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Synthesis and Optical Characterization of Polyaniline /Iron Oxide Nanocomposite

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Abstract

Polyaniline-iron oxide nanocomposites were successfully synthesized by in-situ polymerization method. The polyaniline metal oxide nanocomposites formed were characterized using StellarNet UV – VIS – NIR spectrometer (Blue – Wave Miniature; Model: UVNb). The optical properties investigated include; absorbance, transmittance, reflectance, refractive index, extinction coefficient and energy band gap. Our results show that the absorbance of polyaniline – iron oxide nanocomposites decreases as amount of iron oxide nanoparticles increased with a peak value of approximately 1.00. Transmittance of polyaniline– iron oxide (PANI/Fe_2O_3) nanocomposites decreases as amount of iron oxide nanoparticles increased with a peak value of 58% at 800nm. Reflectance within the regions of the electromagnetic spectrum considered was found to be very low. A peak refractive index value of 2.64 was obtained at 700nm for the synthesized iron oxide nanoparticles. The extinction coefficient of our synthesized nanocomposites decreased with increase in the concentration of iron oxide nanoparticles. Optical band gap of polyaniline iron oxide nanocomposites ranged from 2.50 eV to 2.20 eV.Our x – ray diffraction result show that the PANI/Fe_2O_3 nanocomposites formed have Orthorhombic crystal structure with preferred orientation in the (111) plane.

Keywords:

Conducting polyaniline;
Polyaniline/Fe_2O_3;
nanocomposite;
Characerization;
Optical properties .

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1. Introduction

Nanoparticles are particles which are 1 to 100 nanometers in size. Investigations on nanoparticles are on the high side because of their special physical and chemical properties different from the bulk materials [1]. Their special properties are high surface area, quantum size effects and lower sintering temperature. Presently, polymer/metal oxide nanocomposites are important class of materials in the area of nanotechnology. Polyaniline (PANI) is the most attractive conducting polymer among the other conducting polymers because of its environmental stability, easy synthesis and low cost [3]. The composites of conducting polymers and inorganic materials are of great interest because they exhibit a good range of electrical, optical and magnetic properties [3]. Therefore, the optical properties of the nanocomposites of PANI/Fe_2O_3 are investigated in this paper.

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2. Materials Research Method

In this research work, polyaniline-iron oxide nanocomposite was synthesized. In the synthesis of the nanocomposite, iron oxide nanoparticles were first synthesized by the reaction between ferric chloride and ferrous sulphate mixed in the molar ratio of 2:1.100 ml of both ferric chloride and ferrous sulphate were transferred to a 250 ml beaker, the mixture was then heated up to 60℃ for 10 minutes. After heating, the solution was precipitated by drop – wise addition of ammonia solutionat the rate of 1 ml per minute for 1 hour. The final solution was allowed to stay under continuous stirring on the magnetic stirrer at 60℃ for another 1hour. At end of the 2 hours, the beaker containing the solution was allowed to cool. Black colored particles of iron oxides were precipitated. These particles were then separated from the solution by the use of a strong magnet and then were washed many times with distilled water. The powder was then dried in hot air oven at 100℃ for 24 hours. The overall reaction can be written as

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_2 + 4H_2O$$

After the synthesis of iron oxide nanoparticles, Polyaniline– iron oxide nanocomposites was then synthesized by in-situ polymerization method. 2 ml of aniline was mixed with 1M of HCl and stirred for 30 minutes to form aniline hydrochloride. 0.5 g of iron oxide nanoparticles were then dispersed in the above solution with vigorous stirring in order to keep the iron oxide homogeneously suspended in the solution. To this solution, 20 ml of ammonium persulphate hydrochloride was added drop – wise with drop rate of 1 drop per minute, the final solution was allowed to age for 24 hours to completely polymerize. The precipitate was filtered and washed with acetone and then with water and finally dried in a hot air oven at 60℃ for 24 hours. In this way, Polyaniline – iron oxidenanocomposites containing various weights of 0.5 g, 1.0 g, 1.5 g and 2.0 g in PANI were synthesized.

