometry [12], titrimetry [13] and flow injection methods [14]. However, some of these methods have drawbacks such as time consumption, high cost of instrumentation, trained personnel for operation and low sensitivity which is inappropriate for regular analysis. Electrochemical technique is a good alternative to the above mentioned methods due to the faster response, higher selectivity, higher sensitivity, easy operation and lower cost [15–18].

Graphene, a two dimensional nanocarbon polymorph has attracted global attention in various applications such as solar cells [19], fuel cells [20], supercapacitors [21] and sensors [22], since its discovery in 2004 [23]. Graphene possesses many unique properties such as good electrical conductivity, large surface area, high chemical and thermal stability which makes it an ideal support for dispersion of noble metal nanoparticles (NPs) [24]. The electrochemical performance and reactivity of graphene could be enhanced by doping with foreign atoms such as nitrogen [25]. In addition, the presence of nitrogen atoms in the graphene lattice increases the active sites which promote a more uniform dispersion of smaller sized metal nanoparticles compared to the undoped graphene [26].

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Currently, many researchers have utilized nanomaterials for the modification of electrodes in sensor applications. The combination of nitrogen-doped graphene (NGr) with nano-sized materials into nanocomposites has broaden the utilization of NGr in sensor applications. Thus, platinum nanoparticles (Pt NPs) have gained enormous attention due to the outstanding conductivity and extremely high electrocatalytic activity as electrochemical sensors [27]. However, Pt has some limitations such as the high cost and low natural abundance. Due to these limitations, Pt utilization can be minimised by decreasing the particle size through dispersion on a low-cost support material which possesses higher chemical stability, electrical conductivity and larger surface area such as NGr [28]. In addition, NGr is recognized as an ideal support material due to the lower agglomeration of Pt NPs, hence increasing the stability and activity of the catalytic nanoparticles [29].

In the light of the above ideas, an effective approach for the modification of glassy carbon electrode (GCE) was developed based on the decoration of nitrogen-doped graphene with Pt NPs by chemical reduction and was utilized for the electrochemical determination of AC. The morphology and electrochemical properties of the Pt/NGr nanocomposite were also investigated. The Pt/NGr nanocomposite showed enhanced catalytic activity toward the oxidation of AC compared to the pure NGr and bare GCE.

2. Experimental methods

2.1. Materials

Acetaminophen was procured from Sigma-Aldrich, while potassium tetrachloroplatinate (K_2PtCl_4), dipotassium hydrogen phosphate (K_2HPO_4) and potassium dihydrogen phosphate (KH_2PO_4) were procured from Merck. All chemicals and reagents utilized in these experiments were of analytical grade and used as received. The supporting electrolyte was 0.1 mol L^{-1} phosphate buffer solution (PBS, pH 7.0), prepared by dissolving equal amounts of KH_2PO_4 and K_2HPO_4 in deionized water. The pH of PBS was adjusted using 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} H_3PO_4. A stock solution of 0.01 mol L^{-1} AC was prepared by dilution in PBS. Deionized water (18.2 MΩ cm) from Millipore water systems was used as the solvent.

2.2. Synthesis

2.2.1. Synthesis of nitrogen-doped graphene (NGr)

NGr was synthesized by a microwave-assisted method [30], which utilized graphene oxide (GO) as the starting material. Firstly, GO was obtained from graphite by the Hummers method [31]. A yellow-brown dispersion of GO was prepared by sonicating 0.2 mg mL^{-1} graphitic oxide dispersion in an ultrasonic bath for 30 min. Next, 0.8 mL hydrazine was added to a 30 mL GO dispersion to start the chemical reduction. This was followed by irradiation for 5 min in a microwave oven under high power mode, to form a stable black dispersion of the NGr sheets. Finally, the NGr was collected by centrifuging the NGr suspension and then dried in an oven at 50 °C.

2.2.2. Synthesis of Pt/NGr nanocomposite

Pt/NGr was synthesized using a similar method reported earlier [32]. Firstly, 20.0 mL of 0.05 mol L^{-1} K_2PtCl_4 aqueous solution was mixed with 2.0 mL of NGr suspension (10 mg mL^{-1}). Then, the pH of the solution was adjusted to 8.0 using 0.1 mol L^{-1} sodium hydroxide solution. The mixture was then stirred and heated to 60 °C for 35 min. This was followed by the addition of 0.01 mL hydrazine hydrate to the mixture with continuous stirring and heating for another 30 min. During this process, Pt nanoparticles were deposited on the surface of NGr nanosheets to form Pt/NGr. Next, the Pt/NGr suspension was left standing at room temperature before centrifuged at 4000 rpm for 15 min. Finally, the sample was dried in a drying oven at 60 °C for 24 h.

2.2.3. Fabrication of Pt/NGr modified electrode

A glassy carbon electrode (GCE) was hand-polished to a shiny surface with 0.05 μm alumina particles on a polishing pad and rinsed repeatedly with deionized water. Next, the electrode was ultrasonically washed for 5 min in ethanol as well as in deionized water to eliminate any adsorbed material, followed by air-drying at room temperature.

For the preparation of Pt/NGr/GCE, 1.0 mg Pt/NGr was dispersed in 1.0 mL deionized water and 10 μL nafion solution, and later sonicated for 1 h to form a homogenous suspension. After that, 10 μL of the suspension was drop-casted on the surface of GCE using a micropipette and was evaporated overnight at room temperature. The NGr/GCE was also prepared using the same procedures as a comparison.

2.3. Characterization

X-ray diffraction (XRD) was performed on a Siemens D500 diffractometer with Cu Kα (λ = 1.541 Å) radiation, to investigate the crystal structure and confirm the presence of Pt NPs. The surface morphology of the nanocomposite was analyzed using a JEOL JSM-7600F field emission scanning electron microscope (FESEM), equipped with an Oxford Instrument energy dispersive X-ray (EDX) spectrometer. A JEOL JEM-2100F high-resolution transmission electron microscopy (HRTEM) was utilized to investigate the lattice spacing of the nanocomposite. Raman spectroscopy was performed on a Horiba Xplora micro Raman spectrometer with a laser source and an excitation wavelength of 532 nm. The elemental composition of Pt/NGr was evaluated by ULVAC-PHI Quantera II X-ray photoelectron spectrometer (XPS) with an Al-Kα X-ray source of 1486.6 eV.

2.4. Electrochemical study

Electrochemical experiments such as electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and square-wave voltammetry (SWV) were performed using an Autolab potentiostat/galvanostat model PGSTAT302 (Eco Chemie, Netherlands). All electrochemical experiments were performed using a conventional three-electrode system. The Pt/NGr modified glassy carbon electrode (GCE, 3 mm diameter) was the working electrode, while a platinum wire and Ag/AgCl (3.0 M KCl) were the auxiliary and reference electrodes, respectively. All experiments were performed at room temperature.

2.5. UV spectroscopy measurement

A Shimadzu UV-1800 UV/Visible Scanning Spectrophotometer with quartz cuvette (1 cm path length) was used to measure the concentration of AC in real sample analysis. The results obtained from UV spectroscopy were compared with those obtained by the voltammetry.

3. Results and discussions

3.1. Characterization of Pt/NGr

The crystalline structure of Pt/NGr nanocomposite was investigated by X-Ray diffraction (XRD). As presented in Fig. 1, the presence of several peaks at 2θ values of 40.00, 46.39, 67.82, 81.62 and 86.00 are attributed to the (111), (200), (220), (311) and (222) crystal planes, respectively, which describes the presence of the