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EVALUATING THE ELECTRIC PROPERTIES OF POLY ANILINE WITH DOPING ZnO AND α-Fe_2O_3 NANOPARTICLES

Noor Sabah Al-Obaidi[1], Zaid Hamid Mahmoud[1]*, Ahlam Ahmed Frayyih[2], Anfal S. Ali[1], Farah K. Ali[1]

1. *Department of Chemistry, College of Science, Diyala University, Iraq.*
2. *Ministry of Education, Directorate of Education of the Second Al-Rusafa, Al-Aser Al-jadeed Secondary School, Baghdad, Iraq.*

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ABSTRACT

The nanocomposites of P-Ani doping ZnO and α-Fe_2O_3 were successfully synthesized using co-precipitation method while the particles of ZnO and α-Fe_2O_3 were prepared utilizing Sol-gel and photolysis method; respectively. The morphology and structure of the product were characterized using SEM, XRD and FTIR while, the electric conductivity was examined using the LCR-meter. The results from XRD and SEM led to the particles prepared in nano size which were 18 nm and 31.50 nm for P-Ani/α-Fe_2O_3 and P-Ani/ZnO; respectively. From FTIR result, the Fe-O and ZnO characteristic bands at 447.87 cm^{-1}, 546.6 cm^{-1} and 516cm^{-1}, showed the main characteristic peaks similar to PANI. The results of LCR meter showed increased conductivity by doping nano particles with P-Ani.

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Introduction

In recent decades, electrically conductive polymers such as poly aniline have gained a lot of attention and interest due to their industrial applications which can be excellent substitutes for semiconductor materials in a lot of electrical devices; and their unique properties like good environmental consultancy, configured in the film form have given them potential utilization in many diverse applications as alternative low cost energy sources [1-6]. At present, researchers are working on the development and improvement of the characteristics of the conductive polymers by associating them with the inorganic nanoparticle compounds. The linkage between them has resulted in the production of new class of materials with excellent properties as well as the improvement of the chemical and physical properties. These properties have been amended by the inorganic fillers of nanoparticles, and resulted in increasing the ratio of surface to volume of the polymer [7]. Even today, there are many reports and papers pointing on how to prepare the PAni/inorganic compound (oxides) nanocomposite by using different methods such as electrochemical polymerization, spray pyrolysis, and chemical oxidative polymerization. However, there is little information available about the preparation of PAni with ZnO and α-Fe_2O_3 nanoparticles and their effect on the electricity conductivity. The problem in the process of preparing the composite lies in the preparation of nanoparticles individually. So, in this research, a new method of preparing nanoparticles using UV-irradiation with excellent properties in energy, cost, low size and narrow range was studied [8-11], and also the paper offers the effect of doped ZnO and α-Fe_2O_3 nanoparticles on the conductivity of P-Ani.

Corresponding Author: Zaid Hamid Mahmoud, Department of chemistry, college of science, Diyala university, Iraq, E-mail: zaidhameed_91 @ yahoo .com

Experimental

Preparation of α-Fe_2O_3 Nanoparticles

The nanoparticles of Hematite (α -Fe_2O_3) were prepared utilizing photolysis method. Firstly, 2g of ferric chloride hexa hydrate ($FeCl_3.6H_2O$) was dissolved in 100ml distilled water. Then, it was irradiated for 2hr using the system of UV-irradiation with power 125W as shown in figure 1. Finally, the fresh precipitate was isolated and washed with acetone for 3 times, and burned at 400°C.