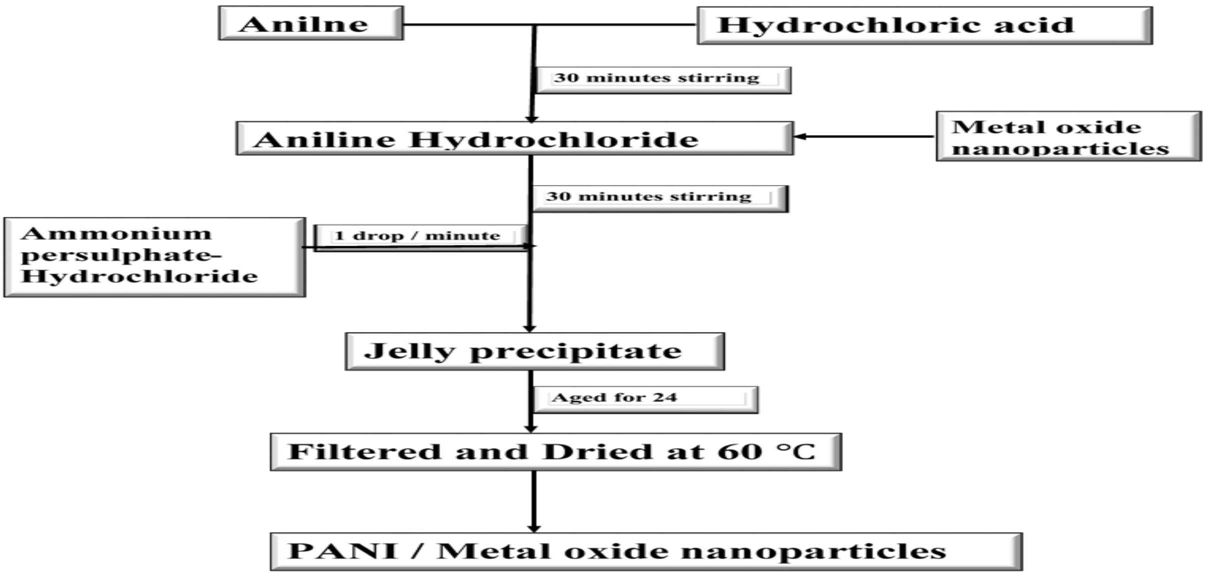

Figure 1: Flowchart of the method of synthesis of Polyaniline – iron oxide nanocomposites

After the synthesis of Polyaniline-iron oxide nanocomposite, optical absorption spectra of the nanocomposites were studied using spectrophotometer within ultraviolet (UV) region (250 nm to 390 nm), visible light (VIS) region (400 nm to 700 nm) and near infrared (NIR) region (710 nm to 800 nm) with a scanning speed of 400 nm/min. Other optical properties such as transmittance, reflectance, refractive index, extinction coefficient and optical band gap were evaluated using theory.

3. Results and Analysis

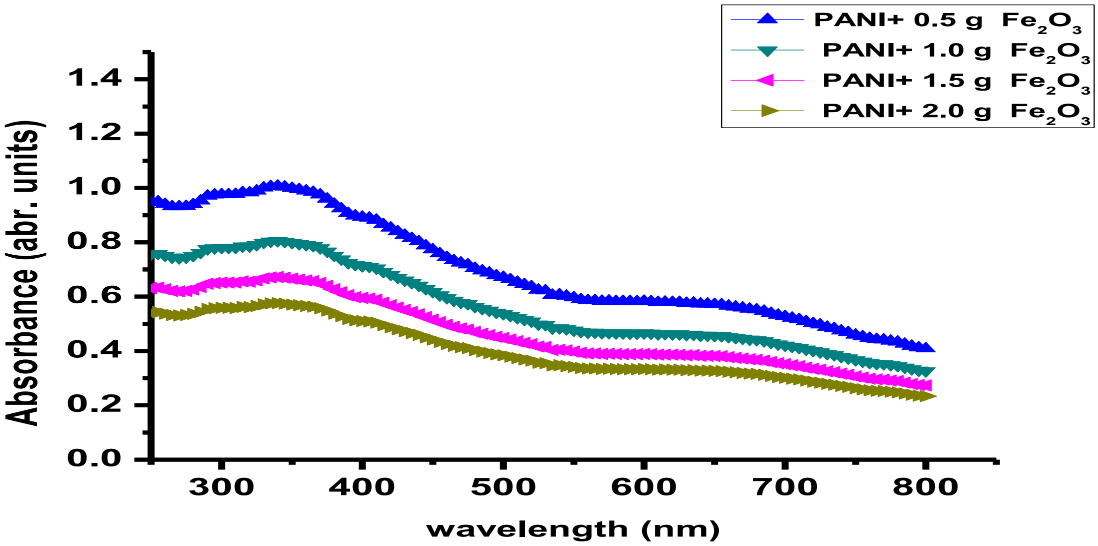

Figure 2: Plot of Absorbance against wavelength for polyaniline – iron oxide(PANI/Fe_2O_3)nanocomposites

