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ORIGINAL ARTICLE

Electropolymerization and Characterization of Poly (O-Phenylenediamine) Thin Films at Different pH

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ABSTRACT

Poly -o- phenylenediamine (PoPD) was deposited as thin films on fluorine doped tin oxide (FTO) conducting substrates by electropolymerization technique using two electrodes at varying acidic pH values of the reaction medium. Dihydrogen sodium phosphate and disodium hydrogen phosphate were used for the preparation of phosphate buffer solution. pH values of 1.0, 1.5 and 2.0 were varied by adding phosphoric acid. 1.2V D.C supply voltage was used with the deposition time of five minutes. The prepared polymer samples were characterized using UV-Vis spectroscopy, Raman Spectroscopy, Scanning Electron Microscope (SEM), X – ray diffraction (XRD) techniques, profilometry and four point probe. The spectral results indicated that the synthesized PoPD film has a head to tail type arrangement with the benzenoid and quinoid structures in the phenazine – like backbone and the absorption bands showed a bathochromic shift. The results also showed that the deposited films have low reflectance and the pH values of the reaction medium affect reflective power of the film produced in such medium and the film deposited at strong acidic condition of (pH = 1.0) has the least reflective power. Also, the optical density (ΔOD) of the PoPD was determined as 0.64 which revealed that the polymer is electrochromic. More unevenly dispersed particles of the Poly (o - phenylenediamine) polymer were observed from the SEM images. The result of the XRD revealed that the samples are amorphous in nature. The results obtained from the Raman spectra confirmed that the PoPD thin film samples contained phenazine ring ladder – structure made of quinoids and benzenoids imine units. The values of the electrical conductivity showed that the PoPD samples fabricated are conducting polymers and pH affect the electrical properties of PoPD thin films.

1 Introduction

The versatility of polymer materials is expanding because of the introduction of electro–active behaviour into the characteristics of some of them. The most exciting development in this area is related to the discovery of intrinsically conductive polymers or conjugated polymers.

Conducting polymers have been a popular area of investigation because of electrical and electrochemical properties and their potential applications in various areas. Among these are corrosion protection [1, 2], electronic devices such as diodes, capacitors or transistors [3–5], electrochromic displays [6], rechargeable batteries and solid electrolytes [7–9], electrostatic materials [10], electromechanical actuators [11], and sensors or biosensors [12–15].

Poly o-phenylenediamine homopolymer has attracted attention because it has been reported to be a high aromatic polymer containing a 2,3-diaminophenazine or quinoxaline repeat unit and exhibiting an unusually high thermostability [16]. Polymerization of a conducting polymer may be performed with chemical or electrochemical methods [17]. Because

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studies have focused mainly on inorganic conductive materials since the discovery of conductivity, the prospect of replacing labour-intensive inorganic and costly materials with cheaper and more flexible organic electronic materials opened up new research. Also, because organic conductive polymers have a higher resistance when compared to inorganic conductors, researchers are currently exploring ways of doping them to boost their conductivity.

These offer a multidisciplinary challenge to scientists, so attention is being strongly given to their improvement because of their availability, durability, recyclability, reduced cost and applications, hence the need for this research.

Conductive polymers such as poly (o-phenylenediamine) continue to be the focus of active research in diverse field including electronics. Different researchers have used chemical method for the synthesis of poly o-phenylenediamine with different oxidizing agents.

But in this work, poly o-phenylenediamine thin films were prepared by electropolymerization at different pH. The investigation of the optical, structural and electrical properties of the thin films was done by subjecting the deposited PoPD thin films to Raman, XRD, SEM, UV-Vis spectroscopy and four point probe. Average film thickness values were estimated using profilometer.

2 Materials & Methods

The o-phenylenediamine (oPD) used in this work was procured from Quallkems. The concentrated Hydrochloric (HCl) acid was procured from Sigma Aldrich, Oceanic chemicals Nig. Ltd. The conducting substrate used was fluorine doped Tin Oxide (FTO), with model number TCO22-15 (5 cm x 5 cm) from SOLARONIX.

Graphite was procured from MERCH, phosphoric acid (H_3PO_4), dihydrogen sodium phosphate (NaH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) were procured from Sigma Aldrich, Oceanic chemicals Nig. Ltd. pH meter (Techmel & Techmel USA, PHS-25) was used to measure the pH of the electrolytic medium. Direct current power supply unit (Koocu 150200) was used as source of power.

