Preparation of nitrogen and sulphur Co-doped reduced graphene oxide (rGO-NS) using N and S heteroatom of thiourea

Refada Adyansa Rochman¹, Sayekti Wahyuningsih¹, Ari Handono Ramelan¹, Qonita Awliya Hanif²

¹ Inorganic Material Research Group, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Surakarta, 57126, Indonesia
² Chemistry Department, Graduate School of Sebelas Maret University, Surakarta, 57126, Indonesia

* Corresponding author: sayekti@mipa.uns.ac.id

Abstract. Graphene oxide (GO) has been synthesized via modified Hummer’s method with graphite powder as a starting material. The synthesized reduced graphene oxide (rGO) was prepared by GO as a precursor. Synthesis of rGO-NS was performed by hydrothermal method using a dopant thiourea as nitrogen (N) and sulphur (S) donors with the ratio of GO: thiourea=1:10, 1:15, and 1:20 (w/w), respectively. Characterization using Fourier Transform Infra-Red (FTIR) spectroscopy shows several peaks that have an agreement with –OH, C=O, C=C, C-BOH, and C-O functional groups for GO and absorption peaks of –SH, C=S, and CO functional groups for rGO with different intensity, while modified materials of variation rGO-NS emerged typical absorptions of –OH, C=C, C=N, C-N, and C-S functional groups. GO and rGO material that have been analysed using X-Ray Diffraction (XRD) shows a dominant peak at 2θ 10.77° (001) and 24.97° (002), respectively. While the distance between layers (d_{spacing}) on rGO (3.56 Å) was lower than GO (8.22 Å). Compared to rGO, XRD analysis also shows that the addition of N and S on GO structure caused shifting of 2θ in 23.73°–24.06° (002) and calculated d_{spacing} of rGO-NS is found to be 3.70 Å–3.74 Å. Morphological observation of rGO-NS using Scanning Electron Microscopy (SEM) shows that rGO-NS is a thin transparent sheets formed because the exfoliation process of GO material.

Keywords: GO, hummers method, rGO-NS, thiourea

1. Introduction

As a new material, graphene has attracted much researcher’s attention because it has excellent chemical, electronic, mechanical, and physical properties that make this material can be potentially applied as electronic components. Graphene oxide (GO) is one of derivative graphene. Graphene is a two-dimensional (2D) material from monolayer graphite with honeycomb structure. Its low cost and easiness to synthesize are other reasons why GO has great interest [1].

GO material can be synthesized with several methods i.e. Brodie, Staudenmaier, and Hummers. Strong oxidizing agent are added to oxidize graphite; the oxygen functional groups are introduced into the graphite structure which leads to expanding of distance between layers. This property enables the graphite oxide to exfoliate its single or few layers in water medium with ultrasonication, known as GO [2]. If Hummers method is used, it will not produce any toxic gases, such as NO₂, N₂O₃, or ClO₂⁻ in the reaction there by making this method more environmentally friendly [3].
There are many methods to synthesize graphene material have been developed. The method includes Chemical Vapour Deposition (CVD) [4], epitaxial growth of graphene on Si substrate [5], plasma treatment [6], solvothermal [7], and hydrothermal [8]. Synthesize of graphene using hydrothermal method was carried out in the study with temperature of 180°C for 12 hours [9]. The hydrothermal method used in this study has several advantages compare to the common reduction method, because it is scalable and simple, environmentally friendly, and was industrially compatible [10].

Reduced graphene oxide (rGO) was result of GO conversion using thermal reduction method or the addition of reducing agents that aim to eliminate the oxygen functional groups found along the GO plane. The reduction agents commonly used to reduce GO were hydrazine or sodium borohydride [11], Zn [12], and ascorbic acid [13]. Research carried out has succeeded in reduce GO using ascorbic acid as a reduction agent [14].

Substitutional doping of graphene with heteroatoms could modify the chemical reactivity, electrical conductivity, and surface activity of graphene material. The results showed that the doping using nitrogen and sulphur atoms in GO material was successfully carried out [9, 15, 16]. Based on these issues, this paper has been synthesis of nitrogen and sulphur co-doped reduced graphene oxide using dopant thiourea as nitrogen and sulphur donors. The existence of this research is expected as a pioneer of graphene research in Indonesian.

