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Electrochemically reduced graphene oxide/Poly-Glycine composite modified electrode for sensitive determination of L-dopa

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ABSTRACT

A facile preparation strategy based on electrochemical technique for the fabrication of glycine (Poly-Gly) and electrochemically reduced graphene oxide (ERGO) composite modified electrode was developed. The morphology of the developed composite (ERGO/Poly-Gly) was investigated using field emission scanning electron microscope (FE-SEM). The composite modified glassy carbon electrode (GCE) was characterized using fourier transform-infrared (FT-IR) spectroscopy, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The electrochemical characterization results revealed that ERGO/Poly-Gly modified GCE has excellent electrocatalytic activity. Further, it was employed for sensing of L-dopa in pH 5.5. Differential pulse voltammetry (DPV) was used for the quantification of L-dopa as well as for the simultaneous resolution of L-dopa and uric acid (UA). The LOD ($S/N = 3$) was found to be 0.15 μM at the proposed composite modified electrode. Determination of L-dopa could also be achieved in the presence of potentially interfering substances. The sensor showed high sensitivity and selectivity with appreciable reliability and precision. The proposed sensor was also successfully applied for real sample analysis.

1. Introduction

L-dopa (levodopa, 3,4-dihydroxy-phenyl-L-alanine) (Scheme 1(a)) is a naturally occurring aromatic amino acid and is a biological precursor of various neurotransmitters, the important ones being dopamine (DA), norepinephrine and epinephrine. It is widely prescribed as a primary drug in the treatment of Parkinson's disease, which is caused by a depletion of DA in the brain [1]. L-dopa has also been used to decrease motor-related movements such as rigidity, tremor, slowness of movement and postural instability. After administration, L-dopa is converted to DA through dopadecarboxylase enzymatic catalytic reaction and is stored in dopaminergic neurons. However, L-dopa has been associated with various side effects such as gastritis, paranoia and dyskinesia when it is used for a long term [2,3]. Besides, L-dopa auto-oxidation causes toxic metabolites such as free radicals, quinones and semi-quinones [4]. Therefore, accurate determination of L-dopa in the analysis of pharmaceutical formulations and biological fluids is important.

Uric acid (2, 6, 8,-trihydroxypurine, UA) (Scheme 1 (b)) is a heterocyclic organic compound and is the primary end product of purine metabolism in the human body. UA exists majorly in the form of urate, a salt of UA. It plays a significant role in the human metabolism in biological fluids as well as in the renal and central nervous systems. Physiological UA levels in human serum are from 0.13–0.46 mM [5]. It has been observed that abnormal levels of UA in the body is the symptom of several diseases like Lesch–Nyan syndrome, gout, obesity, cardiovascular and kidney damage [6–8]. In addition, abnormal concentrations of UA also cause disorders of purine biosynthesis and purine catabolism. Moreover, low concentration of UA is associated with Parkinson, Alzheimer or multiple sclerosis [9].

Graphene is a two-dimensional sheet of carbon atoms in a hexagonal configuration with atoms bonded by sp^2 bonds. The unusual properties of graphene comprise of extremely large surface area, room-temperature Hall effect, a tunable band gap, excellent mechanical strength (approximately 200 times greater than steel), high elasticity and thermal conductivity, which is due to sp^2 bonds and electron configuration [10]. Graphene oxide (GO) is an electrically insulating material due to its disrupted sp^2 bonding networks. The exact process parameters used when reducing GO into reduced GO (RGO) play a major role in the quality of the material, affecting how close a structure to perfect graphene is achieved. The reduction of GO can be achieved a number of ways such as thermal, chemical and electrochemical methods. The methods which are capable of producing the highest quality graphene tend to be more complex. Nowadays, chemical vapour deposition, mechanical cleavage, chemical reduction, thermal reduction and electrochemical reduction of GO are generally used methods for the preparation of graphene sheets. On the other hand, thermally reducing GO at above 1000 °C temperature produces a high surface area RGO

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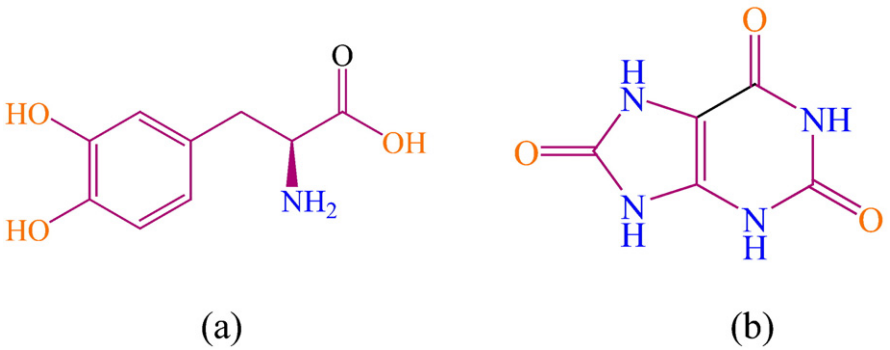

Scheme 1. Chemical structures of (a) L-dopa (b) UA.

which is similar to a pristine graphene. However, a major disadvantage of this process is that the structure of the graphene sheets is damaged by the heating course resulting in a significant mass loss and potentially impacting the mechanical strength of the RGO. Chemical reduction of GO also has several disadvantages. In particular, the method involves use of hydrazine monohydrate which is toxic and introduces heteroatomic impurities as well. This affects the removal of oxygen functionality and also nitrogen remains bounded to the surface of GO in the form of hydrazones, amines, aziridines or other comparable structures [11].