Phosphate buffer was prepared with 0.08 M of Na-2HPO 4 (11.36 g) and 0.02 M of NaH_2PO_4 (2.40 g) in the ratio of 4:1 using 1000 ml of volumetric flask by dissolving the two compounds with 800 ml of distilled water. Then 200 cm^3 of distilled water was added to make it up to 1 litre.

0.15 M of (o phenylenediamine) was prepared by dissolving 4.06 g of the compound in 250 cm^3. 1.0 M of phosphoric acid (H_3PO_4) was prepared by dissolving 24.50 g of the compound in 250 cm3. The electrolyte consists of the prepared solutions of o-phenylenediamine and phosphate buffer.

Before the deposition, the FTO conducting substrates were washed with 0.17 M molar solution of sodium lauryl sulphate, rinsed with distilled and dried in an oven at 60 ℃ before being used. The conducting side of FTO was detected using multimeter and was dropped vertically into the electrolyte for the deposition process at 1.2 V. Electropolymerization of poly – o – phenylenediamine was done using two – electrode (2E) setup. The two electrodes used were the working electrode (FTO) which served as anode and the counter electrode (graphite rod) which served as cathode.

Three samples were deposited at different pH values of 1.0, 1.5 and 2.0 at same deposition time of 5 minutes each. The pH was varied with drop-wise addition of phosphoric acid to the electrolyte to make it acidic while stirring with pH probe inserted in the electrolyte.

The first of PoPD film was electropolymerized at pH value of 2.0 because the phosphate buffer prepared was at pH value of 7.4, so drop-wise addition of phosphoric acid was done till the pH was 2.0. At the end of 5 minutes deposition time, the FTO substrate was removed and allowed to dry in open air. Two other samples were prepared at pH value of 1.5 and finally 1.0 with drop-wise addition of phosphoric acid to the electrolyte.

The three pH values of 1.0, 1.5 and 2.0 was chosen because thick films were deposited within the range of 1.0 to 2.0 with thickest film deposited at 1.5 which supposed to give a better result for the electrochromic properties of the deposited PoPD film.

The electropolymerized thin films were characterized with Raman spectroscopy (Mod. No Pro Raman-L-785-B1S with serial number: 196166), X-ray diffractometer (XRD) (Thermo scientific model: ARL'X TRA X-ray and serial number: 197492086), scanning election microscopy (SEM) (PRO:X: Phenonm world. Serial Number: MVE01570775, Model Number: 800-07334)), UV-vis spectroscopy (Axiom medical Ltd. UK, UV 752), profilometer (Veeco, ektat 150, Vintage: 2010 software: ektat) and four-point probe ((Signatone 393–J Tomkins CT, Model Quadpro 6,220V, Serial number: 0104636, Software: Quadpro 3.7.0.)

3 Results and Discussions

3.1 UV – Vis Analysis

Figure 1 shows the graph of absorbance plotted against wavelength for thin film samples of poly–o– phenylenediamine (PoPD) prepared in different acidic pH values. The absorbance of the PoPD films increases as pH of the films increases towards weak acidic region. The wavelengths of electromagnetic radiation used were between 290 nm to 1100 nm. PoPD deposited at a pH of 1.0 shows absorption bands at 336 nm and 428 nm. PoPD deposited at pH of 1.5 shows an absorption bands at 342 nm and 439 nm. PoPD deposited at pH value of 2.0 shows absorption bands at 344 nm, and 445 nm.

From the spectroscopic analysis, it could be suggested that the synthesized PoPD film has a head to tail type arrangement with the benzenoid and quinoid structures in the phenazine – like backbone which is in line with what was obtained by [18].

The difference in the absorption peaks observed may be as a result of disruption of the phenazine structure formed at strongly acid solution by the presence of 1, 4 – disubstituted benzenoid and quinoid defect caused by decreasing acidity of the deposition solution as suggested by [19].

Comparative study of the absorbance spectra of the films presented in figure 1 shows that the absorption bands of deposited PoPD slightly shifted to longer wavelength (lower energy) commonly known as red shift or bathochromic shift.

