



Synergistic electrocatalytic effect of graphene/nickel hydroxide composite for the simultaneous electrochemical determination of ascorbic acid, dopamine and uric acid



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ABSTRACT

A novel solar graphene-nickel hydroxide modified glassy carbon electrode was developed and used for the simultaneous detection of ascorbic acid (AA), dopamine (DA) and uric acid (UA). The sensor exhibited appreciable electrocatalytic effect for the simultaneous detection of lower concentrations of the analytes compared to solar graphene modified glassy carbon electrode. The detection limits attained by differential pulse voltammetry (DPV) were 30 μM , 120 nM and 0.46 μM for AA, DA and UA respectively. Recovery values ranging from 98 - 104% were obtained for the analysis of real samples.

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1. Introduction

Dopamine (DA), Ascorbic acid (AA) and Uric acid (UA) are important biomolecules that coexist in the extracellular fluid of the central nervous system and serum. These compounds play implicit roles in neurochemistry and biomedicine. DA is one of the most prominent catecholamines, functioning as a neurotransmitter in the central nervous system. Abnormal levels of DA result in serious neurological disorders such as Parkinson's disease and addiction [1,2]. AA is a water soluble vitamin that takes part in many important life processes. It has been used in the prevention and treatment of scurvy, common cold, mental illness, hepatic disease and cancer [3,4]. UA the primary product of purine metabolism in the human body is normally present in the milli molar range in urine and in micro molar levels in serum [5]. Abnormal levels of UA are symptoms of several diseases such as gout, hyperuricaemia and Lesch-Nyhan syndrome [6,7]. Therefore monitoring the levels of these compounds is of great importance and has always been the target of researchers.

Diverse methods like capillary electrophoresis [8], fluorometry [9,10], chromatography [11], spectrophotometry [12] and chemiluminescence [13] are being employed for the detection of AA, DA

and UA. Electroanalytical techniques having advantages of easy fabrication, low cost, fast response, and portable nature of the sensor are more suitable for the detection of these biomolecules due to their electroactive nature. Unfortunately, these biomolecules give a single overlapped voltammetric signal at most solid electrodes and the separation of their voltammetric peaks become a challenging problem. Hence the need to modify the electrodes becomes significant in order to attain well resolved signals. Various polymers [14–18], noble metals [19–23], metal oxides [24,25] and metal complexes [26–28] have been used as effective modifiers together with carbon based materials to achieve this goal.

Graphene—a one atom thick planar sheet of sp^2 bonded carbon atoms densely packed in a honey-comb crystal lattice is the latest discovered nanoscale form of carbon and has drawn immense attention in the fields of electronics, optical, magnetic, biological medicine, catalysis and energy storage due to its special nanostructure and unique electronic properties [29]. It is reported that compared to single walled carbon nano tubes, graphene exhibits 60 times more conductivity, better sensitivity and stability, greater sp^2 character and also more surface negative charge density [30,31]. Hence it is now being widely used in sensor applications because of its large surface area, high electrocatalytic effect, rich edge defects and elevated mechanical strength [32]. It is an excellent 2D support to load polymers and other nanoparticles. The incorporation of such species effectively avoids the problem of aggregation of graphene sheets arising from the Van der Waals interaction [33].

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Several reports on the simultaneous detection of AA, DA and UA utilizing graphene modified electrodes are available [32–42]. Sun et al. [43] has developed a size selected platinum - graphene nano composite for the simultaneous electrochemical determination of AA, DA and UA. The electrocatalytic effect of palladium - graphene composite towards their simultaneous determination has also been recently explored [44]. Sensitive and selective simultaneous detection of these electroactive species has great significance in complex real systems as it eliminates the need for pre-separation, thus saving time and money. Therefore the necessity of continuing further studies with an intention to attain lower detection limits exists even now.

Nickel oxide and hydroxide have awakened great interest for development of biosensors due to their cost effectiveness, high electrocatalytic effect, biocompatibility, non toxicity and high chemical stability [45–48]. Some researchers have investigated the electrocatalytic effect of graphene-nickel oxide modified glassy carbon electrode towards the electro oxidation of glucose [49–52]. A few of them have also considered the catalytic effect of nickel oxide and hydroxide for the electrochemical oxidation of DA [46–48]. But till date there are no reports on graphene-nickel hydroxide composites for the simultaneous detection of AA, DA and UA. Therefore we aim to exploit the synergistic effect of the catalytic activity of nickel hydroxide; together with the high conductivity and surface area of graphene sheets to serve as a potential electrode material for the simultaneous detection of AA, DA and UA.

The current paper presents for the first time, the use of a nickel hydroxide modified solar graphene coated glassy carbon electrode (Ni-sG/GCE) as a highly sensitive sensor for the simultaneous detection of AA, DA and UA. Well resolved peaks for the three were obtained at Ni-sG/GCE by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The voltammetric resolution of AA, DA and UA at their low concentrations, which could not be achieved at solar graphene modified glassy carbon electrode (sG/GCE), was easily obtained at Ni-sG/GCE. Excellent reproducibility, low detection limits and good recovery values attained for real sample analysis, exhibit the reliability of the modified sensor.

