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A novel one step synthesis of graphene via sonochemical-assisted solvent exfoliation approach for electrochemical sensing application

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HIGHLIGHTS

- Novel, green and one-step facile exfoliation approach in ethanol/water mixture.
- Comprehensive parametric study yielding optimised synthesis parameters.
- Biosensing application of produced graphene shown through electrochemical analysis.
- Cyclic voltammetry and amperometric study of graphene towards hydrogen peroxide.
- As produced graphene is up to 22 times more sensitive compared to control specimen.

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ABSTRACT

Graphene, an extraordinary two-dimensional carbon nanostructure, has attracted global attention due to its remarkable electronic, mechanical and chemical properties. This work reports a novel one-step green and versatile route to produce up to 1 mg/mL of graphene by facile exfoliation of raw graphite in ethanol–water mixtures. This approach is viable due to the predictions of material solubility by exploiting the Hansen Solubility Parameters. The effective surface area of the graphene was estimated to be about 1000 m^2/g while Atomic Force Microscopy (AFM) analysis was adopted to evaluate the surface characteristics of the samples, whereby the graphene sheets were found to have an average thickness of below 2 nm. The electrochemical characteristic of the graphene was investigated by cyclic voltammetry tests and amperometric detections of hydrogen peroxide (H_2O_2), a by-product of most oxidase based enzymatic reactions. The graphene was deposited onto the surface of screen printed carbon electrodes (SPCEs) and the modified electrode was found to demonstrate enhanced electro-catalytic response of more than two-fold compared to unmodified electrodes, while the detection of H_2O_2 showed excellent stability with a 22 times improvement in sensitivity by optimising the number of deposition layers on the electrode surface.

1. Introduction

Graphene, a 2D planar single sheet of sp^2 hybridized carbons atoms arranged in a honeycomb lattice is currently, the youngest and most fascinating nanomaterial. Ever since its discovery in 2004 by Novoselov et al. [1], researchers around the world have been intrigued by its unique combination of properties. A single layer of graphene has a thickness of only 0.34 nm, a Young's modulus of 1.06 TPa [2], excellent electrical and thermal conductivity [3], flexibility [4], optical transparency with a transmittance of 99.7% [5], and electron mean free path ballistic transport [1]. Recently, few layered graphene (FLG) sheets have also drawn interest owing to their unique electronic transport properties [6].

When first discovered, Geim et al. manually 'cleaved' graphite using duct tape until a single sheet of graphene could be imaged under an optical microscope [1]. Although this method is effective

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for experimental studies, it is low in yield and throughput. As such, scientists focus on more efficient processing methods, among which the most popular involved the oxidative exfoliation of natural graphite via the Hummers method. This chemical processing method involves harsh acid treatments, followed by chemical reduction, producing what is commonly termed reduced graphene oxide (rGO). The use of harsh acids results in graphene product that is decorated with residual functional groups such as epoxyls, hydroxyls, carboxyls and carbonyls [7], which are not completely removed even with subsequent reduction or annealing processes [8]. These covalently bonded functional groups not only make rGO electrically insulating, the hydrophilicity renders it unsuitable for use in applications that requires dispersibility in organic solvents [9]. Furthermore, oxidative approaches are not only debilitating to the integrity of the graphene, but also harmful to the researcher and the environment.

Recent approaches focus on the direct exfoliation of natural graphite through extended hours of mild sonication to produce defect-free monolayer graphene [10]. Hernandez et al. reasoned that full exfoliation of graphite is facilitated when the surface energy of the solvent matches that of graphene. This balance in graphene and solvent surface energies was estimated via the Hildebrand–Scratchard equation [11] in which successful exfoliation through mild sonication treatment was reported using various solvents, namely N-Methyl-Pyrrolidone (NMP), γ-butyrolactone (GBL), N,N-Dimethylacetamide (DMA) and 1,3-dimethyl-2-imidazolidinone (DMEU). The drawback in these methods are that the solvents used have high boiling points, expensive, toxic and not eco-friendly [10,12]. The use of organic solvents in the exfoliation of graphene from graphite or GO also resulted in some residual solvent that adsorbs onto the surface of the graphene. In most cases, these have to be rinsed off with acetone or ethanol [12], requiring laborious post-processing and causing loss in the final yield. In a further improvement from this approach, O'Neill et al. studied the exfoliation of graphite in low boiling solvents such as chlorofoam and isopropanol. Although the group produced homogenous dispersions of few layered graphene, the flexibility of choosing solvents are hindered by the intrinsic properties of the solvent itself and actual synthesis required long processing times of up to 48 h [13].

