

Preparation of Polymer Nanocomposites and Their Application as Supercapacitors

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ABSTRACT

In this study, a Nano metal oxides (SnO_2 and MnO_2) and Ag nanoparticles have been prepared diagnosed using infrared spectroscopy, x-ray diffraction, and atomic force microscopy. Aniline polymer has been prepared and characterized through IR and x-ray diffraction. Polymeric membranes of polyaniline and polyvinyl alcohol with and without metal oxides and Ag nanoparticles have been prepared. The electrical properties of these membranes (conductivities and real and imaginary isolation constants) have been examined through LCR meter. Capacitors of pristine and doped polymeric films have been made and their voltages have been examined with time. The best behavior was for the capacitor of polymer nanocomposite of MnO_2 with Ag Nanoparticles which gave 1.334 volts at charging and kept 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 most 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 kinds of apparatuses for storing electric energy. They were developed continuously through the last years of this century. In fact, they are important nowadays because of their distinctive characteristics. The most important properties are their ability to keep energy for long periods, they can be used for long times, they can be charged many times without causing any damage, they have very high energy, and they represent low-cost apparatuses [1-7]. Nanocomposites are a distinctive types of materials which resulting from the blending of a material such as a polymer with a nanosized material (note: nano material means a material with nano size)to form a new material with unequaled properties and diverse applications in many fields [8-11]. The nanocomposite of polymers and metal oxides has gotten much interest due to the considerable thermal, mechanical, magnetic and electrical properties in comparison with the bulk of metal oxide and polymer [12]. Metal oxides form an ideal mixture with conducting polymers, therefore they give high capacity and low stability cycling as pseudo-capaciting behavior [13]. The capacitors of polymer composites with nano metal oxides have been an active area of researches during the previous few years [14-22].

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2. MATERIALS AND METHODS

2.1 Chemicals

Stannic Chloride obtained from BDH, Potassium Permanganate obtained from poison, Ammonium Hydroxide provided by Fluka; Aniline, Ammonium Persulphate obtained from HI-MEDIA; Nitric Acid obtained from Scharlau; Manganese Sulphate obtained from SCHUCHARDT; Polyvinyl Alcohol obtained from AFCO; Sulphuric Acid and Hydrochloric Acid were supplied by Riedel-de Haen. The materials have been used without further purification.

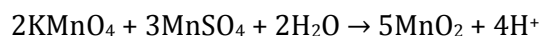
2.2 Preparation of Materials

2.2.1 Preparation of SnO₂ nanoparticles

3.5 grams of SnCl₄·5H₂O 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 get rid of the impurities. The residuum was dried in 85 C for five hours. The resulting residuum was burned for two hours at 400 °C. It became a grayish residuum as hard crystals [23].

2.2.2. Preparation of MnO₂ nanoparticles

3.68 grams of KMnO₄ (dissolved in 62.5 ml of H₂O) was reacted with 5.5 grams of MnSO₄ (dissolved in 19 ml of H₂O) at ambient temperature and pressure. Concentrated HNO₃ 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:



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 min, 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) it has been added as drops with keeping the temperature at 0 °C. The solution was stirring 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 ammonium hydroxide 1M, 20 ml 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 min and dried at 80 °C for 6 hours.

2.2.4 Preparation of Ag nanoparticles

3 grams of silver nitrate was dissolved in 800 ml distilled water and then the solution heated at a temperature 95-100 °C, 5 grams from tri Sodium Citrate dissolved in 125 ml of distilled water and 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 Baker, after that the solution stirred for 15 minutes as well. After completing the stirring, the solution left to the second day to let the precipitate settle well. The precipitate was washing 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 dried at 80 °C for 4-5 hours in order to obtain the nanoparticles powder [26].

2.3 Polymer Composites Films

10 grams 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 till the solution converted to a transparent solution. 1gram 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 grams of each of SnO₂ and MnO₂ nano particles 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 min, after that they installed in the glassy mold. The same procedure was repeated for the mixture of 0.5 g of Ag particles with 0.2 g of SnO₂ and another with 0.2 g of MnO₂. After drying the films, they have been hardened for 10 hours under heating.

