Synthesis of reduced graphene oxide modified Cu (rGO-Cu) by gamma irradiation and its electroactive properties

Fifi Nurfiana, Giyatmi, Nidha Anggita

Department of Nuclear Chemical Engineering, Polytechnic Institute of Nuclear Technology, National Nuclear Energy Agency

E-mail: fifi.nurfiana@batan.go.id

Abstract. Electroactive materials with excellent performance are developed to be applied in different fields. In this study, Graphene Oxide (GO) was synthesized using the Hummer method then reduced and modified with Cu through gamma irradiation (radiolytic reduction) for dose variations. The optimum dose that produces the highest electroactive is 35 kGy which was tested with cyclic voltammetry. The results of FTIR analysis show the characteristics of functional groups found in GO and rGO are different. The modification of rGO with Cu was successfully shown from the results of XRD and SEM-EDX analysis. The results of the XRD analysis showed that there are two peaks at position 2 theta 10.58° which showed the presence of GO and at position 2 theta 42.55° which indicates the presence of Cu. The results of the SEM-EDX analysis showed that there is 2.25% wt of Cu on the surface of the rGO.

1. Introduction

The development of new materials that have good corrosion resistance, mechanical and electrical properties is very important to improve efficiency and reliability uses in the future. Graphene, as one of them, attracted many researchers and made significant progress in the fields of applied electrochemistry and electricity [1].

Graphene oxide (GO) is a chemically modified graphene, which is prepared through oxidation and exfoliate sheets from graphite [2]. In this research, we are the synthesis of GO-based on the method reported by Hummers which graphite can oxidize by a solution of potassium permanganate in sulfuric acid [3].

Graphene oxide is reported to have limited electrical and thermal transport due to oxygen functionalization on the surface of the base plane [4]. Polar oxygen does not only have a positive effect on water dispersion, but also a negative effect which results in conductivity decrease. It is necessary to reduce the oxide with reduced graphene oxide. Reduced graphene oxide (rGO) will increase the ratio of carbon to oxide in the sheet that will produce higher conductivity [5]. Electrical conductivity can be increased by reducing GO to reduced graphene oxide (rGO) although it cannot be the same as pure as graphene conductivity. This is caused by defects and voids that cannot be completely removed during reduction.

Some methods that have been used to make graphene-based composites include solvothermal [6], hydrothermal, chemical reduction and chemical vapor deposition (CVD) synthesis methods with the help of microwaves [7]. Previous research, graphene sheets were doped with Ag nanoparticles [7], Pt nanoparticles[8], Ni nanoparticles [9], prepared using reduction by gamma rays irradiation to improve the electroactive properties. Gamma irradiation is an efficient, easy, and environmentally friendly...
method for preparing composites from doped graphene using metal nanoparticles. Modifications with radiolytic reduction are carried out with contacting the material with a metal precursor under alcoholic conditions. This suspension is then subjected to a radiation dose that will cause the formation of free radicals such as solvated electrons that can reduce the ion precursor and graphene oxide itself.

In this research rGO is modified with copper metal (Cu). Copper is used to having excellent thermal and electrical conductivity. Modification rGO with Cu particle will reduce the aggregation of the two components and maintain stability and improve the electronic properties.

The modification process of rGO-Cu was done by gamma irradiation under alcoholic conditions. Graphene oxide (GO) and Cu\textsuperscript{2+} are reduced together by the electrons which originated from the gamma radiolysis of ethanol. The structure and morphology of the obtained rGO–Cu composites were analyzed using FTIR, XRD and SEM-EDX. The electrochemical response (electroactive) of GO and rGO-Cu of each sample is observed by cyclic voltammetry.

2. Materials and Methods

2.1. Materials
NaNO\textsubscript{3}, KMnO\textsubscript{4}, CuCl\textsubscript{2}.2H\textsubscript{2}O, H\textsubscript{2}O\textsubscript{2} 30%, H\textsubscript{2}SO\textsubscript{4} 98%, K\textsubscript{4}(FeCN)\textsubscript{6} and absolute ethanol are form Merck, aqua dest, graphite, paraffin, and Whatman filter paper number 41.

2.2. Synthesis of graphene oxide
Graphene oxide (GO) was synthesized using the Hummers method [4]. Graphite powder (10 g) and NaNO\textsubscript{3} (5g) were added to 230 mL of H\textsubscript{2}SO\textsubscript{4} maintained in an ice bath at 5 °C and stirred for 1 hour. The mixture was added with 30 grams of KMnO\textsubscript{4} and still maintained in an ice bath at 5 °C. The solution was stirred for 3 hours at room temperature (30 °C). distilled water (460 mL) was added to the reaction slowly. Then, 230 mL of distilled water and 10 mL of H\textsubscript{2}O\textsubscript{2} 30% were added. The solution was filtered and washed using 5% HCl and distilled water respectively. Graphene oxide (GO) was filtered and the filtrate was checked if there is SO\textsubscript{4} content with BaCl\textsubscript{2} 1 M. If there is no white precipitate then GO is dried at 60 °C in the oven for 24 hours.

