Sensors and Actuators B 256 (2018) 488–497

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Research Paper

# Physiological level and selective electrochemical sensing of dopamine by a solution processable graphene and its enhanced sensing property in general

Aswathi Ramachandran [a], Sriniwas Panda [b], Sandhya Karunakaran Yesodha [a,*]

[a] Department of Chemistry, Indian Institute of Space Science and Technology, Thiruvananthapuram, 695 547, India
[b] Vikram Sarabhai Space Centre, Thiruvananthapuram, 695 022, India

ARTICLE INFO

*Article history:*
Received 16 July 2017
Received in revised form 10 October 2017
Accepted 16 October 2017
Available online 18 October 2017

*Keywords:*
Electrochemical sensing
Selective
Pulverized graphite
Dopamine
Ascorbic acid
Solution processable

ABSTRACT

Here in, for the first time, mechanically pulverized graphite (pGr) has been used as an electrode material for the electrochemical (EC) sensing of analytes such as dopamine (DA) and ascorbic acid (AA). The pGr modified electrode exhibits a wide linear response range over the physiological concentration range of DA and AA, and the lowest limiting value of detection (LOD) so far reported for DA and AA of 1 nM, subjected to S/N = 3. The PGr demonstrates selectivity towards DA in the presence of AA and is able to simultaneously detect DA, AA and uric acid (UA). The enhanced and selective sensing of pGr towards DA is assigned to its intact aromatic basal plane structure which promotes the preferential adsorption of DA due to the similarities in their structures. The dispersibility of pGr in water and the formation of Gr nanosheets are explained by the hydrophilic edges. The sensing performance of pGr towards DA and AA is found to be superior to that of reduced graphene oxide (rGO) and graphene oxide (GO). Our results demonstrate the feasibility and the merits of pGr in the EC sensing applications and give insight to its structure.



## 1. Introduction

Graphene (Gr), with its superior mechanical, electronic, electrochemical (EC)/electro-catalytic properties and high surface area (SA) fascinates the scientific communities as a potential candidate for many applications, of which EC sensing application is no exception [1]. However, in order to use Gr for EC applications effectively, it should have (i) processability (ii) better conductivity, i.e., low oxygen content on the surface, i.e., lesser collateral damage to the honeycomb structure in the sheets and iii) methods to produce solution procesable Gr nanosheets in multi-gram scale. Chemical exfoliation method fails to produce Gr with low collateral damage whereas mechanical (Scotch-tape) exfoliation fails to produce Gr in large scale, due to the tedious procedure. Moreover, in both the cases the Gr obtained are not solution-processable.

Mechanical exfoliation and epitaxial growth even though can produce single or bilayer Gr sheets, the elaborate procedures make them unsuitable for mass production. Consequently, other alternatives for producing processable Gr should be exploited. Solid state mechanical ball-milling of graphite yields pulverized graphite (pGr), which is composed of graphite particles of controlled-sizes and a homogeneous structure [2–4] The utilization of pGr had been limited to composite reinforcement, and recently has been extended to Li-ion batteries [5], double layer capacitors [6,7], hydrogen storage [8,9], Li-ion capacitors [10] etc. However, so far no studies have explored the possibility of utilization of pGr as EC sensing electrodes.

Here in this work, the EC sensing property of pGr was studied using dopamine (DA) and ascorbic acid (AA) as analytes. DA, a monoamine neurotransmitter is crucial for the function of brain, metabolic system of human body [11], cardiovascular, central nervous, renal, and hormonal systems [12] and the variation in its concentration can lead to neurological disorders such as Schizophrenia, Huntington's disease, and Parkinson's disease [13]. Thus, the sensing of DA is important, however is rather difficult due to (i) its lower physiological concentration levels (~25–50 nM) and (ii) interferences from the structurally similar AA and uric acid (UA) which are present in fairly higher concentrations (in mM), in biological tissues. Due to the structural similarities of DA, UA and AA, most of the conventional electrodes such as Au, Pt, and glassy carbon electrode (GCE) lack selectivity to them [14,15]. Therefore,

* Corresponding author.
*E-mail addresses:* sandhya@iist.ac.in, kysandh14@gmail.com (S. Karunakaran Yesodha).

https://doi.org/10.1016/j.snb.2017.10.094
0925-4005/

various carbon materials, such as carbon nanotubes (CNT), boron-doped diamond, carbon nanofibers, rGO and graphite [16] have been employed to elaborate the surface of the working electrodes, and were not successful enough.

The EC sensing studies revealed the physiological level sensing property of pGr towards DA and AA and gives insight in to the structure and the water dispersibility of pGr. Further, the pGr modified electrode (pGr/GCE) exhibited selectivity towards DA in the presence of AA, simultaneous sensing of DA, AA and UA, and the lowest limit of detection (LOD) for AA (in the absence of DA) and DA (in the absence and presence of AA) subjected to S/N = 3. Comparison of the values with that of the control-rGO (SA 416 $m^2/g$), graphene oxide (GO) and other reported Gr based DA sensors ascertain the merit of pGr as an EC sensing electrode towards DA and AA. Our results give indication about the structure, the reason behind the excellent and selective sensing properties and the water dispersibility of pGr.

## 2. Materials and methods

### 2.1. Raw materials

Graphite (21 μm particle size), DA and ACh were purchased from Sigma Aldrich India Co. Ltd., GO from Anderlab Technologies Pvt. Ltd., rGO was prepared by chemical reduction using hydrazine hydrate. N,N dimethyl formamide (DMF), hexane, Tetrahydrofuran (THF), AA and UA from Merck, India Ltd., and N-methyl pyrrolidone (NMP) and Isopropanol (IPA) from Spectrochem Pvt. Ltd. Distilled water was used in all the procedure unless specified otherwise.