2.4 Super Capacitor (Electro-Chemical Cell)

The capacitors were constructed from the following materials:

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

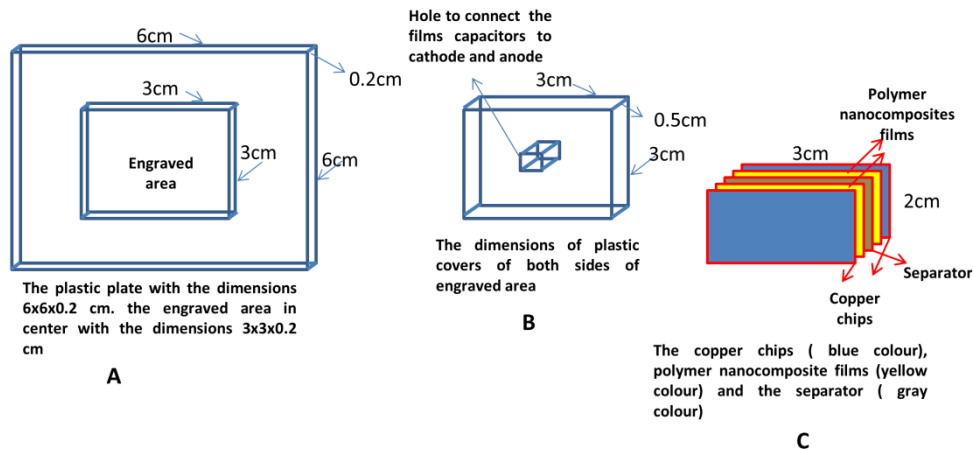


Figure 1. The structure of the prepared capacitors. A represents the engraved plastic plate. B represents the plastic plate using in covering the engraved area. C represents the polymer nanocomposite films, the copper chips and the separator.

3. RESULTS AND DISCUSSION

3.1 FTIR measurements

Infrared spectrum of SnO_2 , shows absorption bands refer to Sn-O stretching 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]. Infrared rays spectrum of MnO_2 shows absorption bands at $437, 522, 600 \text{ cm}^{-1}$ belongs to stretching of Mn-O, and 1382 cm^{-1} which are associated with water molecules present on the sample surface. The band in 3439 cm^{-1} 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. While 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 $2\theta = 33.87^\circ, 51.79^\circ$ and 26.60° . These angles match the values 101, 211 and 110) successively as shown in Figure 2. The average of the size of these nanoparticles equals 48nm.

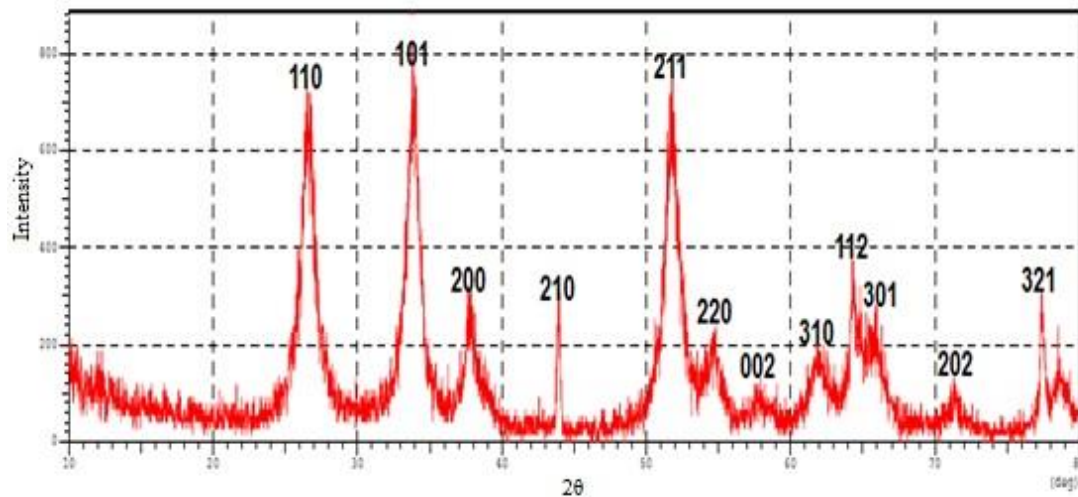


Figure2. X-ray diffraction of SnO₂ Nanoparticles

The x-rays diffraction of MnO₂ 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. The diagram shows that MnO₂ nanoparticles are pure because there are no overlapping summits of the impurities (Figure3). The average of the size of these nanoparticles equals 114.7nm.