Absorbance graph of PANI / 0.5g of Fe_2O_3 show that the absorbance values range from 0.95 at 250nm to a peak value of approximately 1.00 at 340 nm. It decreases slightly to 0.90 at 395nm. In VIS region, the absorbance values range from 0.89 at 400 nm to 0.53 at 700nm. In NIR region, the values range from 0.52 at 705 nm to 0.41 at 800 nm. Absorbance graph of PANI/1.0 g of Fe_2O_3 shows that the absorbance values range from 0.76 at 250 nm to a peak value of 0.81 at 340 nm. It decreases slightly to 0.72 at 395 nm. In VIS region, the absorbance values range from 0.71 at 400 nm to 0.42 at 700 nm. In NIR region, the values range from 0.42 at 705nm to 0.33 at 800nm. Absorbance graph of PANI / 1.5g of Fe_2O_3 shows that the absorbance values range from 0.63 at 250nm to a peak value of 0.67 at 335nm. It decreases slightly to 0.60 at 395 nm. In VIS region, the absorbance values range from 0.60 at 400nm to 0.35 at 700nm. In NIR region, the values range from 0.35 at 705nm to 0.27 at 800 nm. Absorbance graph of PANI / 2.0g of Fe_2O_3 show that the absorbance values range from 0.54 at 250nm to a peak value of 0.57 at 340nm. It decreases slightly to 0.51 at 395nm. In VIS region, the absorbance values range from 0.51 at 400nm to 0.30 at 700nm. In NIR region, the values range from 0.30 at 705nm to 0.23 at 800nm. These results show that the absorbance of polyaniline – iron oxide nanocomposites decreased as amount of iron oxide nanoparticles increased. This may be as a result of low absorbing nature of iron oxide nanoparticles which confirms the presence of iron oxide particles in the polyaniline matrix.

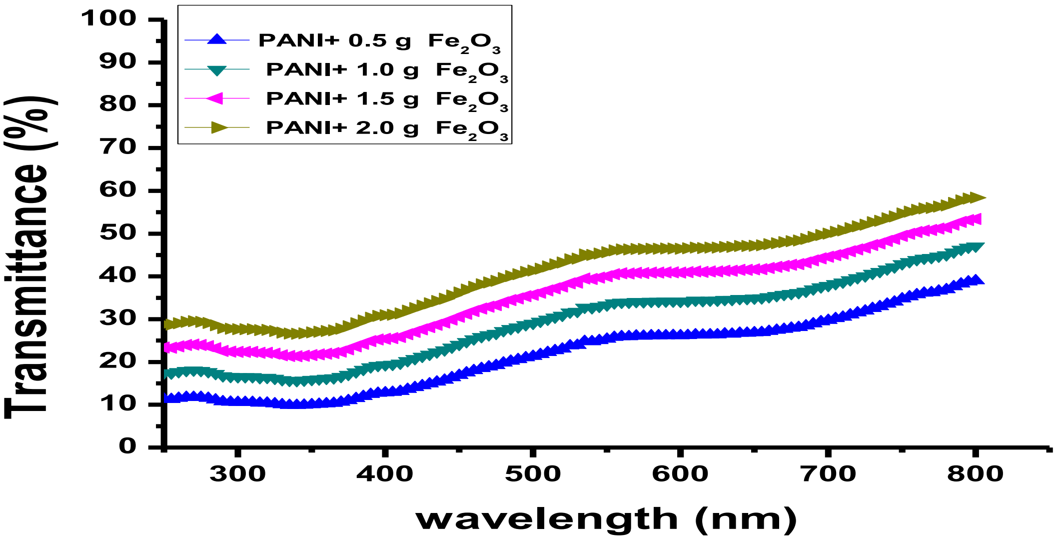

Figure 3: Plot of Transmittance against wavelength for polyaniline – iron oxide nanocomposites