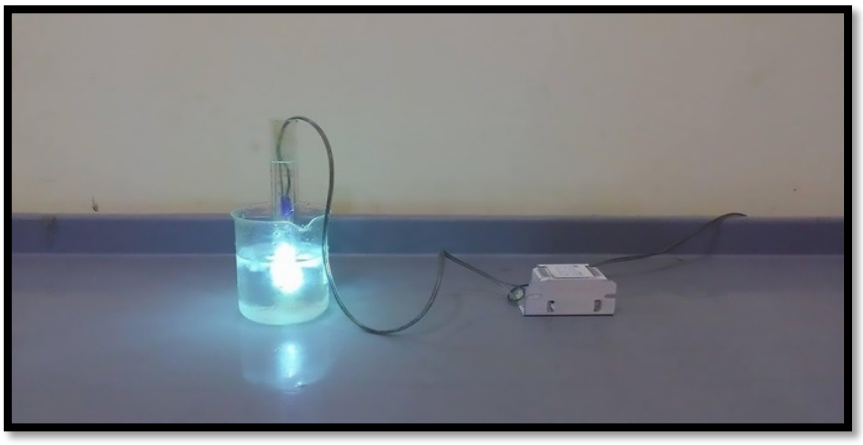

Figure 1: Irradiation system

Preparation of ZnO Nanoparticles

Sol gel method was used to prepare Zinc oxide (ZnO) nanoparticle. Briefly, Zinc acetate was used as a precursor material, while citric acid was used as a precursor to prepare a homogenous solution. Zinc acetate (0.1M) and citric acid (0.1M) solutions with an equivalent ratio were mixed and stirred for 30min. Then, 1M of sodium hydroxide solution was added drop wise until the pH of solution got equal to 7. After that, the solution was left on the hot plate with 80C until the solution evaporated. The product gel was burned at 400°C for 3hr.

Preparation of Poly aniline

3 ml of distillated aniline in a 50 ml beaker was put in an ice bath at 0 °C for 10 min. After that, 20 ml of 1M HCl was added drop wise, and then 20 ml of (2 g of ammonium per sulphate (APS) dissolved in 20 ml of 1M HCl) was added drop wise; the temperature was maintained at 0 °C. Then, the solution was stirred for 2 hours in an ice bath, then it was maintained in the refrigerator the whole night. The obtained yield was filtered and washed with distillated water 4 times with 20 ml ammonium hydroxide 1M, and stirred for 30 minutes. After that, it was filtered and washed with distillated water until the PH was neutral. At the end, 15 ml of benzene was used to wash the precipitate, and then the precipitate was stirred for 15 min and dried at 80 °C for 6 hours.

Preparation of Poly aniline with ZnO, α-Fe_2O_3 Nanocomposites

0.6 g of Ferric oxide was sonicated with 6 ml of distillated aniline for 20 min and filtered, after that it was put in a small beaker immersed in an ice bath at 0 °C. Then, 20 ml of 1M HCl was added drop wise and 10 ml of (1 g of Ammonium per sulphate (APS) dissolved in 10 ml of 1M HCl) was added drop wise; the temperature was kept at 0 °C. Then, the solution was stirred for 2 hours in an ice bath, consequently, the solution was maintained in the refrigerator the whole night. The yield was filtered and washed with distilled water 4 times and 20 ml ammonium hydroxide 1M, and it was stirred for 30 minutes, then it was filtered and washed with distilled water until the PH was neutral. Finally,15 ml of benzene was used to wash the precipitate, and it was stirred for 15 minutes, and dried at 80 °C for 6 hours.

Characterization

FTIR spectra were performed on (65 FT-IR Perkin Elmer Spectrophotometer) in the wavelength range of 400–4000 cm^{-1}, The prepared materials were characterized by x-ray diffraction using (Shemadzu– XR – 6000) device with Nickel - Cooper filter for the x-ray radiation (Cu Kα, λ = 1.5406 Å), and the electrical measurements of the compounds were prepared using the device (LCR- 8105-G).

Conductivity, Dielectric Constant Measurements

The conductivity and the dielectric properties (dielectric constant ε' and dielectric loss ε'') were measured as a disc of (5) mm diameter, and the thickness of (0.00032) mm was prepared by pressing the powdered samples at 10 tons/cm^2 and the frequency range from 50 Hz to 1 MHz using (LCR- 8105-G). The dielectric constant ε', of the prepared composites were calculated from the measured capacitance according to the equation:

$$C_o = \varepsilon_o A / d , \quad (1)$$

$$\varepsilon' = C_p / C_o \quad (2)$$

$$\varepsilon'' = \tan \delta * \varepsilon' \quad (3)$$

$$\sigma_{ac} = \varepsilon_o \varepsilon'' * 2 * pi * f \quad (4)$$

$$\varepsilon_o = 8.85 * 10^{-14}$$

Results and Discussion

Spectroscopic study by FT-IR spectrum

Fig. 2 shows the FTIR spectra of PANI, PANI- α-Fe_2O_3 and PANI-ZnO nanocomposites, FTIR spectra of PANI showed the main characteristic peaks at 3264 cm^{-1}, 1590.8 cm^{-1}, cm^{-1}, 1294.6 cm^{-1}, 1163 cm^{-1}, 833.83 cm^{-1} corresponding to PANI. The bands at 3264 cm^{-1} were attributed to N–H stretching vibration peak. The bands corresponding to stretching vibrations of N-B-N and N=Q=N structures appeared at 1590.6 and 1501 cm^{-1}; respectively, and the stretching mode of C-N bond appeared at 1163 and 1294.6 cm−1; respectively. The band corresponding to out of plane bending vibration of C-H bond of p-substituted benzene ring appeared at 833.83 cm^{-1}. FTIR spectra of PANI- α-Fe_2O_3 showed the main characteristic peaks similar to PANI with α-Fe_2O_3 peak attributed at 447.87 cm^{-1}, 546.6 cm^{-1} while, the FTIR spectra of PANI-ZnO also showed the main characteristic peaks similar to PANI with ZnO peak attributed at 516.69 cm^{-1}.

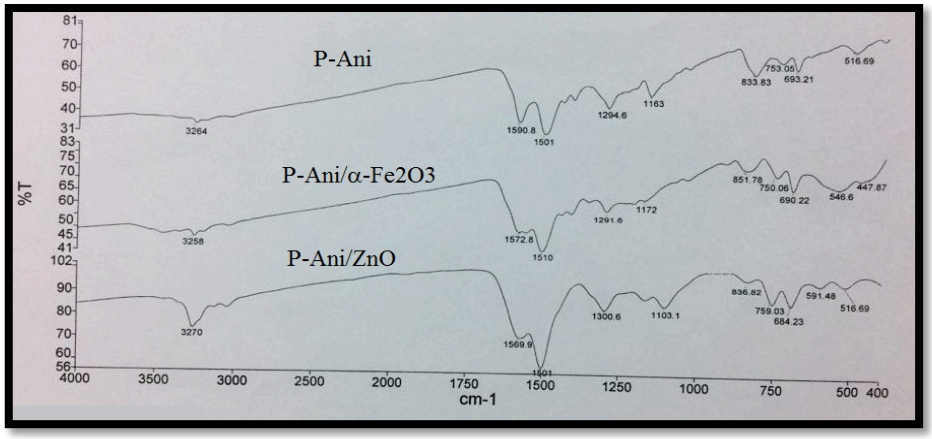

Figure 2: FTIR spectrum of P-Ani, P-Ani/□-Fe_2O_3 and P-Ani/ZnO

XRD

The structure of P-Ani doping with ZnO and α-Fe_2O_3 was investigated using X-ray diffraction pattern analysis (XRD). Figure 3 and 4 show the XRD spectrum of P-Ani doping with ZnO and α-Fe_2O_3; respectively. The spectrum of P-Ani with doping ZnO showed the characteristic peaks at 31.76, 34.42, 36.25, 47.53, 56.60, 62.86, 66.37, 67.96, 69.09, 72.55 and 76.95 corresponding to the hexagonal structure as shown in figure 3, while, many peaks appeared at 24.13, 33.15, 35.61, 39.27, 40.85, 43.15, 49.47, 54.08, 56.15, 57.42, 62.44, 66.02, 69.59, 71.93, 72.26 and 75.24 corresponding to the rhombohedral structure as shown in figure 4. All results of P-Ani with ZnO nanocomposite were in agreement with (JCPDS card No. 36.1451). The spectrum showed the significantly enhanced powder when doping the P-Ani with the nanoparticles of ZnO and α-Fe_2O_3, and indicated high intensity assigned to P-Ani, otherwise the disappeared peaks got back to ZnO and α-Fe_2O_3 due to the low percent of the nanoparticles during polymerization.