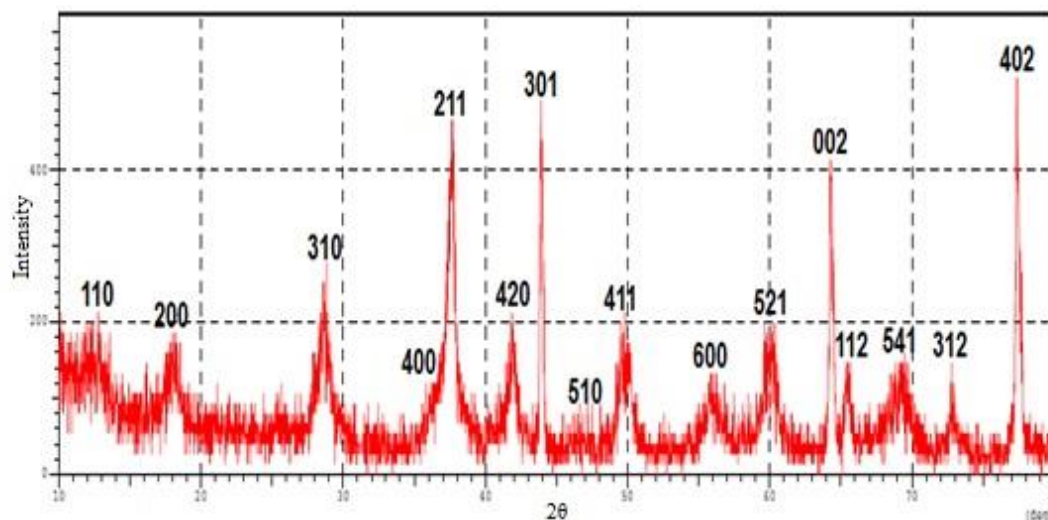


Figure3. X-ray diffraction of MnO₂ Nanoparticles

PAni powder exhibits narrow peaks than that found in nanoparticles. XRD of pure PAni shown in Figure4. The main peaks appeared at the following 2θ angles: (19.8, 20.9° and 25.2). The centered 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].

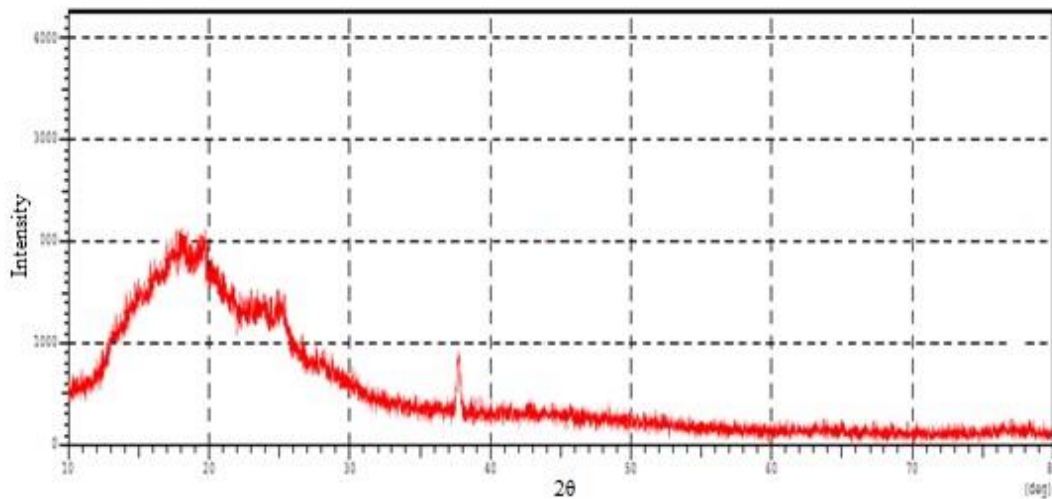


Figure4. X-ray diffraction polyaniline (the values of peaks are not labeled here because the structure of polyaniline does not have crystalline structure like nano oxides or nano composites : see the picture attached with this file under the name: PaniXRDjustification2.jpg)

Ag nanoparticles x-ray diffraction shows the highest 2θ angle values of (38.2° , 44.4° , 77.4° , and 64.5°) as shown in Figure5. 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 30.7nm.

