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Preparation of Polymer Nanocomposites and Their Application as Supercapacitors

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ABSTRACT

In this study, nano metal oxides (SnO_2 and MnO_2) and Ag nanoparticles were prepared and diagnosed using infrared spectroscopy, x-ray diffraction, and atomic force microscopy. Aniline polymer was prepared and characterized through IR and x-ray diffraction. Polymeric membranes of polyaniline and polyvinyl alcohol with and without metal oxides and Ag nanoparticles were prepared. The electrical properties of these membranes (conductivities and real and imaginary isolation constants) were examined through LCR meter. Capacitors of pristine and doped polymeric films were made and their voltages were examined with time. The best behaviour was for the capacitor of polymer nanocomposite of MnO_2 with Ag nanoparticles, which gave 1.334 volts when charging and store the electrical energy even after 24 hours.

Keywords: Electrical Properties, Nano Metal Oxides, Polymer Nanocomposites, Supercapacitors.

1. INTRODUCTION

The increasing request for energy and the pollution issue are of the are one of the major challenges that people are facing recently. This motivates researchers to develop clean, inexpensive and renewable apparatus for energy storage. Supercapacitor or super electrochemical cells are used for storing electric energy. They have been developed throughout the last years of this century. In fact, they are important because of their distinctive characteristics. Among the important properties of the supercapacitor are the ability to store the energy for long periods, can be used for long times, rechargeable without causing any damage, have high energy, and represent low-cost devices [1-7]. Nanocomposites are distinctive types of materials resulting from the blending of a material such as a polymer with a nanosized material (note: nanomaterial means a material with nanosize) to form a new material with unequalled properties and usable in diverse applications in many fields [8-11]. The nanocomposite of polymers and metal oxides have gained much interest due to its considerable thermal, mechanical, magnetic and electrical properties in comparison with the bulk of metal oxides and polymer [12]. Metal oxides form an ideal mixture with conducting polymers therefore, they give high capacity and low stability cycling as pseudo-capacitive behaviour [13]. The capacitors of polymer composites with nano-metal oxides have been an active area of researches during the previous twenty years [14-22].

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2. MATERIALS AND METHODS

2.1 Chemicals

The materials in this research were obtained from specific companies as the following: (1) Stannic Chloride was obtained from BDH, (2) Potassium Permanganate was obtained from poison, (3) Ammonium Hydroxide was provided by Fluka, (4) Aniline and Ammonium Persulphate were obtained from HI-MEDIA, (5) Nitric Acid was obtained from Scharlau, (6) Manganese Sulphate was obtained from SCHUCHARDT, (7) Polyvinyl Alcohol was obtained from AFCO, and (8) Sulphuric Acid and Hydrochloric Acid were supplied by Riedel-de Haen. The extracted materials will be used in the experimental test without further purification.

2.2 Preparation of Materials

2.2.1 Preparation of SnO_2 Nanoparticles

3.5 g of $SnCl_4.5H_2O$ was melted with 100 ml of methanol. Concentrated ammonium hydroxide was added to the previous solution as drops. The result was a thick white solution. The resulting solution was filtered, then the residuum was washed with methanol to rid of the impurities. The residuum was dried at 85°C for five hours. Next, the resulting residuum was burned for two hours at 400°C, the result was a greyish residuum as hard crystals [23].

2.2.2. Preparation of MnO_2 Nanoparticles

3.68 g of $KMnO_4$ (dissolved in 62.5 ml of H_2O) was reacted with 5.5 g of $MnSO_4$ (dissolved in 19 ml of H_2O) at ambient temperature and pressure. Concentrated HNO_3 was added to the reaction vessel to adjust the pH to ~1. The reaction product was then aged at 80°C for 24 hours. The product was filtered and washed in water until the pH reached 6, the product dried at 110°C [24-25], and the reaction equation depicted below:

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

2.2.3 Preparation of Polyaniline (PAni)

A 50 ml beaker contains 6 ml of distilled aniline was placed in ice bath at 0°C for 10 minutes, then 40 ml of 1M HCl was added as drops and 20 ml of (5 g of Ammonium Persulphate (APS) dissolved in 40 ml of 1M HCl) has been added as drops while keeping the temperature at 0°C. The solution was stirred for 2 hours in an ice bath, then the solution was kept in the refrigerator overnight. The yield filtered and washed with distilled water four times and with 20 ml of 1M ammonium hydroxide with stirring for 10 minutes. The yield then filtered and washed with distilled water until the pH became neutral. Finally, the precipitate was washed with 15 ml of benzene with stirring for 15 minutes and dried at 80°C for 6 hours.

