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Short Communication

Study on Electrical Conductivity of Graphene Oxide Decorated with Silver Nanoparticle for Electrochemical Sensor Development

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This research aims to characterize the conductivity of synthesized silver-decorated with graphene oxide (Ag-GO) as a new material that offers better performance in electrochemical sensors. Graphene oxide (GO) was produced using a modified Hummer's method and then decorated with silver nanoparticles to produce Ag-GO. The samples were analyzed using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive Spectroscopy (EDS), X-Ray Diffraction (XRD) and Raman analysis, while conductivity was calculated using impedance spectroscopy. The FESEM imagery showed the difference in the structure between GO and Ag-GO, with the Ag-GO presenting white particles on top of the GO structure. The presence of these particles was confirmed by the EDX spectra, which also showed the weight percentages of the silver nanoparticles. The XRD spectra demonstrated the crystallinity of the sample before and after the silver nanoparticles were added to the GO. Raman spectroscopy revealed detailed information on the samples with the appearance of the 1578 G band and 1342 D band of GO. Finally, the conductivity increased to 3.67 x 10-10 S cm-1 when 60 mg of silver nanoparticles were added to the samples.

Keywords: graphene oxide, modified hummer's, silver nanoparticles, electrical conductivity

1. INTRODUCTION

Graphene is the basic building block of 0D fullerene, 1D carbon nanotubes and 3D graphite, which has a unique planar structure. Graphene has successfully being employed in the development of

new biosensors as it is a carbon material with a honeycomb structure with a one-atom thickness. Graphene has excellent properties, including high electrical conductivity, high surface area properties, and other unique mechanical and electronic properties [1], making it suitable for use in electrochemical applications. During electrochemical applications, electron transfer can be achieved between the graphene and biological elements, such as enzymes, thus benefitting enzyme-based sensor development. Graphene also has good mechanical properties, allowing it to be used as a nano-scale filler in polymer nano-composite technology for gas molecular barrier applications [2].

In order to detect biological analytes, enzymatic electrochemical biosensors work by immobilizing enzymes on the electrode surface and measuring them based on the loss or gain of electrons through oxidation and reduction reactions, also known as the electrochemical redox process [3]. According to [4], graphene and graphene-related materials can be used to manufacture biosensors for the detection of glucose, bacteria, DNA and biomarkers relevant to cancer.

Graphene has attracted widespread interest as researchers have attempted to enhance its properties and characteristics with the aim of upgrading devices. This is due to graphene's considerable potential use in many applications, including in electronic devices, energy storage and conversion, e.g. solar cells, and others [5-8]. The graphene family includes members such as reduced graphene oxide (rGO), graphene oxide (GO) [5], graphene sheets and layered graphenes. Chemical vapor deposition and mechanical and chemical methods are the most popular methods to synthesize GO. Organic solvents can exfoliate graphite to form GO in a manner that is different from dispersion, with different long-term stability and a single-layer thickness [9].

In recent years, graphene-related materials have opened new avenues for novel hybrid materials with great potential for the detection of several clinically relevant biomarkers, such as glucose, bacteria, DNA and cancer-relevant biomarkers. Silver has great potential for use in such hybrid materials due to its unique characteristics, including high electrical and thermal conductivity and antimicrobial activity. However, silver nanoparticles can easily undergo agglomeration as they are unstable when isolated due to the small particle size. To avoid this, silver can be hybridized with graphene-related materials, thus improving the growth of the nanoparticles.

In this paper, graphene oxide (GO) and silver-decorated with graphene oxide (Ag-GO) are prepared using the chemical reduction method and the resulting material's electrical conductivity is tested using impedance spectroscopy.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Graphite powder was obtained from Sigma-Aldrich (USA), potassium permanganate powder and sulfuric acid were purchased from R & M Chemical, silver nitrate was bought from Synerl, sodium hydroxide was purchased from Merck (Germany), and ethanol was purchased from John Kollin Chemical.

