



Stable determination of paracetamol in the presence of uric acid in human urine sample using melamine grafted graphene modified electrode



Srinivasan Kesavan, S. Abraham John *

Centre for Nanoscience and Nanotechnology, Department of Chemistry, Gandhigram Rural Institute, Gandhigram-624 302, Dindigul, Tamilnadu, India

ARTICLE INFO

Article history:

Received 21 July 2015

Received in revised form 12 November 2015

Accepted 25 November 2015

Available online 26 November 2015

Keywords:

Electrografting

Melamine

Graphene oxide

Self-assembly

Raman spectroscopy

Paracetamol

ABSTRACT

Electrochemically reduced graphene oxide (ERGO) on aminotriazine (AT) grafted glassy carbon (AT/GC) electrode was prepared by electrochemical reduction of graphene oxide (GO) attached through 2,4-diamino-1,3,5-triazine on GC electrode and the resulting electrode was utilized for the selective determination of paracetamol (PA) in the presence of higher concentration uric acid (UA). The GO attached on AT/GC (GO/AT/GC) and the ERGO films on AT/GC (ERGO/AT/GC) electrodes were characterized by scanning electron microscopy (SEM), Raman spectroscopy and cyclic voltammetry (CV). The ERGO modified electrode showed excellent electrocatalytic activity towards PA and UA. This electrode not only enhanced the oxidation currents of PA and UA but also shifted their oxidation potentials towards less positive potentials in contrast to bare GC, AT/GC and GO/AT/GC electrodes. Bare and GO modified electrodes failed to separate the voltammetric signals of UA and PA. However, the ERGO/AT/GC electrode successfully separated the voltammetric signals of them in a mixture and hence used for the simultaneous determination. Further, the modified electrode was effectively used for the selective determination of PA in the presence of 50-fold excess of UA. Using amperometry, detection of 40 nM PA was achieved. The current response of PA was increased linearly while increasing its concentration from 4.0×10^{-8} – 1.0×10^{-4} mol/L and the detection limit was found to be 6.8×10^{-10} mol/L ($S/N = 3$). The practical application of the present modified electrode was demonstrated by simultaneously determining the concentrations of PA and UA in human urine samples.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Paracetamol (PA) (N-acetyl-p-aminophenol or acetaminophen) (Chart 1A) is an effective analgesic and antipyretic drug used for the reduction of fever [1]. It acts as a painkiller by inhibiting prostaglandin's synthesis in the central nervous system and reduces fever by sedating hypothalamic heat regulating center [2]. It is also a useful drug for the treatment of osteoarthritis therapy, headache, backache, arthritis and postoperative pain [3–7]. At usual therapeutic doses, PA is rapidly and completely metabolized by undergoing glucuronidation and sulfation to inactive metabolites which are eliminated in the urine [1,6]. However, PA produces toxic metabolite accumulation at higher doses that mainly causes severe fatal hepatotoxicity and nephrotoxicity [8,9] besides skin rashes and inflammation of the pancreas [10].

Uric acid (UA) (Chart 1B) is the main end product of purine metabolism in the human body [11]. Increased uptake of serum UA acts as a scavenger of radicals and thus preventing from Parkinson's disease

[11]. Low concentration of UA is associated with multiple sclerosis [12]. UA is a major interfering agent for the determination of PA in human urine [1]. The electrochemical method has many advantages over the traditional methods due to its high sensitivity, selectivity, low cost and less time consuming. But, it is very difficult to separate UA and PA using conventional electrodes because both of them are oxidized at similar potential. However, accurate and selective determination of PA in human urine sample is essential for the clinical point of view. Therefore, it is a challenging task for the electrochemists to find a suitable electrode system for the determination of PA in the presence of UA. While searching the literature, few reports are available in the literature for the determination of PA and UA using multiwalled carbon nanotube (MWCNTs)/chitosan composite [13], nanocomposite of ferrocene thiolate stabilized $\text{Fe}_3\text{O}_4/\text{Au}$ nanoparticles with graphene sheet/chitosan [14], ionic liquid/MWCNTs/chitosan modified GCE [15], cetylpyridinium bromide/MWCNTs paste electrode [16] and MWCNTs-cobalt nanoparticles modified electrode [17] prepared by drop cast method. However, these methods involve either tedious procedures or series of steps involved to fabricate composite films on electrode surface besides the stability of these films is questionable. Further, the drop-casting method has intrinsic drawbacks such as lack of control over film thickness and less reproducibility. Hence, it is essential for the