2.2.4 Preparation of Ag Nanoparticles

3 g of silver nitrate was dissolved in 800 ml distilled water and then the solution was heated at a temperature 95-100°C. 5 g from tri Sodium Citrate was dissolved in 125 ml distilled water and was added as drops to the silver nitrate solution with stirring at a range of temperature 95-100°C. The mixture then left on stirring for 15 minutes without heat and then the adhesive material was stuck on the walls of the beaker. After that, the solution was stirred for 15 minutes. After the stirring, the solution was left to the next day to let the precipitate settle well. The precipitate was washed with an excess of water and placed in the ultrasonic device for 1 hour to break the aggregation of the large particles of the precipitate. The precipitate was dried at 80°C for 4-5 hours in order to obtain the nanoparticles powder [26].

2.3 Polymer Composites Films

10 g of PVA was dissolved in 100 ml of distilled water and left overnight at room temperature to homogenize it. On the second day, the solution stirred at 70°C until the solution converted to a transparent solution. 1 g of polyaniline was dissolved in 10 ml of distilled water, added into the solution and the mixture stirred at 70°C (the stock solution). An amount of 0.2 g of each of SnO_2 and MnO_2 nanoparticles were added to 25 ml of the stock solution with vigorous stirring. These mixtures need to be maintained at 70°C for 10 minutes and sonicated for 10 minutes, after that they installed into glass moulds. The same procedure was repeated for the mixture of 0.5 g of Ag particles with 0.2 g of SnO_2 and another with 0.2 g of MnO_2. After drying the films, they were hardened for 10 hours under heating.

2.4 Super Capacitor (Electro-Chemical Cell)

The capacitors were constructed from the following materials which are plastic plates, polymeric nanocomposites films, copper plates, and separators.

Two dimensions of plastic plates were used. The first plastic plate as shown in Figure 1(a) has dimensions of 6 × 6 × 0.2 cm and the plate was engraved from the centre with dimensions of 3 × 3 cm. The second plastic plate has dimensions of 3×3×0.5 cm (length × width × thickness) and one hole in each piece (to connect the capacitor to anode and cathode). Plastic covers used to cover the upper and lower parts of engraved pieces as shown in Figure 1(B). Polymeric nanocomposites films (3 × 2 cm) with the same dimensions of plastic separators and copper plates (copper chips) were arranged in the engraved plates according to the following order: the copper chip, the polymer nanocomposite film, the separator film, the polymer nanocomposite film, and the copper (see Figure 1(C)). Both template sides were covered with plastic plates and sealed with silicone adhesive. The cell was injected with an electrolyte solution (sodium sulphate 0.75M, 7 ml).

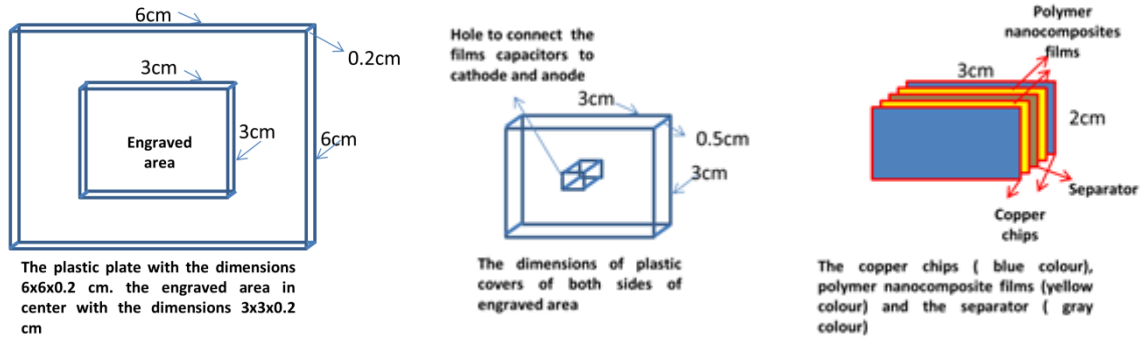

Figure 1. The structure of the prepared capacitors: (a) represents the engraved plastic plate, (b) represents the plastic plate using in covering the engraved area, (c) represents the polymer nanocomposite films, copper chips and the separator.

3. RESULTS AND DISCUSSION

3.1 FTIR Measurements

The infrared spectrum of SnO_2 shows absorption bands where Sn-O stretches at 577 cm^{-1}. The broad peak at 3444 cm^{-1} refers to O-H (of water molecules) present between crystals of tin oxide [26]. The infrared spectrum of MnO_2 shows absorption bands at 437,522,600 cm^{-1} belongs to stretching of Mn-O and 1382 cm^{-1} which is associated with water molecules present on the sample

surface. The band in 3439 cm^{-1} is due to O-H stretching [27]. The IR peaks of Polyaniline appeared at 1583 and 1494 cm^{-1} corresponding to C=C quinonoid and benzenoid deformation vibrations. 1242 and 1670 cm^{-1} are assigned to the C-N of aromatic amine stretching deformation and C=N stretching of (-N=quinoid=N-), respectively. On the other hand, the band at 825 cm^{-1} is attributed to C-H of the aromatic ring. The stretching vibration of N-H shows a broad peak at 3377 cm^{-1} [28].