2. Methods

2.1. Synthesis of GO
In this research, GO was synthesized by the modified Hummer’s method. Next, 2 grams of flake graphite was added to 150 mL of H₂SO₄ (98%). Then, 4 grams of NaNO₃ was added during stirring lasts for 1 hour. Then, 8 grams KMnO₄ was added and this solution was stirred for 4 hours at room temperature. Then, 200 mL of water was slowly added to the solution and stirred for 1 hour. 20 mL of 30% of H₂O₂ was added to the solution so that the mixture solution was changed from light brown to yellowish green colour. The mixture obtained was centrifuged. Then, the filtrate obtained was washed with water until the pH was neutral. The mixture was dried for 6 hours at 80°C. Then, graphite oxide powder was obtained. A total of 100 mg of graphite oxide was grounded until become smooth. Then, 100 mL of water was added then stirred for 30 minutes to obtain a homogeneous solution. The solution was sonicated for 30 minutes to obtained GO solution.

2.2. Synthesis Nitrogen and Sulphur Co-doped Reduced Graphene Oxide (rGO-NS)
Suspension of GO (1 mg/mL) was added with thiourea 1 gram, 1.5 gram, and 2 grams. Then, stirred for 30 minutes until homogenous followed by sonication for 30 minutes. Subsequently, the solution was heated at temperature of 180°C in a Teflon for 12 hours. After the hydrothermal process, the autoclave was naturally cool down to room temperature. Product from hydrothermal reaction was washed with water. Then, sample was freeze-dried overnight and dried at 60°C for 4 hours. Finally, rGO-NS product with mass variation (rGO-NS-x) where x is mass from thiourea was added. The rGO material also was conducted under similar conditions using only GO with ascorbic acid.

2.3. Characterizations
X Ray Diffractograms were obtained on a Bruker D8 Advance with Cu anode. The 2θ angle range of operation was 5°-70°. FTIR spectrophotometer (Shimadzu type 8201PC, KBr pellet) was used to analyse the functional groups that might present in the samples and the wavenumber range was 4000-400 cm⁻¹. The surface morphology of obtained products were carried out using SEM FEI Inspect-S50.
3. Result and Discussions

3.1. X-Ray Diffraction

Fig. 1 shows a schematic illustration for the synthesis rGO-NS. Fig. 2 shows the X Ray diffractogram of graphite, GO, and rGO. The XRD spectra of graphite as starting precursor material shows diffraction peak at \(2\theta=26.42^\circ\) (hkl 002). GO material has a sharp diffraction peak at \(2\theta=10.74^\circ\) (hkl 001) and small peak at \(2\theta=42.42^\circ\) (hkl 100). The sharp peak shows that on the GO there is an oxygen functional groups. The rGO sample exhibit a broad peak at \(2\theta=24.97^\circ\) (hkl 001), indicating that GO was successfully transformed became rGO via hydrothermal method with the help of reduction agent [17].

When compared with rGO, the diffractogram peak value of \(2\theta\) in rGO-NS experienced a shift in the diffraction peak in the lower direction during the doping process. While the peak diffractogram value of \(2\theta\) was obtained respectively in rGO-NS-1 of 23.73\(^\circ\) (hkl 002), rGO-NS-1.5 of 23.98\(^\circ\) (hkl 002), and rGO-NS-2 of 24.06\(^\circ\) (hkl 002). The interlayer spacing (d_{spacing}) calculations can be determined using the Bragg Law in equation (1). The equation (1) is written below:

\[
n\lambda=2d \sin \theta
\]  

where \(n\) is a integer, \(\lambda\) is wavelength of the electrons (nm), \(d\) is interlayer spacing of the crystal planes (Å) and \(\theta\) is the Bragg angle.

![Figure 1. Schematic illustration for the synthesis rGO-NS.](image)

![Figure 2. XRD patterns of graphite, GO and rGO.](image)
The distance between two layers is an important parameter to give the structural information of material. $d_{\text{spacing}}$ of the graphite, GO, and rGO samples is indicated to be 3.37 Å, 8.22 Å, and 3.56 Å, respectively as shown in Fig. 3. This indicates the presence of oxygen functional groups that formed during oxidation. Results from calculation of $d_{\text{spacing}}$ of the rGO-NS also shows of $d_{\text{spacing}}$ in rGO-NS variation samples is indicated to 3.74 Å (rGO-NS-1), 3.71 Å (rGO-NS-1.5), and 3.70 Å (rGO-NS-2). Decrease in the $d_{\text{spacing}}$ value indicates that the GO has been successfully reduced by removal of oxygen functional groups in GO structure [18]. The addition of doping will cause defects resulting in uneven bond length in rGO because of C atoms lost during doping and vacancy in crystal structure which are not completely covered by heteroatoms N or S doped. Adding doping will cause defects in rGO structure and $d_{\text{spacing}}$ changes [19].

