

# Preparation and Characterization of Nitrogen Doped Reduced Graphene Oxide Sheet

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## I. INTRODUCTION

**Abstract:** In this study, nitrogen doped reduced graphene oxide were synthesized from chemically produced graphite oxide. Both the as-synthesized graphite oxide (GO) and the nitrogen doped reduced graphene oxide (N-rGO) were characterized for their functional chemical bonds, surface morphology, chemical structure and elemental compositions by Fourier transform Infrared spectroscopy (FTIR), Scanning electron microscope (SEM), transmission electron microscope (TEM), Energy dispersive X-ray spectroscopy (EDX) and Ultraviolet Visible spectroscopy (UV-Vis). The characterization analysis confirmed the reduction of graphite oxide into graphene sheet doped with nitrogen.

**Keywords:** Graphite oxide; reduced graphene oxides sheet; nitrogen doped graphene.

Graphene nanosheets (GNS) is a monolayer  $sp^2$  hybridized carbon atoms arranged in a honeycomb lattice [1]. The synthesis of GNS has attracted great attention as one of the most interesting and challenging materials with applications found in different fields such as gas storage, electronics, semiconductors, and fuel cells [2]. Graphene is commonly associated with characteristics such as large surface area and high thermal, chemical and mechanical stabilities. These made it a desirable 2-D support for metallic and bimetallic nanoparticles especially for heterogeneous catalysis applications [3]. Nitrogen-doping has become a key-functionalization technique in graphene synthesis. This is due to the ease at which local electronic structure of the N-doped graphene can be manipulated and thus enhance its active sites and capacitance abilities. This feature of N-doped graphene has improved its application in several processes such as biosensor, fuel cell and electronic device [4]. Functionalization using Nitrogen is associated with the changes in the electron donor/acceptor characteristics of graphene or reduced graphite oxide, contributing to the enhancement of capacitance property[5]. Among all known graphite (graphene) oxide synthesis approaches, chemical method has become one of the most favourable technique used despite the defects formed and significant amount of oxygen functional groups present on the products [6]. The chemical route involves the exfoliation of graphite bulk to form hydrophilic graphite oxide layers followed by chemical reduction to form hydrophobic reduced graphene oxide [7]. The reduction process has been evaluated based on various factors including the quality of product produced, the hazards of the process and the scalability of the process [8]. The chemical route which is the most common reduction process is often associated with a lot of drawbacks. Firstly, the usage of hydroquinone, pyrogallo, KOH, or  $NaBH_4$  often produce a typical low conductivity rGO. Secondly, its leads to the prolonged reaction time (up to 40 h) when using gamma irradiating GO dispersions. Thirdly, the use of reducing agents such as hydrazine and hydroxylamine has raised environmental concerns due to their toxic nature. Fourthly, the technological bottlenecks created by the highly explosive nature of hydrazine regarding its handling. Finally, the need

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to efficiently separate the resulting rGO from other components has been a big technological challenge, since vacuum filtration takes too long and waste disposal is too expensive [9]. Hence, there is growing interest by researchers to develop simplify and environmental friendly methods for the reduction of graphene oxide [10]. One of such method that has been reported by [11] who utilized a hydrazine free method for graphene oxide reduction. These authors successfully applied a hydrazine free method for reduction of graphene oxide through continuous stirring in hot water under acid condition. This paper focuses on using a simplified approach for the reduction of graphene oxide to graphene sheet doped nitrogen. The objective of this work is to investigate the feasibility of using ammonia as the reducing agent in the synthesis of nitrogen doped reduced graphene oxide.