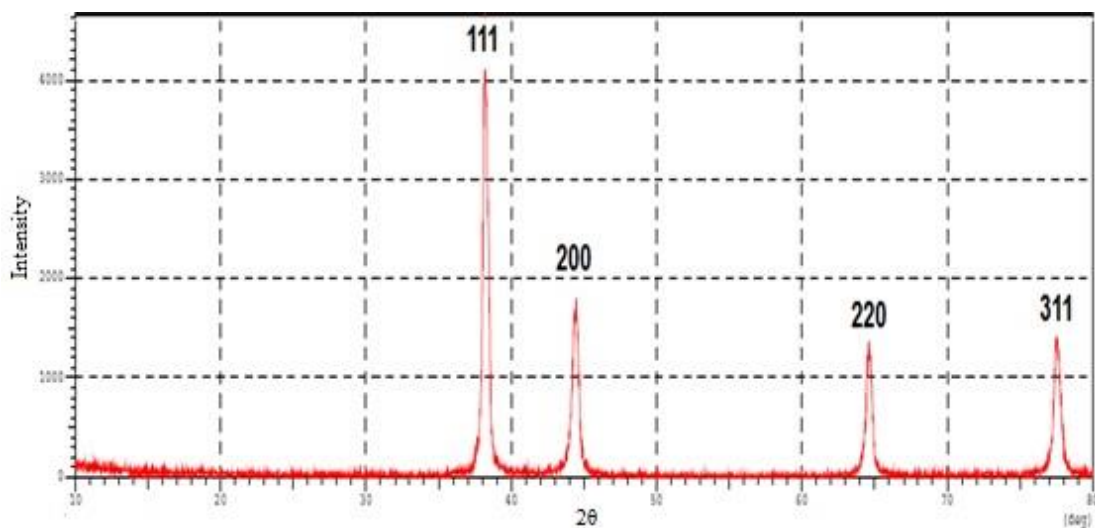


Figure5. X-ray diffraction of Ag nanoparticles

3.3 Atomic Force Microscope measurements

The goal of AFM study is to investigate the topography of the prepared nanostructure materials, average diameter, and size distributions. The later properties are tabulate in Table 1. The AFM features images of the prepared nanomaterials in three and dimensions are illustrated in Figure 6 – 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