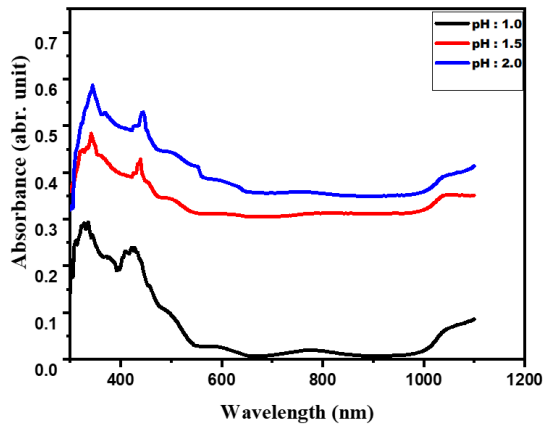


Figure 1: Graph of absorbance plotted against wavelength for the PoPD samples

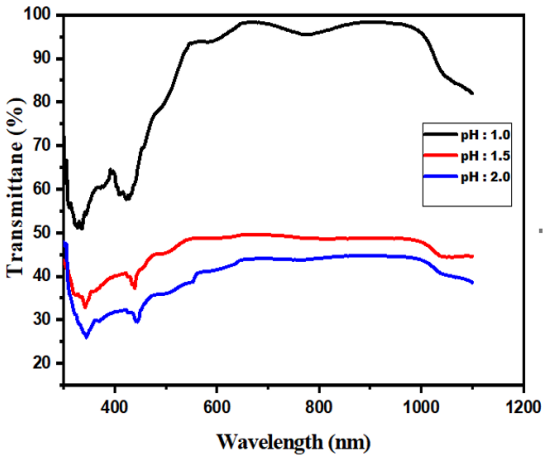


Figure 2: Graph of transmittance plotted against wavelength for the PoPD samples

Figure 2 shows the graph of transmittance plotted against wavelength for thin film samples of poly – o – phenylenediamine (PoPD) prepared in different acidic pH values.

The transmittance of the films was found to decrease as pH of the electrolytic medium tends towards weak acidic medium. The transmittance of the polymer films increases slightly as the wavelength increase.

The film deposited at a pH of 1.0 has the highest value of transmittance within all regions of the spectrum while film deposited at pH of 2.0 has the least value of transmittance. This suggests that PoPD films with higher transmissive power could best be produced under acidic condition while PoPD films with lower transmissive power could best be produced weak acidic condition.

Figure 3 shows the graph of reflectance plotted against wavelength for thin film samples of poly – o – phenylenediamine (PoPD) prepared in different acidic pH values. The reflectance of the polymer film is generally low. The values for the films fall between 0.9 % and 20.5 %.

The patterns of the reflectance spectra for films deposited at pH values of 1.5 and 2.0 are similar. This shows that pH values of the reaction medium affect reflective power of the film. Film deposited at strong acidic condition of pH of 1.0 has the least reflective power.

The graphs of $(\alpha hv)^2$ against photon energy are presented in Figure 4. The optical energy band gaps (E_g) of the films were estimated from the plot of $(\alpha hv)^2$ versus photon energy (hυ) curves shown in Figure 4 for samples deposited at pH of 1.0, 1.5 and 2.0 respectively. The straight nature of the plots indicates the existence of direct transition. The direct band gap energies of grown films were determined by extrapolating the straight portion of the graph to the photon energy (hυ) axis at $(\alpha hv)^2 = 0$.

It was found to be 3.20 eV for film deposited at pH of 1.0, 2.98 eV for film deposited at pH of 1.5 and 2.80 eV for film deposited at pH of 2.0 These results showed that the energy band gaps of deposited PoPD films decreases as the pH of the reaction increases.

Figure 5 shows the graph of transmittance plotted against wavelength for films deposited at pH of 1.5 and its reverse voltage values. A reverse voltage of $(-0.7\ V)$ was applied. The graph of figure 5 was used to determine electrochromic behavior of the film.

The optical transmittance spectra showed the colored and bleached state of the PoPD thin film with pH of 1.5 in the wavelength range from 300 nm to 1100 nm. The optical transmittance of the colored and bleached (T_c and T_b) state at the wavelength of 685 nm are $T_c = 49.53\ \%$ and $T_b = 93.93\ \%$ respectively.

The optical transmittance difference:

$$\Delta T = T_b - T_c = 44.40\ \% \quad (1)$$

The optical density (ΔOD) was calculated using the equation [20, 21]:

$$\Delta OD = \ln\left(\frac{T_b}{T_c}\right)_{\lambda=685\ nm} = \ln\left(\frac{93.93}{49.53}\right) = 0.64 \quad (2)$$

The contrast ratio (CR) defined as the ratio of the optical transmittance at the bleached state to the optical transmittance

at the colored state at a particular wavelength (685 nm) was calculated using equation [20]:

$$CR = \left(\frac{T_b}{T_c}\right)_{\lambda=685\ nm} = \left(\frac{93.93}{49.53}\right) = 1.896 \approx 1.9 \quad (3)$$

The values of ΔT, ΔOD and CR obtained for deposited PoPD thin film positioned it as a potential material for use in electrochromic devices, energy saving glass industry for building and automobiles. According to [22], an optical density (ΔOD) above 0.3 is suitable for monitors and smart glasses/windows and display applications.