2.2. Preparation of graphene oxide by a modified Hummer's method

GO was synthesized using a modified Hummer's method. First, 1.049 g graphite powder and 3.062 g potassium permanganate powder were weighted at a 1:3 ratio and mixed in 80 mL sulfuric acid. The solution was then stirred with a magnetic stirrer for 3 hours at a constant 50℃. Next, the solution was left at room temperature before adding 50 mL deionized water and stirring for 15 minutes. The mixed solution was then quenched for 15 minutes in an ice bath. The solution was centrifuged at 6000 rpm for 15 minutes with 20 ml distilled water; then, ethanol and hydrochloric acid were added until normal pH was achieved. Finally, the solution was dried in an oven at 110℃ for 24 hours to produce GO powder.

2.3. Silver nitrate decoration on graphene

3ml of Tollen reagent and 0.1 g of silver nitrate was mixed with GO suspension. Next, the mixed solution was stirred for 1 hour in room temperature. The mixture left undisturbed for 24 hours before centrifuging and washing with deionized water [10].

2.4. Preparation of thin film

Three types of thin film were prepared, namely poly(methyl methacrylate) (PMMA), poly(methyl methacrylate)-GO (PMMA-GO) and poly(methyl methacrylate)-GO-silver (PMMA-GO-Ag). First, the PMMA thin film was prepared by adding 1 g PMMA to 40 mL acetone. Next, the solution was stirred at 220 rpm for 3 hours before drying at room temperature overnight. The PMMA-GO thin film was prepared by adding 0.05 g GO powder to 40 mL acetone and then stirring for 15 minutes or until all the GO was dispersed. Then, 1 g PMMA was added to the solution and stirring was continued for 3 hours, after which the dispersion was transferred into a petri dish. The solution in the petri dish was left at room temperature to dry overnight. This step was repeated for the PMMA-GO-Ag thin film using a different weight of Ag-GO powder range from 20 – 60 mg produced in section 2.3.

2.5. Testing methods

The morphologies of the GO and Ag-GO were analyzed using Field Emission Scanning Electron Microscopy (FESEM) and Energy-Dispersive X-ray Spectroscopy (EDS). The measurements were conducted at magnifications of 1.0 kx, 10.0 kx, 20.0 kx and 50.0 kx with an accelerating voltage of 1.0 kV. EDS receives x-rays from the surface of the sample when the beam passes over it, thereby providing qualitative and quantitative analytical information at the selected point or area on the sample surface. Meanwhile, X-Ray Diffraction (XRD) patterns were obtained using Cu Kα radiation with a step size of 0.02° and a scanning step time of 2Θ to identify the composition of the sample. Next, the samples were tested by Raman spectroscopy using laser excitation at 514 nm. Finally, impedance spectroscopy was used to measure the electrical conductivity of the thin film.

3. RESULTS AND DISCUSSION

3.1. FESEM and EDS

The FESEM images of the surface morphology of GO are shown in Figure 1. The multilayer structure of GO in particular can be observed in Figure 1d. The GO is dispersed throughout the image for all magnifications. The working distance is approximately 3.8 mm in the high vacuum mode with 1.0 kV. In addition, the morphology of the GO structure shows large agglomerates stacking with each other at 1.00 kx magnification. The FESEM images clearly show that the surface of GO is free from any particles.