* Corresponding author.

E-mail addresses: abrajohn@yahoo.co.in, s.abrahamjohn@ruraluniv.ac.in (S. Abraham John).

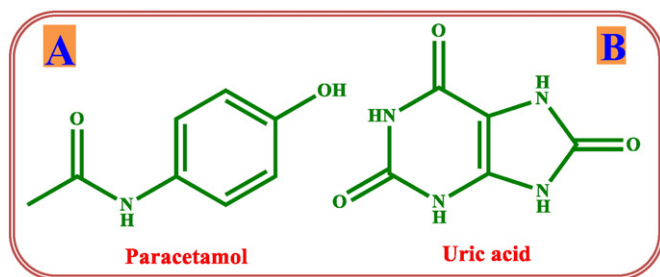


Chart 1. Structures of (A) paracetamol and (B) uric acid.

researchers to develop a simple method for the simultaneous determination of PA and UA in clinical point of view.

Chemical grafting of aryldiazonium salts derivatives is a widely used method for the modification of conducting substrates over the last two decades [18]. The methodology involves reduction of an aryldiazonium ion followed by elimination of dinitrogen to give an aryl radical which attacks the substrate with a formation of a covalent bond [18,19]. Grafting of diazonium salts is a powerful method to graft aryl groups bearing a wide variety of functionalities on different substrates like carbon [20,21], semiconductor [22], gold nanoparticles [23,24], graphene [25,26] and single-walled carbon nanotubes [27]. Graphene, an allotrope of carbon has received much attention because of its excellent electronic conductivity, high mechanical strength, large specific surface area and high stability [28]. It plays a predominant role in the fields of sensors, nanoelectronics, batteries, solar cells and electrochemical double-layer capacitors [29–31]. Graphene modified electrodes show excellent electrocatalytic activity towards biomolecules and toxic chemicals [32–34]. Most of the researchers reported drop casting method for the fabrication of graphene on different electrode substrates [34–40]. But, self-assembly is the best method to fabricate graphene because film thickness can be easily controlled [41].

Melamine (1,3,5-triazine-2,4,6-triamine) is mainly used as a precursor for pyrolysis processes and permits the insertion of nitride-like units in the carbon structure [42]. Be'langer et al. reported the selective diazotization of one amine group of melamine to graft on carbon powder [20]. However, grafting of melamine on electrode surface has not been reported so far. The presence of three amine functionalities in the melamine molecule could be useful for chemical grafting. In the present study, the GO is assembled on melamine grafted GC electrode. Then, the GO was electrochemically reduced at more negative potential to retain the aromatic backbone of graphene and used for the selective determination of PA in the presence of high concentration of UA.

2. Experimental

2.1. Chemicals

Graphite powder was purchased from Alfa Aesar. Uric acid (UA) and paracetamol (PA) were purchased from Sigma-Aldrich and were used as received. Potassium permanganate (KMnO_4), sodium nitrate (NaNO_3), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), melamine, sodium nitrite (NaNO_2) and hydrochloric acid (HCl) were purchased from Merck (India). The selective diazotization of one amine group of melamine has been described in the reported patent [43]. 1 equivalent melamine was solubilized in 0.5 mol/L HCl, to which 1 equivalent cold NaNO_2 was added drop wise to generate the aryldiazonium cations in situ in the electrochemical cell. Indium tin oxide (ITO) substrates were purchased from Asahi Beer Optical Ltd., Japan. GC plates were purchased from Sigma-Aldrich. 0.2 mol/L phosphate buffer (PB) solution (pH 7.2) was prepared by using Na_2HPO_4 and NaH_2PO_4 . All other chemicals

were of analytical reagent grade and were used as received. Double distilled water was used to prepare the solutions.