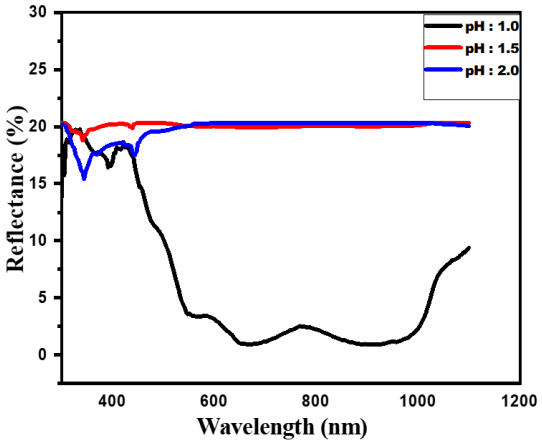


Figure 3: Graph of reflectance plotted against wavelength for the PoPD samples

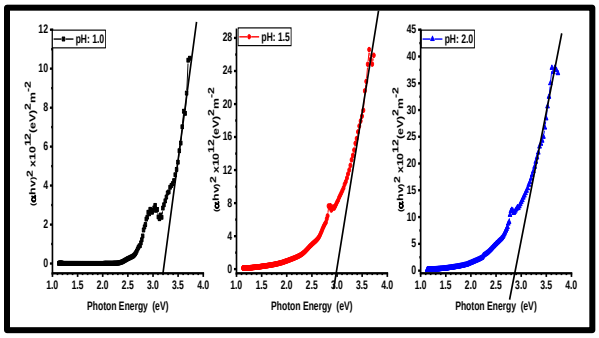


Figure 4: Graph of $(ahv)^2$ plotted against photon energy (eV) for the PoPD samples

3.2 Scanning Electron Microscopy (SEM)

Figures 6 showed the micrograph images of the thin film poly (o – phenylenediamine) samples. The surfaces of the samples look rough and show few spaces that were not properly coated on the FTO conducting glasses. More unevenly dispersed particles of the Poly (o-phenylenediamine) polymer were observed.

ImageJ for Microscopy Image Analysis [23] software was used to determine the average grain size of the films from the micrograph images. Analysis of the micrograph of the deposited PoPD thin films showed that the particle sizes ranged from 100 µm – 25 µm, 200 µm – 50 µm and 50 µm –10 µm for PoPD films deposited under pH values of 1.0, 1.5 and 2.0 respectively.

From the results of the SEM analysis, particle sizes of the polymer samples increase as pH value moves towards low acid region from 1.0 to 2.0, reaching an optimal grain size ranging from (200 µm – 50 µm) at pH of 1.5, then it decreases to grain size range of (20 µm – 1 µm) as the pH of the reaction medium moves towards weak alkaline medium of pH value of 2.0.3.3.

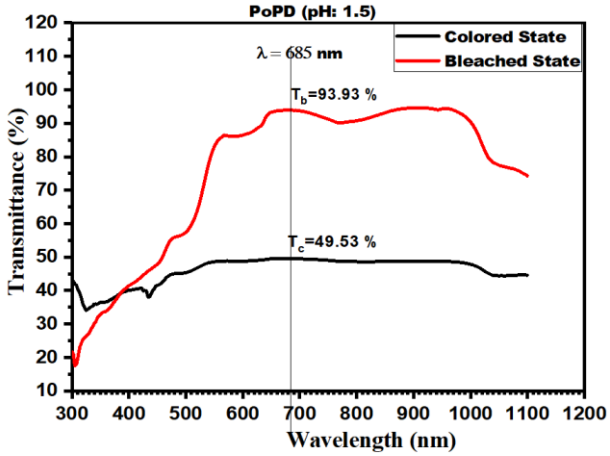


Figure 5: Graph of transmittance plotted against wavelength for pH 1.5 PoPD samples

3.3 X–ray Diffraction Analysis

The X–ray pattern of the fabricated films of poly – o – phenylenediamine (PoPD) at 25.0℃ with 2 theta angles step of 0.030° and scanning rate of 12.0 °/min is shown in figure 7. The angle ranged from 5.0° - 70.0° at Cu-k_α1 wavelength of 1.5405 Å. The result revealed that the samples are amorphous in nature due to its broad features which is not defined by crystalline model and amorphous materials do not produce sharp diffraction peaks.