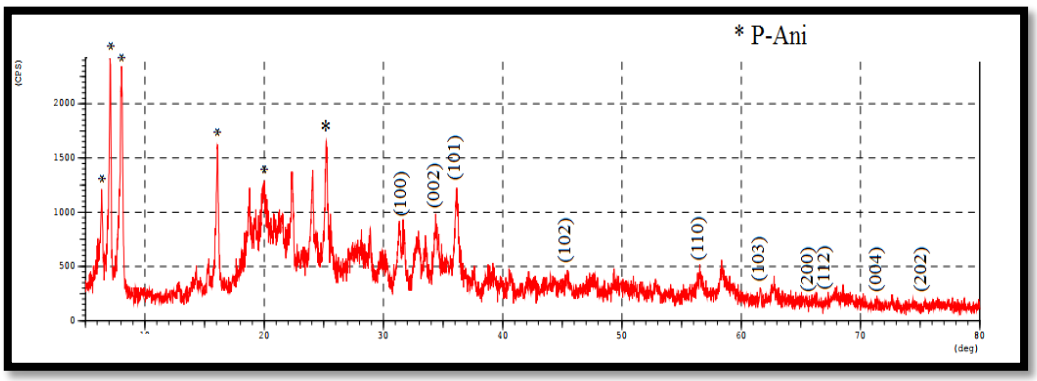

Figure 3. XRD of P-Ani/ZnO nanocompsite

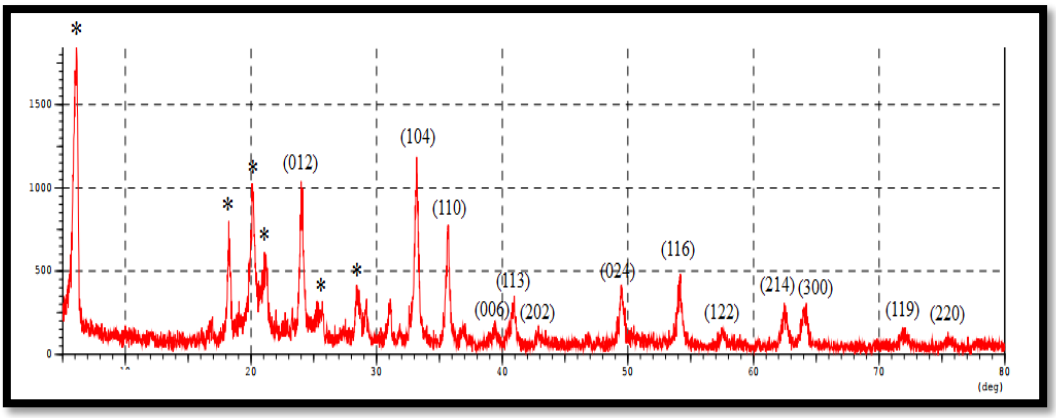

Figure 4. XRD of P-Ani/α -Fe_2O_3 nanocompsite

D*eb*ye-scherrer equation was utilized to calculate the size of particles, and the results indicated particles in nano size as shown in ta*b*le 1.

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Table 1: The particle size of P-Ani/ZnO and P-Ani/□-Fe_2O_3

No.	Compound	FWHM	D
1	P-Ani/ZnO	0.2633	31.50 nm
2	P-Ani/α-Fe_2O_3	0.4343	18.52 nm

SEM

The surface morphology of P-Ani/ZnO was examined using scanning electron microscope. The results represented large agglomeration of particles with a smooth surface as shown in figure 5. The particles were prepared in nano size with the range of 34nm. The results from SEM indicated to be corresponded to XRD result.

