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Synthesis and Characterization of Hybrid Graphene Oxide/Gold Nanoparticle

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Abstract. Nanostructures has been recognized in achieving high level of functionality for not be able to reach from bulk materials. However, hybrid nanostructured materials have proven that it can increase these functionalities such as reactivity and conductivity through improvement of chemical, physical and environmental stability. The objectives of this research are to understand the synthetization method of hybrid GO/Au nanoparticles and analysis of characteristics of GO/Au nanoparticles based on its thermal degree, morphology of size and molecular bonding. GO/Au nanoparticles has been synthesis using one-step synthesis method from GO and Au as precursors where GO is synthesis using Hummer's method. Synthesizing of GO/Au nanoparticle required sodium citrate as stabilizing agent. A mixture of GO/Au is sonicated in sonicator for 2 hours then dried in an oven for 2 hours before centrifuging it at 700 rpm for 6 mins and dried it in an oven overnight will gives powder GO/Au hybrid nanoparticles. The synthesized nanoparticles are further characterized using UV-VIS, TGA, FTIR and FESEM analysis. UV-vis analysis peak absorbance of GO at 255 nm with 2.612Au and GO/Au nanoparticles at 320 nm with 2. 569Au. Thermogravimetric analysis result shows both GO and GO/Au nanoparticles shows that there is significant weight loss in GO as compared to GO/Au nanoparticles. FTIR analysis result shows GO and GO/Au nanoparticles have same phenols and alcohols functional group with different % transmittance. As for GO, carboxylic functional group is presence with C=O bonding as carbon and oxygen exist in GO sample. This is supports by EDX analysis showing that carbon element in GO is 61.26 weight % and oxygen is 38.47 weight %. Whilst in GO/Au nanoparticles, alkynes functional group is presence with C≡C bonding stretch. This is supports by EDX analysis showing gold element is higher than carbon element at 53.06 weight % and 35.92 weight % respectively. FESEM analysis showed that wrinkle formation occurred in GO where it shows surface morphology of GO. However, using hummer's method, GO produced have even wrinkle formation on the plane. As for GO/Au nanoparticles, FESEM analysis shows that gold particle is evenly distributed on GO nanosheets with approximate diameter of 14 nm ± 1 nm.

INTRODUCTION

Graphene is one of the allotropes for Carbon element along with Diamond and charcoal, exist in sp^2 hybridized monolayer of carbon atoms have honeycomb lattice structure arrangement has been recognized as well-diverse material due to its properties[1], [2]. Due to its crystallographic, electronic and chemical structure, graphene conveys an extraordinary both in mechanical and electronic properties. Its mechanical properties includes high thermal conductivity (25 times of silicon) [3], high mechanical strength (strongest nanomaterials measured with tensile strength of 130 GPa and Young's Modulus of 1TPa[4], [5].

Graphene can be extract using various method such as graphite exfoliation and chemical vapor deposition(CVD) [6], [7]. In this report, synthesizing of graphene will be using CVD method. However, these properties can be further improved by studying modification of surface corrugation of graphene. Common surface corrugation for graphene

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consist of wrinkled, rippled and crumpled. These types of corrugation improve particular properties based on their aspect ratio, physical dimension, topology and order[8].

GO preparation is done using Hummer's method years ago[9] and several modified Hummer's method[10]. Common preparation of oxidation of graphite are using several chemical reagents such as KNO3 KMnO4 NaNO3 and H2SO4. Resulted materials is then exfoliating in water using mechanical energy. Huang and colleagues[11] have standardised and improved method of high yield synthesis of pristine GO nanosheets using modified Hummer's method. This is from the basis chemical reagent used is KMnO4-H2SO4, where KMnO4-H2SO4 is cut larger nanosheets of GO into smaller nanosheets continually. The GO nanosheets sample is then can be reduced into reduced GO by using chemical reducing agent or other method such as thermal annealing[12]. This method would produce unique properties of reduced GO in which sustainable in application such as biomedicine, bio-imaging and bio-sensing[13]. Reduced GO has significant functional group that can be further analysed which enable easy surface modification to be done. This is important as reduced GO is more valuable than other carbon materials. This is proven by research that fully oxidized GO can act as insulator, while semi oxidized GO act as semiconductor[14]. Other than that, a functionalized GO can be apply in interfacial polarization, in which has improved dielectric constant as this property is important in the application of capacitors[15].