2.3. Modification of reduced GO with Cu
The solution of CuCl\textsubscript{2}.2H\textsubscript{2}O of 0.01 M (alcoholic) concentration was prepared. GO was dissolved in the solution of CuCl\textsubscript{2} (alcoholic) and sonicated for 1 hour. The solution is put into a glass bottle for gamma irradiation using irradiator type I Ob-Servo Ignis with 12 kCi Co-60 radioactive sources located in STTN BATAN. The irradiation process was done by varying the dose at 20, 25, 30, 35 and 40 kGy. After irradiation, rGO-Cu products were separated by filtration washed with distilled water and dried.

2.4. Electroactive characterization
Electroactive characterization was done through cyclic voltammetry with eDAQ potentiostat STTN BATAN. There are three electrodes: Ag/AgCl electrodes as reference electrodes; Pt dish as counter electrodes; and graphite, GO and rGO-Cu as working electrodes where redox reactions occur. The analyte used was 5 mM K\textsubscript{4}(FeCN)\textsubscript{6} in 0.1 M KCl given a different potential. This measurement will get a current curve for the given potential.

Fabrication of GO and rGO-Cu as the working electrode was done by mixing GO and paraffin in a ratio 7: 3. The GO paste mixture was inserted into an insulator pipe that has the same diameter (Eppendorf 100 µL) and then compacted. The copper wire was inserted into the insulator pipe about 1 cm. The GO electrodes were left on for 24 hours. The same thing is done in the manufacture of working electrodes rGO-Cu.
2.5. Materials Characterization

Functional groups of Graphite, GO and rGO-Cu samples were analyzed by using Shimadzu Prestige 21 spectrophotometer in the range 400-4000 cm\(^{-1}\). The XRD pattern was recorded by using the D2 Phaser Bruker X-ray diffractometer in the 2\(\theta\) range 5-100\(^\circ\). The SEM-EDX was performed on a Hitachi SU 3500 to capture sample morphology.

3. Results

The formation of GO can be indicated from the change in color in the synthesis process as shown in Figure 1. Potassium permanganate that is added slowly to the mixture of graphite powder and sulfuric acid (Figure 1(a)) produces a dark green color with a slight exothermic as shown in Figure 1(b). The dark green color indicated that Mn\(_2\)O\(_7\) has formed. Stirring the mixture at room temperature and then added distilled water results in the release of heat by exothermic H\(_2\)SO\(_4\) so that the color turns brown as shown in Figure 1(c). The addition of H\(_2\)O\(_2\) to the solution also causes heat release and there is a yellow froth (evolution of vapor and oxygen gas) as shown in Figure 1(d) and GO is formed in a yellowish-brown color as shown in Figure 1(e).

![Figure 1](image)

\(\text{(a) (b) (c) (d) (e)}\)

*Figure 1. Color changes in GO synthesis (a) black after mixing graphite, NaNO\(_3\), and H\(_2\)SO\(_4\), (b) dark green after adding KMnO\(_4\), (c) dark brown after adding aqua dest, (d) brownish-yellow after adding H\(_2\)O\(_2\); (e) GO yellowish-brown*

We compare the electroactive performance of the graphite electrode and GO electrode. Graphite electrode had the oxidation and reduction peak current at 36.9722 \(\mu\)A and -16.3368 \(\mu\)A while GO had the oxidation and reduction peak current at 42.46 \(\mu\)A and -144.6 \(\mu\)A. The current response can be seen that graphite has lower current because of the interlayer distance close to the surface area that so needs to be increased by oxidation of graphite to GO. The GO current is higher than graphite and it shows GO is more conductive than graphite.
The electroactive trough current response in cyclic voltammetry increases when GO is reduced to rGO and modified with Cu by gamma irradiation. In Figure 3, the voltammogram of sample results from 20 kGy, 25 kGy, 30 kGy, 35 kGy and 40 kGy gamma irradiation doses, there is a significant increase in current at 35 kGy irradiation dose. At this dose, GO could be optimally reduced at this dose. This result also supported by research conducted by Shahriray et al in 2015 concerning the reduction of GO with gamma irradiation affecting the Cu particles that can bind to rGO [10]. Reduction of GO and modification with Cu metal to increase the electroactive surface area affected by the diffusion of OH and -O- [11]. The incorporation of Cu particles into rGO can increase access to electronic and ionic transport pathways. rGO provides a conductive network for electron transport during the charge and discharge process thereby increasing poor electrical properties and filling the transfer pathways of Cu particles [12].
Figure 3. Cyclic Voltammogram of rGO-Cu result from irradiation dose 20, 25, 30, 35 and 40 kGy.

