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Functionalised carbon nano spheres modified electrode for simultaneous determination of dopamine and uric acid

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ABSTRACT

In this paper we report the interaction of functionalised carbon nano spheres (FCNSs) with dopamine (DA), Uric acid (UA) and L-ascorbic acid (AA). FCNSs were characterised using SEM, AFM, spectroscopic and electrochemical measurements. Functionalised carbon nano spheres paste electrode (FCNSPE) has shown excellent preconcentration property of DA over its surface. UA also has also shown good electrochemical activity over the modified electrode. Parameters were optimised for the enhanced oxidation signal of DA in connection with simultaneous determination of DA and UA. An analytical method was developed for the simultaneous determination of DA and UA using the simple method of fabrication of electrode with detection limits (S/N of 3) of 10 nM and 42 nM for DA and UA respectively. Electrochemical oxidation signals of DA and UA were interference free from the oxidation of AA and other commonly occurring interfering agents. The method was applied for the determination of DA in spiked blood serum sample and for UA in real blood serum samples.

1. Introduction

DA is one of the most important neurotransmitter in our brain. It has significant role in modulating the brain function [1]. In presence of lower concentration of DA in human leads to various neurological disorders, Parkinson's disease and hyperactivity. Higher level of DA leads to the mental disorder due to the abnormal brain function. UA is another important metabolic product in biological system. In human body system UA is the catabolic product of purin. An elevated UA concentration in body system may cause renal failure and gout. It may even cause leukaemia and lymphoma at adverse conditions [2]. Therefore determination of DA and UA in blood, urine and any biological fluids is important to evaluate the metabolic functioning of the body system. Electrochemical method is one of the important techniques for the determination of DA and UA in biological samples, has important advantage over other available techniques, as the electrochemical methods offers direct measurement. Other techniques based on spectroscopy and chromatography have disadvantages like, sample pre-treatment and removal of sample from the sample chamber for the analysis [3]. Electrochemical methods are highly sensitive, selective and offer better understanding of the chemical process in addition to the detection. AA is also one more constituent present in biological system along with DA and UA. The major challenge is to separate the electrochemical peak due to DA, UA and AA, since the electrochemical potential of these three biological molecules are close and it is important to generate the separate electrochemical response from three molecules [4]. Electrochemical methods based on modified electrode have been discussed for the determination of DA [5–38] and these methods are better suited for the determination of biological compounds due to the easy fabrication of the modified electrode, disposability and the possibility of onsite/online determination.

Among different modifications, carbon-based nano materials such as activated carbon, graphene and carbon nanotubes (CNTs) are important materials of modifications, due to their good electrochemical activity and the large active surface area and these modified materials are either used in the form of carbon paste or modified over glassy carbon electrode surface by casting through physical or chemical means [5–27].

Graphene doped with nitrogen has been used for this purpose and it has shown good activity for the determination of DA [39]. In the recent time carbon in the form of nano spheres (CNSs) has been used in various electrochemical applications. CNSs, are the spherical carbon material, are attractive in various functional nano devices due to their excellent physical and chemical properties. In addition to that CNSs have good structural stability, thermal insulation and excellent conductivity [40]. These materials are applied widely in lithium ion batteries [41–44], adsorption [45], catalyst supports [46,47] and so on. Therefore it is likely that carbon nano spheres would be good candidate for electrode modification for electroanalytical application by improving the redox response of analyte. Different nano particles in polymeric matrices also have shown good detection sensitivity of the DA and UA [48–51]. Some of the recent papers have reported the simultaneous methods of

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determination of DA and UA using modified electrode based on different from carbon [52–55].

In this manuscript we have functionalised the carbon nano spheres and the functionalised materials were characterised using spectroscopic and microscopic measurements. The modified electrode, FCNSPE was fabricated using the functionalised carbon nano spheres. The functionalisation has improved the pre-concentration of DA over the modified electrode surface. The electrode was applied for the determination of DA and UA simultaneously. Except some limited studies [35,51], where carbon nano particle was applied for the determination of DA, no such investigation reported about the simultaneous determination of DA and UA in a simple way of modification as presented in this investigation. The concern about the electrode fouling due to the electro-polymerization of these molecules after electrochemical oxidation has also been addressed. Present method is simple, inexpensive and suitable for realization of the determination of DA and UA.

2. Experimental

2.1. Reagents and chemicals

Graphitic CNSs used for functionalisation were of 'VULCAN XC 72 R', Suprapur HCl, HNO_3 & H_2SO_4 were purchased from MERCK. Di-sodium hydrogen phosphate and sodium di-hydrogen phosphate used for the preparation of phosphate buffer solution (PBS) were of GR grade from BDH Chemicals. DA, UA and AA were of spectroscopic grade from Sigma-Aldrich. Deionised water (Resistivity = 18.2 MΩ cm) was used for the preparation of all the aqueous solutions and washing purposes.

