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Synthesis, Characterization and Electrical Properties of Polyaniline Doped with Different Acids

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Abstract
The polyaniline were prepared by using different inorganic and organic acids via oxidative polymerization method. The prepared samples were characterized by FTIR, the peaks are found to be at 507 cm^{-1}, 592 cm^{-1}, 798 cm^{-1}, 1138 cm^{-1}, 1244 cm^{-1}, 1302 cm^{-1}, 1471 cm^{-1} and 1556 cm^{-1}. These predominant peaks may be confirming the formation of polyaniline. The structural analysis was studied by employing XRD; found that polyaniline is amorphous in nature. The SEM studies reveal that they are agglomerated, irregular and size of these grain increases with increasing amount of polyaniline with different organic and inorganic acids. The dc conductivity (σ_{dc}) as a function of temperature (T) for polyaniline is studied in the temperature range from 30 to 1600C. At higher temperature it is found that conductivity increases because of hopping of polarons from one localized states to another localized states. The σ_{ac} conductivity of polyaniline was prepared by oxalic acid show high conductivity at 106 Hz. This is due to the space charge polarization and electrode polarizations.

Keywords: Polyaniline, Inorganic acid, Organic acid, FTIR, SEM, Transport property

I. INTRODUCTION

Conducting polymers have attracted significant attention in recent decades because of their potential applications in various fields. Among these polymers, polyaniline (Pani) is unique because of its high electrical conductivity, good environmental stability and ease of preparation. As a result, it has been studied extensively and has emerged as the most promising candidate for commercial applications. However, a major problem related to its successful utilization lies in its poor mechanical properties and processability, resulting from its insoluble nature in common organic solvents. The preparation method of polyaniline involves two main techniques (chemical and electrochemical polymerization) using suitable protonation media. A number of papers report the synthesis of polyaniline by using different dopants and its characterization. One important feature of these materials is the great dependence of the final properties, which is determined during the polymer synthesis. The possibility of synthesizing and doping polyaniline with protonic acid dopants containing different types of counter-ions is one of the key factors responsible for the versatility of this class of polymers. Polyaniline has moderate conductivity upon doping with conventional acids (Bronsted acids) and has excellent stability under ambient conditions [1].

The conductivity is largely affected by the nature of the doping acid and the doping rate [2–4]. Previously, various acids [5–18] have been used to protonate PANI, to enhance its conductivity, understand the effect of the dopants in the charge transport mechanisms, and correlate the structure and the properties. By the doping process, polarons and bipolarons are generated [19], and they contribute to the conduction by phonon-assisted hopping or by tunneling between electronic localized states randomly distributed. The variable-range hopping (VRH) conduction mechanism was originally proposed by Mott for amorphous semiconductors [20], assuming a phonon-assisted hopping process. However, this model is reported by previous studies to explain the charge transport in conducting polymers and their composites at low temperature [21–22]. The bulk conductivity of conducting polymers depends upon several factors, such as the structure, the number charge carriers, their transport along and between the polymer chains and across the morphological barriers [23]. The ac conductivity measurements are used to give rich additional information about the conduction mechanism in conducting polymers that dc conductivity measurements alone do not provide [24]. Several theoretical models [25, 26] have been proposed to explain the ac conduction mechanism in amorphous semiconductors [27], chalcogenide glasses [28], conducting polymers and their composites.

In this present work, we synthesize PANI by the chemical oxidative polymerization method using organic acid and inorganic acids as dopants. The effect of the dopants structure and reaction conditions on the morphology, size, and physical properties of the resulting PANI was investigated, and the formation mechanism of PANI was discussed.

II. EXPERIMENTAL

Preparation of polyaniline by inorganic acid

Ammonium persulphate (0.1 mole aqueous solutions in protonic acid) is added drop wise to a stirred solution of 0.1 mole aniline dissolved in 1 mole of aqueous solution of hydrochloric acid, pre cooled to 5 ^{0}C. Ammonium persulphate solution is added very slowly to prevent the warming of the solution. After completion of the addition, stirring is continued for 2 hours by suing a mechanical stirred to ensure the completion of reaction. The time of initial coloration on mixing of reactants depends upon the temperature and protonic acid. During the polymerization reaction, HCl is used as a protonic acid and a temperature of 0 – 5^{0}C is maintained by using a freezing mixture. The end product of green color precipitate is obtained. The precipitate was filtered, washed with deionised water and finally dried in an oven for 24 hrs to achieve a constant weight [29].

