Optoelectronic Properties of Conducting Polyaniline (PANi-ES/HCl)

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***Abstract*-Samples of PANi (emeraldine salt) were prepared with protonic acid dopant, namely hydrochloride acid. Easiest chemical method for the preparation a conducting polymer of Polyaniline (PANi-ES) emeraldine salt has been reported in this paper. This polymer microstructure are characterized and analyzed with, HR-XRD diffraction, UV-vis spectroscopy, Fourier transform infrared spectroscopy (FTIR) and Field emission scanning electron microscopy (FESEM). Polyaniline-ES exhibit amorphous nature confirmed that from XRD diffraction pattern and FESEM analysis study, the format ion of the polymer. The presence of characteristic bonds of PANI-ES was observed from FTIR spectroscopy technique. With absorption peak has been attributed due to quantized size of polyaniline conducting polymer. Which forms an emeraldine salt ES. It was characterized by XRD, UV-Vis FT-IR Spectrophotometer and FESEM.**

Keywords: **PANI-ES, Optoelectronic properties, XRD, FT-IR, and UV-vis.**

I. Introduction:

The conducting polymers are highly conjugated π-electron systems that display unusual electronic properties such as low ionization potentials and high electron affinities; they are also called “synthetic metals.” Many of researches are now focused on studying conducting polymers such as, polyaniline among others [1]. Polyaniline PANi exists in a variety of forms that differ in chemical and physical properties. The most common protonated emeraldine has a conductivity at the semiconductor level of the order of 100 $S.cm^{-1}$ [2]. The emeraldine base PANi-EB can be made conducting by doping with a protonic acid dopant. After protonation, there will be dissociation of bipolaron to form two of polarons, where a bipolaron form will be achieved.

It is believed that for the non-degenerate conducting polymers, the bipolarons are the charge carriers. In the polaron form, there will be delocalization of polarons after which polarons will be delocalized yielding a green conducting emeraldine salt PANi-ES [3-5]. As show in Fig. 1.

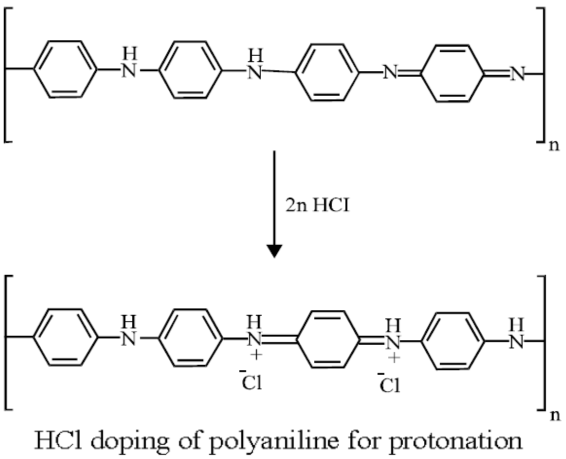

Fig.1. Doping of Polyaniline by Protonic acid media HCl.

The efficient polymerization of monomer aniline is achieved only in protonic acid, where aniline exists as aniline cation. A variety of organic and inorganic acids at different concentrations have been used in the syntheses of PANi; the resulting PANi-ES, protonated with various acids, differs in solubility, conductivity, and stability [6]. The changes in physicochemical properties of PANi that occur in response to various external exciting are useful for various applications [7]. Many of these applications are based on the electro active properties of PANi such as bioelectronics, polymer-modified electrodes [8]. ln this work, a systematically investigation on the oxidative chemical polymerization of aniline is made as simple as possible by easy in situ chemical method at low temperature, which results in good quality, semi conducting Polyaniline PANi-ES in the thin film form suitable for large area deposition. Our efforts are focused onto development of easiest and cheapest synthesis method for the preparation of Polyaniline emeraldine salt form ES commercially, so that to achieve compatibility in applications. Further, in situ grown films are characterized for study of structural, morphological and optical properties. These properties were characterized by XRD, FT-IR, FESEM and UV-Vis Spectrophotometer.