Figure 3 shows the transmittance plotted against wavelength for polyaniline – iron oxide nanocomposites with different iron oxide nanoparticle compositions. Transmittance of PANI / 0.5 g of Fe_2O_3 nanocomposites ranges from 11.30 % at 250 nm to 9.83 % at 340 nm which increases to 12.68 % at 395 nm in UV region. In VIS region, it ranges from 12.80 % at 400 nm to 29.73 % at 700 nm while in NIR region, the transmittance values are between 30.14 % at 705 nm and 39.01 % at 800 nm. Transmittance of PANI / 1.0 g of Fe_2O_3nanocompositesranges from 17.48 % at 250 nm to 15.63 % at 340 nm which increases to 19.16 % at 395 nm in UV region. In VIS region, it ranges from 19.32 % at 400 nm to 37.89 % at 700nm while in NIR region, the transmittance values are between 38.31 % at 705 nm and 47.09 % at 800 nm. Transmittance of PANI / 1.5 g of Fe_2O_3 nanocompositesranges from 23.31 % at 250nm to 21.42 % at 345nm which increases to 25.23 % at 395nm in UV region. In VIS region, it ranges from 25.40 % at 400nm to 44.54 % at 700nm while in NIR region, the transmittance values are between 44.95 % at 705nm and 53.39 % at 800nm. Transmittance of PANI / 2.0 g of Fe_2O_3nanocompositesranges from 28.78 % at 250nm to 26.57 % at 340nm which increases to 30.72 % at 395 nm in UV region. In VIS region, it ranges from 30.90 % at 400nm to 50.00 % at 700nm while in NIR region, the transmittance values are between 50.93 % at 705nm and 58.40 % at 800nm. These results show that the transmittance of polyaniline– iron oxide (PANI/Fe_2O_3) nanocomposites decreased as amount of iron oxide nanoparticles increased. This shows that incorporation of iron oxide into the polyaniline matrix improve the transmittive properties of polyaniline.

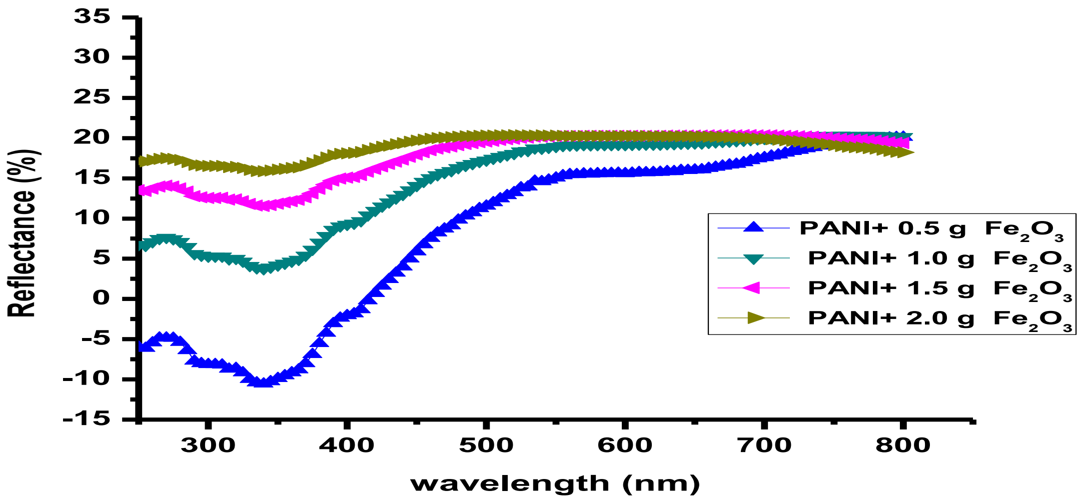

Figure 4: Plot of Reflectance against wavelength for polyaniline – iron oxide nanocomposites

Figure 4 shows the plot of reflectance plotted against wavelength for polyaniline – iron oxide nanocomposites. Reflectance of PANI / 0.5 g of Fe_2O_3nanocompositesranges from −5.98 % at 250 nm which decreases to −10.60 % at 340 nm before increases to −2.38 % at 395 nm in UV region. In VIS region, it ranges from −2.07 % at 400 nm to 17.59 % at 700nm while in NIR region, the reflectance values are between 17.77 % at 705 nm and 20.11 % at 800nm. Reflectance of PANI / 1.0 g of Fe_2O_3 nanocomposites ranges from 6.78 % at 250nm to 3.77 % at 340nm which increases to 9.08 % at 395 nm in UV region. In VIS region, it ranges from 9.28 % at 400nm to 19.96 % at 700 nm while in NIR region, the reflectance values increase slightly from 20.02 % at 705 nm to 20.20 % at 800 nm. Reflectance of PANI / 1.5 g of Fe_2O_3 nanocomposites ranges from 13.50 % at 250 nm to 11.66 % at 345 nm which increases to 14.97 % at 395nm in UV region. In VIS region, it ranges from 15.09 % at 400nm to 20.34 % at 700nm while in NIR region, the reflectance values decrease slightly to 20.32 % at 705 nm and 19.36 % at 800 nm. Reflectance of PANI / 2.0 g of Fe_2O_3 nanocomposites ranges from 17.13 % at 250 nm to 15.87 % at 340nm which increases to 18.02 % at 395 nm in UV region. In VIS region, it ranges from 18.09 % at 400nm to

19.90 % at 700nm while in NIR region, the reflectance values are between 19.84 % at 705 nm and 18.24 % at 800nm. The negative values of reflectance obtained for polyaniline and PANI formed with 0.5 g of iron oxide is due to high absorbing nature of the nanoparticles which results to very low values of reflectance within the regions of the electromagnetic spectrum under consideration.

