



Boron and nitrogen dopants in graphene have opposite effects on the electrochemical detection of explosive nitroaromatic compounds

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ABSTRACT

A multitude of strategies to alter the properties of graphene, a representative two-dimensional material, has been proposed with the aim of improving its performance and capabilities. Whilst in general doping with any element is reported in the literature as an electrochemistry enhancing process, there is no real reason for dopants to always be beneficial. Here we doped graphene with boron or nitrogen and show that they have completely opposite properties for electrochemical detection of 2,4,6-trinitrotoluene (TNT). Nitrogen-doped graphene enhances the signal of TNT, whereas boron-doped graphene reduces the response when compared to undoped graphene. This debunks most of the papers claiming that doping results in excellent electrochemistry.

1. Introduction

Doping has been widely used to enhance the electronic and electrochemical properties of graphene, a representative of two-dimensional materials [1–2,3,4]. Leveraging on dimensionality, dopants would not be trapped within the bulk structure, but rather present on the surface of the nanosheets, thereby actively altering their properties [5]. The implications of substituting foreign or heteroatoms for carbon atoms include changes in band gap, density of states and specific surface area which may be beneficial to electrical conductivity or catalytic activity [6,7]. Regarding the nature of dopants, a wide range of elements have been studied, from metals [8,9] to non-metals [10]. However, boron and nitrogen take centre stage as dopants since both of them are direct neighbours of carbon in the periodic table, having similar interatomic bonding distances (B-C, C-C, N-C) and thus may be easily substituted into graphene [11–13].

Taking a closer look at the literature, there have been mixed results regarding the role of boron- and nitrogen-doped graphene (B-graphene, N-graphene) in enhancing electrical properties. For example, both types of doped graphene demonstrate higher electrocatalytic activity than pristine graphene in the oxygen reduction reaction, and this has even been explained by molecular orbital theory [14–16]. In contrast, there are also reports claiming that the conductivity of pristine graphene is better than B-graphene but worse than N-graphene [17]. This raises the question, does the type of dopant matter? Nevertheless, doped graphene is considered as a promising metal-free catalyst [18]. Findings

that graphene and doped graphene exhibit high sensitivity and high specificity as well as fast response times, suggest the potential of the material as a sensor to detect trinitrotoluene (TNT) [19]. The detection of TNT is necessary to signal potential threats from mines and unexploded ordnance (UXO). These explosives have the potential to detonate and their timely detection may enable appropriate action to be taken before any undesirable events occur [20,21]. In addition to potentially undermining security, TNT also poses environmental and health risks. It is one of the most abundant nitroaromatic contaminants in soil and groundwater in many military areas, and exposure can trigger public health issues such as dermatitis and anaemia [22–25]. The detection of TNT is therefore critical in addressing pressing security, environmental and health concerns. Rapid warning followed by the remediation of contaminated sites could then take place. Electrochemical sensors offer an alternative method of detecting TNT. The nitro moiety (NO₂) has redox properties that result in a flow of electrons, generating an electrochemical response. Overcoming the disadvantages of the current HPLC method, the electrochemical analytical approach is rapid and more portable [26]. It also offers a viable option for miniaturisation, rendering it a suitable method for on-site detection [27].

The primary aim of this study is to evaluate the performance of graphene, B-graphene and N-graphene in the detection of TNT. The materials were prepared by chemical oxidation of graphite, using the Hoffman method as its superiority has been proven, followed by vacuum-assisted microwave reduction in the appropriate gaseous

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atmosphere [28,29]. Boron trichloride and ammonia saturate the atmosphere, providing elemental sources which yield B-graphene and N-graphene, respectively. Apart from analytical parameters such as linearity and sensitivity, the Hoffman chemical oxidation is considered to achieve efficient doping [30,31]. Both cyclic voltammetry and differential pulse voltammetry were carried out to observe the influence of dopants on the electrochemical responses towards TNT.