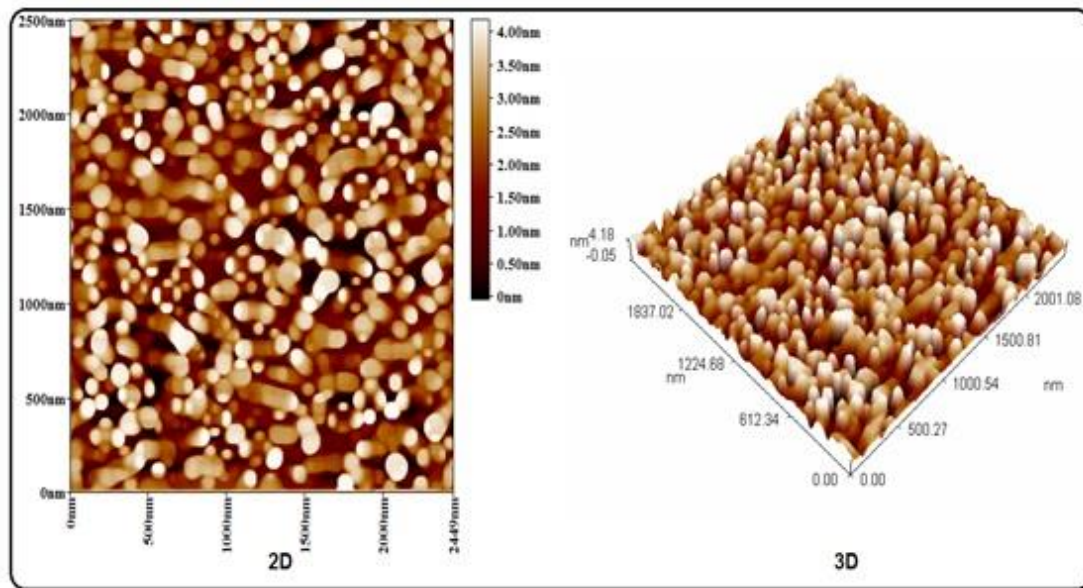


Figure 6. The atomic force microscope image in two (2D) and three (3D) dimensions of SnO₂ particles

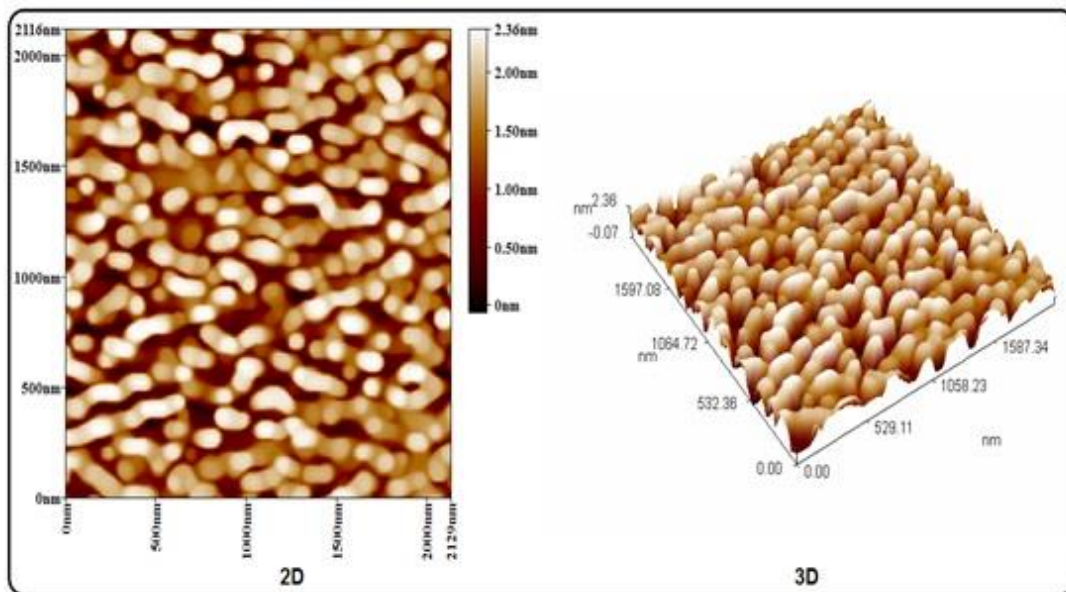


Figure7. The atomic force microscope image in two (2D) and three (3D) dimensions of MnO_2 particles