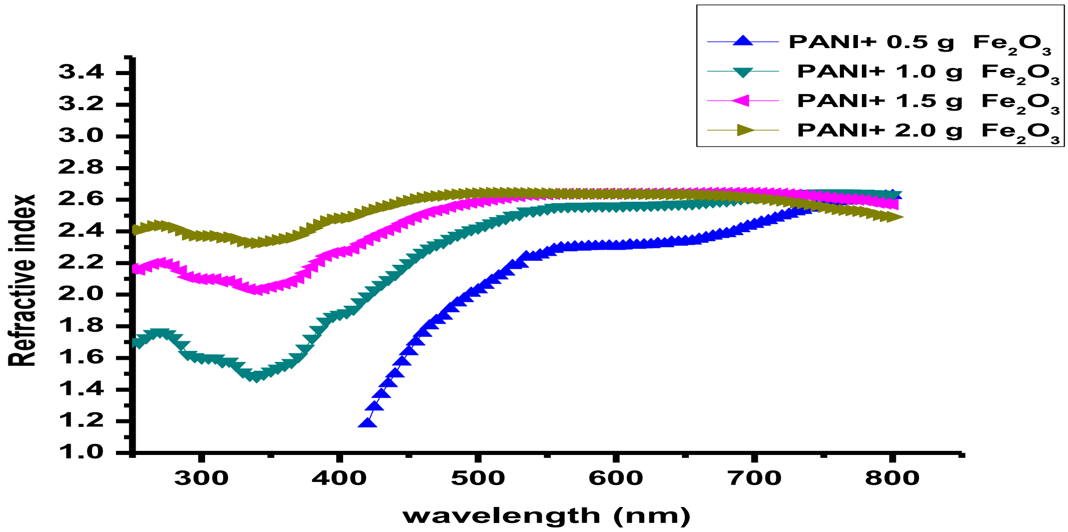

Figure 5: Plot of Refractive index against wavelength for polyaniline – iron oxide nanocomposites

Figure 5 shows the refractive index of polyaniline – iron oxide nanocomposite. Polyaniline formed with 0.5g of Fe_2O_3 has refractive index of 1.18 at 420nm to 2.43 at 700nm. In NIR region, its values range between 2.44 at 705nm and 2.63 at 800nm. Polyaniline formed with 1.0g of Fe_2O_3 has refractive index of 1.70 at 250nm to 1.86 at 395nm within UV region. In VIS region, the refractive index values range from 1.88 at 400nm to 2.62 at 700nm. In NIR region, its values range between 2.62 at 705nm and 2.63 at 800nm. Polyaniline formed with 1.5 g of Fe_2O_3 has refractive index of 2.16 at 250 nm to 2.26 at 395 nm within UV region. In VIS region, the refractive index values range from 2.27 at 400nm to 2.64 at 700nm. In NIR region, its values range between 2.64 at 705nm and 2.57 at 800nm. Polyaniline formed with 2.0 g of Fe_2O_3 has refractive index of 2.41 at 250nm to 2.48 at 395 nm within UV region. In VIS region, the refractive index values range from 2.48 at 400 nm to 2.61 at 700nm. In NIR region, its values range between 2.61 at 705nm and 2.49 at 800nm. Peak value of 2.64 is obtained at 700nm for the synthesized with 1.5g iron oxide nanoparticles.