3.2 X-Ray Diffraction

SnO_2 nanoparticles were diagnosed through x-ray diffraction. Three high values of the angles appeared at 2θ = 33.87°, 51.79° and 26.60°. These angles match the values 101, 211 and 110) successively as shown in Figure 2. The average size of these nanoparticles is 48 nm.

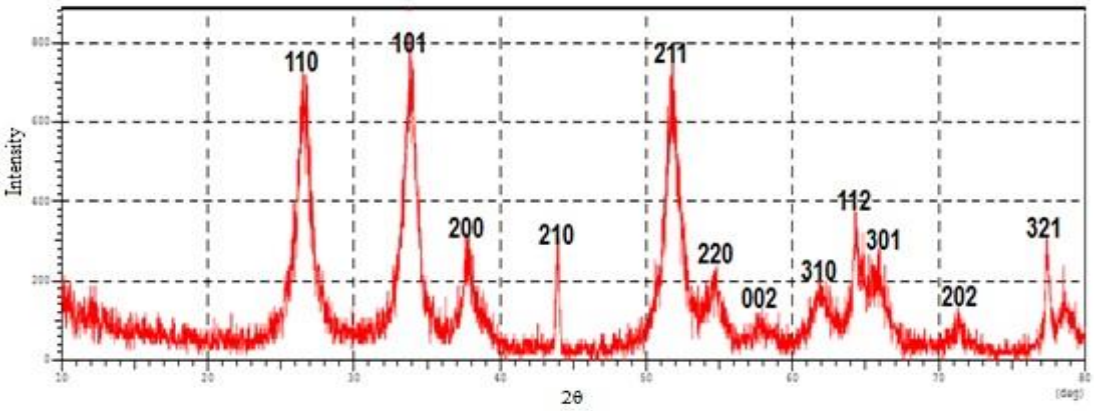

Figure 2. X-ray diffraction of SnO_2 nanoparticles.

The x-rays diffraction of MnO_2 refers to the highest obtained 2θ angles. These values appeared at 77.4°, 43.9°, 37.5° and 64.3°. The obtained angles match the following values 402, 301, 211 and 002, respectively. This indicates that MnO_2 nanoparticles are pure because there are no overlapping summits of the impurities as shown in Figure 3. The average size of these nanoparticles is about 114.7 nm.

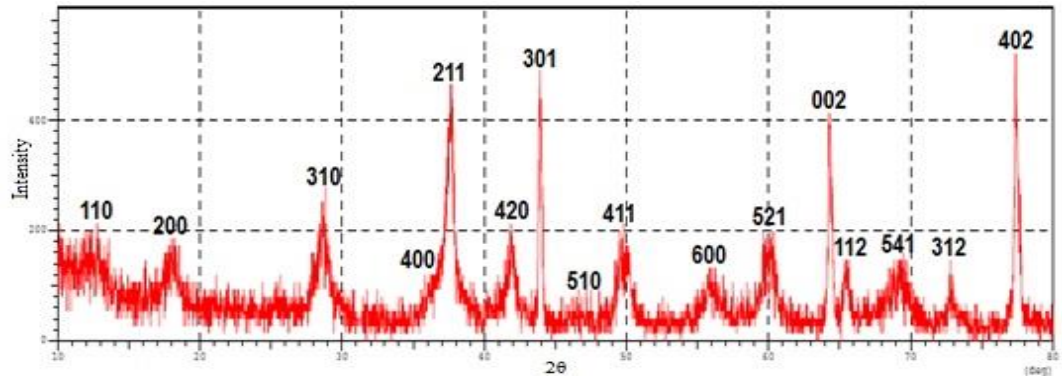

Figure 3. X-ray diffraction of MnO_2 nanoparticles

PAni powder exhibits narrow peaks than that found in nanoparticles. XRD of pure PAni is shown in Figure 4. The main peaks appeared at the following 2θ angles: 19.8°, 20.9° and 25.2°. The centred peak may be ascribed to the repetition of benzenoid and quinoid rings in PAni chains and the peak at (2θ = ~25°) may be caused by the periodicity perpendicular to the polymer chain, while the peak at (2θ = ~20°) represents the typical distance between the ring planes of benzene rings in nearby chains or the close-contact inter-chain distance [27].

