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Study on the Synthesis of GO-AgNP Mixture Assisted by AgNP Based on UV-Vis, SEM-EDX, XRD, and FTIR

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Abstract. This study aims to determine the effect of silver nanoparticles (AgNP) towards graphene oxide-silver nanoparticles (GO-AgNP) formation using liquid sonication exfoliation (LSE) method. The synthesis results are characterized using UV-Vis spectroscopy, scanning electron microscope (SEM-EDX), X-ray diffraction (XRD), and Fourier transform infra-red (FTIR) spectroscopy. This research begins by making two type of solutions. The first solution is $AgNO_3$ solution which is being varied in concentration, i.e.: 1 mM, 2 mM, 3 mM, and 4 mM. The second solution is the graphite solution. Via the LSE method, $AgNO_3$ that has been heated into becoming AgNP solution is mixed with the graphite solution. The mixture is subjected to 6 hours of ultrasonication. From this study GO or rGO material has been produced through the assistance of AgNP solution by varying the concentration of the $AgNO_3$ solution. The UV-Vis result for 4 mM concentration shows two absorbance peaks with wavelength values of 265 nm and 416.5 nm. This also leads to a redshift of the GO absorbance peak with a wavelength of 252 nm to 265 nm resulting in reduction of GO (rGO) material. The SEM results of GO-AgNP samples do not show the presence of AgNP granules corresponding to the EDX results showing that the oxygen element has the highest percentage. The XRD results are shown by comparing the diffraction patterns of the GO-AgNP sample and that of GO sample. Furthermore FTIR results indicate the presence of C-H alkanes, C=O bonds, and O-H bonds in the GO-AgNP samples.

Keywords: GO, GO-AgNP, AgNP, UV-Vis spectroscopy, SEM-EDX, XRD, and FTIR.

1. Introduction

Graphene is an exciting material being developed in the field of nanotechnology today. As a precursor for graphene, thin sheets of graphene oxide (GO) appeared as carbon-based nanomaterial. GO is a derived compound of graphene that contains not only carbon, but also oxygen and hydrogen. GO has also been developed for its benefits in areas such as eco-friendly paint to improve building thermal [1], transparent electrode for LEDs [2], solar cell devices [3], and biomedical especially as drug delivery material [4] and biological imaging [5]. One of the most widely studied GO applications today is the treatment of anti-bacterials [6]. This is done by using GO as a substrate or stabilizer of silver

nanoparticles (AgNP) to form AgNP/GO nanocomposites [6]. This nanocomposite uses GO that has a large specific surface area that can prevent AgNP aggregation. Silver nanoparticles have a relatively large surface area also which may increase their contact with bacteria or fungi hence increasing the effectiveness of bactericide and fungicide [7]. The synthesis of AgNP/GO or AgNP/rGO composites have been reported by several researchers. Zainy *et al*. reported a straightforward and scalable method for the preparation of high purity reduced graphene oxide/silver (rGO/Ag) composites via a rapid thermal reduction method [8]. Liu *et al*. reported that graphene oxide-Ag nanoparticle composites are synthesized through a two phase (toluene-water) process [9]. Sun and his group has prepared Ag nanoparticles/reduced graphene oxide nanocomposites by direct adsorption of performed negatively-charged AgNPs [10, 11] or in situ chemical reduction of silver salts on reduced graphene oxide sheets [12] and prepared by oxidizing pristine graphite according to the modified Hummers method [13].

Based on the unique properties of GO and AgNP, we are interested in synthesizing a mixture of GO-AgNP. In this study, GO is synthesized by mixing AgNP solution into graphite or graphite oxide material. The aim is to investigate the interaction between GO and AgNP, as well as comparing the GO and mixture of GO-AgNP produced. The method which is used to synthesize the mixture of GO-AgNP is liquid sonication exfoliation (LSE) method. In this case, GO is synthesized in liquid phase via ultrasonic waves to exfoliate graphite surfaces into graphene sheets [14]. The AgNP solution is synthesized using chemical reduction method. This method uses reducing and stabilizer agents to stabilize the nanoparticles produced [15].

GO-AgNP mixture that has been created is characterized using UV-Vis spectrophotometer, scanning electron microscope-energy dispersive X-ray (SEM-EDX), X-ray diffraction (XRD), and Fourier transform infra-red (FTIR). The characterization is conducted to compare GO material and GO-AgNP mixture and determine the effect of AgNP on the formation of GO. This study is expected to provide information in the preparation and synthesis of GO-AgNP mixture and its characterization results, which can be used as a research reference in the field of nanotechnology and can be further developed.