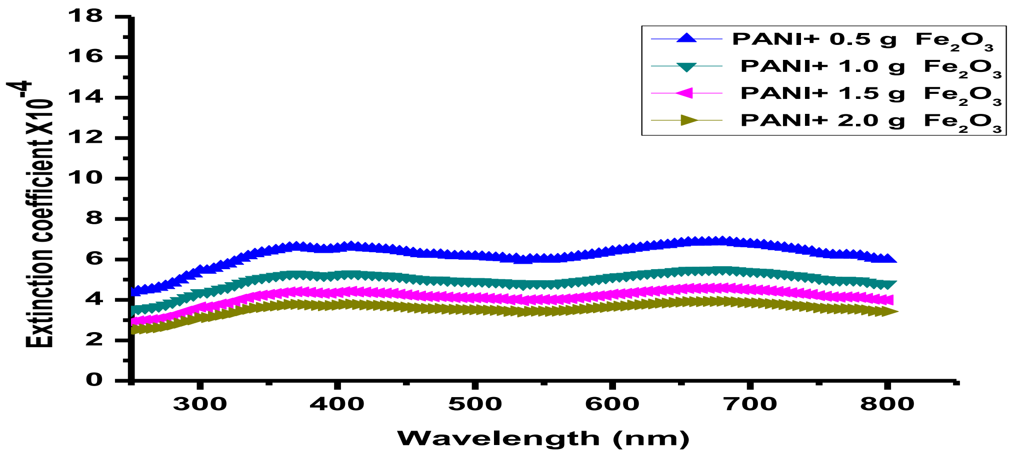

Figure 6: Plot of Extinction coefficient against wavelength for polyaniline – iron oxide nanocomposites

Figure 6 shows the graph of extinction coefficient plotted against wavelength for polyaniline- iron oxide nanocomposites. Polyaniline formed with 0.5 g of iron oxide nanoparticles has extinction coefficient of 4.34×10^{-4} at 250 nm which increase slightly to 6.49×10^{-4} at 395 nm within UV region. In VIS region, the extinction coefficient is between 6.54×10^{-4} at 400nm and slightly increases to 6.76×10^{-4} at 700nm while in NIR region, its values range from 6.73×10^{-4} at 705nm to 5.99×10^{-4} at 800nm. Polyaniline formed with 1.0 g of iron oxide nanoparticles has extinction coefficient of 3.47×10^{-4} at 250 nm which increase slightly to 5.19×10^{-4} at 395 nm within UV region. In VIS region, the extinction coefficient is between 5.23×10^{-4} at 400nm and slightly increases to 5.41×10^{-4} at 700 nm while in NIR region, its values range from 5.38×10^{-4} at 705 nm to 4.79×10^{-4} at 800 nm.Polyaniline formed with 1.5 g of iron oxide nanoparticles has extinction coefficient of 2.89×10^{-4} at 250nm which increase to 4.33×10^{-4} at 395 nm within UV region. In VIS region, the extinction coefficient is between 4.36×10^{-4} at 400nm and slightly increases to 4.51×10^{-4} at 700 nm while in NIR region, its values range from 4.49×10^{-4} at 705nm to 4.00×10^{-4} at 800nm. Polyaniline formed with 2.0 g of iron oxide nanoparticles has extinction coefficient of 2.48×10^{-4} at 250nm which increase slightly to 3.71×10^{-4} at 395 nm within UV region. In VIS region, the extinction coefficient is between 3.74×10^{-4} at 400nm and slightly increases to 3.86×10^{-4} at 700nm while in NIR region, its values range from 3.85×10^{-4} at 705nm to 3.42×10^{-4} at 800nm. From our result it can be concluded that the extinction coefficient decrease with increase in the concentration of iron oxide nanoparticles.