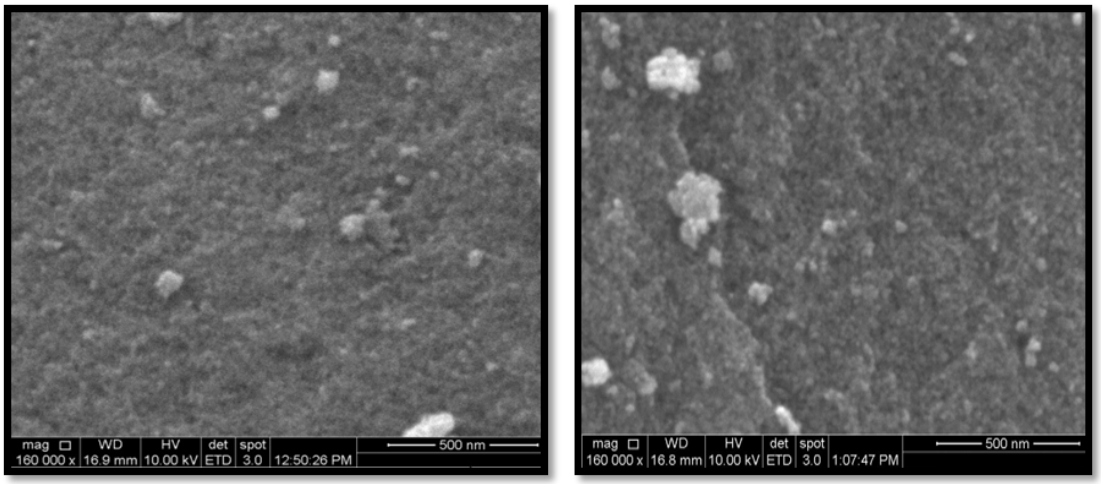

Figure 5: SEM of P-Ani/ZnO

Studying Electrical Properties

In the electrical study of composites by measuring their conductivity, the dielectric properties at different frequencies is one of the most important characters to investigate their use in electrical devices. Basically, dielectric constant ε' is the measure of how easily a material is polarized in the presence of an external electric field. For heterogeneous dielectric materials, the changes in the value of ε as a function of frequency have been attributed to the space charges polarization because of moving the free charges at the interfaces of the composites and dielectric relaxation due to the segmental movement [12, 13]. The electrical conductivity has been shown in Tab.2, the conductivity increased with nano oxide (α-Fe_2O_3, ZnO) additive; and the increase of conductivity was due to the increase of the charge carriers which increased with the increasing filler content [14-16] (See Tab 3, Figures 6,7,8, & 9).

Table 2: the conductivity calculation of PANI/□-Fe_2O_3

No.	Hz	log Hz	F	D	$C_o=\varepsilon_o A/d$	$\varepsilon'=C_p/C_o$	$\varepsilon''=\tan\delta*\varepsilon'$	$\sigma_{ac}=\varepsilon_o\varepsilon''*2*pi*f$
1	50	1.69897	2.93E-08	1.844	8.69E-13	3.37E+04	6.21E+04	1.73E-04
2	226178.4	5.354451	3.42E-12	0.0508	8.69E-13	3.94E+00	2.00E-01	2.52E-06
3	477432.2	5.678912	3.38E-12	0.0323	8.69E-13	3.89E+00	1.26E-01	3.34E-06
4	728685.9	5.86254	3.38E-12	0.0681	8.69E-13	3.89E+00	2.65E-01	1.07E-05
5	979939.7	5.991199	3.40E-12	0.0573	8.69E-13	3.92E+00	2.24E-01	1.22E-05
6	1231194	6.090326	3.32E-12	0.0499	8.69E-13	3.81E+00	1.90E-01	1.30E-05
7	1482447	6.170979	3.38E-12	0.0479	8.69E-13	3.89E+00	1.86E-01	1.54E-05
8	1733701	6.238974	3.37E-12	0.0435	8.69E-13	3.87E+00	1.69E-01	1.63E-05
9	1984955	6.297751	3.37E-12	0.0354	8.69E-13	3.88E+00	1.37E-01	1.52E-05
10	2236209	6.349512	3.36E-12	0.0352	8.69E-13	3.86E+00	1.36E-01	1.69E-05