2. Experimental
The experimental method in this study may be explained as follows.

2.1. Preparation of the graphite solution
Graphite solution is prepared by mechanical mixing method using a blender. This is conducted as follows. 1 gram of graphite powder is dissolved into 100 ml of distilled water, and then mixed using a blender with a rotation speed of ±3000 rpm for 3 minutes. After that, the solution is stored into a sample container under room temperature. The graphite solution is obtained from carbon rods of zinc-carbon battery wastes.

2.2. Preparation and synthesis of silver nanoparticle solution (AgNP)
AgNP solution is prepared using a chemical reduction method with 1% trisodium citrate as the reducing agent [16]. To make AgNP solutions with $AgNO_3$ concentration variation of (in mM) 1, 2, 3, and 4, we start with a 4 mM titration of silver nitrate ($AgNO_3$) solution to become 3 mM and so on. Each concentration of $AgNO_3$ as much as 2 ml is heated via a heater for 10 minutes. After that, 1% trisodium citrate is added drop by drop as many as 5 drops into each solution. The solutions are further heated until they turn yellowish. The yellowish color is an indication of the presence of AgNP in the solution.

2.3. Synthesis of GO-AgNP Mixture
Synthesis of GO-AgNP mixture is conducted via the LSE method. The graphite solution is prepared into 4 separate beaker glasses, each with a volume of 50 ml. As much as 2 ml of the AgNP solutions of each $AgNO_3$ concentration is mixed with 50 ml of distilled water. Each mixture is then poured into

the 50 ml of graphite solution and gradually stirring it. Hence, we obtain a mixture, which is ready to be ultrasonicated. Ultrasonication is performed on the graphite oxide solution and the graphite oxide-AgNP mixture. The ultrasonication uses a self-custom made ultrasound generator with a frequency of 30 kHz for 6 hours. Finally, the two solutions are ready to be characterized.

2.4. Characterizations

UV-Vis spectrophotometer. The UV-Vis spectrophotometer is used to determine the absorption wavelength and peak absorbance. The wavelength ranges from 200 to 800 nm. This wavelength range is selected because the sample needs to be tested using UV light that is in the range of 200 nm to 400 nm and visible light in the range of 400 nm to 800 nm. In this study, the UV-spectrophotometer, which is being employed is Shimadzu UV-Vis 4250.

SEM-EDX. Sample characterization using SEM-EDX is done by attaching a solidified sample solution on a 1 x 1 cm^2 glass slides. SEM-EDX is performed to determine the surface morphology of GO and GO-AgNP mixture of 4 mM concentration and to determine the chemical composition found in both samples. The SEM-EDX being used is JSM-6510LA.

XRD. XRD is used to determine the crystal structure and lattice parameters of the samples. Data that are obtained from XRD characterization are diffractograms. The diffractogram shows the intensity as a function of the diffraction angle (2θ). The resulting diffractogram is then analysed by Rietica program of Le Bail method. The XRD used in this study is Rigaku Miniflex600.

FTIR. FTIR are used to determine functional groups contained in the samples by showing the graph of transmittance and wave number. FTIR is conducted for GO solution and GO-AgNP mixture. The FTIR used here is FTIR Nicolet Avatar.

3. Results and Discussion

The GO-AgNP synthesis is divided into two stages, i.e.: chemical reduction and followed by the LSE method. The synthesis of AgNP using chemical reduction method is to reduce $AgNO_3$ solution with trisodium citrate. AgNP has a characteristic of agglomeration between each other and oxidation so that in general the process of AgNP formation should also include other compounds such as stabilizers. In this study no other compounds are used because trisodium citrate can simultaneously functions as a stabilizer. The result of the reaction can be seen physically as shown in Figure 1 below. The chemical reaction of making silver nanoparticles from $AgNO_3$ with sodium citrate ($Na_3C_6H_5O_7$) is follows:

$$4Ag^+ + C_6H_5O_7Na_3 + 2H_2O \rightarrow 4Ag^0 + C_6H_5O_7H_3 + 3Na^+ + H^+ + O_2$$