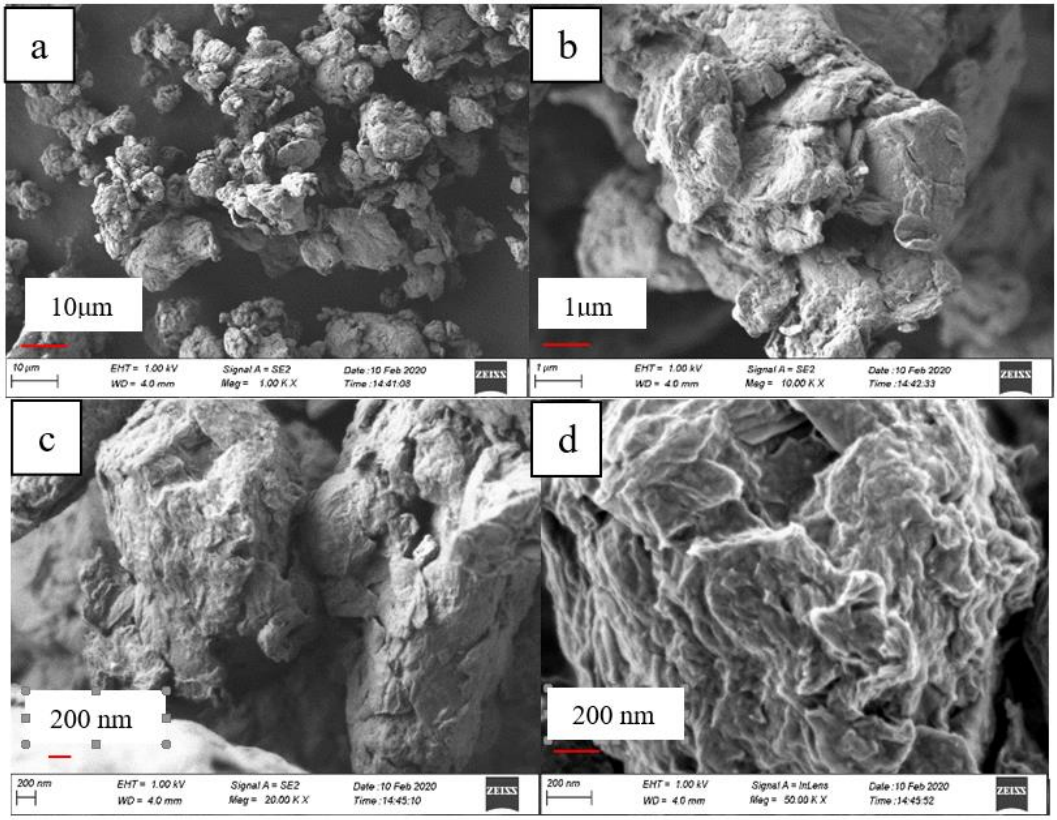

Figure 1. FESEM image of GO at **(a)** 1.00 kX **(b)** 10.00 kX **(c)** 20.00 kX **(d)** 50.00 kX

The presence of carbon particles in the synthesized GO is confirmed in the EDS spectrum presented in Figure 2. Carbon has the highest atomic percent, at 75.4%. Furthermore, the EDS spectrum shows a strong carbon peak, which is in agreement with the high percentage of carbon in GO. However, a sulfur peak can also be detected, which is thought to be from unsettled washing during the reduction process as sulfuric acid was used in the graphite powder synthesis.

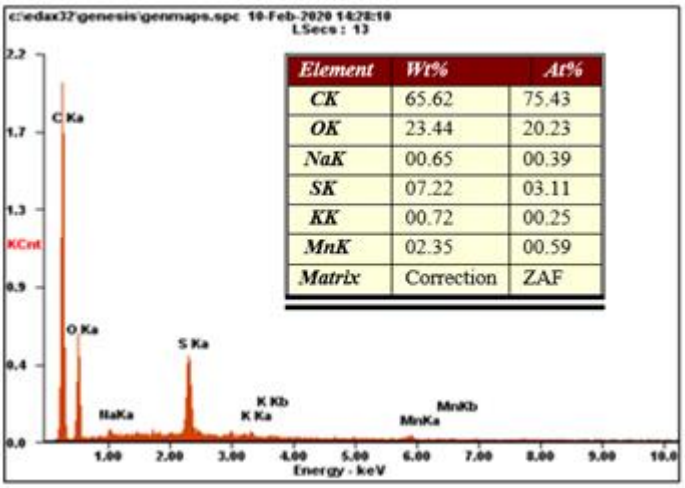

Figure 2. EDS analysis of GO.