The pattern is as a result of the incoherent scatter of the x–ray radiation by the molecules of the polymer samples. Several minor peaks centered between 2θ=15° and 2θ=17°. The shift in the pH values from strong to weak acidic region caused an increase in the intensity of the X-ray radiation.

3.4 Raman Spectroscopy Analysis

The bond structures of the electrodeposited polymers were analyzed by Raman spectroscopy analysis. The characteristic vibrational bands obtained from the Raman spectra of the polymers are shown in figure 8 to 10.

In general, all the samples have sharp band. Figure 8 shows the Raman spectra of PoPD films deposited at a pH of 1.0. A total of nine sharp bands were observed. The strong vibrational bands appearing at 2881 cm^{-1}, 2278 cm^{-1} and 2188 cm^{-1} are attributed to the stretching of aromatic $C-H$ bond, primary amine ($-NH_2$) and secondary amine ($-NH-$) benzene derivatives.

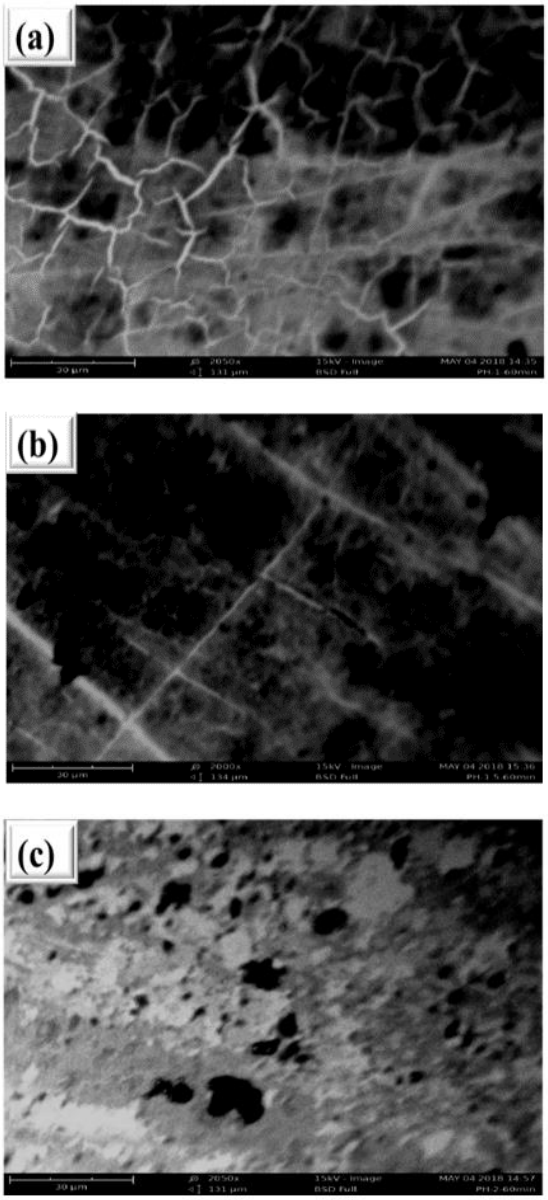


Figure 6: SEM micrograph of PoPD films electropolymerized at (a) pH: 1.0, (b) pH: 2.0 and (c) pH: 1.5

The weak band at 1814 cm^{-1} is due to stretching vibrations of $C = C$ bonds in the quinoid and benzenoids rings. The band could also be attributed to bending vibrations of $C - H$ bonds in the quinoid and benzenoid rings.

Weak band at 1673 cm^{-1} could be due to stretching vibrations of $C = C$ in quinoid and benzenoid rings, bending vibrations of $C - H$ bonds in quinoid and benzenoid rings inside the phenazine ring ladder structured polymers and bending vibrations of amine $(-NH-)$ bonds.

Band at 1499 cm^{-1} is attributed to both stretching vibrations of $C = C$ bond in the benzene derivative rings and $C - N$ bond attributed to aromatic amine. The characteristic vibrational frequency at 853.1 cm^{-1} is attributed to out of plane bending deformation of $C - H$ bonds in 1, 2 disubstituted benzene derivatives. The band at 694.6 cm^{-1} and 595.1 cm^{-1} are due to bending deformation of $N - H$ functional group attached to benzene ring in primary aromatic amines.