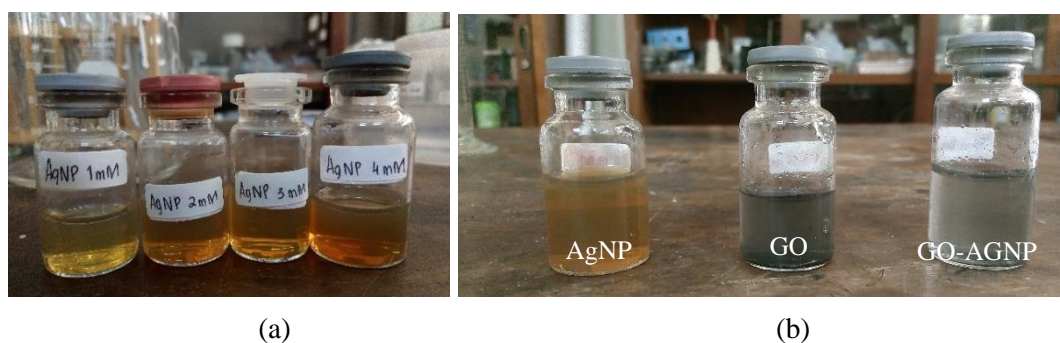| (a) | (b) |

Figure 1. Solutions produced in this study are a) AgNP solution with concentration variation of (from left to right) 1 mM, 2 mM, 3 mM, and 4 mM, and b) AgNP, GO, and GO-AgNP solutions after 6 hours of ultrasonication.

Figure 1(a) shows the color comparison of AgNP samples with concentration variation. The color difference can be seen clearly from left to right, which goes from bright to dark yellowish color. As the concentration value of the solution increases, the color of the solution also gets stronger. Figure 1(b) shows the solutions of AgNP, GO, and GO-AgNP mixture. The GO and GO-AgNP mixture have been ultrasonicated for 6 hours. The GO solution drawing from 6 hours of ultrasonication of the graphite solution shows dark grayish color, whereas the GO-AgNP mixture obtained after 6 hours of sonication resulted in a light grayish color.

In this study, samples of the AgNP solution with different concentration are tested by UV-Vis spectrophotometer to determine the presence of the AgNP materials. The UV-Vis characterization shows a relation between the absorbance and the wavelength of the tested solution.
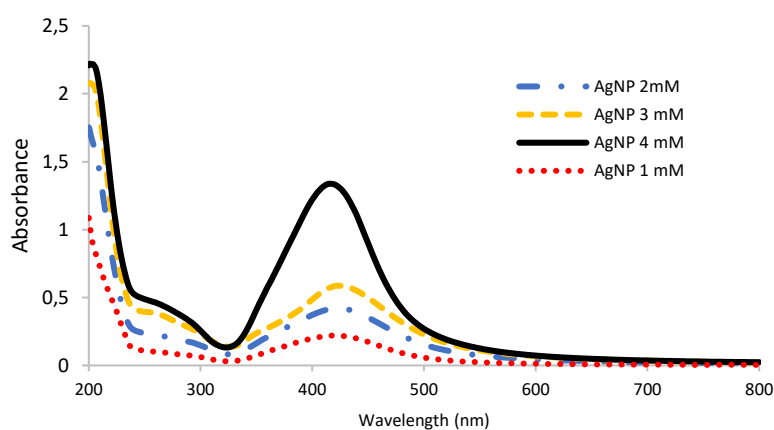

Figure 2. The absorbance spectrum of AgNP with different concentration of $AgNO_3$.