II. Instruments and Characterization

The synthesized a conductive polymer was used to study the structure and morphology of polymer. XRD diffraction studies were carried out using high resolution a diffractometer (Model: PANAlaytical X pert Pro MRD PW3040). The X-ray patterns were recorded in the range of 2θ: 10–70° with a step width of 0.02° and a step time 1.25 sec, using (CuKα) radiation (λ=1.5406A°). UV-Vis the spectra of the samples, which were dispersed in demonized water under ultrasonic action, which were recorded on a Shimadzu -1800 UV-vis spectrophotometer. Fourier Transform Infrared spectroscopy (Model: Perkin Elmer Spectrum Gx) of PANi was studied in the frequency range of 400–4000 cm^{-1}. Morphological study of the thin films of PANi was carried out using field effect scanning electron microscopy (FE-SEM) (Model: FEI NanoSEM 450).

III. Chemical Preparation of Polyaniline PANi-ES

The conducting polymer PANi was prepared by chemical oxidative polymerization of aniline in the presence of hydrochloric acid HCl, and ammonium peroxydisulphate APX, as an oxidant. For the prepare, we took 1M of protonic acid HCl, and 0.2M of aniline monomer solution were added into a 250ml beaker equipped with a Teflon coated magnetic stirrer at about -4°C temperature. Then 0.25 M ammonium peroxydisulphate APS in aqueous medium combined with an equal molarities hydrochloric acid HCl, 1M acid was drop wise added into the above solution. Both of solutions are mixed in a round bottomed flask and stirring to polymerize the mixture. The mixture was left to rest to the next day. The precipitate PANi was collected, filtration and washed with three times of 0.2M HCl and 150 ml of Acetone. After that PANi was keep in vacuum oven at 80°C for 6 hours, annealed to avoid any effect of moisture absorption. The Polyaniline powder dark green colored of conductive Polyaniline emeraldine salt form ES was thoroughly grounded in a mortar to obtain very fine particles.

IV. Results and Discussion:

X-ray diffraction of doped polyaniline PANi-ES with protonic acid with HCl in Fig. 2 show wide peaks at $2\theta=22^{o,}$ 25^{o}. The x-rays spectrum to film of Polyaniline as the angel at 22^{0} refer to diffraction levels parallel in the polymeric chain , and the angle at 25^{0} shows diffraction levels orthogonal [9]. Doped polyaniline represents the diffraction of the film of polyaniline at used of protonic acid to doping polymer and the results was one of the terms of the film of the peaks at angle 22^{0}, 25^{0}, no matter what type of doping. The average of crystallite grain size is calculated according to Debye Scherer equation:
$Gs=K \lambda/\beta \cos \theta$ ……………….. (1)

Where: K is the shape factor 0.9, Gs is the average grain size; λ is the wavelength of x-ray radiation (1.5406Ǻ); β is the full width at half maximum, θ is the diffraction angle. The pattern of thin film polymer PANi-ES exhibit structure by the x-ray peaks confirmed amorphous and the semi crystalline nature of the synthesis polymer [10]. The peaks at $2\theta=22^{o}$, 25^{o}, may also represent the characteristic of distance between the ring planes of benzene and quionied rings respectively in the adjacent chains [10]. The characteristic broadening of the observed peaks implies that the films are nano crystalline. Table (1) x-ray parameter of polymer PANi-ES acid dopant HCl.

Table 1. Effect of acidic media on grain size and Bragg angle and intensity in PANi-ES.

Polymer	**Pos. [2θ º] (degree)**	**FWHM (degree)**	**d- spacing (Å)**	**Gs (nm)**
PANi-ES	22^{0}	0.59	3.9	38.3
	25^{0}	0.78	3.5	10.2