The current response of the rGO-Cu electrode when applied is +0.6 V to -0.6 V as shown in Table 1.

| Dose irradiation of rGO-Cu | Peak current of oxidation | Peak current of reduction |
|---------------------------|--------------------------|--------------------------|
| 20 kGy                    | 35.54 μA                 | -86.17 μA                |
| 25 kGy                    | 44.72 μA                 | -141.17 μA               |
| 30 kGy                    | 122.382 μA               | -296.372 μA              |
| 35 kGy                    | 0.1146 mA                | -0.2477 mA               |
| 40 kGy                    | 0.1063 mA                | -0.2477 mA               |
In Table 1. It can be seen that the highest current response at the irradiation dose of 35 kGy which shows that at that dose GO can be reduced and Cu can decorate the surface of GO that confirmed on the results of SEM-EDX analysis.

Thus, we measured the Fourier transform infrared (FTIR) spectra to analyze the chemical structures in detail, which are shown in Figure 4, the success of graphite oxidation which was confirmed by the characteristics of the oxygen functional group from graphite to GO [13], rGO and rGO-Cu. In the graph it can be seen that the wave number that appears is 3402 cm\(^{-1}\), 1720 cm\(^{-1}\), 1620 cm\(^{-1}\), 1381 cm\(^{-1}\), 1226 cm\(^{-1}\), 1049 cm\(^{-1}\). Various types of oxygen groups in GO were confirmed at wave number 3402 cm\(^{-1}\) (stretch OH), at 1720 cm\(^{-1}\) (stretching vibration of C=O) and showed that the carboxyl group was on the edge of the GO sheet, at 1620 cm\(^{-1}\) (C=C skeletal vibrations from the non-oxidized graphite domain), at 1381 cm\(^{-1}\) (stretching C-OH vibrations), at 1226 cm\(^{-1}\) and 1049 cm\(^{-1}\) (CO stretching vibrations). The functional groups contained in GO have wave numbers almost the same as rGO and rGO-Cu but have different intensities.

XRD result in Figure 5 (upper) shows a sharp graphite peak at position 2 theta 26.54° so that it can be seen that graphite (element C) has a very crystalline structure [14]. Figure 5 (middle) shows when the oxidation process in graphite is completed, GO will form which has a peak at position 2 theta 9.67°. Figure 5 (lower) irradiation of rGO-Cu at a dose of 35 kGy there is a new peak at position 2 theta 42.55° which after being observed using a software match at that peak is Cu. In position 2 theta 42.55° is a crystalline Cu according to the research of Yan et al in 2012 and (JCPDS: 04-0836). Peak intensity at position 2 theta 10.58° increases indicating more formation of C. Peaks in Figure 5 (lower) provides information that the modification of rGO with Cu by irradiation has been successfully carried out and has good crystallinity.
The morphology of rGO-Cu can be seen from Figure 6 with different magnifications showing that rGO-Cu is piled up so it looks very dense and has an irregularly shaped morphology. It is possible that a large agglomeration of rGO occurs during gamma irradiation due to the absence of a stabilizer or stirring. According to research conducted by Rojas in 2012, the use of gamma irradiation Co-60 functional groups such as carboxyl groups that have a high affinity for metal ions will hold molecules in the surface group and protect from fusing with other atoms so that a suitable stabilizer is needed [15].

EDX analysis to confirm the number of elements in rGO-Cu that produces the spectrum shows the intensity of the element at specific energy as shown in Figure 7.
The EDX spectrum shows the dominant elements as representations of functional groups formed with each number of elements as in Table 2. It can be confirmed that Cu metal is formed with a concentration of 2.25% wt.

Table 2. Percentage element of rGO-Cu 35 kGy

| Element | % wt  | %At  |
|---------|-------|------|
| C       | 53.60 | 62.64|
| O       | 39.92 | 35.02|
| S       | 4.23  | 1.85 |
| Cu      | 2.25  | 0.50 |

Distribution of elements from the mapping results can be confirmed the number of elements contained in the rGO-Cu in the EDX spectrum in Figure 7. The Cu element contained in rGO-Cu is 2.25% wt. And from elemental mapping we can see that the Cu particle distribution (Figure 8 (c)) is homogenous along the rGO surface.

Figure 8. SEM mapping (a) Area of rGO-Cu 35 kGy; (b) mapping overlay; (c) element Cu; (d) element C; (e) element O; (f) element S
4. Conclusion

Synthesis of GO from commercial graphite with the Hummer method which was further reduced using gamma irradiation was carried out successfully. The electroactive characteristics of graphite, GO and rGO-Cu prove that there is an increase in electronics properties. The optimum current response is coming from the rGO-Cu result in 35 kGy irradiation.

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