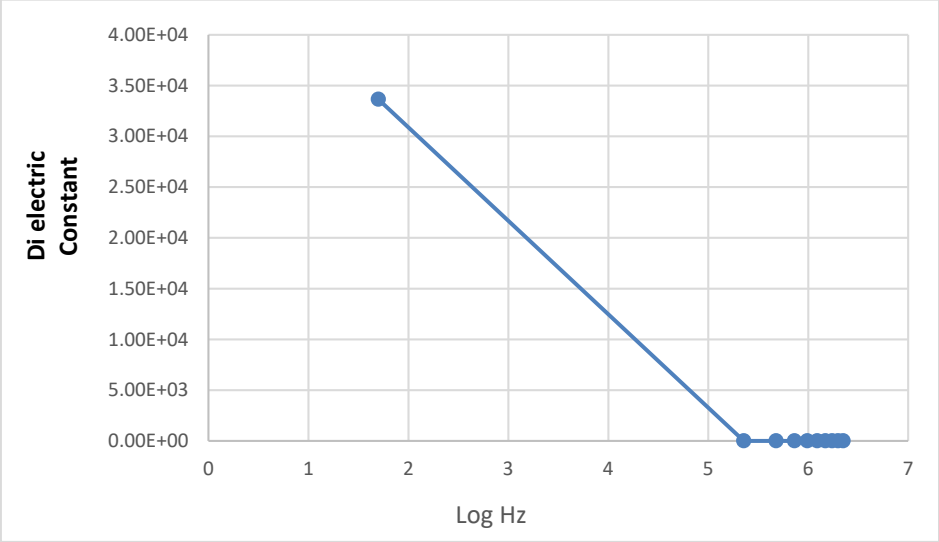

Figure 6: Dielectric constant as function with log Hz

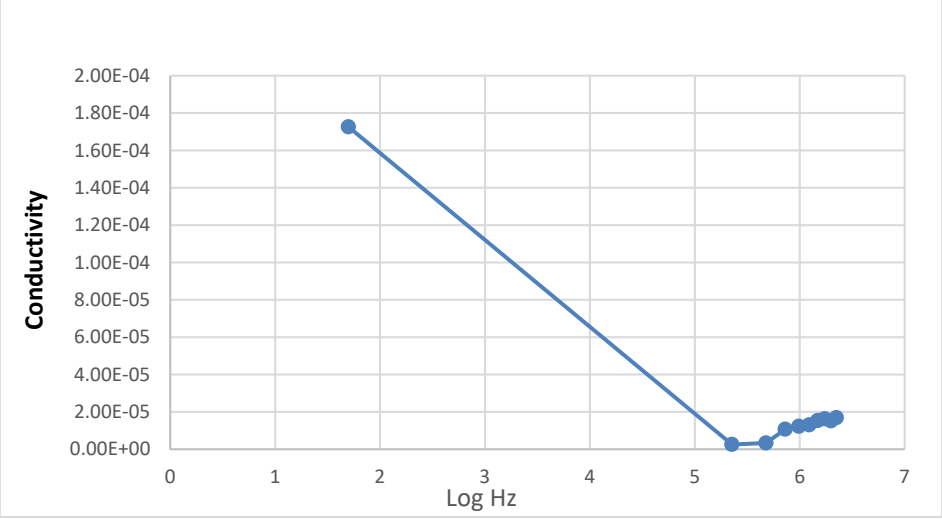

Figure 7: conductivity of P-Ani/α-Fe2O3 as a function with log Hz

Table 3: the conductivity calculation of PANI/ZnO

Unit	Hz	log Hz	F	D	$C_o=\varepsilon_o A/d$	$\varepsilon'=C_p/C_o$	$\varepsilon''=\tan\delta*\varepsilon'$	$\sigma_{ac}=\varepsilon_o\varepsilon''*2*pi*f$
1.	50	1.69897	7.73E-09	8.547	8.69E-13	8.90E+03	7.60E+04	2.12E-04
2.	226178.4	5.354451	8.98E-12	0.0217	8.69E-13	1.03E+01	2.24E-01	2.82E-06
3.	477432.2	5.678912	8.99E-12	0.0054	8.69E-13	1.03E+01	5.58E-02	1.48E-06
4.	728685.9	5.86254	9.10E-12	0.0368	8.69E-13	1.05E+01	3.85E-01	1.56E-05

5.	979939.7	5.991199	9.11E-12	0.0349	8.69E-13	1.05E+01	3.66E-01	1.99E-05
6.	1231194	6.090326	8.84E-12	0.0301	8.69E-13	1.02E+01	3.06E-01	2.10E-05
7.	1482447	6.170979	8.82E-12	0.0219	8.69E-13	1.01E+01	2.22E-01	1.83E-05
8.	1733701	6.238974	8.71E-12	0.0049	8.69E-13	1.00E+01	4.91E-02	4.73E-06
9.	1984955	6.297751	8.89E-12	0.0014	8.69E-13	1.02E+01	1.43E-02	1.58E-06
10.	2236209	6.349512	8.88E-12	0.013	8.69E-13	1.02E+01	1.33E-01	1.65E-05