Figure 2 above is the results of the UV-Vis characterization for samples with concentration variation of the $AgNO_3$. Based on Figure 2, the four samples characterized using UV-Vis have relatively high peaks appearing at wavelengths of 423.0 nm, 423.5 nm, 417.5 nm and 415.5 nm for the $AgNO_3$ concentration of 1 mM, 2 mM, 3 mM, and 4 mM, respectively. All of the $AgNO_3$ concentrations show the formation of silver nanoparticles that has an absorbance peak at wavelengths between 410 nm to 420 nm. The graphs also show that as the concentration of the solution increases, the values of the absorbance peaks become higher. The best synthesis for the AgNP solution is obtained for $AgNO_3$ concentration of 4 mM with an absorbance peak of 1.338 at wavelength of 415.5 nm. Furthermore, UV-Vis spectrophotometer is tested also for the characterization of GO-AgNP mixture with $AgNO_3$ concentrations of 1, 2, 3, and 4 mM that have been ultrasonicated for 6 hours. This are shown in Figure 3.
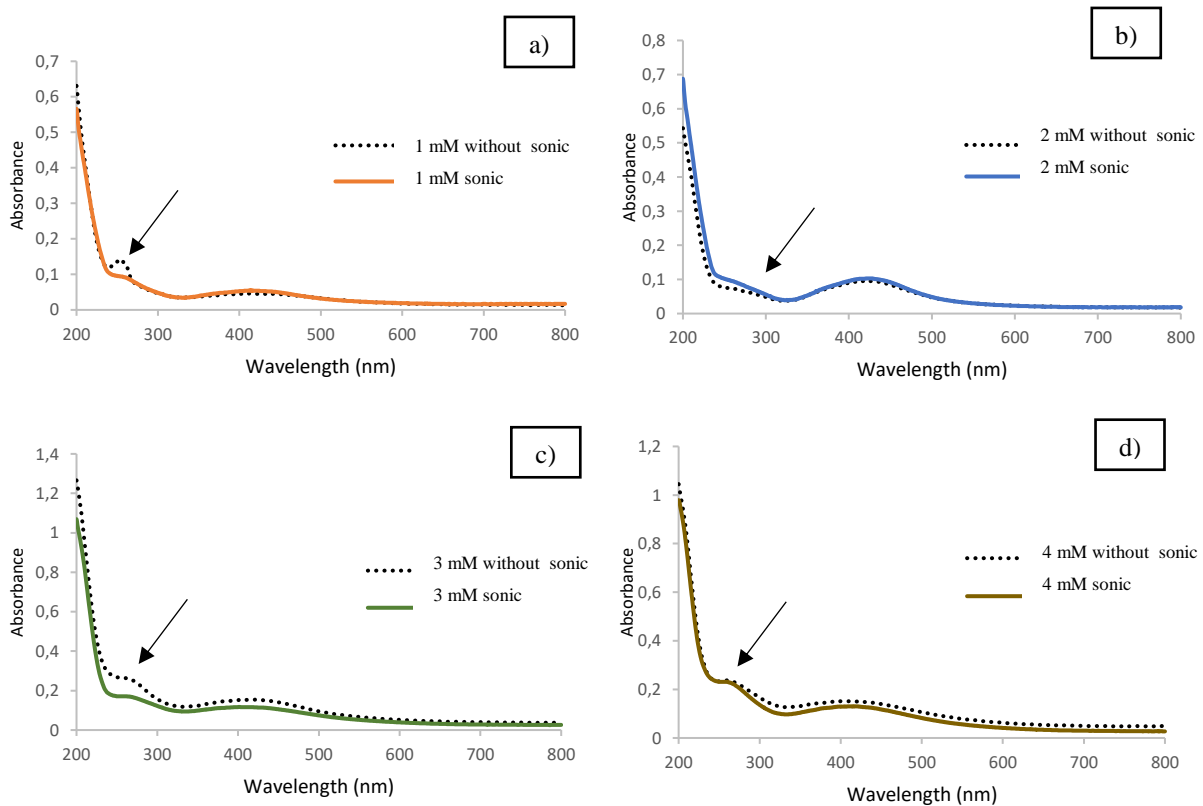
Figure 3. GO-AgNP absorbance spectrum with $AgNO_3$ concentration variation of 1 mM (a), 2 mM (b), 3 mM (c), and 4 mM, (d) with and without ultrasonication.