2. Experimental

N,N-dimethylformamide (DMF), potassium chloride (KCl), sodium chloride (NaCl), potassium phosphate monobasic (KH_2PO_4), sodium phosphate dibasic (Na_2HPO_4) and sodium tetraborate decahydrate were purchased from Sigma Aldrich. 2,4,6-trinitrotoluene diluted in MeOH: AcCN (1:1) with a concentration of 1000 $\mu\text{g}/\text{mL}$ was obtained from Accustandard. The chemicals were used as received.

Graphite (99.9995%, 2–15 mm) was acquired from Alfa Aesar, Germany. Silver nitrate (> 99.8%), barium nitrate (> 99%), potassium chlorate (> 99%), nitric acid (68%) and hydrochloric acid (37%), were acquired from Penta, Czech Republic. Nitrogen (99.9999%) and ammonia (99.9995%) were acquired from SIAD, Czech Republic. Lastly, boron trichloride (99.99%) was acquired from Koch-Light Laboratories Ltd., England.

2.1. Graphite oxide synthesis

Concentrated sulfuric acid (98%, 87.5 mL) and nitric acid (68%, 27 mL) were added to a reaction flask with a magnetic stirring bar. The flask was immersed in an ice bath to be cooled to 0 °C, and graphite (5 g) was then added. The mixture was stirred vigorously to ensure a homogeneous dispersion as well as to avoid agglomeration. While maintaining the temperature of the reaction flask at 0 °C, potassium chlorate (55 g) was added slowly. This was necessary to avoid a sudden increase in temperature along with the resulting formation of explosive chlorine dioxide gas. When the potassium chlorate had completely dissolved, the reaction flask was loosely capped to allow escape of the gas evolved during dissolution. The mixture was continuously stirred vigorously for 96 h at room temperature. After the reaction has completed, the mixture was poured into deionised water (3 L) and decanted. The resulting graphite oxide was first re-dispersed in HCl (5%) solution to remove sulfate and chloride ions (with $\text{Ba}(\text{NO}_3)_2$ and AgNO_3 respectively), then repeatedly centrifuged and re-dispersed in deionized water for complete removal of all chloride and sulfate ions. Finally, the graphite oxide slurry was dried for 48 h in a vacuum oven at 50 °C.

2.2. Microwave plasma treatment

2.2.1. Graphene

Graphite oxide (300 mg) was placed in quartz glass ampoules and evacuated to a base pressure of 5×10^{-5} mbar with an oil diffusion pump. The graphite oxide was heated to 60 °C during the evacuation procedure to remove any traces of moisture. The ampoule was sealed off in vacuo with an oxygen–hydrogen flame. The ampoule was then put inside the microwave reactor and irradiated for 3 min (1 kW, 2.45 GHz). The resultant heating of GO was related solely to the direct absorption of radiation itself. There was no secondary heating of exfoliated material from the reaction vessel as microwave radiation was not absorbed by quartz glass, unless standard labware glass (like Pyrex glass) was used. Formation of plasma was noted inside the evacuated ampoule during the start of the exfoliation procedure, which was accompanied by the intense evolution of large amounts of gases. The increase in pressure led to the plasma discharge being quenched a few seconds after the start of the exfoliation procedure. The ampoule was

then broken to obtain the microwave vacuum exfoliated graphene.

2.2.2. Boron-doped graphene

250 mg of graphite oxide was placed in a quartz glass (500 mL) reactor equipped with a 1000 W magnetron (2.45 GHz). The reactor was evacuated thrice and flushed with nitrogen. Thereafter, the reactor was repeatedly filled with boron trichloride and evacuated. The exfoliation was performed at 10 mbar for 3 min with a continuous flow of boron trichloride (about 50 mL/min). The resulting boron-chlorine plasma accelerated the exfoliation of graphite oxide that followed soon after plasma formation. Lastly, the reactor was flushed with nitrogen and cooled down under a nitrogen atmosphere.