## II. EXPERIMENTAL

### A. Materials and methods

The reduced graphite oxide was synthesized from purified extra-pure graphite powder, concentrated  $\text{H}_2\text{SO}_4$ , (98 %), concentrated  $\text{HNO}_3$ , (65 %) and  $\text{KClO}_3$ , (99 %) (Fisher Scientific (M) Sdn. Bhd),  $\text{NH}_3$  solution (analytical grade) (RM chemicals). The graphite powders were first treated with concentrated  $\text{HNO}_3$ , concentrated  $\text{H}_2\text{SO}_4$  and  $\text{KClO}_3$ , using modified Staudenmaier's method [12] to produce graphene oxide. The resulting graphene oxide was then exfoliated and reduced into reduced graphene oxide (rGO) by treating with ammonia solution. The resulting graphene oxide was subsequently calcinated at temperature of 200 oC under a flow of laminar  $\text{N}_2$  gas. The obtained samples were studied by FTIR, UV-vis, SEM, EDX, and TEM methods.

### B. Synthesis of Graphene Oxide (GO)

Modified Staudenmaier's method as reported by [12, 13] was employed for the synthesis of graphite oxide from graphite powder. Graphite powder (5 g) was gradually added to a mixture of concentrated  $\text{HNO}_3$  (65 %, 25 mL) and concentrated  $\text{H}_2\text{SO}_4$  (98 %, 50 mL). The solution was cooled down to 5 °C in an ice bath and subsequently followed by the gradual addition of 25 g of  $\text{KClO}_3$ . A special precaution was observed in this step due to enormous heat produced when  $\text{KClO}_3$  was added into the mixture. Subsequently, the solution was further heated up to 75 °C and kept constant for 24 h. This was followed by air-cooling for another 72 h and thereafter transferred into 1 L of distilled water for washing purpose. The resulting solution was allowed for settling for two days. The final solution was filtered at room temperature and dried at 75 °C for 24 h .

### C. Synthesis of Nitrogen Doped Reduced Graphene Oxide (N-rGO):

The N-rGO was synthesized by dispersing 200 mg of GO in 20 ml  $\text{NH}_3$ . The solution was stirred and subsequently heated at 60 °C for 24 h. This resulted to the formation of a homogeneous brown GO aqueous suspension which was obtained by filtering the solution. The black product formed was thereafter washed with distilled water and dried at 70°C for 24 h. The dried samples were heated to 200 °C for 40 minutes in  $\text{N}_2$  (99.999%) atmosphere to produce N-rGO. This method was adapted and was previously used to prepare reduced MWCNT as that described in the literature [14].

### D. Characterization of GO and N-rGO

Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer, Spectrum 100) was employed for the analysis of nature of chemical bonds in terms of functional group of the synthesized GO and N-rGO. The spectra was analysed in the range of 4000 to 650  $\text{cm}^{-1}$  in the attenuated total reflectance (ATR) mode. Scanning electron microscope (SEM) (Hitachi, S-3400N) and transmission electron microscope (TEM) (Hitachi, H-7100) operating at 80–120 kV were used for the morphological analyses of the as-prepared samples. The absorbance of sample solutions was detected by UV-Vis Spectrophotometer (Shimadzu, UV-1800).

## III. RESULTS AND DISCUSSIONS

### A. Fourier transform Infrared spectroscopy analysis

The FTIR spectra of the GO and N-rGO are shown in Fig. 1 respectively. As it can be seen from the FTIR of the GO, the characteristic peaks of graphite oxide such as the absorption peaks included 801, 720 and 685  $\text{cm}^{-1}$  for aromatic C-H deformation, 1028 and 1308  $\text{cm}^{-1}$  for C-O stretching, 1577  $\text{cm}^{-1}$  for O=C-O stretching, 1706  $\text{cm}^{-1}$  for C=O stretching, and a broad peak at 3119  $\text{cm}^{-1}$  for the O-H stretching vibrations of C-OH groups [15]. The small peaks at 2879  $\text{cm}^{-1}$  in the spectrum were attributed to the  $\text{CH}_2$  stretching vibration [16]. The FTIR spectra of the N-rGO showed that the intensities of absorption bands of oxygen-containing functional groups such as C-O (1048  $\text{cm}^{-1}$ ) and C=O (1724  $\text{cm}^{-1}$ ) were dramatically reduced (60 and 50%) and became sharper as shown in Fig. 1. This observation can be attributed to the presence of carboxyl groups that were still remained after reduction. However, it can be seen that the spectrum retains a broad absorption band centered at 3400  $\text{cm}^{-1}$ , which was attributed to the residual O-H groups of rGO [16]. Interestingly, the band at 2806  $\text{cm}^{-1}$  representing the C-H stretch vibrations of the methylene group were formed which is consistent with the findings of [17]. The peak between 1430  $\text{cm}^{-1}$  and 1480  $\text{cm}^{-1}$  are related to the  $\text{sp}^3$  C=N as that described by [5].

