



# Simultaneous and sensitive determination of ascorbic acid, dopamine, uric acid, and tryptophan with silver nanoparticles-decorated reduced graphene oxide modified electrode



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## ABSTRACT

In this paper, we report the synthesis of silver nanoparticle-decorated reduced graphene oxide composite (AgNPs/rGO) by heating the mixture of graphene oxide and silver nitrate aqueous solution in the presence of sodium hydroxide. This material was characterized by means of X-ray diffraction, UV–vis spectroscopy, and transmission electron microscopy. AgNPs/rGO based electrochemical sensor was fabricated for the simultaneous determination of ascorbic acid, dopamine, uric acid, and tryptophan. Electrochemical studies were carried out by using cyclic voltammetry, linear sweep voltammetry, and chronoamperometry. AgNPs/rGO modified electrode exhibited excellent electrocatalytic activity, stability, sensitivity, and selectivity with well-separated oxidation peaks toward ascorbic acid, dopamine, uric acid, and tryptophan in the simultaneous determination of their quaternary mixture. The analytical performance of this material as a chemical sensor was demonstrated for the determination of ascorbic acid and dopamine in commercial pharmaceutical samples such as vitamin C tablets and dopamine injections, respectively. The applicability of this sensor was also extended in the determination of uric acid in human urine samples.

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## 1. Introduction

The last three decades have witnessed the development of electro-analytical methods to detect important bio-molecules present in living species such as human beings and plants [1]. Thousands of different bio-molecules exist in the human body/plant and it is almost impossible to detect them in one run, because of their different physical–chemical properties. However, if an analytical method is developed, which can detect at least a class of compounds in one run, then it is of great importance in the medical science, food, and pharmaceutical industry [2]. Theoretically, a class of compounds present in the living organism having similar electrochemical properties can be detected in one run by suitable electro-analytical tools [3]. The objective of this study is to develop a non-enzymatic electrochemical method for the simultaneous determination of ascorbic acid, dopamine, uric acid, and tryptophan. Numerous attempts have been made for the determination of these bio-molecules, but the simultaneous determination of four analytes has been paid less attention [4,5].

Ascorbic acid (AA) prevents scurvy and is known to take part in several biological reactions. It has been widely used in foods and drinks as an antioxidant and also for the prevention and treatment of common cold, mental illness, infertility, cancer, and AIDS [6]. Dopamine (DA) is an important neurotransmitter and present in the mammalian central nervous system [7]. Low levels of DA may cause neurological disorders such as schizophrenia and Parkinson's disease [8]. Uric acid (UA) is the end product of purine metabolism and its concentration in the body should be maintained [9]. Its abnormal concentration level leads to several diseases such as hyperuricemia, gout, leukemia, and pneumonia [10]. Tryptophan (Trp) is an essential amino acid required for the biosynthesis of proteins (precursor molecules of hormones, neurotransmitters and other relevant bio-molecules) and finds importance in nitrogen balance and the maintenance of muscle mass and body weight in humans [11]. To correct possible dietary deficiencies, Trp is added to dietary and food products as a food fortifier and to pharmaceutical formulations.

Graphene, a flat monolayer of sp<sup>2</sup>-bonded carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, has attracted tremendous attention due to its high surface area, high chemical stability, and unique electronic and mechanical properties [12]. High electrical conductivity is one of its important properties. Physico-chemical properties of the graphene can be tailored by

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chemical modification of its surface. Organo-functionalization and attachments of metal nanoparticles on the graphene surface significantly tailor its physico-chemical properties and largely extend the application area of graphene. Numerous efforts have been made to decorate the surface of graphene with noble metal nanoparticles and to find their applications in electrochemical sensing, fuel cell, and catalysis [13–18]. In order to develop economical and highly active protocol, significant efforts have been made to develop Ag nanoparticles (AgNPs) decorated graphene and have been used in optics, electronics, catalysis, and electrochemistry [19–28]. Various synthesis protocols have been reported for the preparation of AgNPs supported on graphene oxide (GO) and AgNPs supported on reduced graphene oxide (hereafter represented as AgNPs/rGO) [29–31]. However, most of these reported methods are multi-step and involve hazardous or toxic reducing agents such as sodium borohydride and formaldehyde to reduce GO and  $\text{Ag}^+$ , posing environmental and health risks. There are only a few reports available in literature, where AgNPs modified electrodes have been used for the detection of biological compounds [32–34].

Therefore, in this paper, an environment friendly, rapid, and one-step synthetic route is adopted for the preparation of AgNPs/rGO nanocomposites. AgNPs/rGO modified electrode was fabricated for the simultaneous and sensitive electrochemical determination of AA, DA, UA, and Trp in their quaternary mixture.

## 2. Materials and methods

### 2.1. Materials

All chemicals used in the study were of A.R. grade and used as received without further purification. Graphite powder (99.5%), sulphuric acid ( $\text{H}_2\text{SO}_4$ , 98 wt.%), silver nitrate ( $\text{AgNO}_3$ , 99%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 wt.%), hydrogen chloride (HCl, 35 wt.%), and potassium permanganate ( $\text{KMnO}_4$ , 99%) were purchased from Merck India Pvt. Ltd., whereas dopamine (98%), L-ascorbic acid (99%), uric acid (99%), and tryptophan (98%) were obtained from Spectrochem Pvt. Ltd. The standard phosphate buffer solutions with different pH values were prepared by adding 7.5 M aqueous NaOH solution to an aqueous solution of ortho phosphoric acid [1 L of aqueous solution containing 10.11 mL of  $\text{H}_3\text{PO}_4$  (85 wt.% aqueous solution)] while magnetically stirring until the pH of the aqueous solution reached the desired value (1.0, 3.5, 5.0, 7.0, and 9.0). The electrochemical measurements were performed in the buffer solution (pH 3.5). Deionized water from Millipore Milli-Q system (resistivity 18  $\text{M}\Omega$  cm) was used in the electrochemical studies.