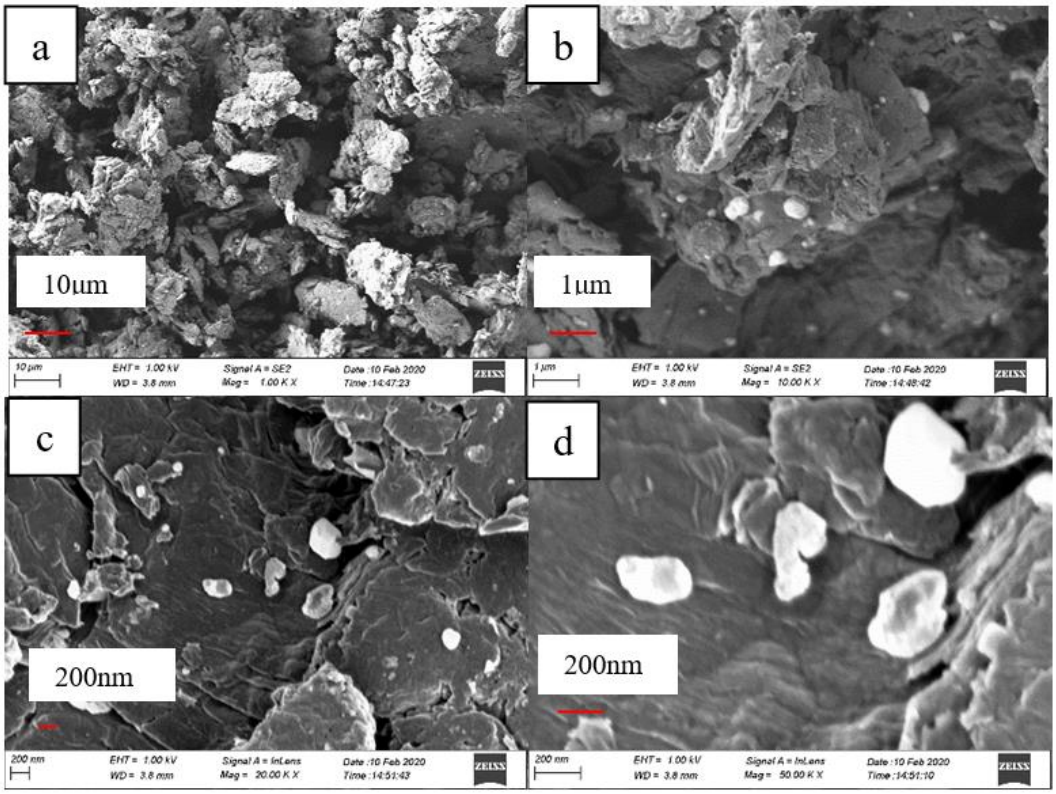

Figure 3. FESEM images of GO decorated with silver at **(a)** 1.00 kx, **(b)** 10.00 kx, **(c)** 20.00 kx, **(d)** 50.00 kx.

The FESEM images of the surface morphology of GO decorated with silver nanoparticles are shown in Figure 3. The working distance is approximately 3.8 mm in the high vacuum mode with 1.0 kV. White particles can be clearly seen in the FESEM imagery; these represent the silver that was decorated onto the GO. The average size of the silver particles is 229.8 nm when calculated using Image

J software. The mapping and EDS analysis of the samples, presented in Figure 4, demonstrate that the white particles are silver.