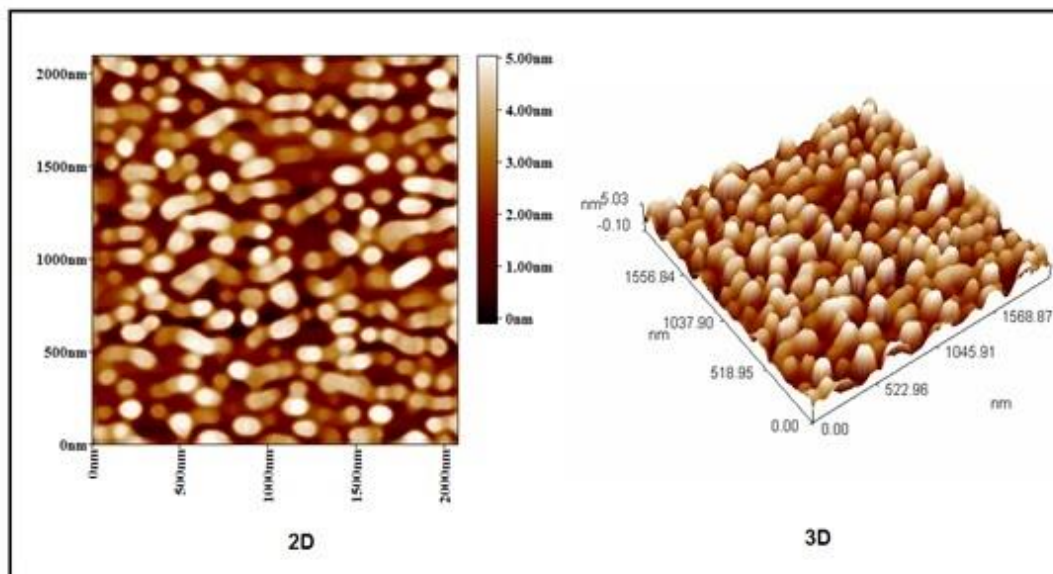


Figure8. The atomic force microscope image in two (2D) and three (3D) dimensions of Ag particles

3.4 Electrical Properties of Polymer Nanocomposites

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

Figure 9 – Figure 12 show the relationship between the real isolation constants and the imaginary isolation constants with frequency logarithm of polymer mixtures nanocomposite, 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 constant which has the same behavior with some diffraction at some points. In the beginning, the imaginary isolation constant is high, then it starts to be lesser gradually with the increase in the frequency noticing some meanders with the change of frequency. The imaginary isolation constant of polymer mixtures nanocomposites with silver particles lower than that 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 behavior 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.

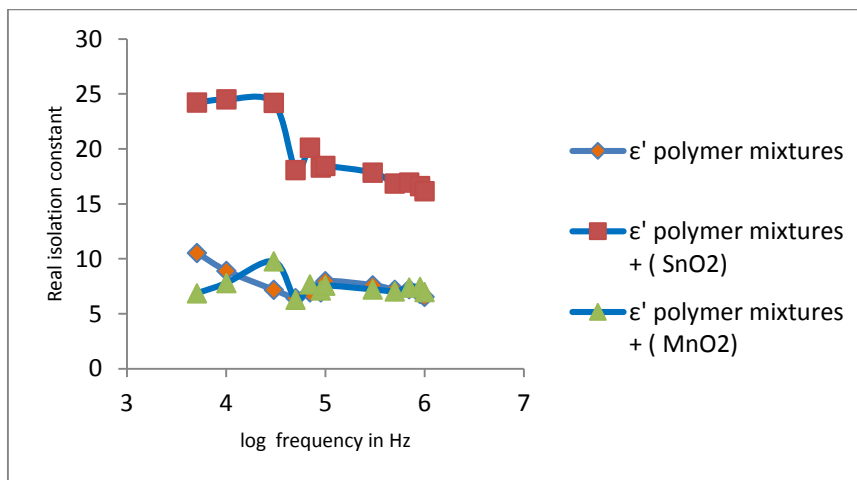


Figure9. The relationship between real isolation constant(ϵ') and frequency logarithm of polymer mixtures nanocomposites and polymer mixtures

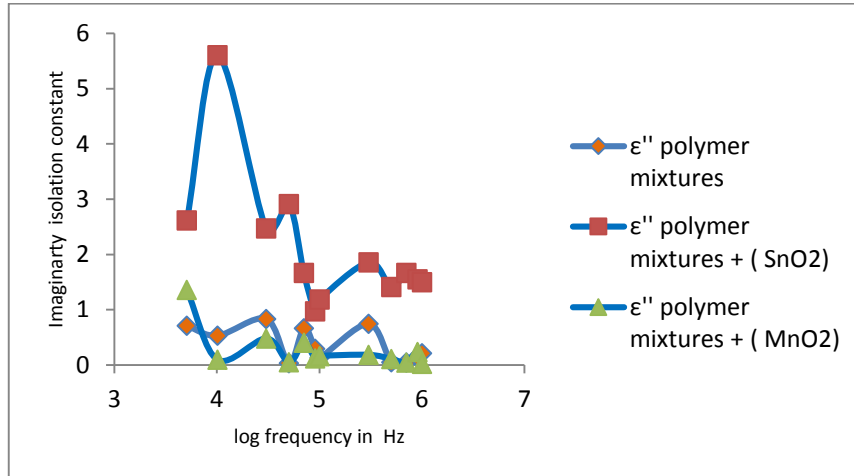


Figure10. The relationship between imaginary isolation constant (ϵ'') and frequency logarithm of polymer mixtures nanocomposites and polymer mixtures