METHODOLOGY

Preparation of Graphene Oxide/Gold Nanoparticles

During this experiment, 230 ml of concentrated H_2SO_4 was poured into a flask and cooled to $0^{O}C$ using ice bath. Graphite powder of 10g and potassium nitrated(KNO_3) of 5g were added into the flask gradually while stirring H_2SO_4 using magnetic stirrer. Temperature of mixture is increased to $20^{O}C$ and 30g of potassium permanganate ($KMnO_4$) is added into the flask. The flask is then placed into water bath at temperature of $35^{O}C$ and stirred for 2 hrs until thick paste is formed. Subsequently, deionized water of 230 ml is slowly added into the mixture while the temperature is maintained at $98^{O}C$ for 30 mins. The mixture is then diluted with warm deionized water of 1.4 L. In order to reduce residual permanganate and manganese dioxide in the mixture, 30% of H_2O_2 is added into the mixture. A deep brown slurry from treating method is taken in dialysis membrane and was dialyzed using distilled water for 7 days. Further method of exfoliation is done using ultra sonification for 1 hr. Any un-exfoliated GO layers are then removed using centrifugation method at 4000 RPM in 10 mins. A GO liquid is obtained after the centrifugation.

Homogenous GO of aqueous dispersion using 1mg/ml was prepared by sonication method of solid 20mg GO in deionized water for a duration of 30 mins. 40 ml of GO with 1 mg/ml is added to 200 ml of $HAuCl_4$ at 0.06mg with 0.01 M concentration. A mixture of GO/Au is sonicated in sonicator for 2 hours. This procedure is done to promote interactions between GO and Au nanoparticles. 8 ml of sodium citrate is added into sonicated GO/Au solution during stirring of GO/Au solution at 300 rpm. GO/Au solution is then kept in the oven for a duration of 2 hours. The solution is then taken out and centrifuged at 7000 rpm for 6 mins. The solution that has GO/Au precipitate is wash in water and then disperse in ethanol solution. GO/Au nanoparticles is then dried in the oven at $60^{o}C$[16].

RESULT AND DISCUSSION

UV–Visible spectroscopy Analysis

Figure 1 shows a graph of uv-vis for both graphene oxide (GO) and graphene oxide/gold nanoparticles (GO/Au). It is found that GO has 2.612 absorbance at 255 nm while GO/Au has 2.569 absorbance at 245 nm. This shows that the presence of GO in GO/Au. During the analysis, the spectrum found to have spikes that shows several peaks, however, most noticeable absorption peak is at 225 nm. This corresponds to several π-π^* transition of aromatic C-C bonding and π-π^* transition of C-O bonding respectively[17]. In GO/Au spectrum, initial peak was at 250 nm which then shifted to 245 nm shows the absorption for GO. Further absorption for GO/Au happen at peak 320 nm where it shows the formation of AuNPs from plasmon resonance process[18].