![Figure 3. XRD patterns of rGO, rGO-NS-1, rGO-NS-1.5 and rGO-NS-2.](image)

3.2. Fourier Transform Infrared (FTIR)

Characterization of a vibration graphite, GO, and rGO can be viewed using FTIR (Fig. 4). The spectrum of graphite (Fig. 4a) gave the absorption spectra of O-H at 3441 cm$^{-1}$ and C=C at 1632 cm$^{-1}$. Then, the spectrum of GO (Fig. 4b) gave the absorption spectra of O-H at 3415 cm$^{-1}$, C=C at 1618 cm$^{-1}$, and new intense band C=O at 1722 cm$^{-1}$, C-OH at 1361 cm$^{-1}$, and C-O at 1057 cm$^{-1}$. These results are consistent with the research that on GO has absorption peaks of functional groups OH, C=O, C=C, C-O, and C=OH which indicated that GO material has been formed from graphite oxidation [20-22]. The FTIR spectra of rGO (Fig. 4c) exhibits band at 3426 cm$^{-1}$ due to O-H stretching. The band at 1631 cm$^{-1}$ appears due to C=C stretching. The band at 1198 cm$^{-1}$ is attributed to the presence C-O stretching. It shows that the stretching vibration of C-OH and C=O bonds in rGO disappears compared to GO, which are caused by the fact that the GO material has been reduced successfully [23]. rGO-NS-1, rGO-NS-1.5, and rGO-NS-2 material in Fig. 5 shows a new intense band at a wavelength of 1522-1573 cm$^{-1}$ which corresponds to the presence of C=N vibration and 1172-1189 cm$^{-1}$ indicates the existence of C-N and or C-S vibrations [24, 25]. The vibration of C=N in the absorption area indicates the occurrence of C double bonds on GO with N dopants from thiourea. Whereas the C-N and or C-S vibrations indicates a C single bond on GO with N and or S dopants from thiourea. The FTIR spectra confirm the presence of C=N, C-N, and C-S bonds indicating that the doping of nitrogen and sulphur atoms has successfully entered the GO structure.
Figure 4. FTIR spectra (a) graphite, (b) GO and (c) rGO.

Figure 5. FTIR spectra of (a) rGO, (b) rGO-NS-1, (c) rGO-NS-1.5 and (d) rGO-NS-2.

3.3. Scanning Electron Microscopy (SEM)
The morphology of the graphite, GO, and rGO samples was characterized using SEM analysis. Graphite material has a form of rough flakes that spread with varying and irregular sizes as shown in Fig. 6a. After graphite undergoes oxidation and sonicated, the morphology GO that occurs was shown in Fig. 6b. Depicted in Fig. 6b, GO shows as a thick material and consists of many layers as the distance between the layers is clearly visible. Thickness of GO morphology is due to the presence of oxygen functional groups that bound to the plane. This indicated that graphite has been peeled off during the oxidation process [26]. Then, the rGO morphology was showed in Fig. 6c indicates that rGO has a thin sheet morphology when compared to GO and the distance between layers is decrease.
Figure 6. SEM images of (a) graphite, (b) GO, (c) rGO, and (d) rGO-NS-1.

The results of SEM images of the rGO-NS variation were shown in Fig. 6d. rGO-NS-1, rGO-NS-1.5, and rGO-NS-2 material have morphology in the form of thin and transparent sheets and consist of several layers which shown the distance between sheets with each other [27, 28]. Fig. 6d shown the existence of morphology in the form of small dots which indicated the possibility of some thiourea that did not react with GO. In addition, morphological observations for rGO shown in Fig. 6c is apparently similar with rGO-NS-1. It is because the doped atoms in rGO-NS-1 was dissolved and very small so that difficult to distinguish. Therefore, it will not make significant change in the morphology of rGO.

4. Conclusions
In summary, thiourea as an N and S doping agent undergo reactions with GO material then rGO-NS was succesfully synthesized as indicated by the changes in the results from XRD, FTIR, and SEM characterizations. It is proved by the shifting 2θ peak and change in \(d_{\text{spacing}}\) 3.70-3.74 Å, new peaks with an agreement C=N, C-N, and C-S bonds, and morphological differences when compared with GO and rGO material.

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