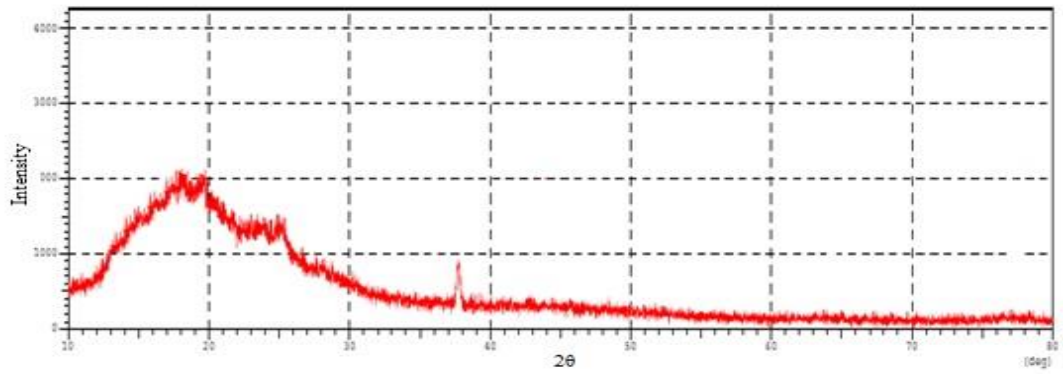

Figure 4. X-ray diffraction polyaniline

Ag nanoparticles x-ray diffraction shows the highest 2θ angle values of 38.2°, 44.4° 77.4, and 64.5°, as shown in Figure 5. These angles corresponded to the following values 111, 200, 311, and 220, respectively. The particles formed in cubic shape and the size of nanoparticles is approximately 30.7 nm.

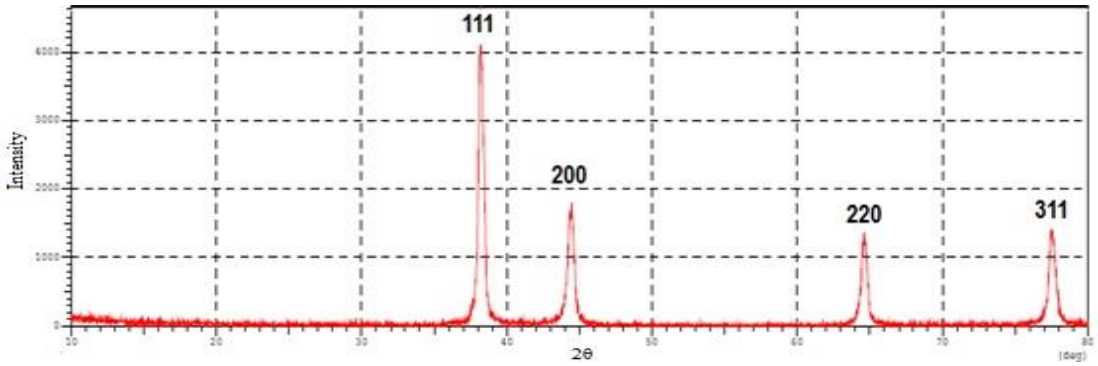

Figure 5. X-ray diffraction of Ag nanoparticles

3.3 Atomic Force Microscope (AFM) Measurements

The goal of the Atomic Force Microscope (AFM) study is to investigate the topography of the prepared nanostructure materials, average diameter, and size distributions. The later properties are tabulated in Table 1. The AFM features images of the prepared nanomaterials in two and three dimensions are illustrated in Figure 6 until Figure 8.

Table 1. Average diameter, size distributions, roughness average, and root mean square of the prepared nanostructure materials (SnO_2, MnO_2, and Ag).

Nanoparticle	Average diameter (nm)	50% diameter (nm)	Particles size distributions (nm)	Roughness average (nm)	Root mean square (nm)
SnO_2	101.7	90	30-190	0.94	1.11
MnO_2	99.7	95	55-125	0.48	0.58
Ag	79	70	60-165	1.07	1.26