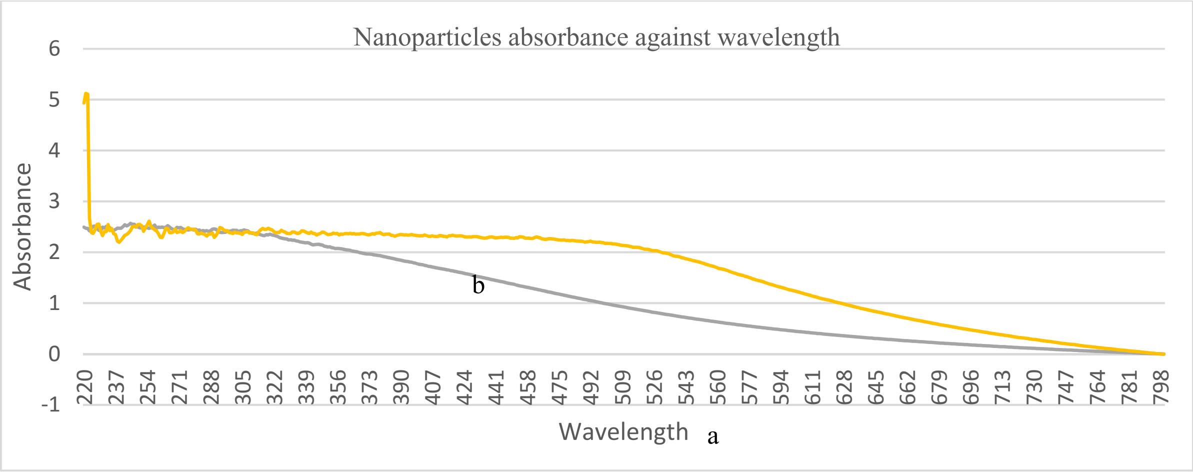


FIGURE 1: UV–Visible spectroscopy of a) Graphene oxide b) Graphene oxide/Gold nanoparticles

Thermogravimetric Analysis

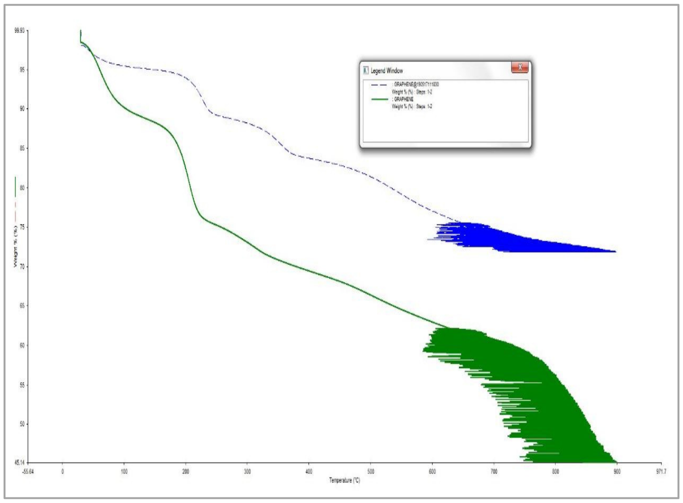


FIGURE 2: Thermogravimetric analysis curve of a) Graphene Oxide b) Graphene oxide/Gold Nanoparticles

Thermogravimetric analysis is done to determine curves for thermal stability of a compound. Thermogravimetric analysis is done using parameters of temperature up to 900^{o}C with a ramping rate of 10^{o}C /min under flows of pure nitrogen gas with 20ml/min flowrate. The holding rate for thermogravimetric analysis is at 30^{o}C for 5 mins as a pre-analysis condition. FIGURE shows thermogravimetric analysis curves for both GO and GO/Au nanoparticles. It is observed that GO has significant weight % loss at 100^{o}C, 200^{o}C and 300^{o}C as compared to Go/Au nanoparticles. GO sample shows 10% loss in weight % compare to GO/Au nanoparticles. This is because of the carbon element presences in GO is higher than in GO/Au nanoparticles. As for thermogravimetric analysis for both GO and GO/Au nanoparticles, GO/Au shows high thermal stability, stemming deoxygenation from the reduction process[18].