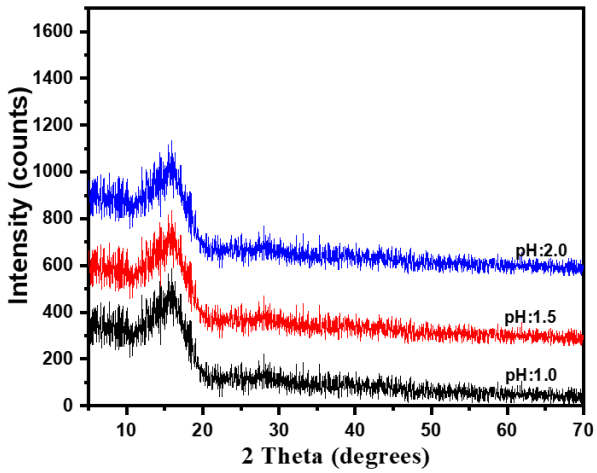


Figure 7: XRD pattern of PoPD films

Figure 9 shows the Raman Spectra of PoPD film fabricated at a pH value of 1.5. A total of eight sharp bands were observed. Weak bands occurred at 1812 cm^{-1}, 1110 cm^{-1}, 852.4 cm^{-1} and 695 cm^{-1} while relatively strong bands were observed at 2880 cm^{-1}, 1906 cm^{-1}, 579 cm^{-1} and 542 cm^{-1}.

Characteristic vibrational frequency observed at 2880 cm^{-1} is attributed to stretching vibrations of $C - H$ bond in aromatic ring, primary amine $(-NH_2)$ and secondary amine $(-NH-)$ functional group.

The band at 1906 cm^{-1} and 1812 cm^{-1} are due to stretching vibrations of $C = C$ bonds in quinoid and benzenoid rings which could also be attributed to bending vibration of $C - H$ bonds in the same quinoid and benzenoid rings.

The band at 1110 cm^{-1} is due to $C - N$ stretching frequency of quinoid and quinoxaline. The bands at 852.4 cm^{-1} and 695 cm^{-1} are attributed to out of plane bending deformation of $C - H$ bond in 1, 2 disubstituted benzene derivatives. The bands at 579 cm^{-1} and 542 cm^{-1} are due to bending deformation of $N - H$ functional group attached to benzene ring in primary aromatic amines.

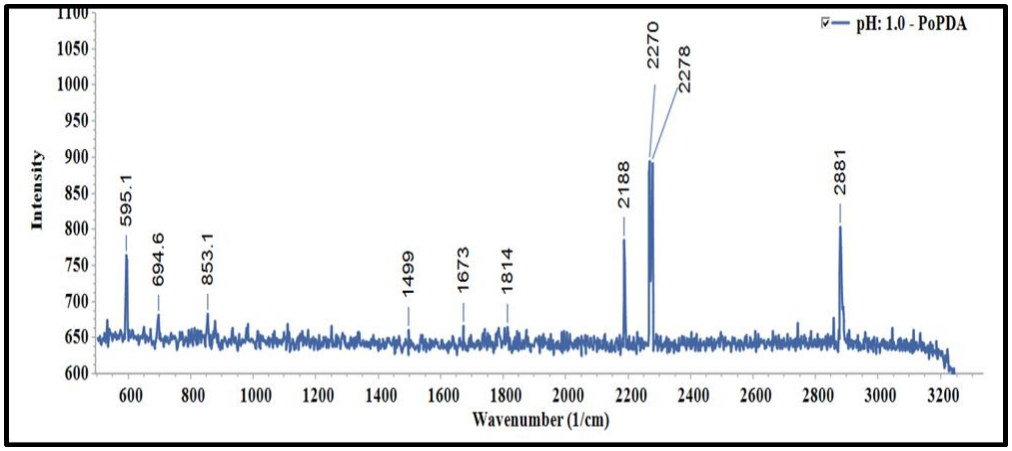


Figure 8: Raman Spectra of Poly – o – Phenylenediamine (PoPD) sample at pH value of 1.0