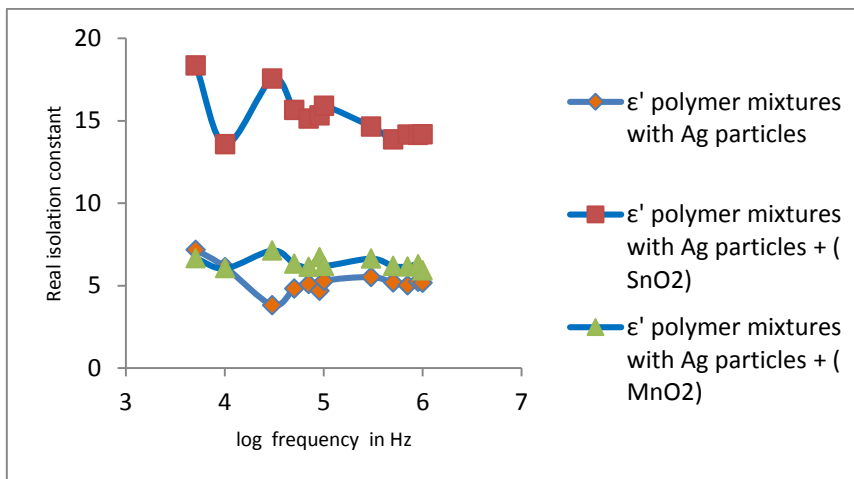


Figure11. The relationship between real isolation (ϵ') constant and frequency logarithm of (polymer mixtures nanocomposites and polymer mixtures) containing Ag nanoparticles

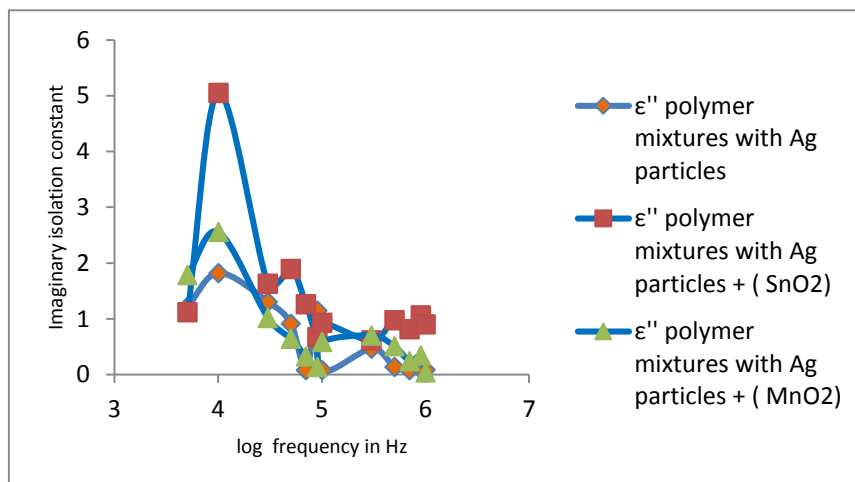


Figure12. The relationship between imaginary isolation constant (ϵ'') and frequency logarithm of polymer mixtures nanocomposites and polymer mixtures) containing Ag nanoparticles

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 Figure14. The mixture of polymer nanocomposites containing Ag nanoparticles shows good conductivities. This behavior expected because the silver nanoparticles is a good conductor. Therefore, if they are added in very small quantities to the polymer nanocomposite, they will be more conductive(according to reviewer inquiry: the conductive increase due to the addition of Ag nano particles). Hence, the storage of the supercapacitor will increase.