Fourier transform infrared (FTIR) Analysis

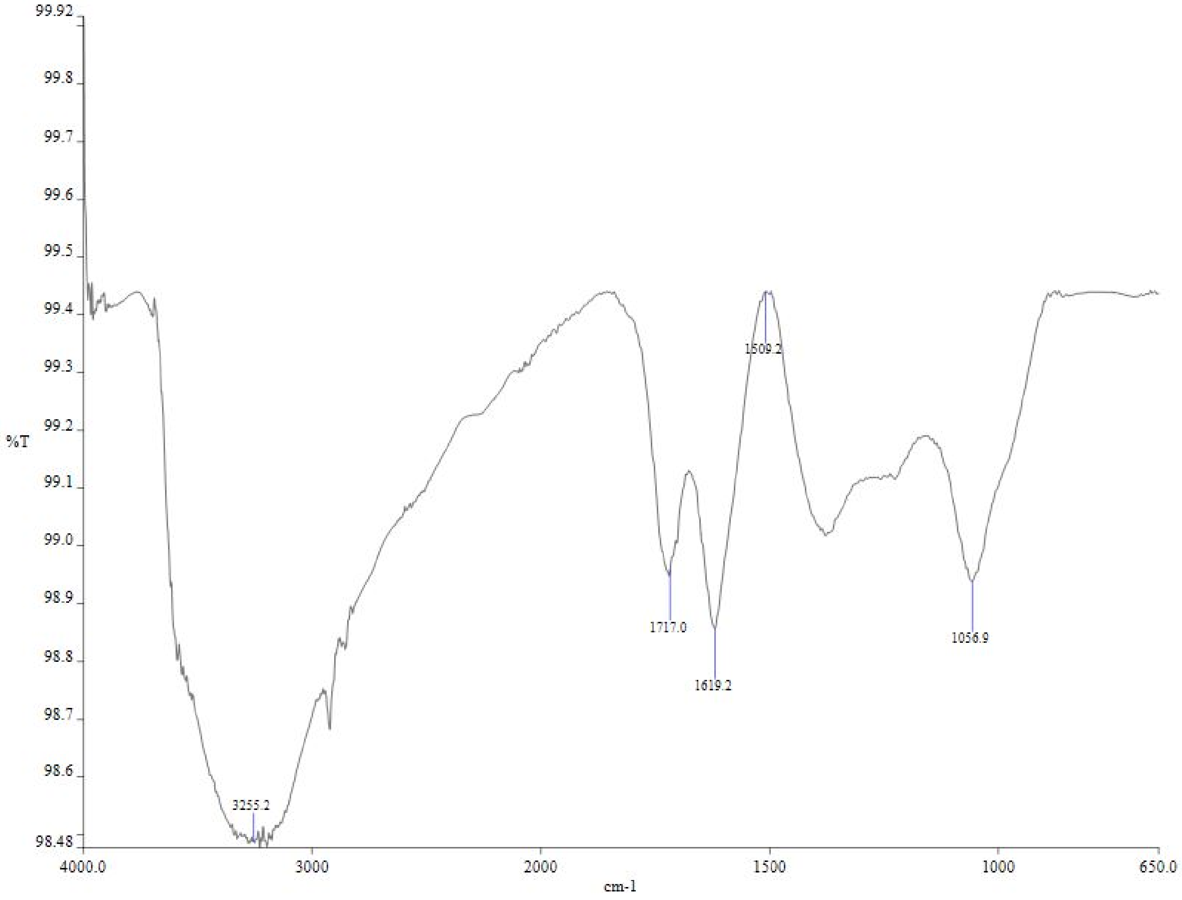


FIGURE 3: FTIR spectrum of Graphene oxide

Figure 3 shows FTIR spectrum for Graphene oxide (GO). FTIR analysis is used to determine the functional group for GO sample prepared. It is observed at ~3255.2 cm-1 that there is strong absorption due to O-H bonding stretching cause from vibration[19]. This shows the functional group of phenols and alcohols. Proving that wavelength number of ~3255.2 cm-1 belongs to phenols and alcohols, their peaks usually appear much broader than other infrared absorptions[19]. The C=O bonding stretch appears in ~1717 cm-1 and ~1619.2 cm-1. Both C=O bonding shows the presence of carboxylic acid and amides functional group respectively. At ~1509.2 cm-1 wavelength number, the functional group is amines-secondary with N-H bending type of vibration which change the angle between N-H bond. Wavelength number of ~1056.9 cm-1 shows the functional group of ethers with C-O stretch.