In similar way polyaniline was synthesized by using different inorganic and organic acids like HCl, H_2SO_4, and HNO_3 etc.

Preparation of polyaniline by organic acid

Ammonium persulphate is added drop wise to a stirred solution of 0.1 mole aniline dissolved in of aqueous solution of oxalic acid acid (solubility is 90g dm^{-3} at 20^{0}C), pre cooled to 5 ^{0}C. Ammonium persulphate solution is added very slowly to prevent the warming of the solution. After completion of the addition, stirring is continued for 2 hours by suing a mechanical stirred to ensure the completion of reaction. The time of initial coloration on mixing of reactants depends upon the temperature and protonic acid. During the polymerization reaction, oxalic acid is used as a protonic acid and a temperature of 5^{0}C is maintained by using a freezing mixture. The end product of green color precipitate is obtained. The precipitate was filtered, washed with deionised water and finally dried in an oven for 24 hr to achieve a constant weight.

In similar way polyaniline was synthesized by using tartaric acid (solubility is 133g / 100ml at 20^{0}C).

Characterization

Infrared Spectroscopy

The IR spectra of all the samples are recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. For recording IR spectra, powders are mixed with KBr in the ratio 1:25 by weight to ensure uniform dispersion. The mixed powders are pressed in a cylindrical dye to obtain clean discs of approximately 1mm thickness.

XRD Spectroscopy

X-ray diffraction phase identification was carried out by X-ray powder diffraction at ambient temperature. A Shintag X1 diffractometer with Cu K_a (1.54 A°) radiation in θ–θ configuration was used. The patterns were recorded in the 2–70^0 range at 0.05^0 step size using 3-s acquisition time per step. The mean particle size was calculated using the Debye–Scherer equation $D = K\lambda/\beta \mathrm{Cos}\theta$, in which K is a constant equal to 0.9, λ is the wavelength of the Cu Ka radiation, β is the full-width half-maxima of the diffraction peak in radiant, and θ is the Bragg's angle of (311) plane.

Scanning Electron Microscopy

The samples were sputtered with gold and then the surface morphology of the composites was investigated by scanning electron microscope (SEM, JEOL/EO JSM-6360).

III. Results and discussion

Infra Red Spectroscopy

Figure 1(a) show the FTIR spectra of pure polyaniline prepared by hydrochloric acid at room temperature. The characteristic vibration of polyaniline is known to be in the region 1000 - 1500 cm^{-1}. The FTIR spectra of PANI Shows the vibration around 507 cm^{-1}, 592 cm^{-1}, 798 cm^{-1} , 1138 cm^{-1}, 1244 cm^{-1}, 1302 cm^{-1}, 1471 cm^{-1} and 1556 cm^{-1}. The band at 507 and 592 cm^{-1} is due to stretching out of the plane, 798 cm^{-1} is C-H vibration of Para coupling benzenoid ring. 1138cm^{-1} is corresponds to C-O-C stretching of excess oxidant, 1244cm^{-1} C-N stretching of benzenoid ring, 1302cm^{-1} C-N bonds of aromatic amines, 1471cm^{-1} C=C stretching mode of vibration benzenoid and1556cm^{-1} C=N quinoid stretching mode of vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline.

Figure 1(b) shows the FTIR spectra of pure polyaniline prepared by using sulphuric acid at room temperature. The predominant peaks of polyaniline are found to be 453 cm^{-1}, 557 cm^{-1}, 850 cm^{-1}, 1068 cm^{-1}, 1170 cm^{-1}, 1228 cm^{-1}, 1298 cm^{-1}, 1400 cm^{-1}, 1491 cm^{-1}, 1583 cm^{-1}and 3151cm^{-1}.The band at 453 and 557cm^{-1} are due to stretching out of the plane, 850 cm^{-1} is attributed to C-C and C-H for the benzenoid unit, 1068 cm^{-1} is corresponds to S-O stretching vibration, 1170 cm^{-1} is due to C-C stretching, 1228 cm^{-1} is C-N stretching and C-C stretching. 1298 cm^{-1} C-N stretching.1400cm^{-1} correspond to C-H in plane to aromatic, 1491cm^{-1} is due to C=C stretching of benzenoid ring and 1583cm^{-1} quinoid stretching mode of vibration.3151cm^{-1} N-H stretching. Therefore, the above characteristic peaks confirm the formation of polyaniline.