Figure 3 is the UV-Vis absorbance data for the GO-AgNP samples. The solid lines are mixture samples with 6 hours of ultrasonication, while the dashed line are the samples without ultrasonication. Based on the above figure, it is seen that the ultrasonic treatment of the solutions does not result in a shift in the absorbance peak, but tends to decrease the absorbance values, except for the mixture with $AgNO_3$ concentration of 2 mM. It may also be observed that the decrease of the absorbance occurs at around the wavelength of 200 nm to 300 nm, which is the location of GO absorbance peaks. Moreover, the absorbance values around the AgNP peaks seem to stay the same with and without the sonication treatment. This indicates that the ultrasonic treatment influences the GO formation, but do not alter the AgNP. The comparison of the UV-Vis results between GO and GO-Ag mixture can be seen in the figure below.
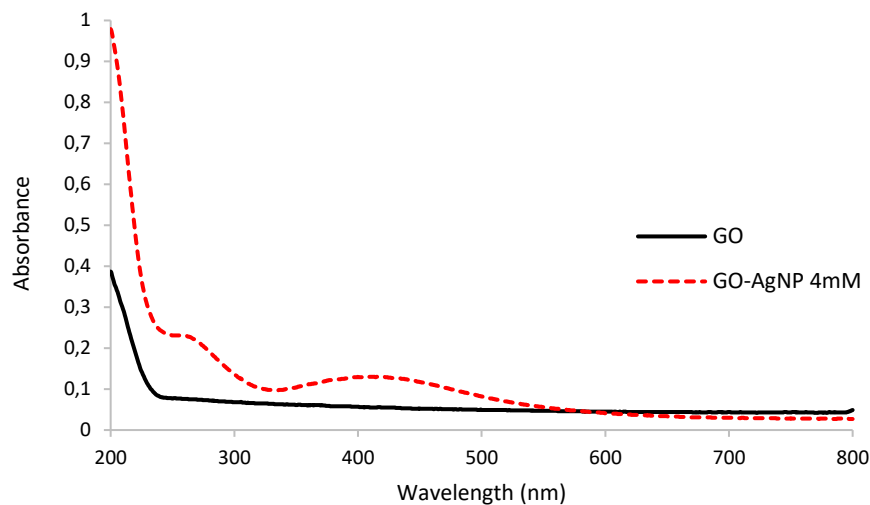
Figure 4. UV-Vis absorbance spectrum comparison of GO and GO-AgNP with 6 hours of ultrasonication.

Figure 4 shows the UV-Vis absorbance spectrums of GO sample (solid-black line) having a very weak absorbance peak at a wavelength of 252.0 nm and two strong absorbance peaks at 265.0 nm and 416.5 nm for GO-AgNP mixture with $AgNO_3$ concentration of 4 mM. This indicates a shift in the absorbance peak toward a larger wavelength or a redshift, that is from 252.0 nm to 265 nm. It also means that the mixing process of the graphite and AgNP solutions throughout the sonication process may reduce GO into rGO.

Further characterization is conducted using SEM-EDX, which produces morphological images and elemental contents of the samples. The samples characterized are GO and GO-AgNP mixture with 6 hours of ultrasonication. The SEM-EDX results can be seen in Figure 5.
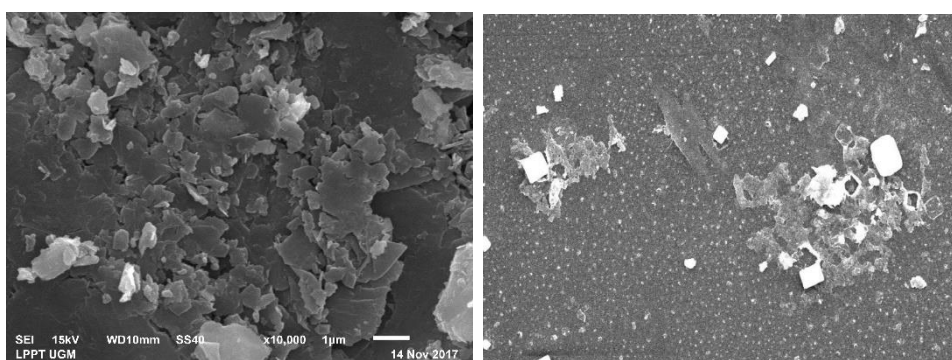
(a)   (b)

Figure 5. SEM-EDX images with 10,000X magnification for GO (a) and GO-AgNP mixture (b).

Figure 5(a) shows the presence of fairly smooth and thin sheets of materials with equal size distribution. The sheets on this SEM image indicate the presence of GO material after the sonication treatment. On the other hand, Figure 5(b) does not indicate the existence of GO-AgNP material. It also