2.2.3. Nitrogen-doped graphene

250 mg of graphite oxide was placed in a quartz glass (500 mL) reactor equipped with a 1000 W magnetron (2.45 GHz). The reactor was evacuated thrice and flushed with nitrogen. The exfoliation was performed at 10 mbar for 3 min with a continuous flow of nitrogen (about 50 mL/min). The resulting nitrogen plasma accelerated the exfoliation of graphite oxide that followed soon after plasma formation. Lastly, the reactor was flushed with nitrogen and cooled down under a nitrogen atmosphere.

2.3. Elemental analysis

An MX5 (Mettler Toledo) microbalance was used for precise sample weighing (1.5–2.5 mg per single sample analysis). Combustible elemental analysis (CHNS-O) was carried out with a PE 2400 Series II CHNS/O Analyzer (Perkin Elmer, USA). The CHN operating mode was chosen as it is the most robust and interference free. The instrument utilised a classical combustion principle to convert the sample elements to gases (CO_2 , H_2O and N_2). The analyzer automatically performed combustion, reduction, homogenization and separation, as well as detection of the gases. The accuracy of CHN determination was better than 0.30 abs.%. Internal calibration was carried out using *N*-phenyl urea.

2.4. Electrochemical measurements

Suspensions of graphene and doped graphene in *N,N*-dimethylformamide (DMF) were prepared. 15.0 mg of the material was weighed, followed by addition of 3.0 mL of DMF to prepare a concentration of 5.0 mg/mL. This was then sonicated for 2 h, with the temperature not exceeding 30 °C, to ensure the material was well dispersed or suspended in DMF.

All electrochemical experiments were performed using a μ Autolab type III connected to a personal computer. Depending on the voltammetric technique used, the control software was either NOVA version 1.10 or General Purpose Electrochemical Systems version 4.9. The former was used for cyclic voltammetry while the latter was chosen for square wave and differential pulse voltammetry.

Measurements were carried out at room temperature using a three-electrode system in a glass cell, comprising a glassy carbon (GC) electrode coated with the material of interest, a platinum auxiliary electrode and a Ag/AgCl reference electrode. In other words, the potentials reported herein are vs. Ag/AgCl. The GC electrode was polished with 0.05 μm alumina powder on a polishing pad. A 1 μL aliquot of the material suspended in DMF was deposited onto the GC electrode surface. It was then left to dry under a lamp where the solvent was evaporated, leaving a randomly distributed film on the GC electrode. Prior to measurement, a solution comprising the desired concentration of analyte in a buffer was deoxygenated for 5 min with nitrogen.

A phosphate-buffered saline (PBS) buffer was prepared by mixing

two solutions. 1.87 g of Na_2HPO_4 , 1 g of NaCl and 0.025 g of KCl were weighed then dissolved in 250 mL of ultrapure water to make up the first solution. 1.70 g of KH_2PO_4 , 1 g of NaCl and 0.025 g of KCl were weighed then dissolved in 250 mL of ultrapure water to make up the second solution. The second solution was added to the first until a pH of 7.20 was obtained. For preparation of a 20 mM borate buffer, 1.90 g of sodium tetraborate decahydrate was dissolved in 250 mL of ultrapure water. The measured pH was 9.26.

The treatment of the electrochemical data first involved baseline correction via moving average, with a peak width of 0.01. Peak picking was carried out thereafter, with peak potential as well as height being recorded. For each material, the scan was repeated twice more, cleaning and coating the GC electrode with fresh material between scans. Among the triplicate measurements, the scan with values closest to the average would be used for further analysis and comparison.

3. Results and discussion

Graphene and its doped counterparts, B-graphene and N-graphene, were synthesised via Hoffman's chemical oxidation to graphite oxide, followed by microwave exfoliation in vacuum, BCl_3 or NH_3 atmospheres accordingly. Combustible elemental analysis reveals 0.34 atomic % B and 2.09 atomic % N for B-graphene and N-graphene respectively. The materials, suspended in DMF, were drop casted onto bare glassy carbon electrodes prior to the detection of TNT. The nitro groups in TNT are excellent electron acceptors, undergoing reduction to a dihydroxylamine by gaining two electrons and protons each (Scheme 1). Subsequently, a water molecule is lost irreversibly, yielding a nitroso moiety. Further reduction via two electrons and protons leads to the hydroxylamine compound. The amine functionality is finally obtained upon an irreversible reduction with concomitant dehydration [32].