2. Experimental

2.1. Chemicals

DA was purchased from Himedia. UA, AA, graphite powder and potassium permanganate were obtained from Merck. All other reagents were of analytical grade and used without further purification. Phosphate buffer solution (PBS) was prepared by mixing stock solutions of 0.1 M Na_2HPO_4 and NaH_2PO_4 and then adjusting the pH with dilute H_3PO_4 and NaOH. High quality deionised water was used throughout.

2.2. Instrumentation

Transmission electron microscope (TEM) images were obtained with JEOL 2010F high resolution transmission electron microscope (HRTEM) using an accelerating voltage of 200 kV. The Raman spectrum of solar graphene (sG) was recorded with Witec alpha 300 confocal Raman spectrometer, using green (532 nm) laser radiation. Scanning electron microscope (SEM) images were obtained with JEOL JSM- 6390 scanning electron microscope. Identification and characterization of functional groups on the surface of sG and nickel oxide modified sG was done using Bruker Fourier transform infrared (FTIR) spectrometer in the range 500–4000 cm^{-1} . DPV was done using CHI 620 B electrochemical analyzer. CV was performed using CHI 604D electrochemical analyzer in a conventional three-electrode glass cell. A platinum wire and Ag/AgCl were used

as counter and reference electrodes respectively. A glassy carbon electrode (GCE) modified with sG and nickel oxy hydroxide/nickel hydroxide i.e. nickel(III)/nickel(II), denoted as Ni-sG/GCE was the working electrode. All experiments were carried out at room temperature.

2.3. Modification of electrodes

The bare GCE (3 mm diameter) was cleaned by polishing with 0.05 μm alumina slurry on polishing pads before it was used. It was then rinsed ultrasonically with methanol and deionized water respectively, and dried at room temperature. 2 mg of sG was mixed with deionized water and methanol in a particular proportion, without a binder. The above mixture was sonicated for 2 hours, and 5 μl of the sG suspension was cast on the surface of GCE and dried at 50 °C in an air oven to produce sG/GCE. Then 5 μl of 4 mM nickel acetate (NiAc) solution was dropped on the sG/GCE surface and dried again at 50 °C to give NiAc/sG/GCE. The electrode was then conditioned by potential cycling (20 cycles) in a limited range (0.2–0.6 V vs. Ag/AgCl) in 0.1 M NaOH solution, containing 0.1 M KCl as supporting electrolyte, until steady state voltammograms were obtained. The as modified nickel(III)/nickel(II) solar graphene GCE (Ni/sG/GCE) was carefully rinsed with water to remove any loosely bound material, and thus employed as the working electrode in 0.1 M phosphate buffer solution (PBS) of pH 4. Electrochemical response of DA at bare GCE, GCE modified with nickel oxide alone (Ni/GCE) and sG/GCE were also followed for comparison.

3. Results and Discussion

3.1. Characterization of solar graphene and nickel hydroxide modified solar graphene

Graphite oxide (GO) was prepared by a modified Hummer's method [53]. sG synthesized from GO by an easy and eco friendly solar exfoliation method [54] was characterized by employing techniques like Raman, FTIR and TEM. HRTEM images of sG (Fig. S1 A) reveal that most of the GO underwent efficient exfoliation to form well separated ultrathin transparent sheets with sharp edge planes. The Raman spectrum of sG (Fig. S1 B) shows two prominent peaks at $\sim 1345 \text{ cm}^{-1}$ and 1596 cm^{-1} . The G-band arises due to the first order scattering of E_{2g} symmetry which is characteristic of most carbon based materials. On the other hand the intensity of the D-band reveals the degree of disorder arising from the presence of oxygenated functionalities, distributed edge planes or defects in the sample. An I_D/I_G value of 1.28 obtained for sG indicates a decrease in the average size of sp^2 domains and an increase in the number of edge planes and defects in sG after solar exfoliation [34]. A broad 2D band around 2700 cm^{-1} indicates that sG is composed of few layers, probably within five layers [55]. The SEM image of Ni/sG/GCE surface (Fig. 1A) shows well exfoliated graphene sheets with numerous edge planes that aid in the effective resolution of the voltammetric signals of analytes during their simultaneous detection. The corresponding EDAX (Fig. 1B) clearly indicates the presence of nickel on the electrode surface. The FTIR spectrum of Ni/sG/GCE surface is shown in Fig S 2. In addition to the peak at 3400 cm^{-1} (O-H vibration) peaks of NiO are also observed around 877 cm^{-1} . All these techniques reveal that the modified electrode (Ni/sG/GCE) consists of nickel hydroxide particles deposited on few layer graphene sheets, with defects and edge planes that are highly advantageous for its application in bio-sensing [33,56].

3.2. Mechanism of electrode modification

The synergistic catalytic effect of sG, together with that of the nickel oxide particles formed insitu on the electrode surface while

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