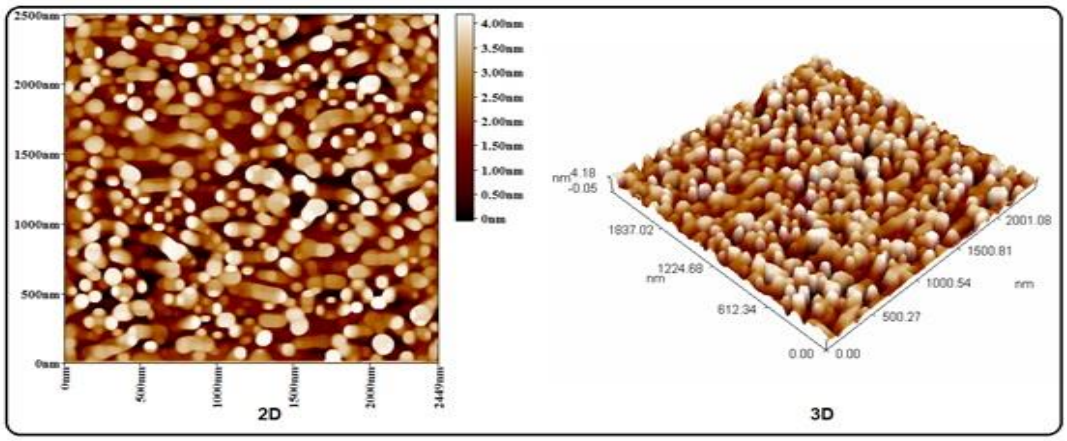

Figure 6. The AFM image in two (2D) and three (3D) dimensions of SnO_2 particles

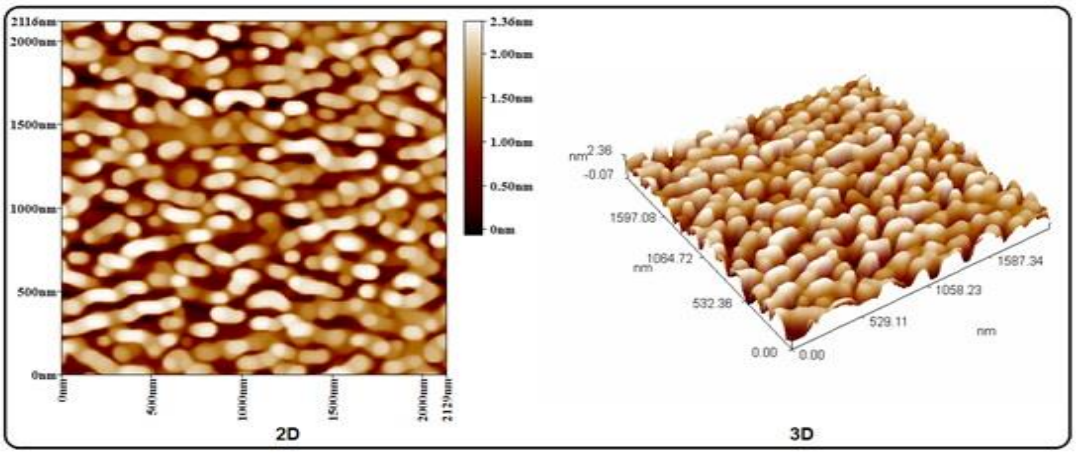

Figure 7. The AFM image in two (2D) and three (3D) dimensions of MnO_2 particles

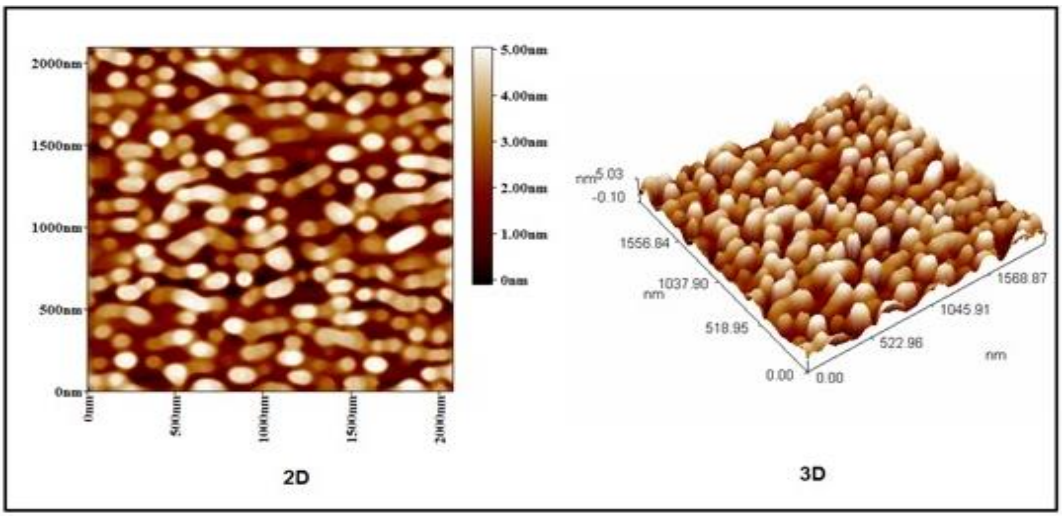

Figure 8. The AFM image in two (2D) and three (3D) dimensions of Ag particles

3.4 Electrical Properties of Polymer Nanocomposites

3.4.1 Real and Imaginary Isolation Constant of Polymer Nanocomposites and Pure Polymer Mixture

Figure 9 until Figure 12 shows the relationship between the real and imaginary isolation constants and the frequency logarithm of polymer mixtures nanocomposites, polymer mixtures nanocomposites containing Ag nanoparticles, and polymer mixture. It appears that the real isolation constant is high at low frequencies while it is lessened at high frequencies. The real isolation constant of polymer mixtures is less than the real isolation constants of polymer mixtures nanocomposites with and without Ag nanoparticles, that is because that the polymer mixtures do not have charge carriers which can hold energy as much as the polymer nanocomposites and polymer nanocomposites containing silver nanoparticles. The polymer nanocomposites with silver nanoparticles give real isolation constants higher than that of polymer nanocomposites without silver nanoparticles and that attribute to good electrical