Figure 1(c) shows FTIR spectra of pure polyaniline prepared by using nitric acid at room temperature. The characteristic vibrations of polyaniline are known to be in the region 1000-1500cm^{-1}. The FTIR spectra of PANI show vibration around 507 cm^{-1}, 558 cm^{-1}, 796 cm^{-1}, 1141 cm^{-1}, 1236 cm^{-1}, 1298 cm^{-1}, 1466 cm^{-1} and 1556 cm^{-1}. The band at 507 and 558 cm^{-1} is corresponds to stretching out of the plane, 796 cm^{-1} is due to C-H vibration of Para coupling benzenoid, $114cm^{-1}$ is C-O-C stretching of excess oxidant,$1236cm^{-}1$ is C-N stretching and C-C stretching. 1298 $cm^{-}1$ for C-N stretching, 1466 cm^{-1} for C=C stretching mode of vibration and 1556 cm^{-1} for C=N quinoid stretching mode of vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline.

Figure 1 (d) shows FTIR spectra of pure polyaniline prepared by oxalic acid at room temperature. The characteristic vibrations of polyaniline are known to be in the region 1000 - 1500 cm^{-1}. The FTIR spectra of PANI show vibration around 418 cm^{-1}, 507 cm^{-1}, 1107 cm^{-1}, 1238 cm^{-1}, 1302 cm^{-1}, 1489 cm^{-1} and 1556 cm^{-1}. The band at 418 and $507cm^{-1}$ is due to stretching out of the plane, $1107cm^{-1}$ is corresponds to C-NH-C secondary amine vibration, $1238cm^{-1}$ is C-N stretching of benzenoid ring, $1302cm^{-1}$ due to C-N bonds of aromatic amines,$1489cm^{-1}$ corresponds to C=C stretching of benzenoid ring and 1556 cm^{-1} is due to C-C quinoid stretching mode of vibration. There for, the above characteristic peaks confirm the formation of polyaniline.

Figure 1 (e) shows FTIR spectra of pure polyaniline is prepared by using tartaric acid at room temperature. The characteristic vibration of polyaniline is known to be in the region 1000-$1500cm^{-1}$. The FTIR spectra of PANI show vibration around 418, 507, 586, 823, 1039, 1151, 1246, 1305, 1494, 1568 cm^{-1}. The band at 418, 507 and 586 cm^{-1} is corresponds to stretching out of the plane, $823cm^{-1}$ is attributed to C-C and C-H for the benzenoid unit, $1039cm^{-1}$ for S-O stretching vibration, 1151cm $^{-1}$ for C-N stretching mode of benzenoid unit, $1246cm^{-1}$ for C-N stretching of benzenoid ring, $1305cm^{-1}$ for C-N bonds of aromatic amines, $1494cm^{-1}$ for C=C stretching of benzenoid ring and 1568 cm^{-1} for C-N quinoid stretching mode of vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline.

X-ray diffraction analysis

Figure 2 shows the X-ray diffraction patterns of polyaniline prepared by different acid dopants. The PANI prepared by HCl, $H_2SO_4$and HNO_3 exhibits a broad peaks at 2θ angles around 26^0 is characteristics of the van der Waals distances between stacks of phenylene rings (polyaniline ring). These broad peaks indicate crystalline domains in the amorphous structure of PANI. The oxalic acid and tartaric acid show broad peak at 26^0 and a weak broad peak at 19^0 indicate amorphous structure of polyaniline. More broadness and decreased intensity in peaks was observed in organic acid dopant polyaniline. This is may be presence of bicarboxlic group of acid increases the intramolecular chain spacing and amorphousness as compared with the PANI prepared by inorganic acids.

Scanning Electron Microscopy (SEM)

SEM micrograph of conducting polyaniline synthesized by chemical oxidative method is shown in figure 3 (a-e). It can be clearly seen that the micrograph of polyaniline that is smooth and homogeneous (figure 3 (a)). Since Hydrochloric acid is used as protonic acid in the preparation of polyaniline, the presence of microcrystalline structure can be seen that is not homogeneously distributed throughout. The presence of microcrystalline structures in polyaniline in these particular samples can be confirmed from XRD studies. Since conducting polymers are very sensitive to the temperature, due to the interaction between electron and the sample, considerable amount of heat is generated which causes the development of mall crackening in the sample during SEM recording. A granular morphology of the microcrystalline structures is measured and is found to be about 200 – 600 Å in diameter for polyaniline which is consistent with other reports[30].The contrast in the image is a result of differences in scattering from different areas of the surface as a result of geometrical differences. The average grain size is calculated by using line intercept method and is found to be in the range of 1.3μm to 2.7μm