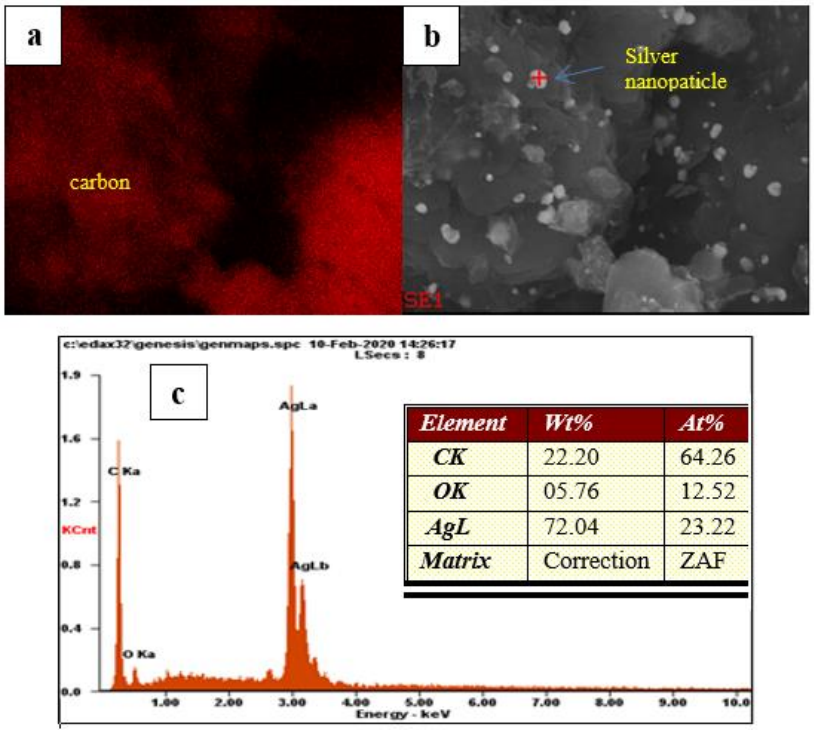

Figure 4. (a) EDS mapping of Ag-GO, (b) silver on GO, and (c) EDS analysis of Ag-GO.

The EDS spectra reveal peaks of silver when the electron beam is focused on the white nanoparticles. The weight percentage of silver is 72.0%. The EDS spectrum also reveals carbon and oxygen, as shown in Figure 4(c). EDS mapping was performed to identify the elementary component of the white particles, and the red dot shown in Figure 4(a) represents the silver (Ag) elements. It is thus confirmed that the white particles visible in the FESEM images are silver nanoparticles.

3.2. XRD

An XRD graph is crucial to obtaining and analyzing the detailed structure of crystalline materials. Figure 5 shows that the XRD patterns for GO and Ag-GO are slightly different, whereby the diffraction pattern of GO exhibits a peak at 10.0° (002), while Ag-GO shows a sharp peak at 37.8°, corresponding to the Ag crystal plane (111). In [11], a sharp peak of GO was observed at around 11.7°, corresponding to the (001) plane, indicating the successful preparation of GO in this study that also matches the reference data. This is followed by another sharp peak at 26.4°. From the calculation, the crystallite size of GO is 148.8 μm, while the crystallite size of a silver particle is 229.8 nm.