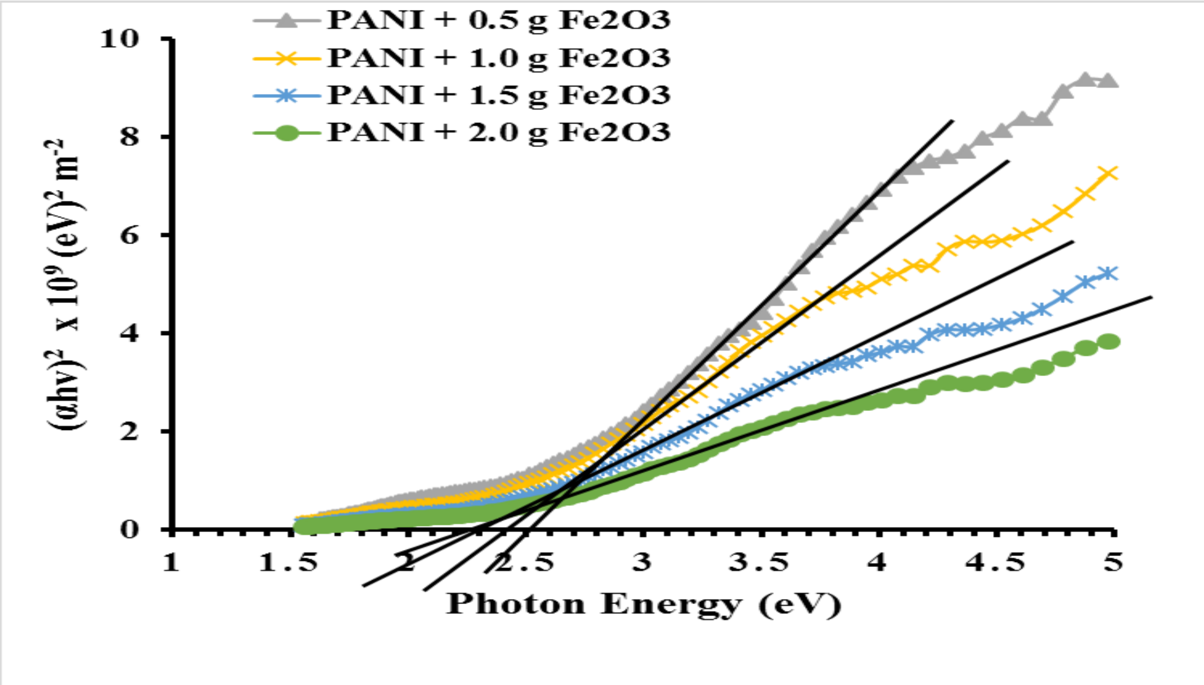

Figure 7: Plot of $(\alpha hv)^2$ against photon energy for polyaniline – iron oxidenanocomposites

Figures 7 shows the plots of $(\alpha h\nu)$squared plotted against photon energy$(h\nu)$. The direct band gap energy was extrapolated at the axis of the photon energy $(h\nu)$ where $(\alpha h\nu)^2 = 0$. Figure 7 gives the band gaps of 2.50 eV for PANI / 0.5g Fe_2O_3, 2.40 eV for PANI / 1.0g Fe_2O_3, 2.27 eV for PANI / 1.5g Fe_2O_3 and 2.20 eV for PANI / 2.0g Fe_2O_3nanocomposites. From Figure 7, it can be seen that the optical band gap of polyaniline iron oxide nanocomposites decreased from 2.50 eV to 2.20 eV as amount of Fe_2O_3 increased. The decrease in the optical band gap may be due to reduction in the disorder of the system and increase in the density of defect states [4] and modifications of the polymer matrix due to the addition of dopant [5].[6] observed a similar decrease in the energy band gap of polyaniline when intercalated with selenium nanowires. They suggested that the decrease in band gap may be due to the broadening of polaron bands, which is attributed to the increase in carrier concentration in the polymer after doping. A similar behavior of decrease in band gap was obtained for polyaniline doped with increasing Zirconium nanoparticles concentrations [7]. According to [7], this decrease in band gap as zirconium concentration increases caused an increase in electrical conductivity of the polyaniline. Corresponding results were observed by other researchers such as [8, 9, 10, 11] for various doping agents. The values of the optical band gap for polyaniline – iron oxide nanocomposites are suitable for application in semiconducting materials.

