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Simultaneous determination of ascorbic acid, dopamine and uric acid by a novel electrochemical sensor based on N_2/Ar RF plasma assisted graphene nanosheets/graphene nanoribbons

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ABSTRACT

A novel nitrogen/argon (N_2/Ar) radio frequency (RF) plasma functionalized graphene nanosheet/graphene nanoribbon (GS/GNR) hybrid material (N_2/Ar/GS/GNR) was developed for simultaneous determination of ascorbic acid (AA), dopamine (DA) and uric acid (UA). Various nitrogen mites introduced into GS/GNR hybrid structure was evidenced by a detailed microscopic, spectroscopic and surface area analysis. Owing to the unique structure and properties originating from the enhanced surface area, nitrogen functional groups and defects introduced on both the basal and edges, N_2/Ar/GS/GNR/GCE showed high electrocatalytic activity for the electrochemical oxidations of AA, DA, and UA with the respective lowest detection limits of 5.3, 2.5 and 5.7 nM and peak-to-peak separation potential (ΔE_p) (vs Ag/AgCl) in DPV of 220, 152 and 372 mV for AA/DA, DA/UA and AA/UA respectively. Moreover, the selectivity, stability, repeatability and excellent performance in real time application of the fabricated N_2/Ar/GS/GNR/GCE electrode suggests that it can be considered as a potential electrode material for simultaneous detection of AA, DA, and UA.

1. Introduction

Ascorbic acid (AA), playing an important role in cancer prevention and immunity development, affects at low concentration the formation of new collagen which causes breakdown of various tissues and thus affects health and repair of our body. Chronic deficiency of ascorbic acid leads to scurvy (Arrigoni and De Tullio, 2002). Dopamine (DA), an important neurotransmitter, acting as a messenger between brain cells, is involved in the functions of central nervous, endocrine, cognition and emotion systems and is also playing a major role in functions of kidneys, blood vessels, pancreas, digestive system and immune system (Wightman et al., 1988). Dysfunction of DA causes various diseases such as Parkinson's disease, attention deficit hyperactivity disorder, restless leg syndrome *etc*. Uric acid (UA), the end product of metabolic breakdown of purine nucleotides, can lead to gout, renal failure, leukemia and lymphoma when its concentration in blood is increased (Dutt and Mottola, 1974). These biomolecules not only play an important role in the physiological and metabolism functions of human, but also for diagnosing diseases (Hadi and Rouhollahi, 2012).

In the last few decades, various analytical methods including chromatography, spectroscopy and electrochemistry (Inoue et al., 2003; Guan et al., 2004; Hong and Huang, 2003) have been used for determination of these biomolecules simultaneously. Among them, electrochemical techniques have been considered as a simple, fast response, sensitive and stable approach (Gumpu et al., 2015; Kimmel et al., 2011; Ronkainen et al., 2010). However, due to the drawbacks such as inability to detect the required low level concentrations of DA (0.01–1 μM), fouling of electrodes and overlapping of their oxidation potential, individual as well as simultaneous electrochemical detection in commercial electrode is very difficult (Kumar et al., 2005; Zare et al., 2005).

To address these issues, various chemically modified electrode materials based on polymers, metal complexes, metal oxide and carbon nanomaterials have been proposed (Chitravathi et al., 2011; Cui et al., 2012; Ensafi et al., 2010; Kalimuthu and John, 2009; Zhang et al., 2012; Zheng et al., 2013). Recently, hybrid graphene (Seo et al., 2012) synthesized by incorporating carbon spacers such as carbon nanotube (CNT) (Tung et al., 2009), graphene nanoribbon (GNR) (J Lavanya and

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Gomathi, 2015) or any carbon based nanomaterial, with graphene oxide sheets (GOS) (Li et al., 2017; Kong, 2013) are used to overcome the limitations such as restacking, inert surface, high charging current, and enhance the surface area and electron mobility of hybrid material which provides intense application in the field of dye sensitized solar cells, active material encapsulation and lithium-ion battery energy storage (Chen et al., 2013; Mani et al., 2013; Tung et al., 2009) and biosensors (Dong et al., 2012)

The performance of hybridized GS can be further improved by functionalization with heteroatoms such as nitrogen. Nitrogen alters the electronic properties and surface chemistry of carbon materials, which in turn may significantly increase the electrocatalytic activity and finds application in supercapacitor and biosensor applications (Sheng et al., 2011; Evtugyn et al., 2014). For the past few years, nitrogen functionalized graphene (Sheng et al., 2012), mesoporous nitrogen rich carbonaceous material (Joshi et al., 2016), nitrogen doped carbon nanofibres (Sun et al., 2015) have been reported as suitable materials for simultaneous electrochemical detection of AA, DA and UA. However, functionalization of these materials *via* chemical method has several drawbacks such as requirement of multiple-steps, longer time, poor control over the chemical homogeneity and reproducibility. Most importantly, sometimes it may lead to destruction of material morphology. Plasma functionalization has received enormous attention because of its controlled functionalization, simplicity, selectivity, fast and energy-saving alternative to the existing functionalization methods (Bon et al., 2009).

In this study, hybrid graphene material of graphene nanosheets/graphene nanoribbons (GS/GNR) with high electrical conductivity and large surface area was functionalized using N_2/Ar RF plasma to improve the performance.