properties of silver particles. Nonetheless, the polymer mixtures nanocomposites without and with silver particles gave an imaginary isolation constants have the same behaviour with some diffraction at some points. In the beginning, the imaginary isolation constant is high, then it starts to reduce gradually with the increase in the frequency noticing some meanders with the change of frequency. The imaginary isolation constants of polymer mixtures nanocomposites with silver particles lower than those without silver particles, this is a good indicator, due to the better electrical properties of any system that has high real isolation constant and lower imaginary isolation constant and that seems obvious in the charge and discharge measurements of electrical capacitors. The polymer mixtures nanocomposites with silver particles showed the best behaviour over the materials, and capacitors of the polymer mixtures nanocomposites of silver particles store the electricity more efficiently than the capacitors of other polymer materials.

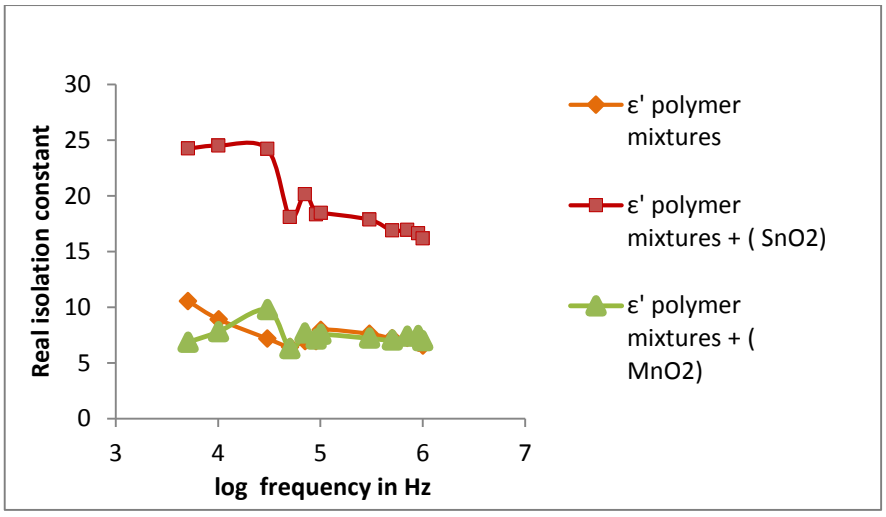

Figure 9. The relationship between real isolation constant (ε') and frequency logarithm of polymer mixtures nanocomposites and polymer mixtures

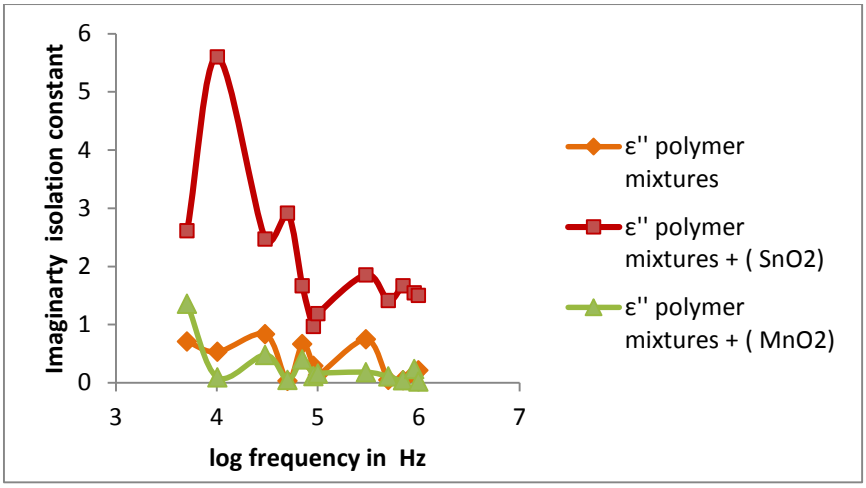

Figure 10. The relationship between imaginary isolation constant (ε'') and frequency logarithm of polymer mixtures nanocomposites and polymer mixtures