The figure 3(b) shows that, most of the particles are agglomerated spherical regular in shape and they are well interconnected to each others. The average grain size is calculated by using line intercept method and is found to be in the range of 5μm to 7μm

It is observed that the particles are highly clustered, irregular in shape; some of them are in fiber form which holds the two polyaniline hips in figure 3 (c). They are well interconnected to each others. The average grain size is found to be in the range of 8μm to 9μm.

It is observed that from the figure 3(d), polyaniline have flaked like structure and lying one above the others. They are highly agglomerated and have porous in nature. The average grain size is found to be in the range of 2.3μm.

From the figure 3 (e), polyaniline have flaked like structure, orientated randomly in different directions and not lying one above the others like as polyaniline prepared by using acetic acid. The networks are well connected and also have porous in nature. The average grain size is found to be in the range of 17μm.

DC Conductivity

Figure 4 shows the variation of dc conductivity as a function of temperature for polyaniline. The conductivity increases with increase in temperature. The dc conductivity of polyaniline exhibit three phases in a temperature range 40 °C to 160 °C. In temperatures between 40 – 100 °C, the conductivity values are almost constant and increases suddenly in the temperature range 100 – 130 °C. In stage III, in between temperatures 130 – 160 °C, a linear increment in the conductivity values is observed. Among all, polyaniline prepared by oxalic acid shows high conductivity because oxalic acid gives a oxalate anion, which is resonances stabilized because the negative charge is shared (delocalized) between the two oxygen atoms and carbon back bone of the polyaniline chain. Oxalic acid gives a oxalate anion, which is resonances stabilized because the negative charge is shared (delocalized) between the two oxygen atoms increasing.

Ac conductivity

Figure 5 shows the dielectric tangent loss (tan δ) as a function of frequency for organic and inorganic acids of PANI. It is observed that the dielectric loss decreases as a function of frequency. PANI exhibit small value of dielectric loss at higher frequencies, which suggests that these materials are lossless materials at frequencies beyond 10^7Hz. The observed behavior is inconsistent with the conductivity and dielectric constant results in these composites.

Figure 6 shows the variation of real permittivity (ε') as a function of log (f) for organic and inorganic acids of PANI. It is found that real permittivity decreases with increase in frequency for PANI prepared by different acids. It is observed that Debye type relaxation mechanism is responsible for higher values of real permittivity at low frequencies, which decreases as the applied frequency increases. Thus above the frequencies of 1 KHz, the real permittivity (ε') becomes independent of that of the applied frequency.

Figure 7 shows that the variation of σ_{ac} versus logarithmic of frequency for organic and inorganic acids of polyaniline. The polyaniline prepared by oxalic acid shows high conductivity at the frequency of 10^6 Hz. This is due to the space charge polarization and electrode polarizations, i.e., positive charges are displaced along the field and negative charges shift in the opposite direction creates an internal electric field which partly compensates the external field inside the composites. Therefore, the σ_{ac} conductivity increases with increase in applied frequency.

IV. Conclusion

The polyaniline were prepared by using different acid dopants via oxidative polymerization method. The prepared samples was characterized by FTIR, indicates the band at 418 and 507cm^{-1} is due to stretching out of the plane, 1107cm^{-1} is corresponds to C-NH-C secondary amine vibration, 1238cm^{-1} is C-N stretching of benzenoid ring, 1302cm^{-1} due to C-N bonds of aromatic amines,1489cm^{-1} corresponds to C=C stretching of benzenoid ring and 1556 cm^{-1} is due to C-C quinoid stretching mode of vibration. There for, the above characteristic peaks confirm the formation of polyaniline. The structural analysis was studied by employing XRD; found that polyaniline is amorphous in nature. From SEM, it is observed that the polyaniline prepared by H_2SO_4 and HNO_3 particles are highly clustered, spherical in shape collecting together to form a bunch like structure. The dc conductivity (σ_{dc}) as a function of temperature (T) for polyaniline is studied in the temperature range from 30 to 160^{0}C. At higher temperature it is found that conductivity increases because of hopping of polarons from one localized states to another localized states and this can be explained by 1D-VRH theory proposed by Mott. The Ac conductivity of polyaniline prepared by oxalic acid show high conductivity at 10^6 Hz. This is due to the space charge polarization and electrode polarizations, i.e., positive charges are displaced along the field and negative charges shift in the opposite direction creates an internal electric field which partly compensates the external field inside the composites. The real permittivity decreases with increase in frequency for PANI prepared by different acids. It is observed that Debye type relaxation mechanism is responsible for higher values of real permittivity at low frequencies.