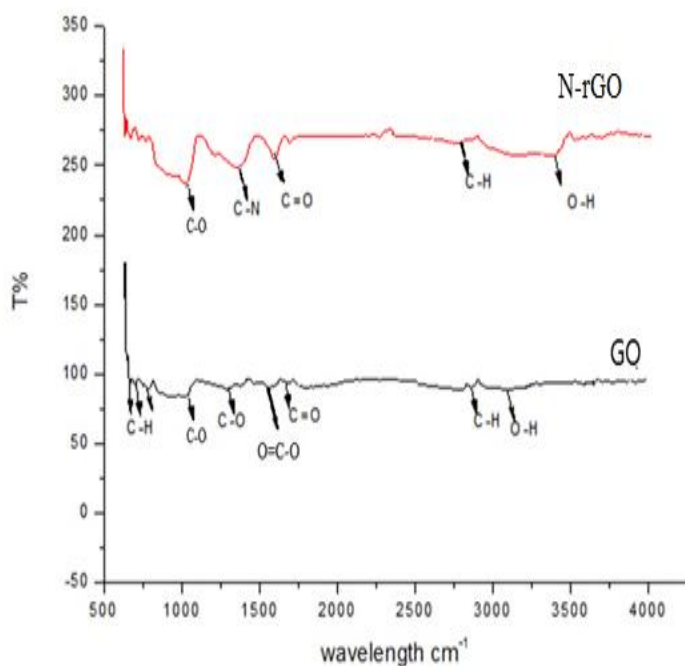


Fig. 1. Fourier transform Infrared spectroscopy analysis (FTIR) analysis of the Graphene Oxide (GO) and Nitrogen Doped Reduced Graphene Oxide (N-rGO).

### B. Morphology Analyses

The morphology and structure of the GO and N-rGO nanosheets are depicted in Fig. 2. The representative SEM image of free standing GO nanosheets is depicted in Fig. 2 (a). Graphite oxide obtained from the acid oxidation were formed by few layers of GO as shown in Fig. 2(c). The image of the GO formed revealed thin and wrinkle nanosheets such that it could allow the passage of electron beam[10]. The GO nanosheets also had crumple and ripple structures as that described by [18]. The appearance of these features might be due to the deformation of the graphite oxide layers that occurred during the exfoliation and restacking processes. The morphology of the N-rGO as analyzed using SEM and TEM are depicted in Fig. 2 (b) and (d). It can be observed that N-rGO wrinkles and can be attributed to the folding of the sheets as shown in the TEM image. This phenomenon can be explained by the thermodynamic instability of exfoliated 2-D structure of GO sheets as well as the van der Waals attractions between the graphene oxide layers [19, 20]. The exfoliated GO sheets are coupled with one another to stabilize into thick layers due to the thermodynamic instability [21]. Moreover, the occurrence of oxygen functional group in the GO layers also contribute to its thermal instability at elevated temperature [6]. The internal and external coupling of the exfoliated GO sheets are perceived to produce microfolding (or microwrinkling) as well as increasing the number of layers,

respectively [22]. It is evident from the SEM micrographs that the extended sheets exhibited a lateral dimensions ranging from a few micrometers to tens of micrometers in