Figure 4 shows FTIR spectrum for Graphene oxide/Gold nanoparticles. At wavelength number of ~3314.6 cm-1, the functional group is phenols and alcohols with O-H bonding. Differ from infrared spectrum of O-H bonding in FIGURE , the absorption is lower in GO/Au compared to GO sample. This shows the intensity of O-H bonding in GO/Au is lower than in GO[20]. Functional group of alkanes presence at peak ~2989.6 cm-1 with H-C-H bonding at symmetric stretch vibration. The absorptions in this region can be observed to have several peaks as shown in FIGURE . At wavelength number of ~2167.8 cm-1, a functional group of alkynes presence with triple bond of C≡C stretch while at 1497 cm-1, functional group presence amines-secondary with N-H bend bonding. Similar at peak ~3314.6 cm-1, N-H bond in ~1497 cm-1 has low %transmittance in GO/Au spectrum as compared to GO spectrum. However, both spectra curves indicate the same intensity of infrared absorption. At ~1299.6 cm-1 and ~1044.6 cm-1 wavelength number, both have same ethers functional group with C-O stretch[19].

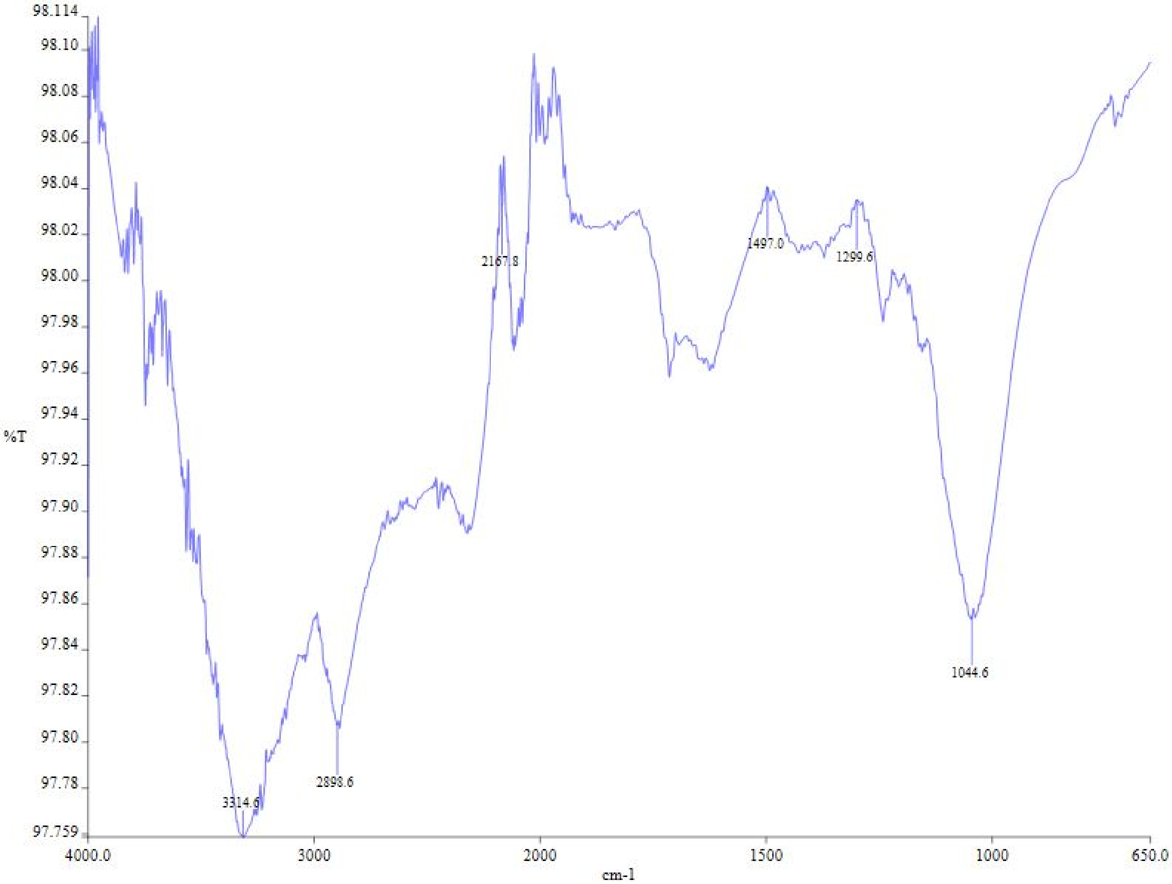
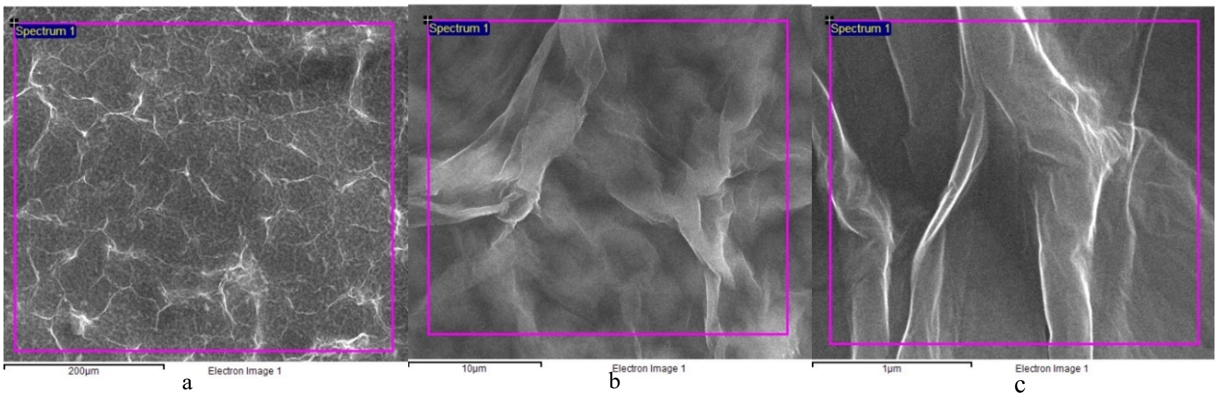


FIGURE 4: FTIR spectrum of Graphene oxide/Gold Nanoparticles



a b c

FIGURE 5: FESEM images of Graphene oxide at a) 200µm b) 10µm and c) 1µm

Field emission scanning electron microscopy (FESEM) Analysis

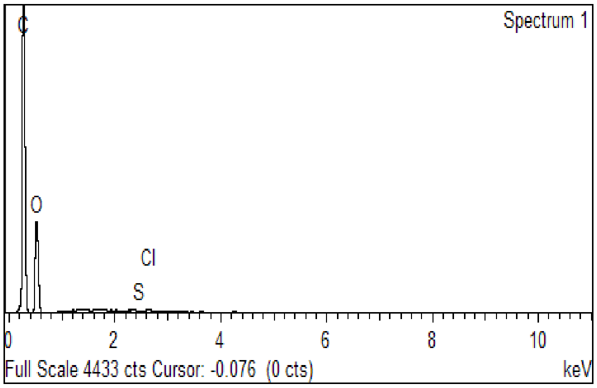


FIGURE 6: EDX spectrum of Graphene oxide

TABLE 1: Composition of element in graphene oxide

Element	Weight%	Atomic%
C K	61.26	67.89
O K	38.47	32.01
S K	0.10	0.04
Cl K	0.18	0.07
Totals	100.00	