shows no granule of silver nanoparticles occurs. This may be due to the GO-AgNP sample heating time on the glass slide which is too long so that the solution is oxidized and does not stick well to the glass. In addition, the sample forms a thin layer on the glass slide which may make the SEM to only detect a small part of the layer. The digital data from the SEM results can be further processed to obtain particle size distributions through Image-J digital data processing software. The result of image processing using ImageJ is shown in Figure 6. Figure 6 shows that the average particle diameter of GO is 62.45 nm. This shows the formation of GO particles in the range of 32 nm to 84 nm and also corresponds to nanoparticles in the size of 1 nm to 100 nm. However, the GO-AgNP sample shows the particle diameter of around 276.59 nm, which may be too large for GO or AgNP sizes.
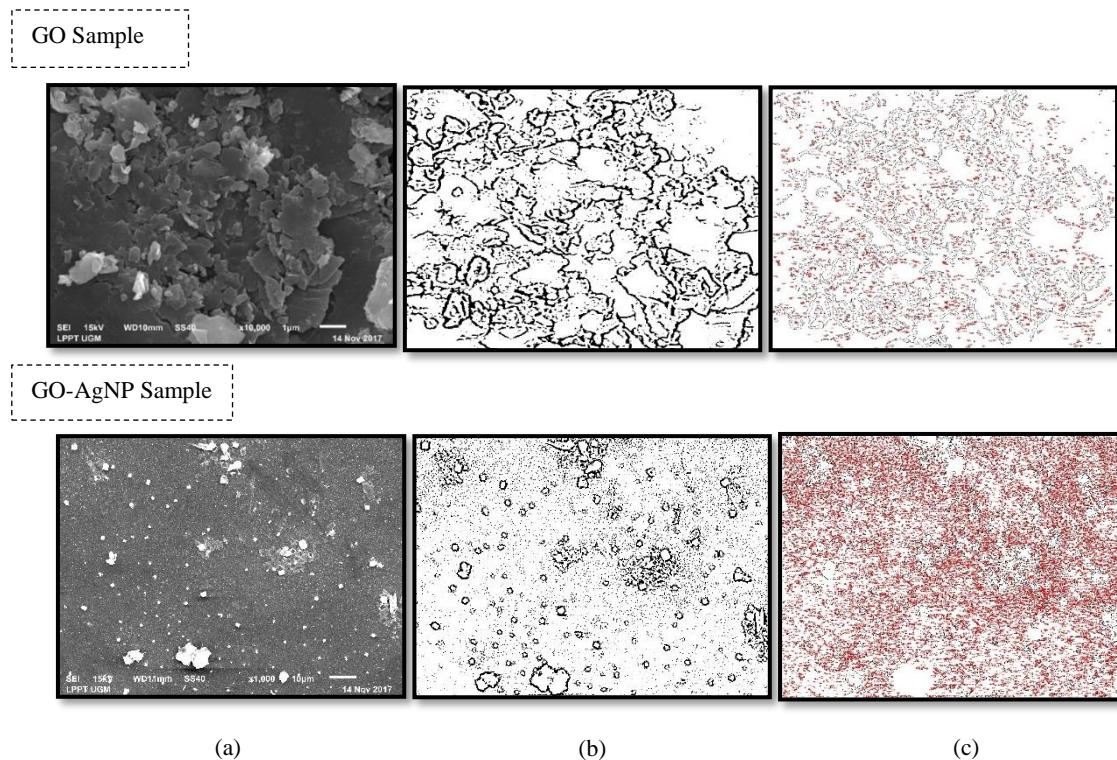

Figure 6. Results of SEM image processing using Image-J: (a) original sampling, (b) sample after threshold, and (c) sample outline image.