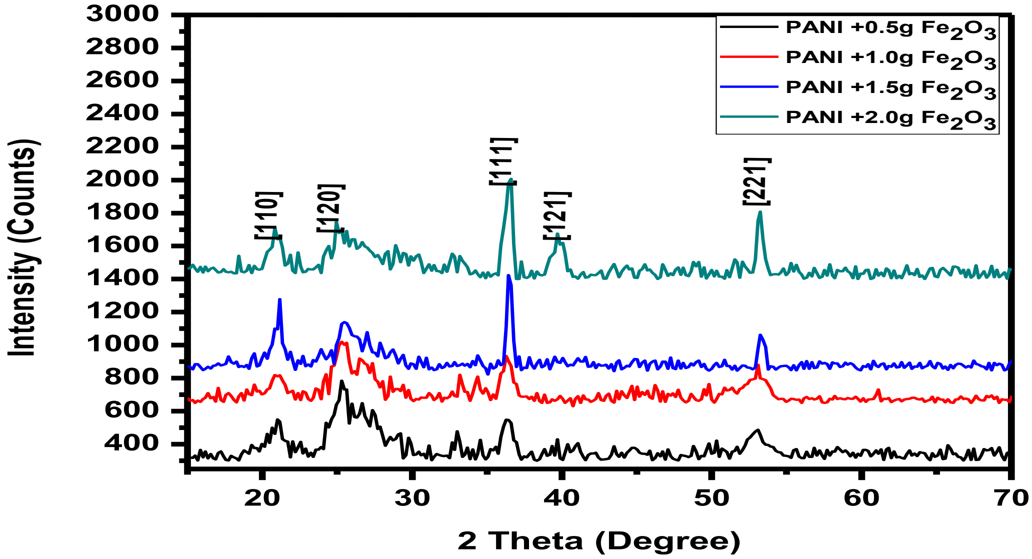

Figure 8: XRD pattern of Polyaniline / Iron oxide (PANI / Fe_2O_3) nanocomposite

Figure 8 shows the x – ray diffraction pattern of PANI/Fe_2O_3 nanocomposites synthesizes with different weights of Fe_2O_3 nanoparticles ranging from 0.5g to 2.0g. Our results show that the PANI/Fe_2O_3 nanocomposites formed have structural phase of iron oxide hydroxide with mineral name Goethite belonging to Orthorhombic crystal structure with space group Pbnm and JCPDS file number (00 – 029 – 0713). The structural parameters such as full width half maximum (FWHM), miller indices (hkl), standard and observed 2 theta angles, standard and observed d – spacings, and crystallite sizes of the PANI/iron oxide nanocomposites are presented in table 1. From table 1, the average crystallite sizes of 8.03 nm, 7.68 nm, 12.85 nm and 13.91 nm were obtained for different Fe_2O_3 compositions of polyaniline matrix. These results show that the polyaniline – iron oxide particles are in nanoscale. [12] obtained similar Goethite structural phase for their synthesized iron nanoparticles.

Table 1: Crystal structural properties of PANI / Fe_2O_3 nanoparticles

PANI/Fe_2O_3	2θ (°)		D – spacing (Å)		[hkl]	FWHM (°)	Crystallite Size (nm)
	Observed	Standard	Observed	Standard			
0.5g	20.92	21.22	4.24	4.18	110	1.086	7.77
	26.00	26.32	3.42	3.39	120	2.846	2.99
	36.37	36.06	2.47	2.49	111	0.655	13.33
	52.96	53.24	1.73	2.72	221	1.153	8.04
1.0g	20.99	21.22	4.23	4.18	110	0.987	8.55
	25.86	26.32	3.44	3.39	120	2.545	3.34
	36.35	36.06	2.47	2.49	111	0.709	12.31
	52.95	53.24	1.73	2.72	221	1.421	6.52
1.5g	21.06	21.22	4.22	4.18	110	0.646	13.06
	26.03	26.32	3.42	3.39	120	2.547	3.34
	36.50	36.06	2.46	2.49	111	0.331	26.39
	53.09	53.24	1.72	2.72	221	1.077	8.61
2.0g	20.89	21.22	4.25	4.18	110	0.866	9.74
	26.26	26.32	3.39	3.39	120	2.123	4.01
	36.44	36.06	2.46	2.49	111	0.490	17.82
	39.77	39.98	2.26	2.25	121	0.692	12.75
	53.21	53.24	1.72	2.72	221	0.368	25.21

4. Conclusion

Polyaniline-iron oxide nanocomposites were successfully synthesized by in-situ polymerization method. The polyaniline metal oxidenanocomposites formed were characterized using Stellar Net UV – VIS – NIR spectrometer (Blue – Wave Miniature; Model: UVNb). From the absorbance values obtained, other parameters which include: transmittance, reflectance, refractive index, extinction coefficient and optical band gap were evaluated using theory. Our results show that the absorbance of polyaniline – iron oxide nanocomposites decreases as amount of iron oxide nanoparticles increased with a peak value of approximately 1.00. Our results show that the transmittance of polyaniline– iron oxide (PANI/Fe_2O_3) nanocomposites decreases as amount of iron oxide nanoparticles increased with a peak value of 58% at 800nm. Reflectance within the regions of the electromagnetic spectrum considered was found to be very low. A peak refractive index value of 2.64 was obtained at 700nm for the synthesized with 1.5g iron oxide nanoparticles.From our result it can be concluded that the extinction coefficient decrease with increase in the concentration of iron oxide nanoparticles. Our result also revealed that the optical band gap of polyaniline iron oxide nanocomposites decreased from 2.50 eV to 2.20 eV as amount of Fe_2O_3 increased. Our x–ray diffraction result show that the PANI/Fe_2O_3 nanocomposites formed have Orthorhombic crystal structure with preferred orientation in the (111) plane. Average crystallite sizes of 8.03 nm, 7.68 nm, 12.85 nm and 13.91 nm were obtained for different Fe_2O_3 compositions of polyaniline matrix.

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