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Preparation of graphene nanoflakes and its application for detection of hydrazine

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ABSTRACT

This work reports the synthesis of graphene nanoflakes (GNF) and its electron transfer characteristics towards hydrazine electro-oxidation. GNF is prepared by a simple chemical route using cationic surfactant mediated exfoliation of graphite. The flakes are formed as a stable colloidal suspension in N,N-dimethyl formamide. Surface morphology and corresponding number of layers are measured using high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and laser Raman spectroscopy. In addition, electrochemical techniques like cyclic voltammetry, amperometry and electrochemical impedance spectroscopy (EIS) are used to quantify electron transfer kinetics and electrochemical properties of GNF. These results inveterate that edge plane sites in GNF promote electron transfer characteristics in graphene nanostructures. GNF modified glassy carbon electrode (GCE) shows hydrazine oxidation at lower overpotential with higher selectivity, sensitivity and stability. Thus, a novel hydrazine sensor is presented using GNF modified GCE. The regression coefficient (R^2) value is found to be 0.99 with a response time less than 3 s. The above observations revealed that these results are the finest reports to scrutinize the electrochemical properties of GNF produced using liquid phase exfoliation with surfactant. Further, it serves as an important benchmark in the development of inexpensive graphene based electrodes for electrochemical hydrazine sensor.

1. Introduction

Graphene is an atomically thin, two-dimensional (2D) carbon material with a fascinating properties like high values of Young's modulus, fracture strength, thermal conductivity, mobility of charge carriers, high specific surface area and mesmerizing transport phenomena such as quantum Hall effect [1–4]. Because of these properties, graphene and graphene derivatives are used in plethora of applications such as nanoelectronics, energy storage and sensors [5–10].

The primary method used for the synthesis of graphene is the micromechanical cleavage of graphite [11], where it lacks scalability and the need is smaller size graphene sheets [12]. The other reported methods for the preparation of GNF includes, chemical vapour deposition [13], epitaxial graphene growth on the substrate surface [14] and solution based chemical reduction of graphene oxide into graphene [15]. Graphene obtained by the aforementioned methods showed limitation in uniformity [16]. However, low productivity, non-viability for commercialization, time consuming nature and use of high temperature makes the above methods unsuitable for large-scale production of graphene [17]. Most of the reported chemical methods use harsh oxidizers, such as sulphuric acid, potassium permanganate or carboxylic acid, for subsequent exfoliation of graphite [18]. In addition to this, the subsequent reduction of graphene oxide sheets to graphene typically requires a strong chemical reductant such as hydrazine or sodium borohydride with high temperature requirement for heating [19]. Since graphene is useful for practical applications, it is important to produce it in large areas and high quality (free from impurities). In this work, a novel and simple chemical route is reported to produce high quality GNF using cetyltrimethylammonium bromide (CTAB) surfactant based method. This approach is having several advantages such as simple, low-cost, finite mass production capability and GNF are obtained by a single step, without using any strong oxidizers.

In this work, the GNF synthesized by novel chemical route is exploited as a powerful sensor platform for hydrazine detection. Since, hydrazine is a neurotoxin, carcinogenic, mutagenic and hepatotoxic substance that affects liver and brain glutathione [20]. It is widely used in rocket fuels, weapons of mass destruction, fuel cells and missile systems [21,22]. Further, in industrial viewpoint it is used as a catalyst, emulsifier, corrosion inhibitor, reducing

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agent, oxygen scavenger and antioxidant [23]. Hydrazine and its derivatives are accounted for having adverse health effects, but it is having potential applications [24–26]. Therefore, sensitive determination of hydrazine is practically important for environmental and biological aspects [27]. Being electrochemically active compound, electroanalytical techniques can be employed for the direct and effective determination of hydrazine using conventional electrodes. Electrochemical oxidation of hydrazine is kinetically sluggish and relatively requires high overpotential. A number of approaches have been reported to reduce high overpotential using noble metal electrodes and chemically modified electrodes [28–36]. To reduce high overpotential followed to enhance the oxidation current for hydrazine oxidation, here the GNF modified GC electrode is reported for electrochemical oxidation of hydrazine. It exhibits outstanding performance for hydrazine determination at low overpotential with a high sensitivity, selectivity and finite limit of detection.

2. Experimental procedure

2.1. Materials

The following chemicals used in this work are of analytical grade. Hydrazine, phosphoric acid, graphite powder received from Alfa Aesar, N,N-dimethyl formamide (DMF) obtained from Sisco Research Laboratories Pvt. Ltd., India. Acetic acid is received from Otto Chemie Pvt Ltd. Sodium hydroxide, boric acid and cetyltrimethylammonium bromide (CTAB) are obtained from Merck. All the solutions are prepared using ultra-pure water of 18 MΩ cm resistivity (Milli Q, Millipore).