This method provides a reagent less approach to fabricate N_2/Ar/GS/GNR hybrid material as electrode materials for simultaneous detection of AA, DA and UA. (Scheme 1). Here various forms of nitrogen moieties incorporated on the hybrid structure, plays a role in enhancement of the electrocatalytic property, whereas inert gas (Ar) reduces amorphous carbon during N_2 functionalization without significantly affecting the structural stability of the GS/GNR.

2. Materials and methods

Graphite flakes (GF) with particle size < 20 μm, carbon nanotube; multi-walled (MWCNT), carbon > 95% 6–9 nm O.D × 5 μm L, DA, UAwere purchased from sigma Aldrich. 98% sulphuric acid (H_2SO_4), 88% ACS ortho phosphoric acid (H_3PO_4), potassium permanganate ($KMnO_4$), 30% hydrogen peroxide (H_2O_2), 35% hydrochloric acid (HCl), 98% hydrazine hydrate $(NH_2)_2{\cdot}H_2O$, 55% hydroiodic acid (HI), ferricyanide, potassium chloride, AA and phosphate buffer solution (PBS) were purchased from Merck India. N_2 and Ar gases (99.99% pure) used in the plasma functionalization process were purchased from Tapaswi enterprises, Kolkata, India. All the chemicals were used as purchased without any further purification. All solutions were prepared with ultrapure water (> 18 MΩ cm) obtained from a Millipore Milli-Q water purification system.

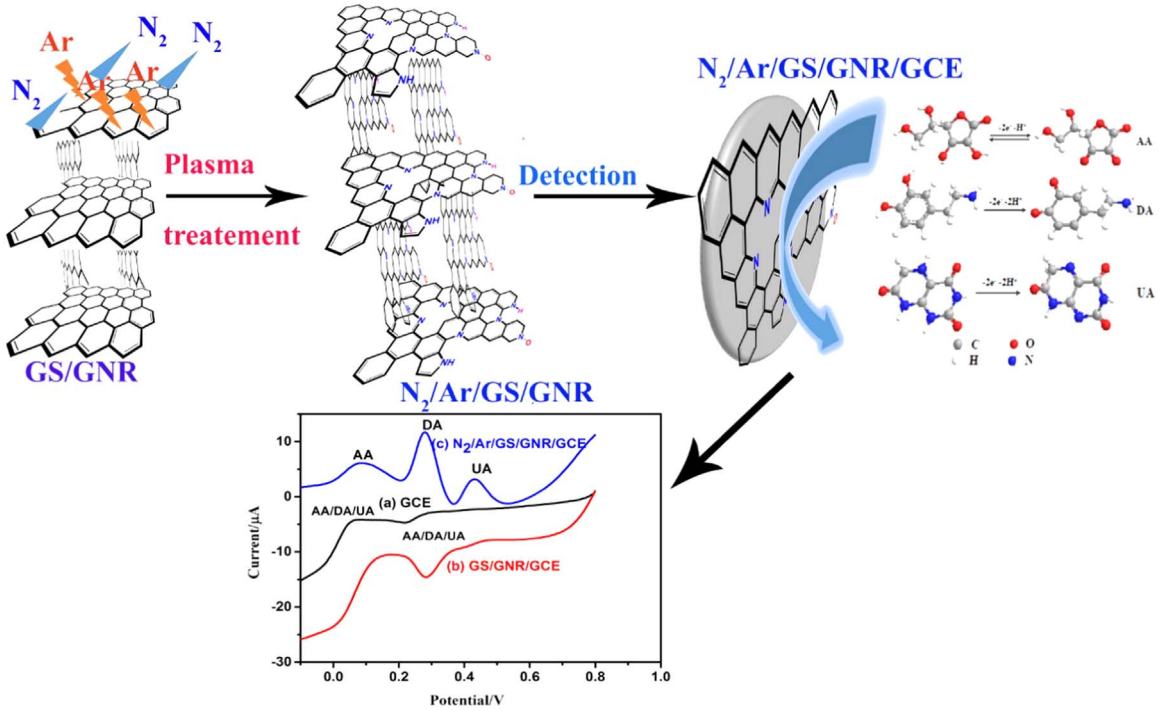
2.1. Synthesis and N_2/Ar plasma functionalization of GS/GNR

2.1.1. Synthesis of GS/GNR

Hybrid material of GS/GNR was synthesized by the integration of two dimensional graphene oxide nanosheets and quasi-one dimensional graphene oxide nanoribbon *via* two step simultaneous chemical reduction as described elsewhere (Lavanya and Gomathi, 2015).

2.1.2. N_2/Ar plasma functionalization of GS/GNR

GS/GNR hybrid was functionalized by using a capacitively coupled plasma reactor [MPECVD-1A] operated at 13.56 MHz, procured from Milman Thin Film Systems, Pune, India. Plasma reactor consists of a vacuum chamber consisting of two parallel plate electrodes namely powered top electrode and grounded bottom electrode (substrate holder). After the system was evacuated to a base pressure of 0.1 Pa, N_2 and Ar gases were introduced through a mass flow controller at a desired flow rate of 10 sccm each. Once the desired process pressure of 50 mTorr was achieved, plasma was generated between the two electrodes by supplying 100 W power for a preset time of 10 min. Various active species generated in plasma interact with hybrid graphene and incorporates various oxygen and nitrogen containing groups.



Scheme 1. Schematic representation of the preparation of N_2/Ar/GS/GNR/GCE biosensor for the simultaneous detection of AA, DA, and UA.