Cyclic voltammetry was first carried out to provide qualitative information about the electrochemical processes of 2,4,6-trinitrotoluene (TNT). The voltammograms of graphene, B-graphene and N-graphene are illustrated in Fig. 1. Various information can be extracted regarding their inherent electrochemistry as well as their responses towards TNT.

The inherent electrochemistry is the first aspect of voltammetry necessary for any study. It is defined as the changes of a material's properties when used as an electrode surface without any analyte [33]. Measurements on blank solutions were performed and the results, represented by dotted lines in the voltammograms, indicate that there are neither oxidation nor reduction peaks. Henceforth, there will be no interference by the materials and peaks can be successfully distinguished in the analysis of TNT. The structures of the materials remain unperturbed, hence the performance of graphene and doped graphene can be studied accurately.

Another observation is the striking appearances of the baseline, which is not at all flat relative to bare GC. A factor affecting the baseline is the background current, sometimes known as the charging current. This is a non-faradaic current i.e. a current not arising from a redox reaction. Rather, it is due to an electric double layer adjacent to the

surface of the electrode. Since charging currents for graphene, B-graphene and N-graphene are observed in the voltammograms, it can be inferred that their capacitance is significant. This is plausibly due to an increase in surface area.

Meanwhile, analyses of 20 $\mu\text{g}/\text{mL}$ TNT are represented by solid lines in the voltammograms. Three peaks were observed in the forward scan for all three graphene materials. A correlation between the number of peaks and the number of nitro groups has previously been established [34]. This is supported by density functional studies where the stability of intermediate compounds in the reduction process has been investigated. It was ascertained that the first reduction requires the most energy and subsequent reductions are thermodynamically easier than the first. As a result, a multielectron overall response will occur [35]. Each peak can therefore be assigned to the reduction of a nitro moiety in TNT.

Moving on from the reduction peaks, there is an oxidation peak as the voltage is switched to more positive values. The peak is due to the oxidation of hydroxylamine [36,37]. Since the reduction process can either be a 4- or 6-electron process [34,38], not all of the hydroxylamine will undergo the final step of reduction to an amine. Therefore a hydroxylamine oxidation peak is observed [32].

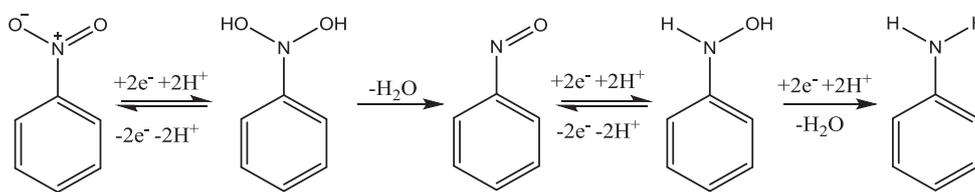
For quantitative analysis of TNT, a different voltage profile has to be employed. Differential pulse voltammetry (DPV) was carried out since pulsed methods have better sensitivity and the peak height is proportional to the concentration. The potential range of -0.3 to -1.0 V is set based on the CV. The voltammograms for the various materials (graphene, B-graphene and N-graphene) in the presence of 20 $\mu\text{g}/\text{mL}$ TNT are shown in Fig. 2.

The first reduction peak of TNT occurs at -0.431 V for both B-graphene and N-graphene, with a more negative potential of -0.440 V for graphene. A less negative potential implies that less energy is required for the process to occur. In terms of peak height, the highest peak is attained by N-graphene, followed by graphene, while B-graphene generates the smallest peak height. The superior performance of N-graphene is observed as its electron transfer is faster and yields the highest sensitivity towards TNT.