2.2. Preparation of graphene nanoflakes (GNF)

GNF are prepared as follows: initially 200 mg of graphite powder was mixed with 0.5 M CTAB surfactant in 15 ml of glacial acetic acid. The resultant solution was sonicated continuously for 4 h at room temperature and this mixture was heated at 100 °C for 24 h under nitrogen atmosphere. After heat treatment, the resultant CTAB assisted graphite mixture was left undisturbed overnight, where the stabilized flakes are settled at the bottom of the container. The supernatant was decanted followed by centrifugation at 13,000 rpm for 1 h. The resultant black residue was thoroughly washed with ultrapure water followed by acetone and the black residue was dried at 40 °C in a vacuum oven for overnight. The resultant material having the flaky structure is called as GNF.

2.3. Preparation of graphene nanoflakes modified glassy carbon electrode (GNF/GCE)

Initially GCE was polished with 1, 0.3 and 0.05 μm alumina powder sequentially followed by sonication in alcohol and deionized water for 5 min respectively. The resultant electrode was dried at ambient condition. Further, 3 μl of 1 mg/ml GNF dispersed in DMF solution was drop-cast on the GC electrode, followed by drying at room temperature for solvent evaporation. The above electrode preparation procedure is maintained uniform for all the experiments. The GNF/GC electrode is washed with deionized water before performing the experiments, in order to remove the loosely bound particles.

2.4. Electrochemical measurements

All the electrochemical measurements were performed using IVIUM portable electrochemical interface and impedance analyzer, Netherlands. A saturated Ag/AgCl electrode, a platinum wire and a GNF modified GCE were used as the reference, auxiliary and working electrodes, respectively. All experiments were performed at room temperature (25 ± 1 °C) in 0.1 M phosphate buffer solution (PBS) [pH 7.0] as a supporting electrolyte. Cyclic voltammetric experiments were carried out in a static electrochemical cell and amperometric experiments were carried out under stirred conditions with a successive addition of hydrazine to the buffer solution by applying a potential of 0.4 V *vs* Ag/AgCl. Impedance measurements were performed in 5 mM of each potassium ferricyanide and potassium ferrocyanide in 0.1 M potassium nitrate solution by applying an alternating voltage of 5 mV in a frequency range from 0.01 Hz to 100 kHz.

2.5. Characterizations techniques

Scanning electron microscopic analysis was carried using Vega3 TESCAN model to study the surface morphology of the GNF. High resolution transmission electron microscopy characterization was carried out using FEI Technai G2 S-Twin and it is operated at 200 kV to observe the morphological features of GNF. X-ray diffraction (XRD) measurements was carried out using Philips PAN analytical PRO X-ray diffractometer using Ni-filtered Cu Kα radiation ($\lambda = 0.15406$ nm) at a scan rate of 3° per minute. Phase identification was performed by referring to the joint committee on powder diffraction standards international centre for diffraction database. The morphological features of synthesized GNF were investigated using Agilent 5500 atomic force microscopy (AFM) instrument. For AFM analysis samples were prepared by ultrasonic treatment of 0.25 mg of GNF dispersed in 1 ml of DMF. The dispersion was drop-cast on a fresh silicon wafer substrate. The silicon wafer was dried at ambient temperature for 12 h and it was directly examined using atomic force microscope at different locations. Laser Raman analysis was carried out using Renishaw Invia Raman Microscope model from the United Kingdom, with He–Ne Laser source of 633 nm wavelength, 18 mW intensity.

3. Results and discussion

3.1. Spectroscopic and microscopic characterization of GNF

Fig. 1(A) shows high resolution transmission electron microscopy (HRTEM) image of multi-layered GNF that is observed on the top of a holey carbon grid. The observed flaky structure resemble the highly oriented large graphene sheets with precise edges and wrinkled structure. HRTEM images of GNF are rippled and knotted with each other. However, these GNF are highly transparent and exhibited extremely stable nature under the electron beam [39]. From the HRTEM image as shown in Fig. 1(A and B), the edges of the suspended GNF is continually fold back, which is confirmed by cross-section view of GNF. This type of conformation is very typical for exfoliated graphite materials since these materials are having huge number of graphene layers. In a cross-section view of one such stack after exfoliation is showed in Fig. 1(B) and observed with a distance between these layers is 3.4 Å. Apart from this larger proportion of flakes with various dimensions, different sizes are observed using scanning electron microscopy analysis [Fig. 1(C)], in which low dissimilarity is observed in few places. This may be due to the multi-layer stacked GNF. Fig. 1(C) also shows a transparent flaky structure and one can easily visualize thin sheets of GNF. The presence of large amount of edge plane sites in GNFs may facilitate the charge transfer properties at interfaces and improved electrochemical property.

3.2. Raman spectroscopy

Fig. 2 shows Raman spectroscopic analysis of GNF that reflects significant structural changes occurred during the exfoliation