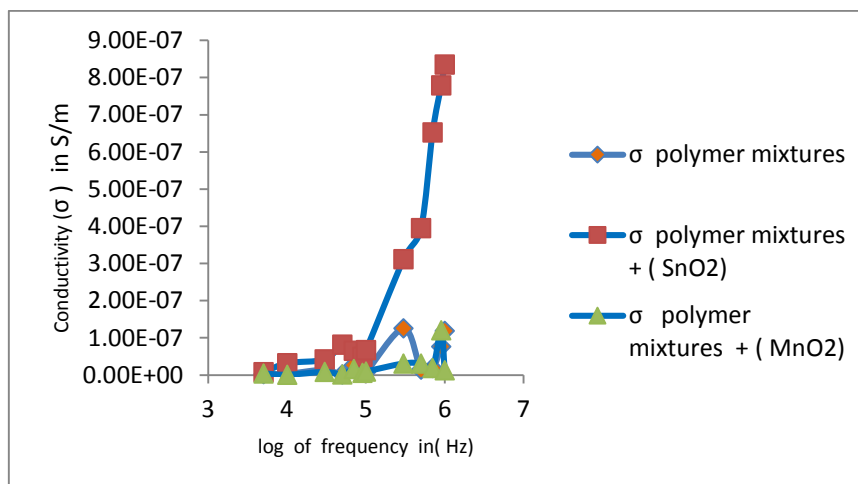


Figure13. The relationship between conductivity (σ) and frequency logarithm of polymer mixtures nanocomposites and polymer mixtures

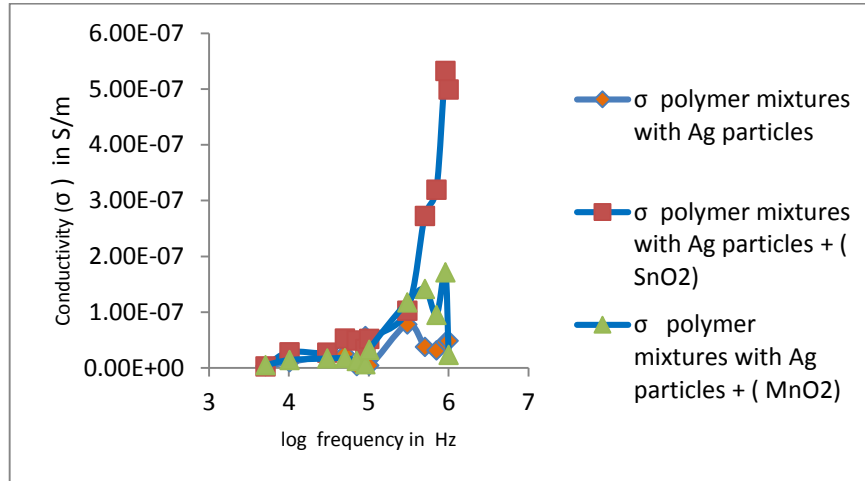


Figure14. The relationship between conductivity (σ) and frequency logarithm of polymer mixtures nanocomposite and polymer mixtures) containing Ag nanoparticles

3.5 Measurement of Supercapacitors Voltages

Through the measurements of the supercapacitors voltage of the polymer nanocomposite with and without silver nanoparticles. The capacitors doped with silver nanoparticles has a voltage higher than the voltage of capacitor 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 at charging, while the supercapacitor which contains polymer nanocomposite of MnO_2 gave 1.123 volt. The supercapacitor of SnO_2 nanocomposite containing Ag nanoparticles gave 1.32 volts, while the supercapacitor of pure SnO_2 nanocomposite gave 0.995 volt. These capacitors kept electrical energy even after 24 hours. This is an excellent step 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	Capacitor voltage of polymer mixtures with ($\text{SnO}_2 + \text{Ag}$) particles	Capacitor voltage of polymer mixtures with ($\text{MnO}_2 + \text{Ag}$) particles	Capacitor voltage of polymer mixtures with SnO_2 particles	Capacitor voltage of polymer mixtures With MnO_2 particles
0	1.32	1.334	0.995	1.123
5	1.216	1.098	0.88	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	0.15	0.371	0.068	0.064

4. CONCLUSION

The prepared oxides were of nano size, and that proven by x-ray diffraction and AFM measurements. It has been founded through measurement of electrical conductivities that the best conductivity and best real permittivity (ϵ') and less imaginary permittivity

(ϵ'') it was for 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 MnO₂ containing Ag nanoparticles, as kept 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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