2.2. Instrumentation

Raman spectra were recorded on a Nanofinder® HE (Tokyo Instruments, INC), 532 nm YAG Laser. SEM measurements were carried out by using VEGA3 TESCAN. Electrochemical measurements were performed in a conventional two compartment three electrode cell with a mirror polished 3 mm glassy carbon electrode (GCE) as a working electrode, Pt wire as a counter electrode and a NaCl saturated Ag/AgCl as a reference electrode. All the electrochemical measurements were carried out with CHI model 634B (Austin, TX, USA) Electrochemical Workstation. For differential pulse voltammetry (DPV) measurements, pulse width of 0.06 s, amplitude of 0.05 V, sample period of 0.02 s and pulse period of 0.2 s were used. All the electrochemical measurements were carried out under nitrogen atmosphere at room temperature.

2.3. Synthesis of GO

GO was synthesized using the Hummer's method with a slight modification [44]. Concentrated H_2SO_4 (12 mL) was added to flake graphite (0.5 g) and NaNO_3 (0.25 g) and the mixture was cooled to 0 °C. KMnO_4 was added slowly into the mixture and the temperature was maintained at 20 °C. The reaction mixture was warmed to 35 °C and stirred for 30 min. Then, 23 mL of water was added, which produce an exotherm to 98 °C and the temperature was maintained for 15 min by external heating. The reaction was terminated by the large addition of water (72 mL) and 0.5 mL of 30% H_2O_2 . Finally, the reaction mixture was cooled, washed with 0.1 mol/L HCl and water to remove the metal ions and then dried.

2.4. Fabrication of AT grafted ERGO electrode

The fabrication of the AT grafted ERGO electrode is schematically shown in Scheme 1. 2,4-diamino-1,3,5-triazine moieties were introduced on the GC electrode by the in situ generation based on the diazotization of melamine. The resulting AT grafted electrode was termed as AT/GC electrode. It was rinsed with water and then immersed into exfoliated GO solution (1 mg/mL) for 12 h. The exfoliation of GO was achieved by the sonication of GO for 45 min. The GO was self-assembled on AT/GC modified electrode via electrostatic interaction between positively charged amine groups and negatively charged carboxyl groups present in the GO solution. In addition to that hydrogen bonding between the amine group in melamine and oxygen containing groups in GO and π - π interaction between the GO and triazine ring of melamine are also possible. This electrode is termed as GO/AT/GC electrode. Then, the GO modified electrode was electrochemically reduced in PB solution (pH 7) for the fabrication of ERGO on GC electrode. After electrochemical reduction of GO, the oxygen functional groups are reduced and strong π - π interaction between ERGO and triazine ring of melamine will anchor it on the electrode surface. This electrode is termed as ERGO/AT/GC electrode.

3. Results and discussion

3.1. Grafting of AT and electrostatic assembly of GO and its electrochemical reduction on GCE

Fig. 1A shows the CV obtained for the reduction of 2,4-diamino-1,3,5-triazine diazonium cations generated in situ from melamine. The CV shows a broad reduction wave at -0.47 V which was assigned to the formation of the aminotriazine radical and which attaches aminotriazine group on the GCE [19,21]. A similar behavior has been previously reported for the electrochemical reduction of several diazonium salts on various substrates [18,45]. We have chosen the electrografted

Download English Version:

<https://daneshyari.com/en/article/217916>

Download Persian Version:

<https://daneshyari.com/article/217916>

[Daneshyari.com](https://daneshyari.com)