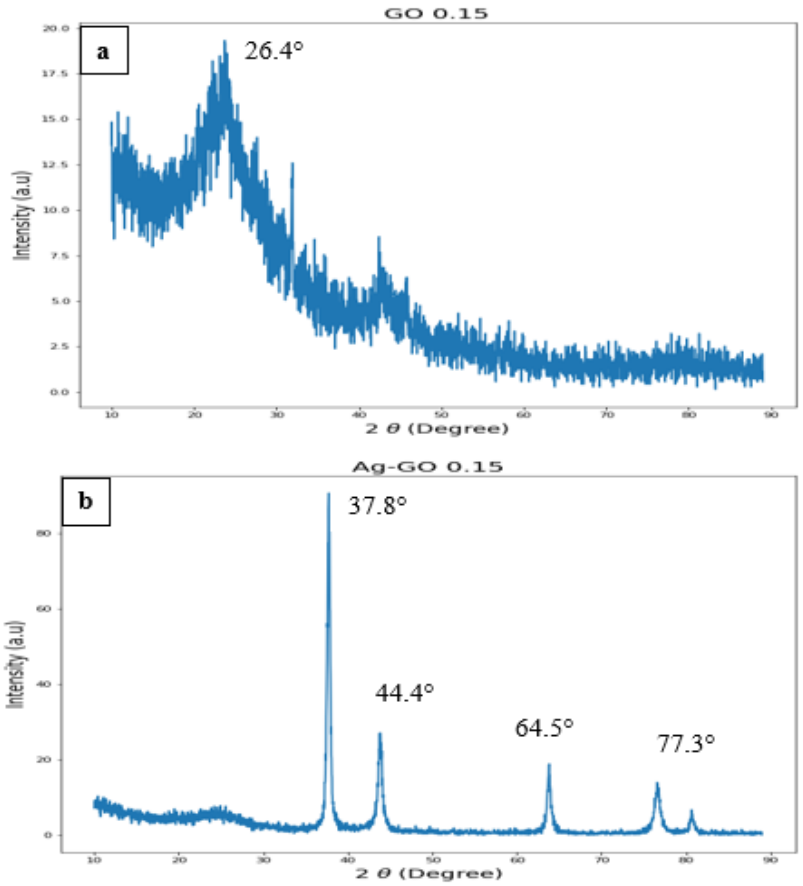

Figure 5. XRD patterns of (a) GO and (b) Ag-GO.

Major peaks of silver present at 37.8°, 44.4°, 64.5° and 77.3°. Hence, the appearance of this spectrum indicates the presence of a crystalline structure in the sample. According to [12], the XRD peak should shift from ~26° to ~11° when graphite is oxidized to GO. The other peak of Ag-GO shows peaks at 44.3°, 64.6° and 77.5°, corresponding to Ag phase (111), (200), (220) and (311) [13]. A previous paper also identified almost the same peaks of intensity, namely 30.1°, 44.3°, 64.4°, 77.4° and 81.5° [14].

3.3. Raman analysis

According to the Raman spectra in Figure 6, the GO spectrum shows a strong G band at 1578 cm^{-1} and also a small band, namely the D band, at 1342 cm^{-1}. The presence of the D band in the Raman spectra indicates a defect in the graphene material, such as a bond-angle disorder or a bond-length disorder [15]. Other than that, the presence of a band at 2677 cm^{-1}, also called the G' band, is used to evaluate the structural parameters of the c-axis orientation as this band is very sensitive to the stacking order of graphene along the c-axis [16].

Next, the addition of silver nanoparticles can enhance the Raman spectra [17], and when silver is decorated onto graphene oxide, the signal shifts. The Ag spectrum can be observed in Figure 6, which

confirms the presence of silver nanoparticles decorated onto GO. All spectra show a D band at 1350 cm^{-1} (due to a defect) and a G band at 1583 cm^{-1} (originating from in-plane optical vibration). The intensity of Ag-GO is lower because the silver nanoparticles do not disperse well on the top of the GO. Based on the Raman spectra, the I_D/I_G ratios were calculated as 0.96 and 0.82 for GO and Ag-GO, respectively. The intensity ratios of these bands help to estimate the defect in the sample [18], whereby GO presents more defects compared to Ag-GO. According to [19], the intensity ratio depends on the structural properties, such as the oxygen content in the sample, crystallinity and disorder degree of GO.

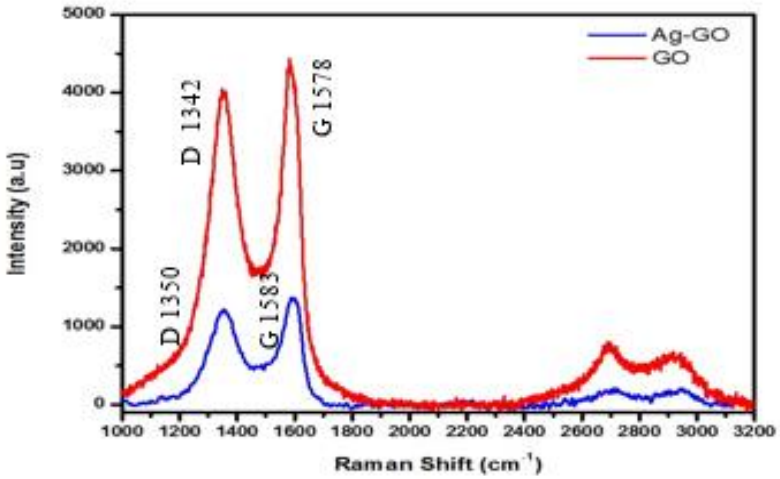

Figure 6. Raman spectra of (a) GO and (b) Ag-GO.