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Figure captions:

1. Figure 1 (a-f) shows the FTIR spectra of pure polyaniline prepared by various dopants like (a) HCl, (b) H_2SO_4, (c) HNO_3, (d) $(C_2H_2O_4.2H_2O)$, (e) $(CHOH\text{-}COOH)_2$ at room temperature
2. Figure 2 shows the XRD spectra of pure polyaniline prepared by various dopants like (a) HCl, (b) H_2SO_4, (c) HNO_3, (d) $(C_2H_2O_4.2H_2O)$, (e) $(CHOH\text{-}COOH)_2$ at room temperature
3. Figure 3 shows that SEM image of pure polyaniline prepared by various dopants like (a) HCl, (b) H_2SO_4, (c) HNO_3, (d) $(C_2H_2O_4.2H_2O)$, (e) $(CHOH\text{-}COOH)_2$ at room temperature
4. Figure 4 shows that the dc conductivity of polyaniline prepared by using different organic and inorganic acids.
5. Figure 5 Shows the dielectric tangent loss (tan δ) as function of frequency for polyaniline with different organic and inorganic acids
6. Figure 6.Shows the variation of real permittivity ε' with frequency for different weight percentage of Polyaniline
7. Figure 7 Show the ac conductivity of polyaniline prepared by using different organic and inorganic acids.

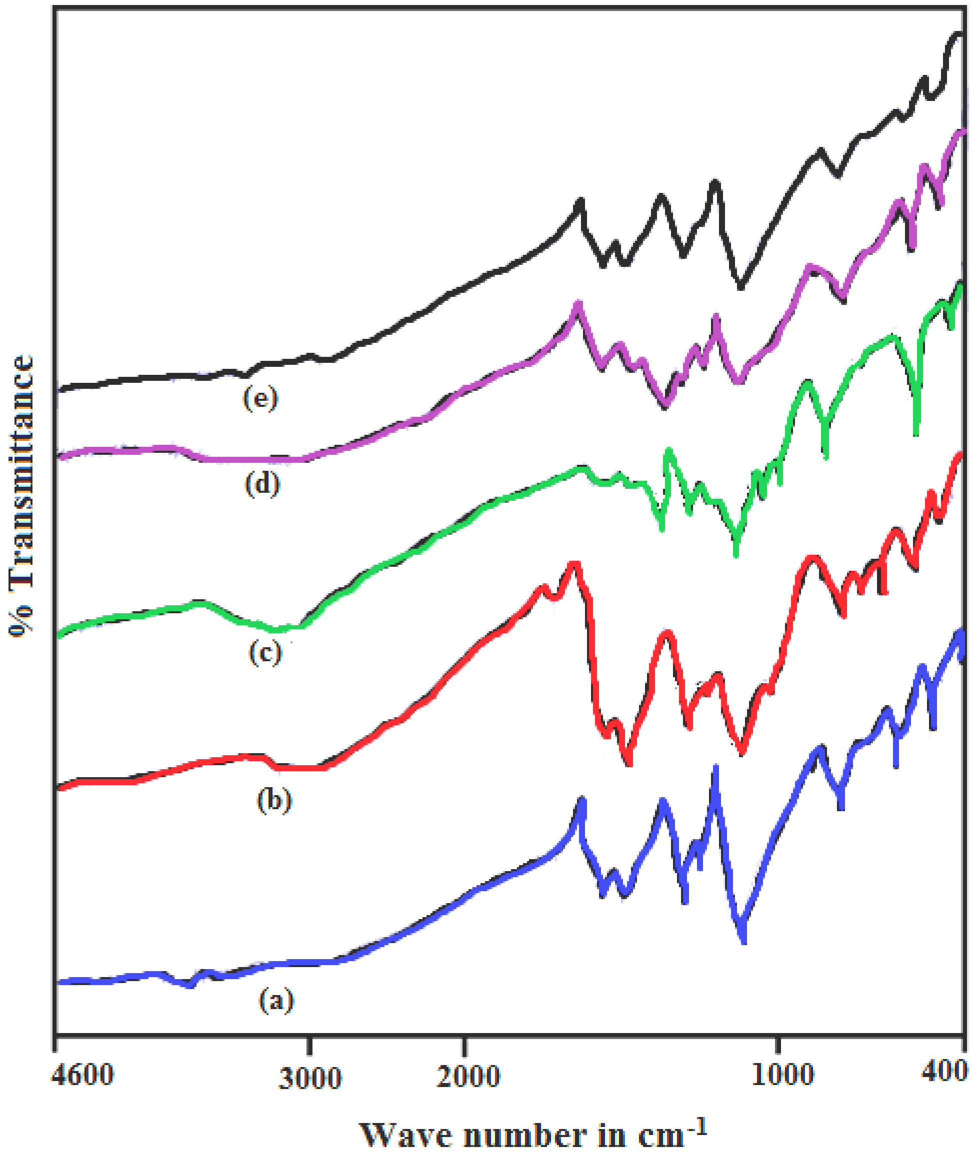
% Transmittance
(e)
(d)
(c)
(b)
(a)
4600
3000
2000
1000
400
Wave number in cm-1