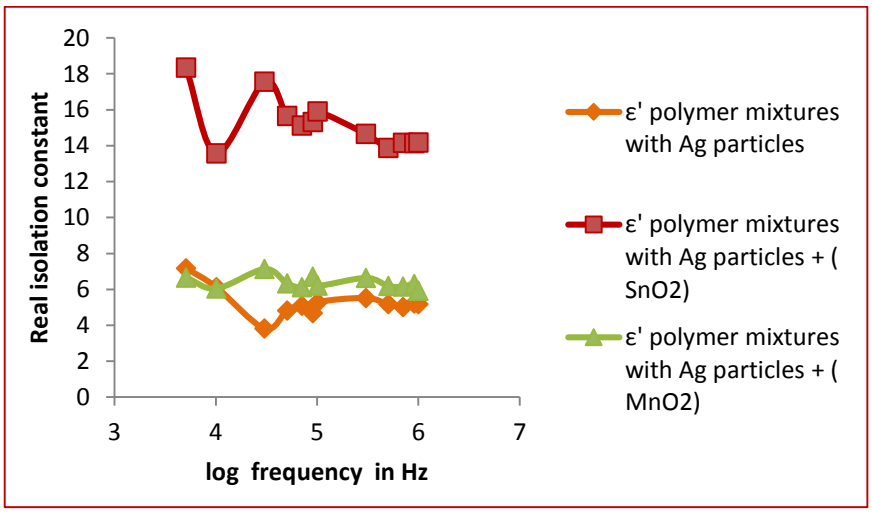

Figure 11. The relationship between real isolation (ε') constant and frequency logarithm of (polymer mixtures nanocomposites and polymer mixtures) containing Ag nanoparticles

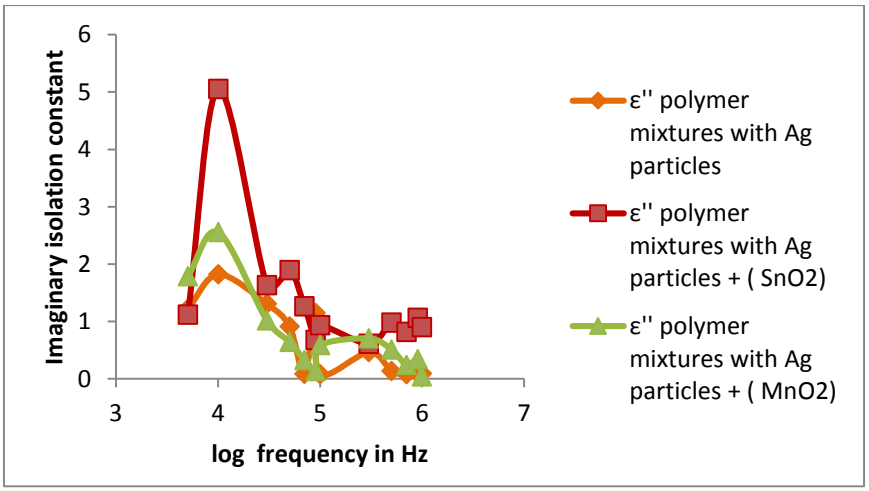

Figure 12. The relationship between imaginary isolation constant (ε'') and frequency logarithm of polymer mixtures nanocomposites and polymer mixtures) containing Ag nanoparticles

3.4.2 Electric Conductivity of Polymer Mixtures Nanocomposite and Polymer Mixtures

Through the measurement of electrical conductivities of polymer nanocomposites and polymer mixtures, their values were low in the beginning and they increase with frequency increasing as shown in Figure 13 and Figure 14. The mixture of polymer nanocomposites containing Ag nanoparticles shows good conductivities. This behaviour is expected because the silver nanoparticles is a good conductor. Therefore, if it is added in very small quantities to the polymer nanocomposite, they will be more conductive. Hence, the storage of the supercapacitor will increase.

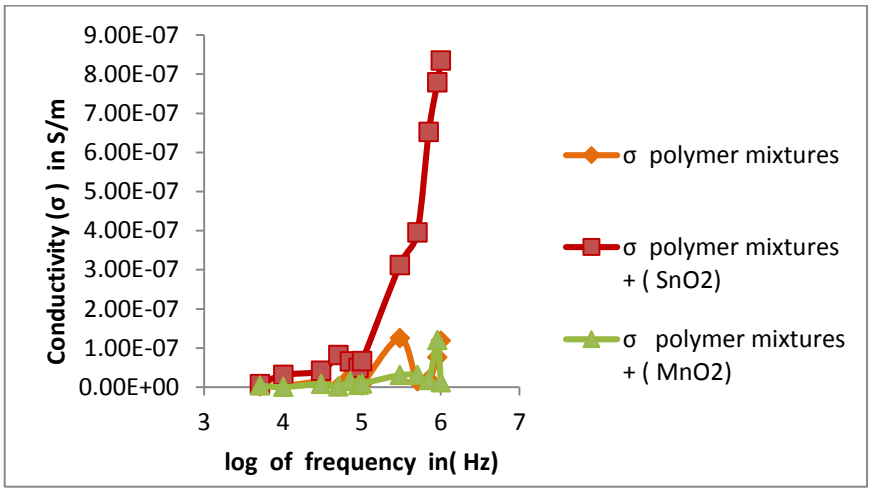

Figure 13. The relationship between conductivity (σ) and frequency logarithm of polymer mixtures nanocomposites and polymer mixtures