Among these methods, electrochemical reduction is most commonly used because it is fast, green, reagent-free and will not result in contamination of the reduced material. Electrochemical reduction of GO (ERGO) is likely to be the preferred commercial method in the future since it produces a material almost identical in structure to pristine graphene. A simple approach for the large-scale production of high-quality graphene sheets via electrochemical reduction of exfoliated GO material was reported by Guo et al. [12]. ERGO for the electrochemical sensing applications was first reported by Liu et al. [13]. The conductivity of ERGO is higher than chemically obtained RGO (CRGO). This might be owing to residual defects in CRGO material, which can be minimized in the reaction of ERGO [14]. RGO is usually an incomplete reduced form of GO and is in the intermediate state between GO and graphene. This reduced GO has few oxygen-containing functional groups and defects which can hold up chemically active sites for usage in catalytic reactions and interacting with layers of polymers due to the incomplete reduction.

Various methods have been developed and applied over the last few decades for L-dopa determination. Among them, chemiluminescence [15], spectrophotometry [16], high-performance liquid chromatography (HPLC) [17], capillary electrophoresis [18], and NMR detection [19] have been extensively employed for the determination of L-dopa in pharmaceutical formulations and biological fluids. However, these methods are still suffering from some disadvantages such as high cost, complicated equipment, low sensitivity, requirements of organic solvents, over time analysis and requirement of sample pretreatment. Compared to these methods, electrochemical techniques attract enormous interest due to less time consuming, simple and rapid procedures, precision, inexpensive and with good sensitivity for the determination of clinically and biologically important compounds.

Chemically modified electrodes (CMEs) have been receiving enormous attention since 1979 due to their sensitivity and selectivity of the analyte at the surface of the electrodes [20]. At conventional electrodes (e.g.: Au, Pt and glassy carbon electrode (GCE)), the redox path of the electrolyte takes place at over potentials due to sluggish electron transfer rate. Unfortunately, most bare electrodes show slow electron transfer rate towards L-dopa determination [20]. Moreover, the oxidation product of the L-dopa also adsorbs easily to the surface of electrodes. Hence, the electrochemical determination of the L-dopa in presence of UA is also very difficult at these electrodes. This leads to poor selectivity and reproducibility at these conventional electrodes. To overcome this problem, modification with catalytic materials onto the surface of electrode is one of the best concepts in the area of electroanalytical methods. The surface of the electrode modification leads to diminishing of over potential and also picks up the rate of electron transfer for the systems having redox reactions. Recently, different types of materials including nanostructured conducting polymer/copper oxide [21], ZnO nanorods [22], GO/ZnO nanocomposite [23], poly(allylamine hydrochloride) [24], gold and palladium nanoparticles [25] have been used for the quantification of L-dopa. Very recently, use of polymers as electrode surface-modifiable material has attracted more attention in electroanalysis. There are different methodologies for the preparation of polymers. Among the various methodologies for the preparation of polymer for the modification of electrode surfaces,

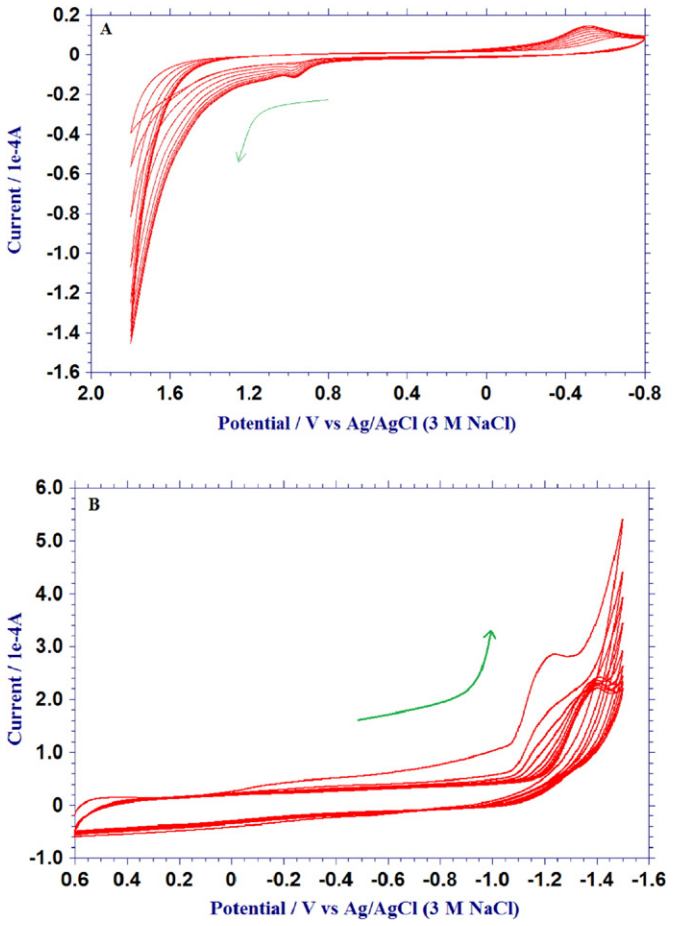

Fig. 1. (A). Cyclic voltammograms obtained for the electrochemical polymerization of glycine onto the surface of GCE. (B). Cyclic voltammograms obtained for electrochemical reduction of GO onto the surface of GO/Poly-Gly/GCE.