Figure 5 shows FESEM images of graphene oxide on the device at 600 x magnification. The working distance is approximately at 9.5 mm in high vacuum mode at 20 kV. It is observed that wrinkled GO formation occurred in GO. This supports that surface morphology occurred during the synthesizing of graphene oxide. The high degree of exfoliation could be attributing to high degree of functionality on the basal plane where this would prevent of stacking layers[21]. From the image in Figure 5c, wrinkle GO shows an even formation through out the layer. It can be visualized that GO layer have enough number of carboxylic groups at the edges, leaving graphene sheets with minimal functionality at the basal plane in which allowing for π-π bond to stacks and forming multilayer sheets[22]. Figure 6 shows EDX spectrum of GO with 3 number of iteration analysis. With carbon element presence at the highest weight % at 61.26 and oxygen element at 38.47 weight %. However, the presence of Sulphur, S element and Chlorine, Cl element are from the measurement standards.

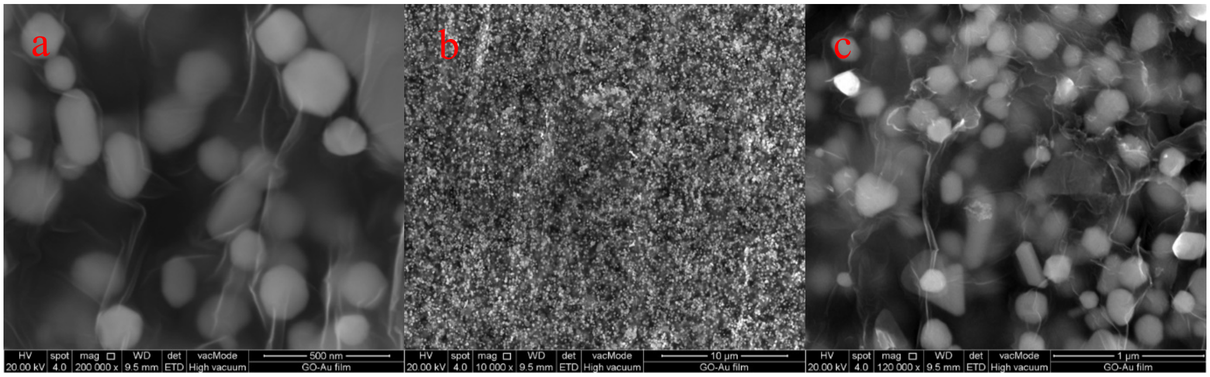


FIGURE 7: FESEM images of Graphene oxide/Gold nanoparticles at a) 200μm b) 10μm and c) 1μm

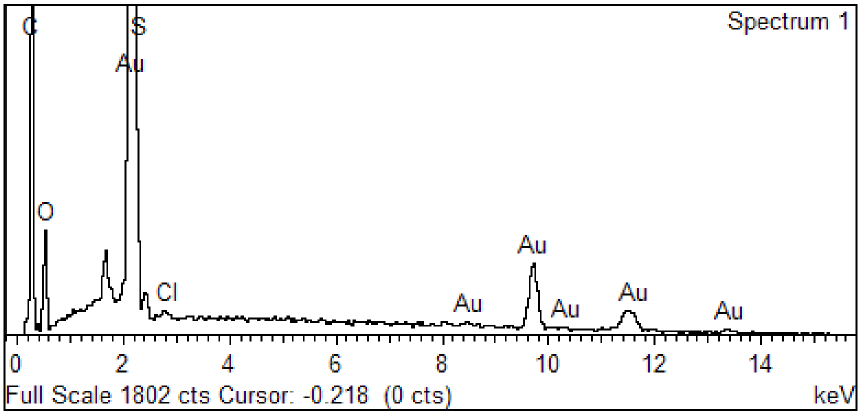


FIGURE 8: EDX spectrum of Graphene oxide/gold nanoparticles

TABLE 2: Composition of element in graphene oxide/gold nanoparticles

Element	Weight%	Atomic%
C K	35.92	75.94
O K	10.68	16.95
S K	0.35	0.27
Cl K	0.00	0.00
Au M	53.06	6.84
Totals	100.00	