3.4. Conductivity study

The conductivity values was calculated by using the equation below:

$$\sigma = \frac{l}{RA} \text{..... (1)}$$

where,

l = the thickness of thin film

R = total bulk resistance

A = surface area

Figure 7 shows the Nyquist plots for poly(methyl methacrylate) (PMMA) polymer and poly(methyl methacrylate)-GO (PMMA-GO), representing the imaginary versus the real part of the complex impedence. The conductivity value was calculated based on (1). The value of the bulk resistance of PMMA is 4.47 x 10^6 Ω and the conductivity value is 3.36 x 10^{-10} S cm^{-1}. Figure 7 (a) shows that the diameter of the semicircle is the largest in the plot, thus it can be said that the larger the diameter, the higher the resistance to the flow and the lower the current flowing in the sample. Next, for Figure 7 (b), the bulk resistance of PMMA-GO decreases to 3.87 x 10^6 Ω. This is because of the presence of GO in the thin film, which increases the conductivity of the sample. Based on the calculation, the electrical conductivity of PMMA-GO increases to 3.71 x 10^{-10} S cm^{-1}.

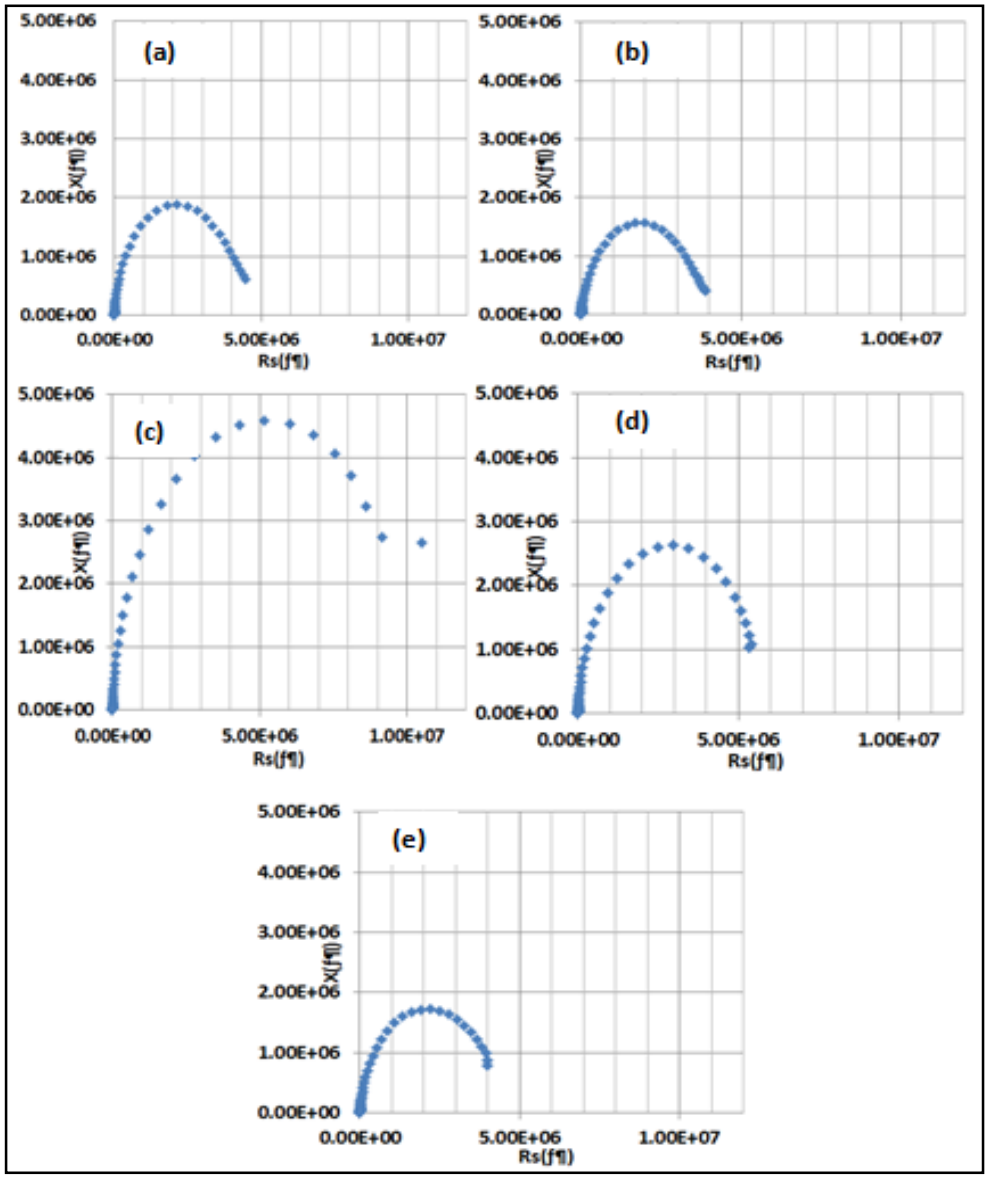

Figure 7. Nyquist plots for (a) PMMA polymer, (b) GO-PMMA, (c) 20 mg PMMA-GO-Ag, (d) 40 mg PMMA-GO-Ag, and (e) 60 mg PMMA-GO-Ag

Figure 7 shows the Nyquist plot for Ag-GO with different concentrations of silver in the nanocomposite. When the silver is added to the samples, the electrical conductivity of the nanocomposite increases, hence underlining the effectiveness of silver nanoparticles in improving the conductivity of GO. Silver is the most conductive element, followed by copper and gold, which is why the conductivity value increases compared to PMMA and PMMA-GO [20]. According to the results, the values of bulk resistance