Figure-1

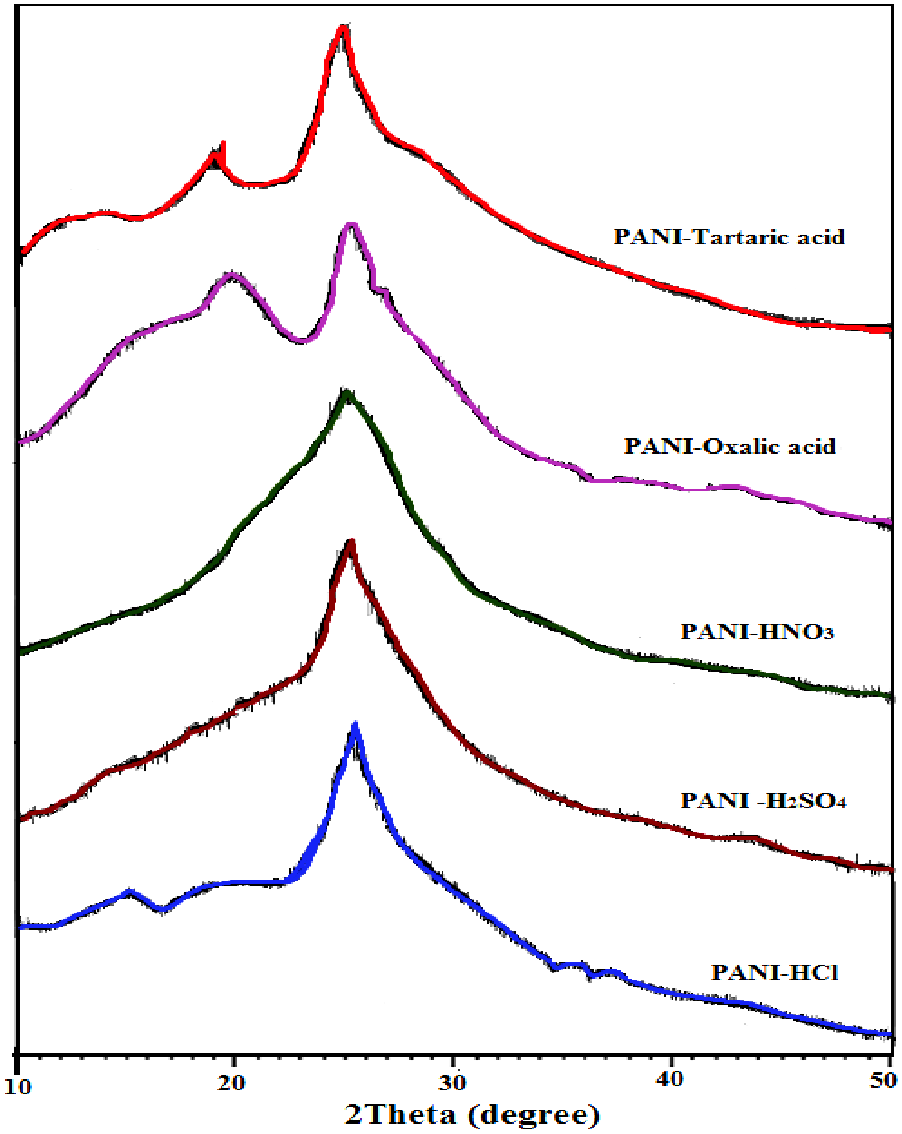
PANI-Tartaric acid
PANI-Oxalic acid
PANI-HNO3
PANI -H2SO4
PANI-HCl
10
20
30
40
50
2Theta (degree)