Figure 7 shows FESEM images of graphene oxide on the device at 600 x magnification. The working distance is approximately at 9.5 mm in high vacuum mode at 20 kV. It is observed that drying method for GO/Au is affecting its structure. Using hydrothermal method for drying GO/AU, a GO nanosheets with decorated Au are produced. From the FIGURE c, it is observed that Au is evenly distributed on GO nanosheets during one step synthesis of GO/Au[13]. However, the result from using conventional oven in one-step synthesis is, GO nanosheets formation occurred in wrinkle formation. The average diameter of Au nanoparticle in GO is 14 nm ± 1nm. These images show the successful of GO preparation, its reduction preparation and synthesizing of GO/Au hybrid nanoparticle. From EDX curve for graphene oxide/Au nanoparticle in Figure 7 with support value in TABLE 2, it is known that carbon element is reduced from 61.26 weight % to 35.92 weight %. Whilst oxygen also reduced from 38.47 weight to 10.68 weight %. In the meanwhile, there is presence of Au with interval of 2 KeV in the spectrum and 53.06 weight %. This proves that Au is Au is synthesis in GO structure.

CONCLUSION

Synthesizing of GO/Au nanoparticle using one step synthesis method using GO and Au as precursor which Go prepared from hummer's method. Produced in highly stable time colloidal suspension, GO/Au nanoparticles is synthesis using chloroauric acid ($HAuCl_4$) and sodium citrate as stabilizing agent for the nanocompound. Improved method of using oven for 2 hours help increase synthesizing GO/Au nanoparticle before centrifuging it at 700 rpm for 6 mins. Powder of GO/Au nanoparticles is obtained from drying in conventional oven at 60 °C. UV-vis analysis shows the peak absorbance of GO at 255 nm with 2.612Au and GO/Au nanoparticles at 320 nm with 2.569Au.

Thermogravimetric analysis for both GO and GO/Au nanoparticles shows that there is significant weight loss in GO as compared to GO/Au nanoparticles.

Using FTIR analysis, showing the presence of functional group in both GO and GO/Au nanoparticle. FTIR analysis showed GO and GO/Au nanoparticles have same phenols and alcohols functional group with different %transmittance. As for GO, carboxylic functional group is presence with C=O bonding as carbon and oxygen exist in GO sample. This is supports by EDX analysis showing that carbon element in GO is 61.26 weight % and oxygen is 38.47 weight %. Whilst in GO/Au nanoparticles, alkynes functional group is presence with C≡C bonding stretch. This is supports by EDX analysis showing gold element is higher than carbon element at 53.06 weight % and 35.92 weight % respectively. FESEM analysis showed that wrinkle formation occurred in GO where it shows surface morphology of GO. However, using hummer's method, GO produced have even wrinkle formation on the plane. As for GO/Au nanoparticles, FESEM analysis shows that gold particle is evenly distributed on GO nanosheets with approximate diameter of 14 nm ± 1 nm.

The synthesis method in this study represent highly efficient procedures, with good characterization of GO and GO/Au nanoparticles. Due to sample produced along with the analysis, further research can be done using hybrid nanoparticle such as GO/Au nanoparticles in electrical properties and thermal conductivity and stability properties. This work paves a new method of transformer oil fabrication where hybrid GO/Au nanoparticles is added into mineral oil to increase its performance based on its high thermal conductivity and high electron mobility. Fully decorated AuNPs on GO shown in FESEM analysis promising a high technological advancement for both GO and AuNPs synthesis based on its high-quality graphene with controllable morphology of size and distribution of AuNPs on graphene sheet.

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