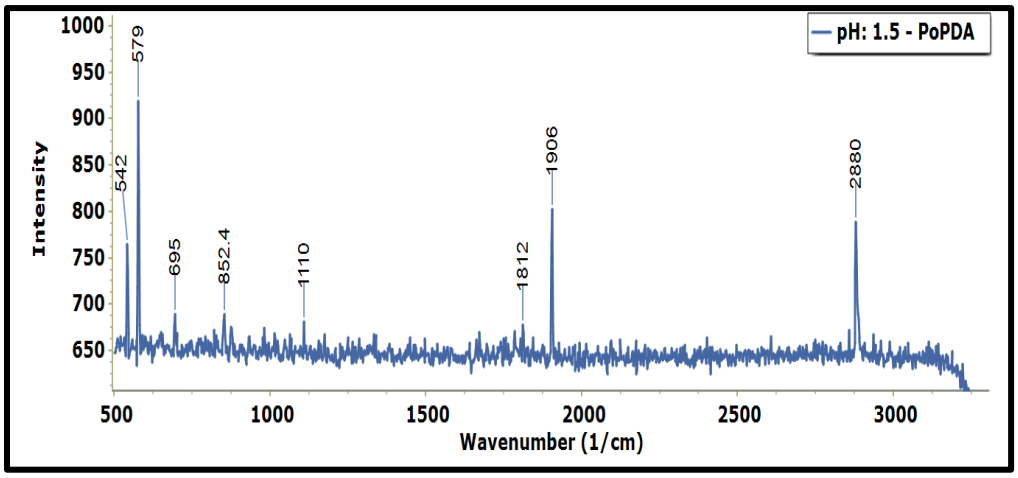


Figure 9: Raman Spectra of Poly – o – Phenylenediamine (PoPD) sample at pH value of 1.5

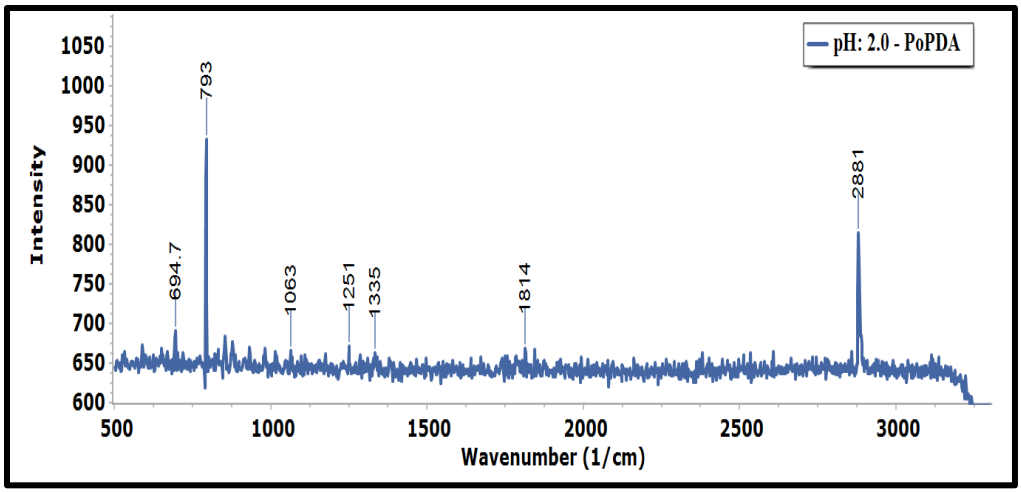


Figure 10: Raman Spectra of Poly – o – Phenylenediamine (PoPD) sample at pH value of 1.5

Figure 10 shows the Raman spectra of PoPD film fabricated at a pH value of 2.0. The Raman spectra obtained has two sharp strong bands at 2881 cm^{-1} and 793 cm^{-1} while five weak bands occurred at 1814 cm^{-1}, 1335 cm^{-1}, 1251 cm^{-1}, 1063 cm^{-1} and 694.7 cm^{-1}. Characteristic vibrational frequency observed at 2881 cm^{-1} is attributed to stretching vibrations of $C-H$ bond in aromatic ring, primary amine ($-NH_2$) and secondary amine ($-NH-$) functional group.

The band at 1814 $cm^{-1}$is due to stretching vibrations of $C=C$ bonds in quinoid and benzenoid rings which could also be attributed to bending vibration of $C-H$ bonds in the same quinoid and benzenoid rings. The bands at 1335 cm^{-1}, 1251 cm^{-1} and 1063 $cm^{-1}$are due to $C-N$ stretching frequency of aromatic amine derivatives (quinoid and quinoxaline).

They are also attributed to the stretching vibrations of $C-N$ bond present in amine functional group. The bands at 793 cm^{-1} and 694 cm^{-1} are attributed to out of plane bending deformation of $C-H$ bond in 1, 2 disubstituted benzene derivatives.

3.5 Electrical Properties of PoPD

The four-point probe apparatus used for the measurement of electrical properties has four probes in a straight line with an equal inter-probing spacing of 1.60 mm and a probe needle radius of 125 µm. Electrical properties of the fabricated polymer samples were presented in table 1 and figure 11 (a, b) gives the graphical representation of the variations in resistivity and conductivity of the films with pH.