The EDX is used to determine the elemental contents of the characterized samples. The EDX results of the samples can be observed in Figure 7. Based on the EDX result in Figure 7(a), it can be observed that carbon element (C) has the largest atomic percentage of 72.1% in the GO sample, and follow by the atomic percentage of nitrogen (N) of 18.62%, and the atomic percentage of oxygen (O) of 7.80%. The elements of carbon and oxygen indicates further that the material is GO. On the other hand, based on Figure 7(b), the highest percentage of the atomic content is oxygen, which indicates that the main constituent of the material is in the form of oxides. This corresponds to the SEM result in Figure 5(b) which does not indicate either GO or silver nanoparticles. Hence, it may be concluded that the SEM-EDX of the sample fails to detect the presence of GO-AgNP material. As mentioned above, this may be caused by the poor preparation of the GO-AgNP sample itself for the SEM-EDX characterization.
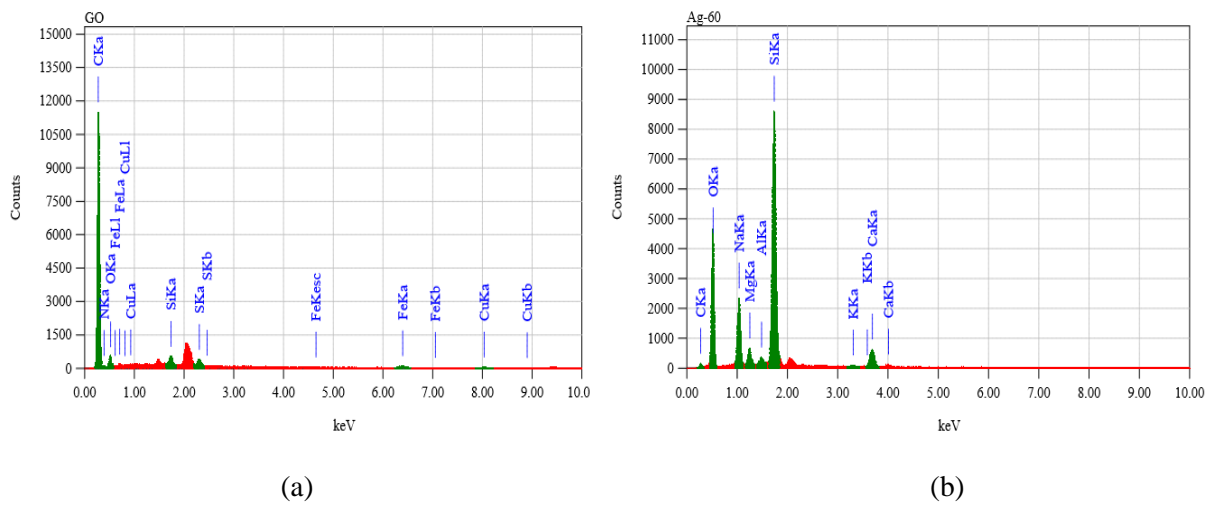
Figure 7. Graphs of EDX test results for (a) GO sample and (b) GO-AgNP sample.

The next characterization of the samples is conducted using XRD. XRD is performed to determine the crystal structure of the samples. The XRD results may be observed in Figure 8. The diffraction pattern of GO sample in Figure 8(a) produces a crystal structure with six peaks at 2θ positions of 20.78^O, 28.75^O, 35.53^O, 38.67^O, 42.32^O, and 46.89^O indicating that GO has been formed with crystal planes of (022) at an angle of 20.78^O, (221) at an angle of 28.75^O, (100) at 42.32^O, and (101) at an angle of 46.89^O. This is obtained by the qualitative matching of XRD data with the appropriate JCPDS data. On the other hand, the diffraction pattern of the GO-AgNP mixture sample in Figure 8(b) suggests an amorphous or semi-crystal structure. Moreover, it consists of a single peak at 2θ position of 24°, which is a crystal plane of (002) at a high enough intensity. Qualitatively, this shows the formation of rGO in the GO-AgNP sample. The XRD data comparison between the GO and GO-AgNP samples show a decrease in the number of peaks after AgNP solution is mixed into the graphite solution and sonicated for six hours. Moreover, the XRD pattern of the GO-AgNP sample tends to be lower and wider than the XRD pattern of the GO sample. This suggests that the insertion of the Ag atoms in the intermodal carbon bonds may destroy the van der Waals bonds so that the graphene layers become exfoliated and disconnected by the sonication and reduces the atoms in the (002) plane. The comparison between GO and GO-AgNP samples show changes in the XRD results. Overall, the peak pattern of the GO-AgNP sample produces a wide peak at an 2θ angle of 24° with a lower intensity than the GO sample.
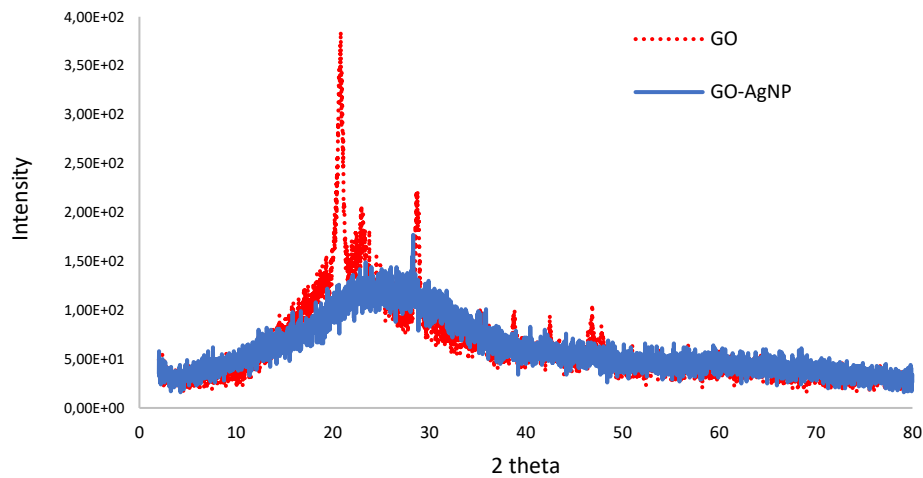
Figure 8. Diffractogram results of GO (dashed-red line) and GO-AgNP (solid-blue line) samples.