Analysis of TNT at different concentrations, from 0 to 20 $\mu\text{g}/\text{mL}$, was then performed to obtain a calibration graph (Fig. 3). Two parameters can be assessed from the graph – sensitivity and linearity. The sensitivity is represented by the gradient, whereas linearity is captured by R^2 . The values are tabulated in Table 1. Among the studied materials, N-graphene is the most promising as an electrochemical sensor for TNT. It enhances the electrochemical response for graphene, generating higher peaks while at the same time not compromising on linearity. The reverse is true for B-graphene, which reduces the performance of graphene [16].

4. Conclusion

The effects of doping together with the nature of dopants have been studied by preparing three materials: graphene, boron-doped graphene and nitrogen-doped graphene. The dopants have different effects on the



Scheme 1. Electrochemical reduction pathway of a nitro group involving six electrons overall.

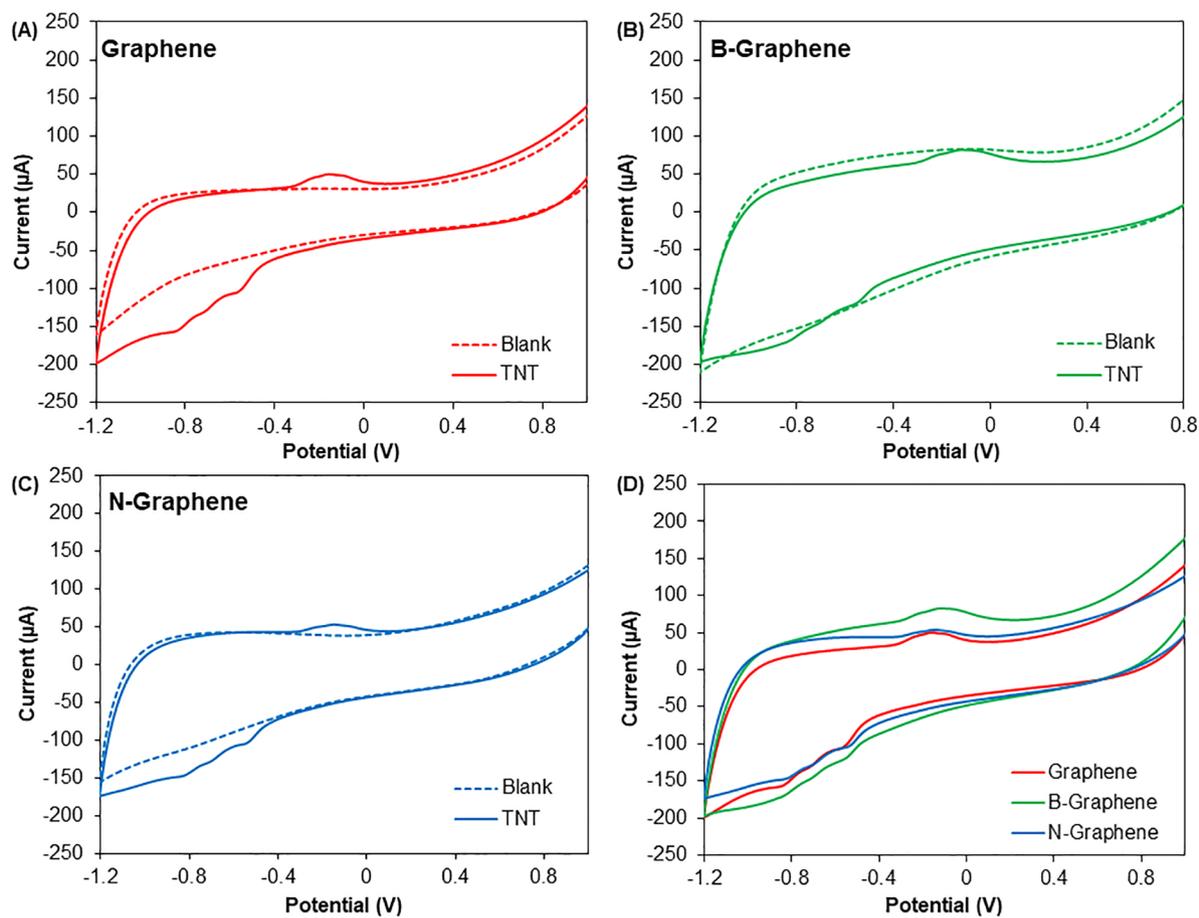


Fig. 1. Cyclic voltammograms of blank (dotted lines) and 20 µg/mL TNT (solid lines) on the following materials: (a) graphene, (b) B-graphene, (c) N-graphene, and (d) all materials. Conditions: 20 mM borate buffer, pH 9.2, scan rate 0.1 V/s.

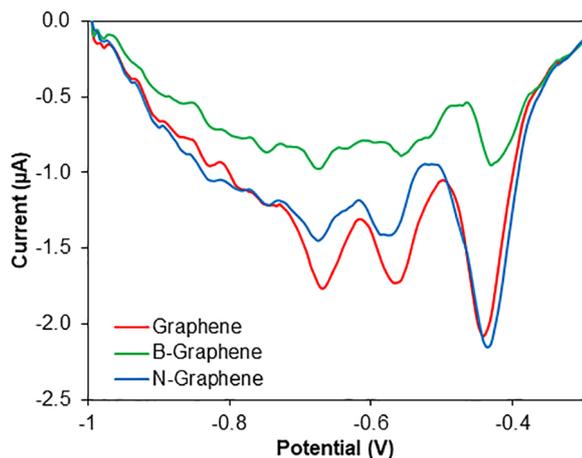