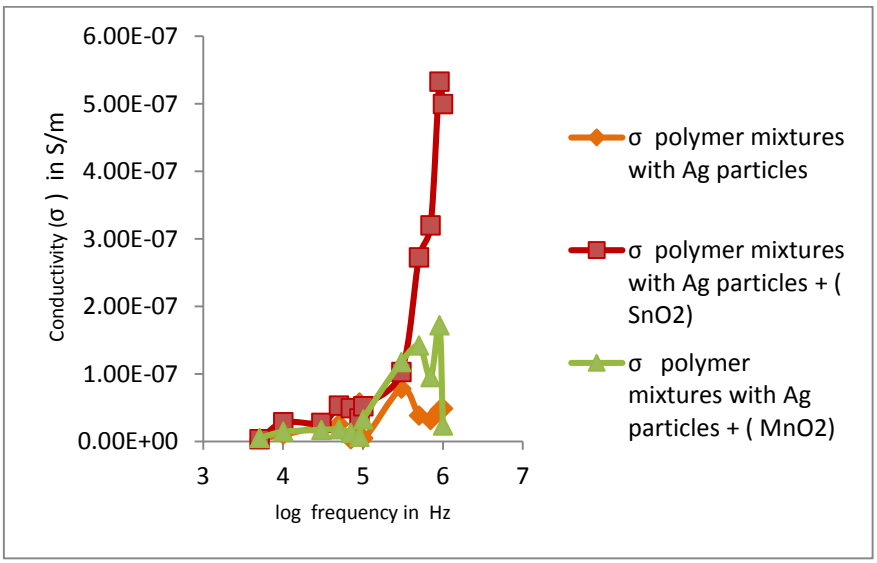

Figure 14. The relationship between conductivity (σ) and frequency logarithm of polymer mixtures nanocomposite and polymer mixtures containing Ag nanoparticles

3.5 Measurement of Supercapacitors Voltages

Through the measurements of the supercapacitor voltage of polymer nanocomposites with and without silver nanoparticles. Capacitors doped with silver nanoparticles has a voltage higher than the voltage of the capacitors without silver nanoparticles which have good electrical properties as depicted in Table 2. The supercapacitor which contains polymer nanocomposite of MnO_2

containing Ag nanoparticles gave 1.334 volts during charging, while the supercapacitor which contains polymer nanocomposite of MnO_2 gave 1.123 volts. The supercapacitor of SnO_2 nanocomposite containing Ag nanoparticles gave 1.32 volts, while the supercapacitor of pure SnO_2 nanocomposite gave 0.995 volts. These capacitors store electrical energy even after 24 hours. This is an excellent characteristic for these supercapacitors.

Table 2 Voltage of capacitors of polymer mixtures nanocomposites of (SnO_2 and MnO_2) with and without Ag nanoparticles at different times

Time/min	Capacitor voltage of polymer mixtures with (SnO_2 + Ag) particles	Capacitor voltage of polymer mixtures with (MnO_2 + Ag) particles	Capacitor voltage of polymer mixtures with SnO_2 particles	Capacitor voltage of polymer mixtures With MnO_2 particles
0	1.320	1.334	0.995	1.123
5	1.216	1.098	0.880	0.844
10	1.184	1.078	0.454	0.522
15	1.112	0.568	0.293	0.379
30	0.779	0.541	0.267	0.187
600	0.441	0.441	0.132	0.105
900	0.151	0.391	0.111	0.085
1200	0.150	0.371	0.068	0.064
1440	0.142	0.342	0.032	0.037

4. CONCLUSION

The prepared oxides were of nano size, and that proven by x-ray diffraction and AFM measurements. It has been found through measurements of electrical conductivities that the best conductivity and best real permittivity (Ɛ') and less imaginary permittivity (Ɛ") is the polymer nanocomposite containing silver nanoparticles because Ag nanoparticles increase the charge carriers in polymeric systems which increase the electrical conductivity and energy storage. The best supercapacitor was the supercapacitor of MnO_2 containing Ag nanoparticles, as it is able to retain 25.63% from the amount of total energy after 24 hours, this is an excellent step in the realm of supercapacitors.

CONFLICT OF INTEREST

None

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