Figure-2

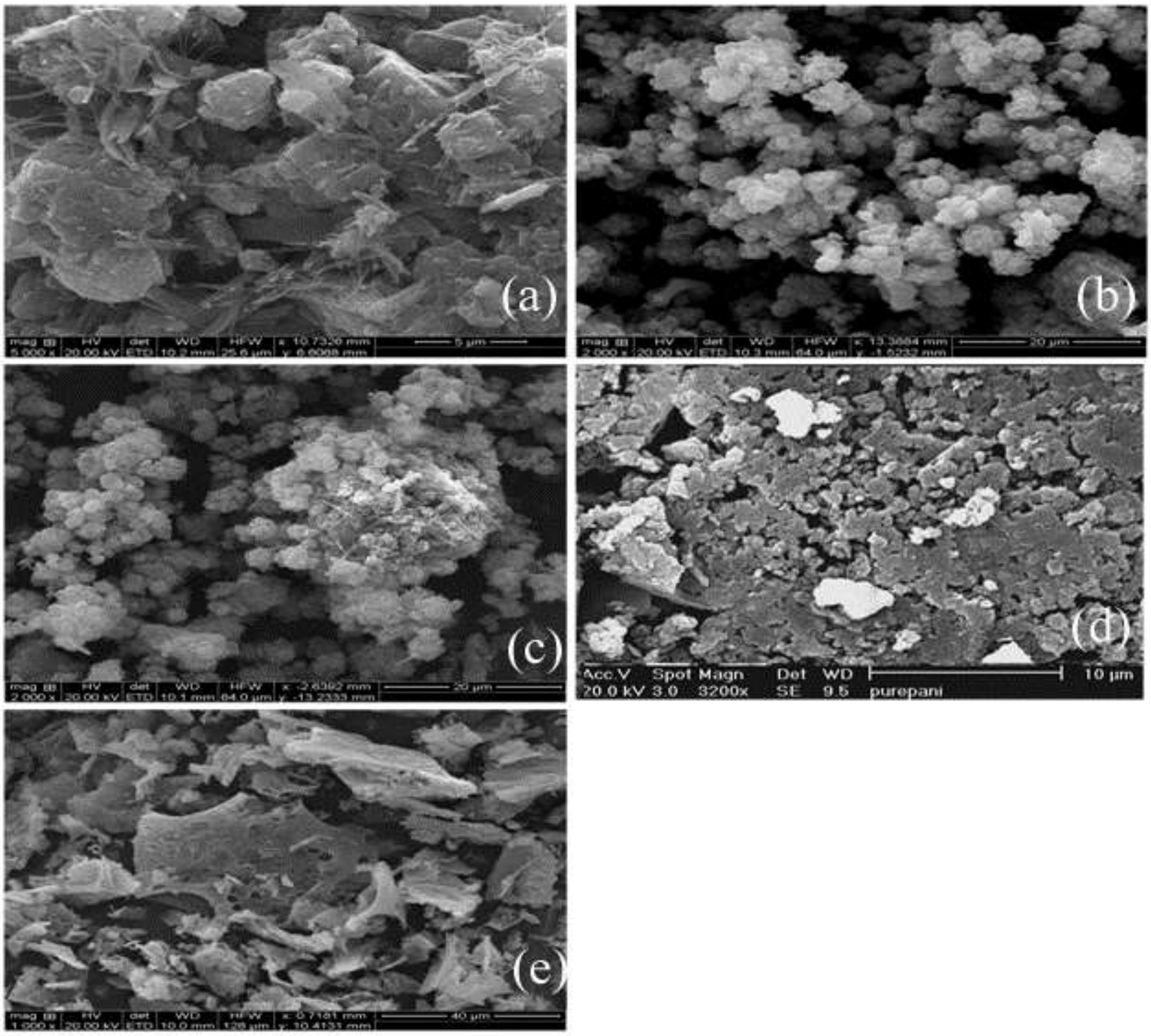

Figure-3

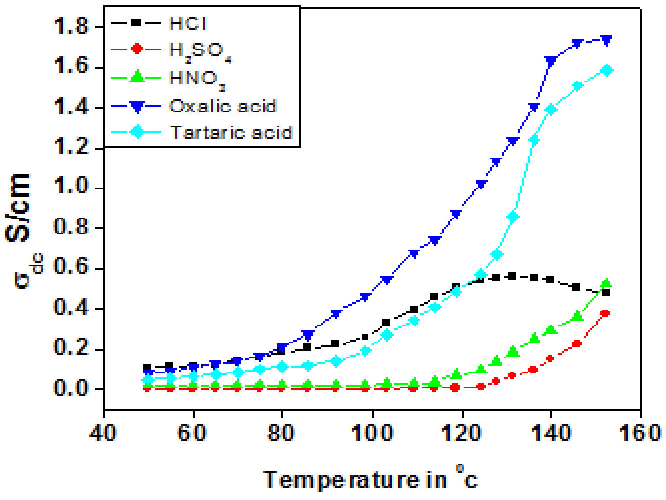

Figure-4

