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Ionic liquid based high performance electrochemical sensor for ascorbic acid in various foods and pharmaceuticals

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ABSTRACT

In the present study, 1-butyl-3-methyl imidazolium tetra fluoroborate ionic liquid (IL), boron nitride (BN) and magnetite nanoparticles (Fe_3O_4NPs) based nanocomposite (IL-BN-Fe_3O_4NPs) was successfully synthesised and used to fabricate glassy carbon electrode (GCE) for the determination of ascorbic acid (AA). The nanocomposite was characterized by Fourier transformation infrared spectroscopy (FTIR), x-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM), electron diffraction spectroscopy (EDS) and transmission electron microscopy (TEM) techniques to observe the surface morphology. Cyclic voltammetry (CV) was performed to assess the electrochemical performance of IL-BN-Fe_3O_4NPs/GCE towards ascorbic acid (AA) in 0.1 M phosphate buffer solution (PBS) at pH 7. The CV results obtained reveal that the significant enhancement of anodic peak current with increased sensitivity and conductivity. The differential pulse voltammetric results obtained indicates the linear increment of electrochemical signals with an increase in the concentration of AA in the range of 1–12 μM. Based on the calibration plot, limit of detection and limit of quantification were calculated and found to be 0.042 and 0.139 μM respectively. The electrochemical sensor showed outstanding sensitivity, selectivity, repeatability and stability. In addition to this IL-BN-Fe_3O_4NPs/GCE sensor was practically applied for the routine analysis of AA in various food and pharmaceutical samples.

1. Introduction

Ascorbic acid (AA) is a commonly known as vitamin-C, and is widely distributed in both the animal and plant kingdom. It plays a significant role in human biological metabolism, predominantly in healing the burns, production of collagen and regulation of cartilage and tendons. [1]. Moreover AA is used for the treatment of cold, neurodisorders, impotency and AIDS [2,3]. In addition, AA is used as antioxidants in various food and beverage industry as well as pharmaceutical and cosmetic industries [4]. Therefore, it is necessary to develop facile and robust methodology for selective and sensitive determination of AA in various food and pharmaceutical products. Previously, numerous methods were reported for the determination of AA such as electrophoresis [5], fluorimetry [6], chemiluminescence [7], liquid chromatography [8] and electrochemical methods [9–12]. Amongst all, these methods need complex sample preparation, expensive instrumentation and are time consuming processes. However the electrochemical methods include relatively low cost instrumentation, easy handling and less sample preparation methodology, with good sensitivity and selectivity [13–17].

Usually in electrochemical techniques, the glassy carbon electrode (GCE) is able to detect the AA at higher oxidation potentials. In principle, some biological compounds like uric acid and tyrosine exhibit similar oxidation potential as AA, so there is a possibility of interferences with bare GCE towards AA. Numerous efforts has been made to improve the sensitivity of the electrode by modifying its surface, which includes nano-materials and conducting polymers [18,19], but they showed some stability issues. In addition to these, carbon nanotubes were used as a fabricating material, due to their larger surface area and high electronic conductivity nature [20].

Alternatively, ionic liquids (ILs) exhibit outstanding physicochemical properties such as high ionic conductivity, greater thermal stability, lowest vapour pressure, higher antifouling capacity and good biocompatibility [21]. Due to unique properties and extensive application of ILs, they have been used as a new generation material binders in the construction of electrochemical sensors [22–24]. Nowadays, various metallic nanoparticles and carbon nanotubes are used in the combination of ILs for the fabrication of various types of electrodes [25–27] which inevitably enhances the electrochemical sensing abilities of electrochemical sensors.

In the present work, a novel electrochemical sensor was developed based on 1-butyl-3-methyl imidazolium tetra fluoroborate ionic liquid (IL), boron nitride (BN) and magnetite nanoparticles (Fe_3O_4NPs) composite for the ultra-sensitive determination of AA. The electrochemical sensing potentiality of the developed sensor was demonstrated. Effect

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of excepients, stability and reproducibility of the electrochemical sensor were also examined. In addition, real sample analysis was carried out in the present investigation.

2. Experimental

2.1. Reagents

IL (1-butyl-3-methyl imidazolium tetra fluoroborate [BMIM] [BF_6]), boron nitride (BN) and L-ascorbic acid was purchased from Sigma–Aldrich, South Africa. Multiwalled carbon nanotubes (95% purity, 10–20 nm in diameter and 30 μm length), anhydrous iron (III) chloride and iron (II) chloride were obtained from Merck. Orthophosphoric acid (H_3PO_4), potassium chloride, potassium hydroxide, sodium hydroxide, ethyl alcohol, sulphuric acid, acetone and potassium ferricyanide were purchased from Capital Labs, Durban, South Africa. All the reagents were of analytical grade and used as received. Millipore water (18 MΩ cm) was used throughout in all experiments. All standard solutions were kept in a refrigerator at 4 °C for stability. The 0.1 M phosphate buffer solution (PBS) was freshly prepared from appropriate amounts of H_3PO_4 and NaOH solutions.

2.2. Apparatus

Electrochemical measurements were performed by using a 797 VA computrace from Metrohm (Herisau, Switzerland) equipped with three electrode conventional system. Glassy carbon electrode (GCE) with 3.0 mm diameter was used as working electrode. The (Ag/AgCl (3 M KCl)) electrode and the platinum wire were used as a reference and counter electrodes respectively.