Finally, the functional groups in the GO and GO-AgNP samples can be determined using the FTIR characterization. FTIR pattern results from both samples can be observed in Figure 9. The results of the FTIR transmittance spectrum for both samples qualitatively indicate that the main functional groups identified are functional groups of C=C and O-H. The C=C functional group is bonded together and cause the formation of hexagonal structures of carbon atoms arranged into layers of GO or rGO. The O-H bond contributes to the oxides in the GO or GO-AgNP samples.
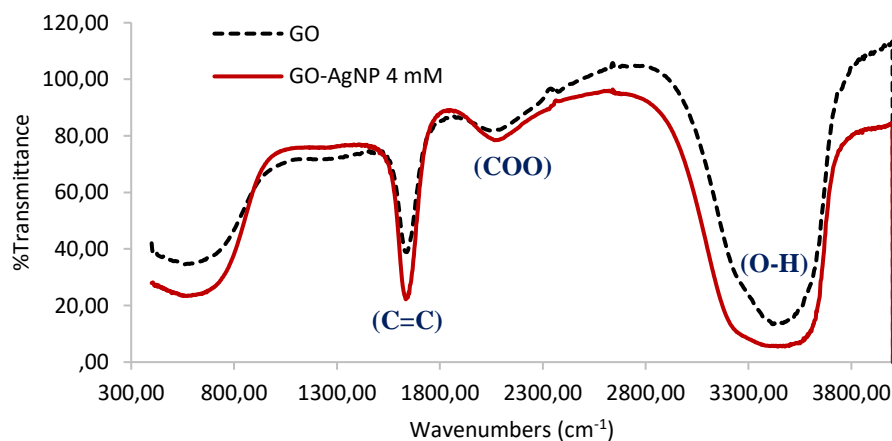

Figure 9. FTIR results for GO and GO-AgNP samples.

The FTIR spectrum result from the GO sample has transmittance peaks, which are quite identical to the FTIR spectrum result from the GO-AgNP mixture. The results of FTIR spectrum from GO and GO-AgNP samples produce O-H bond at wavenumbers of 3441.3 cm^{-1} and 3433.75 cm^{-1}, respectively, and C=C bond at wavenumbers of 1634.71 cm^{-1} and 1638.88 cm^{-1}, respectively. Furthermore, the

peaks at wavenumbers of 2066 cm^{-1} and 2055.26 cm^{-1} are areas where small transmittance peaks occur, so that COO bond is presence. It may also be observed that the values of the transmittance peaks for the GO-AgNP sample are smaller compared to the GO sample. This is expected as mixing the graphit with AgNP solutions increases the oxides and functional groups in the mixture, hence, decreasing the transmittance value at the peaks.

4. Conclusions

GO and GO-AgNP materials have been synthesized and characterized. The UV-Vis spectroscopy shows the best result for the GO-AgNP mixture is at the concentration of 4 mM with two absorbance peaks at 265 nm and 416.5 nm. The SEM images for the GO sample shows thin sheets of materials with diameters of around 62.4 nm. SEM images for the GO-AgNP sample fails to show the presence of GO and silver nanoparticles in accordance with EDX results indicating that the oxygen element has the highest percentage. However, the XRD data for the GO-AgNP sample shows the forming of reduced GO. The FTIR results show the functional groups in the GO and GO-AgNP samples, which consist of O-H bonds at wave numbers of 3441.3 cm^{-1} and 3433.75 cm^{-1}, respectively, and C=C bonds at wave numbers of 1634.71 cm^{-1} and 1638.88 cm^{-1}, respectively.

5. Acknowledgement

6. References

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