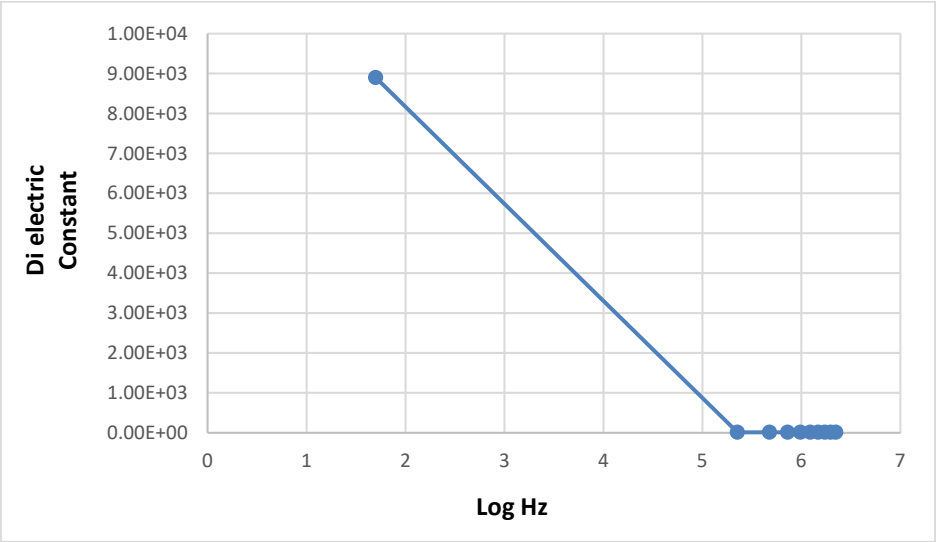

Figure 8: Dielectric constant as function with log Hz

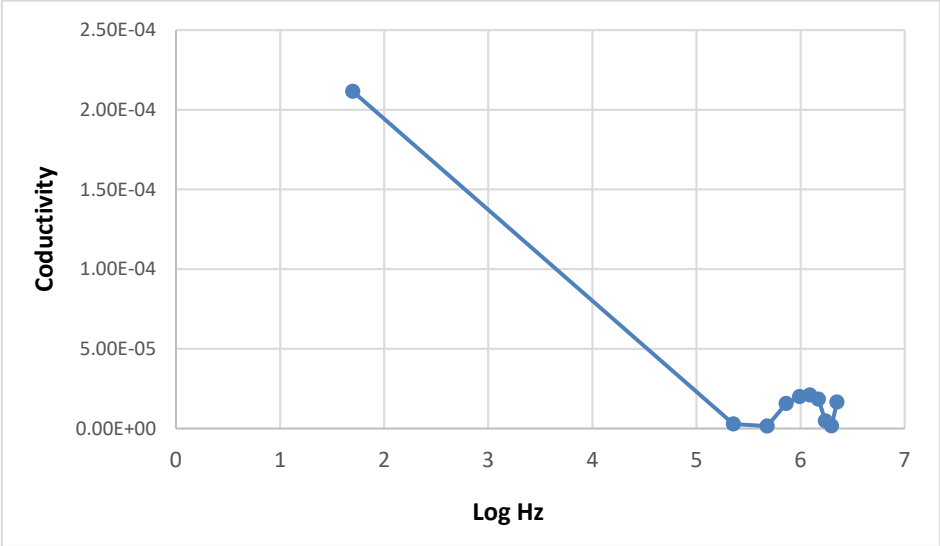

Figure 9: conductivity of P-Ani/ZnO as a function with log Hz

Conclusion

The small amount of α-Fe_2O_3 and ZnO was utilized in P-Ani/α-Fe_2O_3, and P-Ani/ZnO nanocomposite was successfully prepared. The compound prepared was analyzed using FTIR, XRD, SEM and LCR. The particles synthesized were in nano scale, which were confirmed by XRD and SEM. The measurement of SEM was used in preparing smooth surface of P-Ani/ZnO, while the results from XRD showed a preference of photolysis method on sol-gel method in preparing nanoparticles with a small range. Investigating the electric properties, P-Ani/α-Fe_2O_3 and P-Ani/ZnO showed conductive properties due to the increase in the charge carriers which were increased by increasing the filler content.

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