2.2. Instrumentation

All the electrochemical measurements were carried out using AUTOLAB 302N potentiostat purchased from Metrohm Autolab B. V., The Netherlands and placed in our institute. Three electrode systems was used for the experiments, where Ag/AgCl/KCl (saturated) electrode was used as reference electrode, glassy carbon rod as counter electrode and the FCNSPE as working electrode. Electrochemical data acquisition and analysis were carried out using GPES 4.9 software. All the experiments were carried out at room temperature (25 °C) and 1 atm pressure. Atomic force microscopy (AFM) measurements were carried out using flex AFM from Nanosurf, Switzerland placed in our institute. The morphology of the functionalised material was examined by using FE-SEM (JEOL Model JSM-7600F, USA placed in IIT, Bombay), operated at 10 kV. The analytical HPLC measurements were performed on a JASCO PU 2080 Plus dual pump HPLC system, Japan, with a JASCO 2075 Plus tunable absorption detector (placed in our institute), using a C18 reversed phase HiQ Sil column (5 μm, 4 × 250 mm). The eluting solvents (1 mL/min) used in HPLC were; H_2O (solvent A) and acetonitrile (solvent B) with 0.1% trifluoroacetic acid.

2.3. Experimental procedure

We have adopted the functionalisation method based on the methods previously reported in the literature [56–57]. The CNSs were washed thoroughly by dilute nitric acid, hydrochloric acid and deionised water to eliminate the possible metal impurities in the carbon powder prior to the functionalisation. 500 mg of the washed CNSs was soaked in 50 mL of an acid mixture (1:1) of 50% HNO_3 and 50% H_2SO_4 for 1 h. Then the whole mixture was refluxed at 90 °C for 6 h under vigorous stirring condition. Subsequently, the solution was centrifuged and the black residue was collected and washed thoroughly with deionised water and kept inside a vacuum furnace for 12 h at 50 °C for drying. The dried FCNSs were characterised using spectroscopic and microscopic techniques. These FCNSs were mixed with CNSs at different proportions. A paste was made with this mixture adding adequate amount of silicon oil (around 20%), the paste was used to make the modified electrode. The modified electrode was fabricated by filling a glass tube with the paste and a Pt wire was used to connect the paste to the

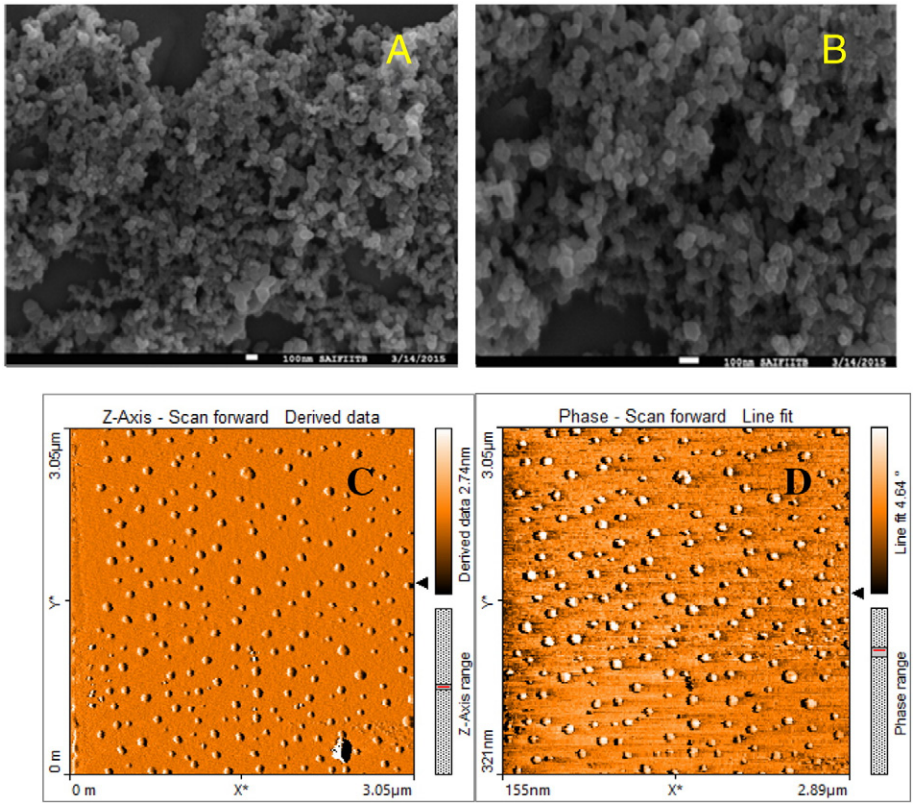

Fig. 1. SEM image of (A) as received graphitic CNS, (B) FCNS, (C) AFM amplitude scan and (D) AFM phase scan of the FCNS.