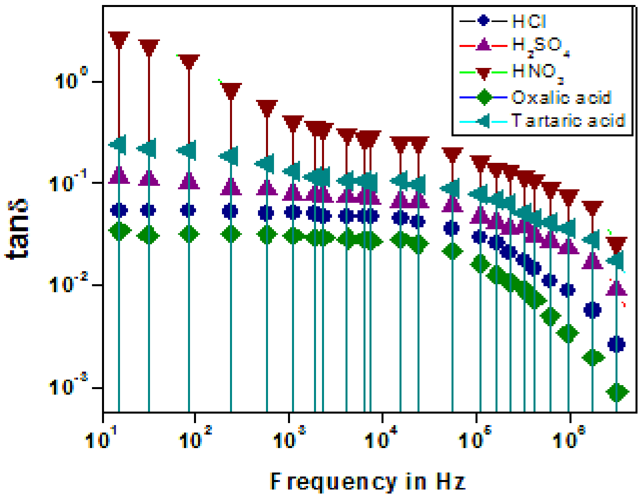

Figure-5

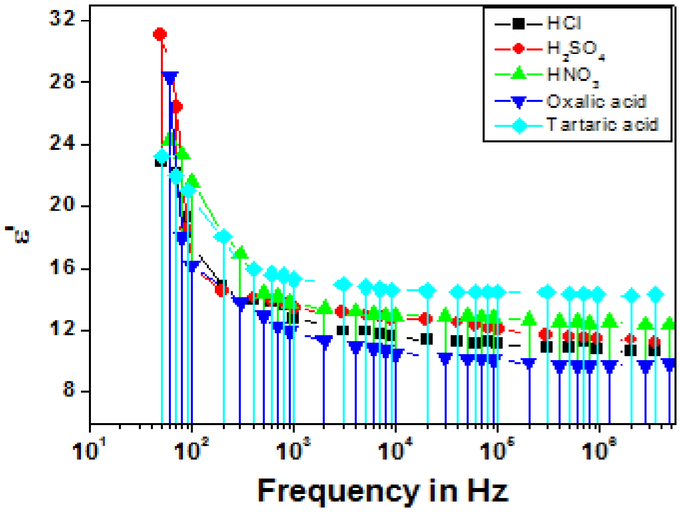

Figure-6

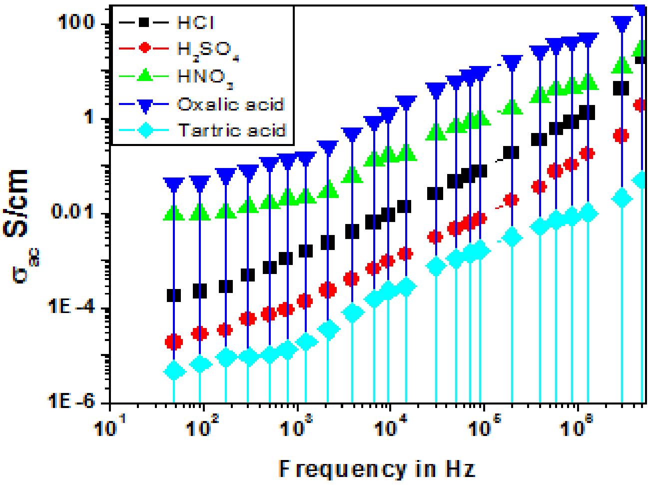

Figure-7