Recently, Zhou et al. reported a method of exfoliating inorganic graphene analogues (IGAs) in a simple ethanol water system [14]. In this work, Zhou et al. predicted the dispersion of IGAs in an ethanol water system using the theory of Hansen Solubility Parameters (HSPs). They reasoned that by matching the solubility parameters as expressed in the HSP, it is possible to exfoliate single to few layered samples from bulk materials, thus revealing an interesting route for the mass synthesis of graphene.

Herein, this work demonstrates that water and ethanol, two otherwise unsuitable solvents if based solely on the surface energy balance between these solvents and graphene, can be used to effectively exfoliate graphite to produce high quality graphene sheets via mild sonication treatments. This is achieved by exploiting the HSP theory of seeking the lowest HSP distance (R_a) value, thus facilitating an economical, green and scalable means of producing bulk quantities of graphene. In comparison with other work reported on the synthesis of graphene, the proposed method omits harsh chemicals which results not only in a safer synthetic procedure, but also preserves the pristine quality of as produced graphene sheets. From an economical perspective, the starting materials are inexpensive while ultrasonication is a mild treatment that does not consume too much power and can be carried out in both a laboratory or scaled for mass production. The final graphene is then used to modify electrodes to demonstrate its viability for biosensing applications.

2. Experimental

2.1. Materials

Graphite flakes (purity $\geqslant$98% carbon) were purchased from Bay Carbon. Ethanol was purchased from Merck. Raw graphite and all solvents were used as received. Deionized water (DI) from the Milipore system was used as a co-solvent. Hydrogen peroxide (30%) was purchased from Sigma–Aldrich and diluted to the required molarity. Phosphate buffer solution (PBS) tablets were purchased from Sigma–Aldrich and diluted in DI water to produce a 0.1 M buffer solution with a pH of 7.4.

2.2. Preparation of graphene flakes

Stable graphene dispersions were formed through a single step approach by sonicating raw graphite flakes in mixtures of ethanol and water. Raw graphite flakes are mixed in the desired ethanol–water mixture (from 10% to 90%) ratio and sonication was carried out at a fixed position, in a conventional ultrasonic bath with a working frequency of 50/60 Hz at room temperature. At this stage, sonication times were also varied from 30 min to 180 min. The sonicated dispersions were then centrifuged at 1000 rpm for 30 min to remove unexfoliated graphite flakes. The supernatant is then filtered and dried at 80 °C overnight to evaporate any residual ethanol.

2.3. Instrumentations and characterisations

Scanning electron microscopy (SEM) on the graphene sample is conducted using the FEI Quanta-400 FESEM. Energy Dispersive X-Ray (EDX) microanalysis (Oxford Instruments X-Max, 20 mm^2 detector) was conducted on graphene sheets deposited from dispersion unto silicon substrates. The graphene sheets in dispersion were deposited from dispersion onto silicon wafers and left to dry overnight at 37 °C. Transmission Electron Microscopy (TEM) (JEOL JEM-2100F) was conducted on the produced graphene powder at an operating voltage of 200 kV. Tapping mode Atomic Force Microscopy (AFM) (NTEGRA Spectra NT-MDT) were performed on samples drop casted on Si wafers (1 cm × 1 cm) using the NT-MDT NSG01 tapping mode probe (typical curvature radius of 6 nm, cantilever length of 125 μm, and cantilever width of 30 μm). Measurements were done under ambient conditions. The Raman spectra on the powdered samples of FLGs synthesized via different ethanol–water ratios were recorded on a Renishaw inVia Raman microscope at room temperature. The system is equipped with a CCD detector and a holographic notch filter, using a 514 nm diode laser excitation source with power below 0.5 mW. UV–Visible spectra (Perkin Elmer, Lambda 35) were measured from 190 to 600 nm. Graphene dispersions at different ethanol–water fractions were first centrifuged at 3000 rpm to sort out single, double and few layered graphene, and the concentration of the supernatant was determined via UV–Vis absorbance spectroscopy. In this instance, UV–Vis absorbance spectroscopy was conducted at fixed wavenumbers of 273 nm for graphene. A calibration curve was then plotted so that the unknown graphene concentration in the dispersions studied can be determined through this method. Electrochemical measurements (Autolab 4130) were carried out on samples drop-casted on a screen printed carbon electrodes (SPCEs) which had a 4 mm diameter carbon working electrode (WE) and silver reference electrode. Graphene modified SPCEs were prepared by pipetting 1.5 μL of graphene solution onto the WE, allowing it to dry at ambient temperature and repeating until the required modification times, n is achieved.