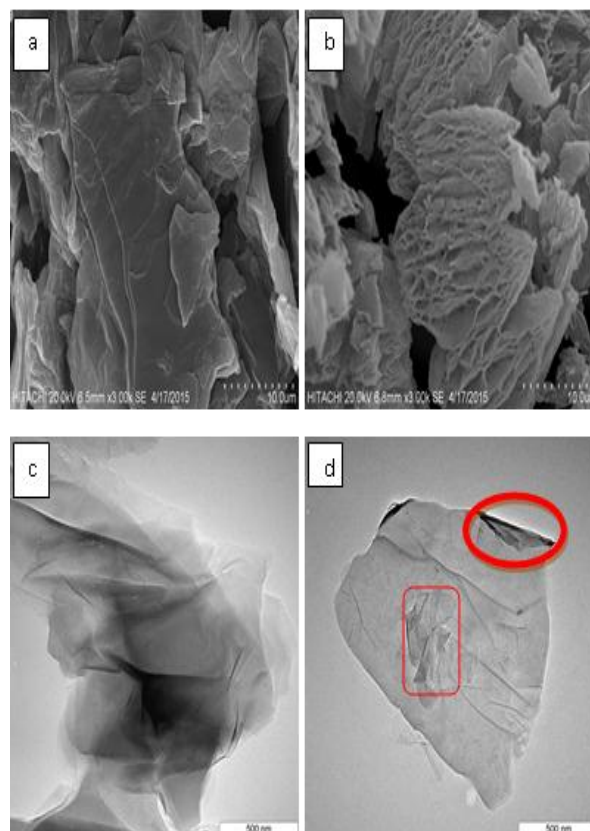


Fig. 2. Microstructure observation of Graphene Oxide(GO) and Nitrogen Doped Reduced Graphene Oxide (N-rGO): (a, b) Scanning electron microscope (SEM) images of GO and N-rGO, while (c, d) transmission electron microscope (TEM) images of (GO) and (N-rGO)

length with layered structures. This is further corroborated from the TEM images (Fig. 2 (c) and (d)) which shows multilayer structures, which might be attributed to the defective structure formed upon exfoliation and the presence of foreign nitrogen atoms [23]. In addition, it can be seen from the TEM images of the folded graphene layers on one edge with isolated small fragments on the surfaces [6].

### C. Energy dispersive X-ray spectroscopy analysis

The synthesized GO sheet using modified Staudenmaier's method entails the utilization of 5.0 g of pure graphite to obtain final quantity of 10.9 g GO sheet. Based on theoretical estimation, the content of C element in GO sheet was calculated to be 45.67% which was based on elemental compositions obtained from the EDX analysis

depicted in Table I. Moreover, the Oxygen composition in the GO sheet obtained from the EDX analysis was 54.33%. This characteristic can be attributed to the presence of oxygen-containing functional groups embedded in the GO sheet [24]. The reduction of the graphite oxide to exfoliated graphite can be further confirmed from the EDX micrograph

TABLE I. The Energy dispersive X-ray spectroscopy (EDX) results showing the elemental compositions of Graphene Oxide(GO) and Nitrogen Doped Reduced Graphene Oxide (N-rGO)

| Element | C (%) | O (%) | N (%) |
|---------|-------|-------|-------|
| GO      | 45.67 | 54.33 | 0     |
| N-rGO   | 78.17 | 15.85 | 5.98  |

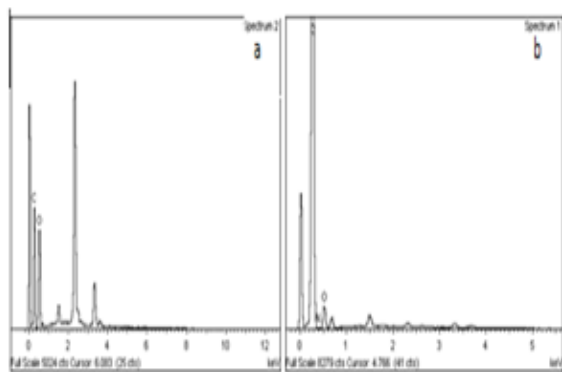


Fig. 3. Energy dispersive X-ray spectroscopy (EDX) micrograph of the (a) Graphene Oxide(GO) and (b) Nitrogen Doped Reduced Graphene Oxide (N-rGO)

shown in Fig. 3(a) and (b). The characteristics of the reduced GO was based on results presented by other's work [25]. The formation of a nitrogen peak from  $\text{NH}_3$  after reduction as shown in the EDX spectra is a further reduction of GO to graphene nanosheets [26].