Fig. 2. Differential pulse voltammograms of graphene, B-graphene and N-graphene in the presence of 20 µg/mL TNT. Conditions: 20 mM borate buffer, pH 9.2.

sensitivity of graphene towards TNT. N-graphene generates the highest current peaks while B-graphene performed worst of the three materials. Based on our study, doping with nitrogen atoms improve the sensing capabilities of graphene while boron atoms impair the response. These findings have important implications for the use of doped graphene in analytical chemistry applications, showing that not all doping is beneficial.

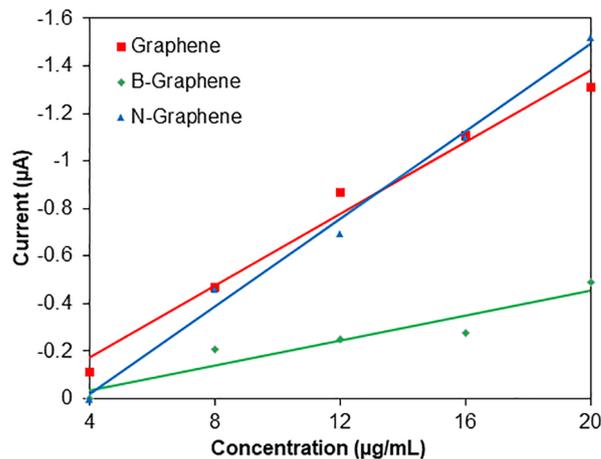


Fig. 3. Calibration graph for graphene, B-graphene and N-graphene with different TNT concentrations (4, 8, 12, 16, 20 µg/mL). Conditions: 20 mM borate buffer, pH 9.2.

Table 1
Gradient and R^2 values of graphene, B-graphene and N-graphene from the TNT calibration graph (Fig. 3).

Material	Sensitivity (Gradient)	Linearity (R^2)
Graphene	-0.076	0.9803
B-graphene	-0.026	0.8938
N-graphene	-0.092	0.9922

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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N.R. carried out electrochemical and materials analysis. Z.S. prepared the doped graphenes. M.P. devised the idea, supervised the project. N.R. and M.P. wrote the manuscript.

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