for the three samples with increasing silver content are 8.8 x 10^6 Ω, 5.5 x 10^6 Ω and 4.1 x 10^6 Ω, respectively, slightly lower than for PMMA and PMMA-GO. The radius of the semicircle of the Nyquist plot also becomes smaller as the resistance decreases. The electrical conductivities of 20 mg, 40 mg and 60 mg were calculated based on the bulk resistance, whereby the results are 1.28 x 10^{-10} S cm^{-1}, 2.63 x 10^{-10} S cm^{-1} and 3.67 x 10^{-10} S cm^{-1}, respectively. Therefore, PMMA-GO with 60 mg silver nanoparticles has the highest electrical conductivity, followed by 40 mg and 20 mg, whereby the

electrical conductivity in GO depends on the silver content in the samples [21]. The conductive thin films produced in this work will be subsequently used for hydrogen peroxide (H_2O_2) detection. Hydrogen peroxide is used in many applications, including pharmaceuticals, food, and industry, and it is also a biomarker for diseases such as cancer, aging, and renal disease [22 – 25]. Hence, the rapid, sensitive, and accurate determination of H_2O_2 is crucial.

4. CONCLUSIONS

GO and Ag-GO were successfully synthesized using a modified Hummer's method and chemical reduction method, respectively. The synthesized nanomaterials were characterized via different material characterization methods. The morphology of the GO structure appeared to feature large agglomerations, while the silver nanoparticles were scattered across the surface of the GO. EDS spectra confirmed the presence of carbon and oxygen in the synthesized GO powder. The electrical conductivity results showed that silver nanoparticle plays a crucial role by increasing the electrical conductivity of the polymer nanocomposite samples.

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