### 2.2. Characterization

Universal Attenuated Total Reflection (UATR) mode of Fourier Transform Infrared (FT-IR) spectroscopy was used for recording IR spectra using Perkin Elmer spectrum100 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) was performed in a Q50 TA instrument USA and Differential Scanning Calorimetry (DSC) in a Q20 TA instrument USA. Raman spectroscopy measurements were carried out on a Renishaw inVia Raman microscope with an excitation laser wavelength of 532 nm. Agilent 5500 Scanning Probe Microscope Atomic force microscopy (AFM) with 9 μ scanner was used in tapping mode for AFM imaging, Scanning electron microscopy (SEM) images were taken on a Zeiss EVO 18 Scanning electron microscope with an acceleration voltage of 15 kV and High resolution transmission electron microscopy (HRTEM) analyses were performed using FEI, TECNAI S twin microscope with the acceleration voltage of 300 kV. Brunauer-Emmett-Teller (BET) SA analyses were done using Tristar II micromeritics SA analyzer.

### 2.3. Pulverization, dispersibility and surface area studies

Graphite (25 g) and zirconia balls (100 Nos.) were taken in a container and ball milled for hours. The SA and dispersibility of the pulverized samples were tested for every 150 h of milling. The dispersibility of pGr was studied in water, DMF, THF, Hexane, IPA and other solvents. The pGr (1 mg) was taken in 1 mL of solvent and dispersed by probe ultrasonication for 30 min. The stability of the dispersion was noted by observing for any settlement for one week. Degasification of the samples was done at 120 °C overnight, prior to nitrogen ($N_2$) adsorption isotherm. The $N_2$ adsorption isotherms were carried out at 77 K using liquid $N_2$ as a coolant taken in the Dewar flask.

### 2.4. Preparation of electrodes for sensing and electrochemical methods

Prior to modification of glassy carbon electrode (GCE) with the samples, they were mechanically polished with a wetted micro-cloth containing alumina powder, and then carefully cleaned in distilled water by ultra-sonication (2 min). After each analysis, GCEs were cleaned by ultrasonicating in DMF and then distilled water. The samples (rGO or pGr) dispersed in DMF were drop casted over the pre-treated GCE carefully and then allowed to dry for 24 h at room temperature (RT). The EC measurements were carried out with potentiostat/galvanostat PG 302N, AUT 83909 (Metrohm, Autolab, Netherlands) with three electrode system using drop casted GCE (3 mm diameter) as the working electrode, platinum wire as the counter electrode and Ag(s)/AgCl(s)/$Cl^{-1}$ (aq.) (saturated KCl) as the reference electrode. The EC behaviors of DA, AA and AA (in 0.1 M Phosphate buffer solution, PBS) were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) at RT. For DPV studies, an optimized scan rate of 50 mV $s^{-1}$ and pulse amplitude of 25 mV were opted. Each GCE was made by dropcasting 20 μL of a 0.5 mg $ml^{-1}$ freshly ultrasonicated dispersion in DMF, to ensure that roughly the same amount of material is deposited onto the electrode surface. Electrochemical Impedance Spectroscopy (EIS) studies were carried out between 100 mHz and 100 kHz at the open circuit voltage.

## 3. Results and discussions

### 3.1. Characterization of pGr

The digital images of graphite powder and pGr are given in Fig. S1A & B (see the supplementary information file), respectively. Unlike graphite, pGr had no metallic lustre, and was a black powder. The pGr samples of pulverization time ≥300 h were dispersible in water and it is evident from Fig. S1C that the dispersibility improved with the pulverization time. Further, the pGr was found to be dispersible in organic solvents such as THF, DMF and NMP and the dispersibility was better in NMP and DMF (Fig. S1D). The specific BET SA values of pGr at different intervals (Table S1) show that the SA of pGr increased with pulverization time and reached an optimum value of ~500 $m^2/g$ at ~1000 h of ball milling. The SA of the control-rGO was 416 $m^2/g$. Dispersibility and SA are two of the important factors which influence the sensing performance of an electrode material. Since the pGr at 1000 h had comparatively higher SA, the samples with lower and higher SA than that of at 1000 h i.e, those at 450, 750, 1000 and 1200 h of pulverization times were tested for their sensing performance. The result (Fig. S1E) clearly shows that the sample with the highest SA (i.e. 1000 h) exhibits the highest current response. Therefore, the pGr at 1000 h was chosen for further sensing studies.

The FTIR spectra of the pGr, rGO (control) and graphite are given in Fig. S2A. The peak at 3500 $cm^{-1}$ in graphite is assigned to the moisture content, whereas in pGr and rGO, it is assigned to the —OH group of the edge functionalities (i.e. C—OH and —COOH) because of the presence of other corresponding peaks. The peak at ~1600 $cm^{-1}$ is assigned to C=C vibration. The spectrum of rGO has a peak at 1065 $cm^{-1}$ and is assigned to the —C—O stretching of the epoxide linkages in the basal plane, whereas the peak is absent in pGr, indicating that the extent of oxidation of the basal plane is less or the nature of oxidation of pGr is different from that of the rGO. The HRTEM images of the pGr dispersion reveal thin and transparent Gr sheets (Fig. 1A and C). The transparent Gr sheet in Fig. 1C has single layer regions as suggested by the single crystalline pattern in the SAED (Fig. 1D). The images show that the Gr sheets have certain roughness feature to it, which is assigned to the partial removal of