### 2.2. Methods

#### 2.2.1. Sample preparation and characterization

A modified Hummers method was used to synthesize the oxidized graphite powder [35]. In a typical synthesis, 2.5 g of natural graphite was added to the pre-cooled (below 5 °C), concentrated  $\text{H}_2\text{SO}_4$  (50 mL). 2.5 g of  $\text{NaNO}_3$  was added slowly to the above reaction mixture, followed by the addition of 7.5 g of  $\text{KMnO}_4$  under vigorous stirring. The mixture was stirred continuously for 1 h at 35 °C to oxidize the graphite completely. 100 mL of deionized water was added into the reaction mixture and the temperature was raised to 95 °C, and the suspension was maintained at 95 °C for 15 min. The suspension was then further diluted with 300 mL of deionized water and treated with 20 mL of aqueous  $\text{H}_2\text{O}_2$  solution (30%) to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulphate. Upon treatment with  $\text{H}_2\text{O}_2$ , the suspension turned bright yellow. The resultant suspension was filtered, washed with 5% HCl aqueous solution and deionized water, and dried to obtain graphite oxide.

For the preparation of AgNPs/rGO, 50 mg of graphite oxide was dispersed in 100 mL of deionized water to obtain a yellow-brown suspension, which was ultrasonicated for 1 h using an ultrasonication bath to form graphene oxide (GO). The temperature of reaction mixture was raised to 80 °C. 44 mg (0.26 mmol) of  $\text{AgNO}_3$  was slowly added under constant stirring. 11 mL of 8 M aqueous NaOH solution was added drop-wise into the reaction mixture and stirring was further continued for 15 min at 80 °C resulting into AgNPs/rGO precipitate. The resulting precipitate was washed with water, centrifuged, and dried in air. For the comparative study, reduced GO (rGO) was also synthesized by following a reported procedure by the reduction of graphite oxide [36].

Details of equipments used for material characterization are provided in the supporting information.

#### 2.2.2. Electrode fabrication

Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometric studies were performed using Potentiostat-Galvanostat BASi EPSILON, USA. A three electrode electrochemical cell was employed with Ag/AgCl as the reference electrode (3 M KCl), AgNPs/rGO mounted glassy carbon (3 mm diameter) as the working electrode, and Pt foil as the counter electrode. Before modification, the polished electrode was ultrasonicated in ethanol and deionized water for 5 min, respectively. 10  $\mu\text{L}$  aliquot of AgNPs/rGO suspension (a homogenous sonicated solution of 2 mg of AgNPs/rGO and a mixture of 10  $\mu\text{L}$  of Nafion and 1 mL of distilled water) was placed onto the electrode surface, dried in air leaving the material mounted onto the GC surface.

#### 2.2.3. Real sample preparation

Dopamine injections (DOMIN, NEON Labs; DOPAA, AAA Pharma; and DOPRESS, UNITED Biotech) were obtained from Kailash Medical Store, Ropar. 10 mL of 0.1 M stock solution of dopamine hydrochloride injection was prepared using deionized water. Required amount of this solution was added to the electrochemical cell consisting 10 mL of buffer solution (pH 3.5).

Vitamin C tablets (Glaxo Smith Kline Pharmaceuticals Ltd., Nicholas Paramil, and CECON ABBOTT), obtained from Kailash Medical Store, Ropar. Vitamin C tablets (labeled 500 mg vitamin C per tablet) were completely grounded and homogenized before preparing 10 mL of 0.1 M stock solution. Required amount of this solution was added to the electrochemical cell consisting 10 mL of buffer solution (pH 3.5).

500  $\mu\text{L}$  of urine samples were diluted to 10 mL using deionized water. Required amount of diluted urine samples were added to the electrochemical cell consisting 10 mL of buffer solution (pH 3.5) for the determination of UA.

## 3. Results and discussion

### 3.1. Synthesis and physico-chemical characterization of AgNPs/rGO

AgNPs/rGO was prepared by heating a mixture of graphene oxide and silver nitrate aqueous solution. The idea behind this synthetic protocol is that GO will serve as a reducing agent for the formation of AgNPs. It is known in the literature that aliphatic alcohols can be used as a reducing agent for the formation of metal nanoparticle [37,38]. GO layer is covered with hydroxyl group, enables it to act as a mild reducing agent. Such a mild reducing capability of GO is finely suited for the reduction of  $\text{Ag}^+$  in alkaline medium [39]. It is well documented that GO can be converted into rGO under alkaline medium [36]. Under our synthesis condition, NaOH not only facilitates the reduction of  $\text{Ag}^+$  by GO to form AgNPs, but also induces reduction of GO to rGO to form AgNPs/rGO. GO and rGO can be visually differentiated based on their color. Pale-yellow

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