Transmission electron microscopy (TEM) and energy dispersive X-ray spectrometry (EDS) were performed on a JEOL-2100F microscope operating at an accelerating voltage of 200 kV (Maxoxford instruments). The scanning electron microscopy (SEM) was performed on a JSM-6701F (JEOL, Japan). Whilst X-ray diffractrometric study was performed with D 5000 Siemens diffractometer having copper source ($K = 154.18$ nm) with the sample secured on quartz mono crystals. The JCPDS-ICDD database has been used to confirm the detected crystalline properties. Fourier Transformer infrared spectroscopic (FT-IR) study was achieved with Scimitar Series supplied by SMM Instruments (Durban, South Africa) respectively. All solutions were sonicated using a Labcon 5019 U ultrasonic bath and the pH measurements were made with the aid of a CRISON micro pH 2000 digital meter.

2.3. Synthesis of Fe_3O_4NPs and IL-BN-Fe_3O_4NPs composite

3.6 mM $FeCl_3 \cdot 6H_2O$ and 1.8 mM $FeSO_4 \cdot 7H_2O$ were completely dissolved in 10 mL millipore water. To the resulting solution 20 mL of ammonium hydroxide solution was added with constant stirring. The pH of the solution was maintained constantly at 8.0, until the reaction was completed. Finally a dark green coloured solution was turned into a black coloured solution indicating the formation of Fe_3O_4NPs. The formed NPs was subjected to repeated washings with millipore water to remove all the impurities. The resultant content was oven dried at 80 °C for about 30 min and then stored at room temperature for further use.

Individually 1.0 g each of both Fe_3O_4NPs and IL was dissolved in deionized water. The IL was kept in an oil bath with a nitrogen outlet and thermometer inlet. The temperature of the system was then raised up to 120 °C and kept constant, followed by continuous stirring for about 24 h. Then after the reaction mixture was allowed to dry at 100 °C for about 12 h, a black coloured product was obtained and was dispersed in 20 mL of ultra-pure water followed by sonication to remove the impurities. Boron nitride (BN) was then dispersed in 50 mL of deionized water and sonicated for about 15 min, and to dispersion dissoluted Fe_3O_4NPs was added with constant stirring. The reaction mixture was transferred into a round bottomed flask and subjected to reflux condensation in a temperature controlled oil bath, followed by constant stirring at 150 °C for 24 h. The resultant was vacuum dried for 10 h to get a brown coloured IL-BN-Fe_3O_4NPs composite. The product was purified by repeated washing with ultrapure water, ethanol and thereafter stored in the refrigerator at 4 °C for further use.

2.4. Fabrication of electrochemical sensor

Prior to use, the bare GCE was polished with 0.05 mm alumina slurry with a soft polishing cloth to obtain a mirror like surface. The GCE was further sonicated in water and ethanol (1:1) mixture to remove the adhered alumina. The pre-cleaned GCE was introduced to potential cycling from -0.5 to 1.5 V in phosphate buffer solution at the scan rate of 0.1 V s^{-1}. To prepare multiwalled carbon nanotubes modified GCE (MWCNT-GCE), 6 μL (1.0 mg mL^{-1}) of an MWCNTs-DMF solution was placed directly onto the surface of GCE and kept for drying at room temperature [28]. The Fe_3O_4NPs/GCE was prepared by adding 0.10 mmol L^{-1} solution of Fe_3O_4NPs to 5 mL of DMF and placed in an ultrasonic bath for 10 min at 50 °C. Thereafter, 6 μL of Fe_3O_4NPs-DMF was directly added on the surface of GCE by means of micro pipette and allowed to dry in an oven for 10 min at 50 °C. Finally, 0.10 mol $L^{-1}$of IL-BN-Fe_3O_4NPs was used to fabricate the GCE surface with the polishing brush. After coating the GCE, the electrode was subjected to drying in an oven for 30 min at 50 °C.

2.5. Electrochemical measurements of IL-BN-Fe_3O_4NPs

10 mL of supporting electrolyte (pH 7.0) was introduced into the electrochemical cell. The working electrode was dipped into electrolyte solution and purged with nitrogen gas for 5 min, in order to remove all the dissolved oxygen and few cyclic sweeps were performed in order to minimise the background currents. A small quantity of AA solution was then added into the cell and stirred at 500 rpm with the deposition at -1.00 V for 120 s. The solution was left to equilibrate for 5 s, prior to sweeping from 1.10 to 2.20 Vat a scan rate of 0.10 V s^{-1} DPV.

2.6. Real sample preparation

Ten vitamin C tablets containing 100 and 250 mg of AA were purchased from a local pharmacy, Durban, South Africa. The tablets were ground to a fine powder in order to obtain a homogenous mixture. A stock solution (0.10 mol L^{-1}) of AA was accurately measured and transferred into a 10 mL volumetric flask, followed by 10 times dilution. The content in the flask was then centrifuged for 15 min to ensure the complete dissolution of AA analyte. Aliquots of PBS were also added for the sample preparation.

The fruit and vegetable samples having visually the same size were purchased from the local market Durban, South Africa. Each fruit and vegetable samples were thoroughly cleaned and cut into pieces; 10 mg of the pulp was then transferred into a mortar and ground with pestle followed by the filtrate which was collected into a 50 mL calibrated flask, by using adsorbent cloth [29]. The content of AA in the filtrate samples were examined using the IL-BN-Fe_3O_4NPs/GCE sensor.

3. Results and discussion

3.1. Characterization of IL-BN-Fe_3O_4NPs composite

The Fourier transform infrared spectra of IL-BN-Fe_3O_4NPs, primarily contain BN exhibited the broad band's at 1516 cm^{-1}, 1218 cm^{-1}, 943 $cm^{-1}$and 820 cm^{-1} which is responsible for B—N, B—N—O, B—N—O stretchings and B—N—B bending respectively [30]. Two broad peaks are observed at 3282 cm^{-1} and 2823 cm^{-1} indicating the presence of IL containing imidazolium moiety stretching vibrations respectively (Fig. 1). In addition to these, two more peaks were noticed