Film thickness values obtained using stylus profilometry were also presented in the table. The values of the electrical conductivity that ranged 1.40×10^{-3} S/cm $-\ 1.9\times10^{-3}\ S/cm$ confirmed the conducting behavior of the deposited PoPD thin films. Electrical conductivity of the PoPD films was found to decrease as pH of the deposition solution moves towards weak acidic region.

This decrease in electrical conductivity could be explained on the basis of continuous deprotonation of nitrogen atoms in the backbone of PoPD thin films due to relatively small amount of phosphoric acid used. As amount of phosphoric acid increased, protonation occurred in the polymer backbone which caused an increase in the electrical conductivity of deposited PoPD films.

This result is in line with trend suggested by [19]. The range of electrical conductivity obtained in this work is close to values obtained by [19, 29] and within range obtained by [30, 31]. The resistivity of the deposited PoPD films increases towards weak acid medium.

4 Conclusion

The poly-o-phenylenediamine thin films have been successfully deposited on FTO substrates at different pH values of reaction medium, using electropolymerization technique. Characterization of the synthesized samples showed that the synthesized PoPD film has a head to tail type arrangement with the benzenoid and quinoid structures in the phenazine – like backbone and the absorption bands showed bathochromic shift.

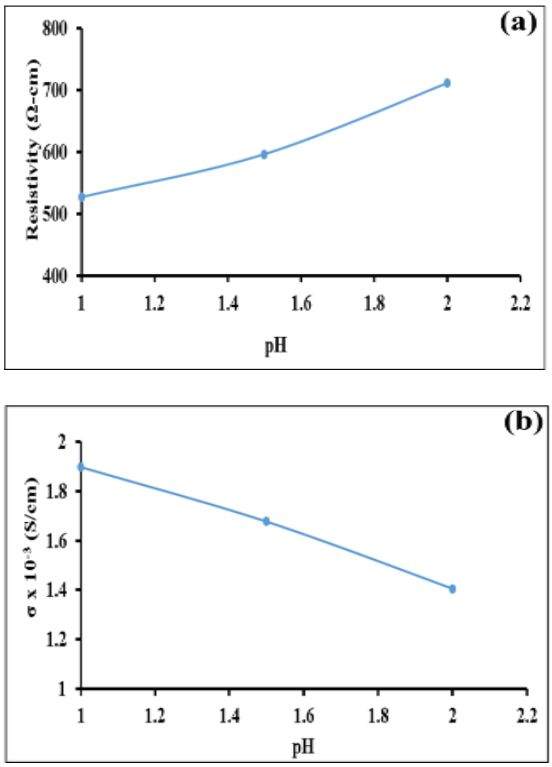


Figure 11: Variation of Electrical Properties of deposited Poly – o – Phenylenediamine (PoPD) thin films against pH in acidic region (a) Resistivity, (b) Conductivity

The results also showed that the deposited films have low reflectance and the pH values of the reaction medium affect reflective power of the film produced in such medium and the film deposited at strong acidic condition of pH of 1.0 has the least reflective power. The energy band gaps of deposited PoPD films decreases as the pH of the reaction increases.

The optical density (ΔOD) of the PoPD was determined as 0.64 which revealed that the polymers exhibited some degrees of electrochromism and are suitable for smart monitors, smart glasses/windows, and display applications. More unevenly dispersed particles of the Poly (o - phenylenediamine) polymer were observed from the SEM images.

Table 1: Electrical properties of fabricated poly-o-phenylenediamine (PoPD) samples

Sample	V (mV)	I (µA)	t ×10^{-5} (cm)	R×10^{6} (Ω)	ρ×10^{2} (Ω -cm)	σ×10^{-3} (S/cm)
pH-1.0	529.3	0.05	1.10	10.59	5.27	1.90
pH-1.5	119.8	0.05	5.50	2.40	5.96	1.68
pH-2.0	165.5	0.04	3.80	4.14	7.11	1.41

The result of the XRD revealed that the samples are amorphous in nature with several minor peaks centered between (2θ = 15°

and 17°) which confirmed the polymeric nature of the deposited thin films. The results obtained from the Raman spectra confirmed that the PoPD polymer thin film samples contained phenazine ring ladder – structure made of quinoids and benzenoids imine units. The values of the electrical conductivity show that the PoPD samples fabricated are conducting polymers.

Acknowledgment

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Declaration of Competing Interest

The authors declare no conflict of interest.

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