#### D. Ultraviolet Visible spectroscopy analysis

Often, the polarity of the graphene layer as well as its solubility in water is usually increased due the oxidation of graphite. These occur due to the attachment of oxygen to the graphene layers. For a well oxidized material, the GO formed should have an absorption maximum at *ca.* 230-270 nm. From literature [10, 27, 28] most of the N-rGO solutions has a shifted absorption peak which reveals the occurrence of the GO reduction. This occurrence can be explained in terms of the change in absorption maxima from 260 nm to 285 nm ( as shown in Fig.4) due to the removal

of oxygen atoms from the graphene layer. During the reduction of GO, there is an upward shift in the absorption band assigned to oxidized graphene at *ca* 285 nm. This shift is as a result of the attached oxygen on the layers which is desorbed by the reducing agent [27], the decreased oxygen functional groups as well as increase in aromatic rings resulting to electrons being excited at a lower energy [10]. It also signifies electronic conjugation within the reduced

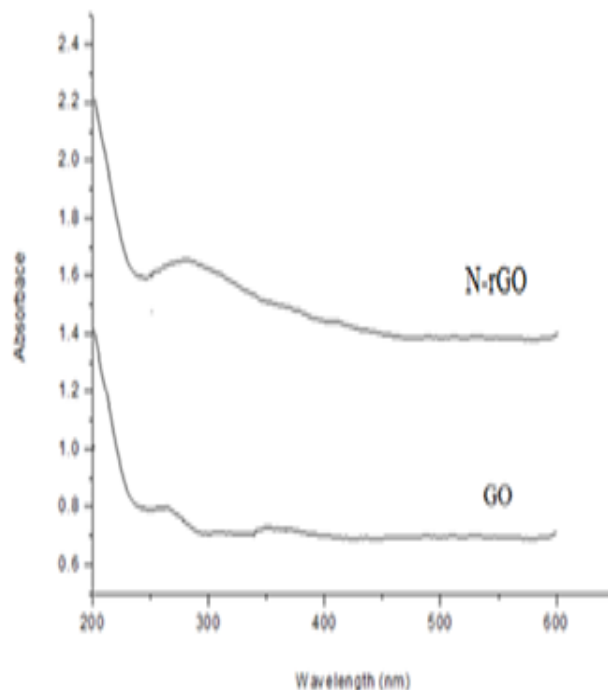


Fig. 4. Ultraviolet Visible spectroscopy (UV-Vis) absorption spectra of Graphene Oxide(GO) and Nitrogen Doped Reduced Graphene Oxide (N-rGO)

graphene sheets which is revived upon reduction of graphene oxide [28]. Furthermore, maximum absorption peak at  $\sim$ 260 nm was observed for graphene oxide (GO) which can be attributed to  $\pi$ - $\pi^*$  transition of the atomic C-C ring and transition of C=O bond. The shoulder peak that present at  $\sim$ 350 nm might show the  $n$ - $\pi^*$  transitions of aromatic C-C bonds [29]. The results of UV-VIS for GO and N-rGO can be shown in the Fig. 4.

#### IV. CONCLUSION

This study has successfully evaluated the synthesis of nitrogen doped reduced graphene oxide via oxidation of graphite flakes. The graphene oxide was successfully synthesized using the Modified Staudenmaier's Method and subsequently reduced to graphene doped with nitrogen by thermal exfoliation chemical reduction. The as-synthesized nitrogen doped graphene as well as the graphene oxide

formed were characterized by SEM and EDX analysis. The SEM results revealed that both the graphene oxide and the nitrogen doped reduced graphene oxide were defected. The FTIR result corroborated that of SEM evident from the disappearance of the OH- and C-O band after the reduction of the graphene oxide. The findings from this study have successfully demonstrated easy procedure for modification of graphene oxide for applications in composites, energy storage devices and heterogeneous catalysis.

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