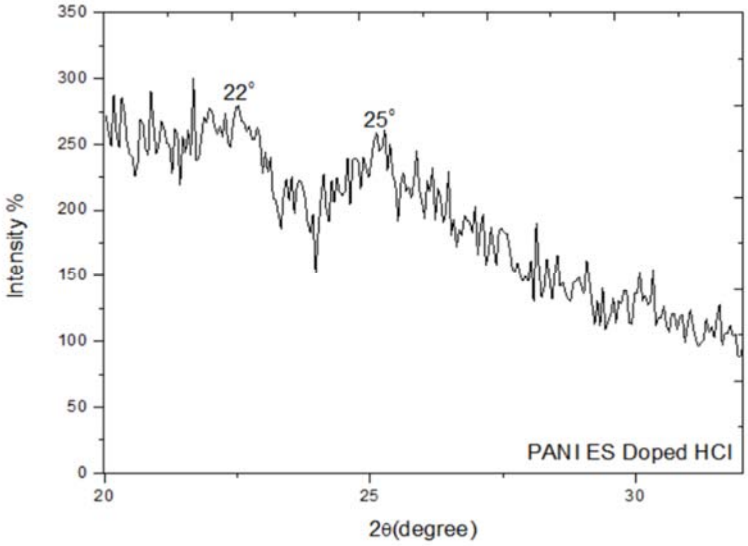

Fig. 2 X-ray diffraction of doped PANi-ES with protonic acid.

The absorption spectrum of the polyaniline dopant ES films prepared at temperatures -4 °C, with 1M doping concentration of protonic acids HCl. At the visible spectrum, which is measured by a Shimadzu UV1800 ultraviolet visible spectrophotometer. Shows in Fig. 3, show the prominent absorption peaks are observed around 300nm, 400nm and 800nm confirming the HCl doping in PANi-ES films [11–13].

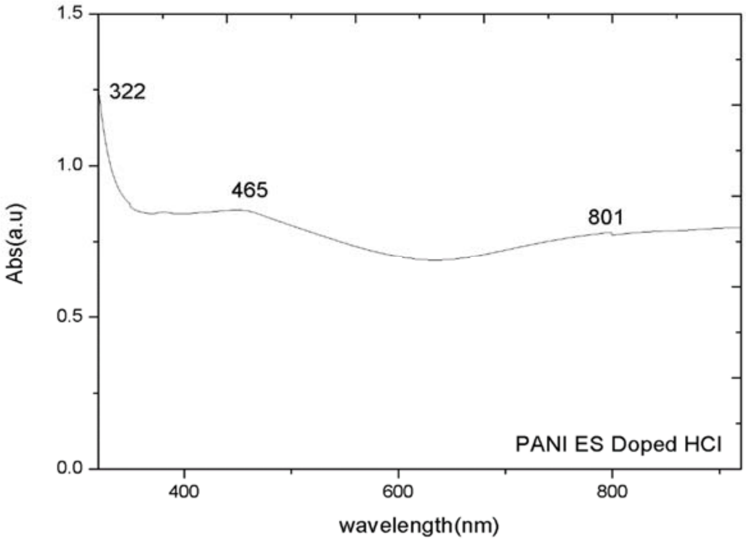

Fig. 3 UV-vis spectroscopy of PANi-ES Doped with HCl.

The peaks at 322nm, 465nm and 801nm for Polyaniline doped with acid HCl, are assigned to: π→π* transition, polaron→π* transition and π→polaron transition, for Polyaniline-ES doping with 1M acid HCl, according to Fig.4.

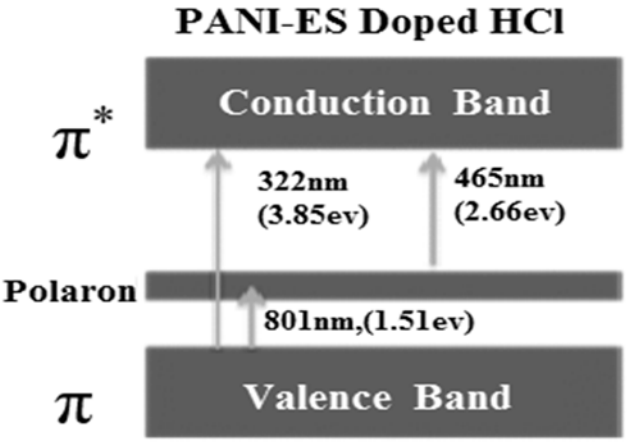

Fig. 4 Optical transitions and energy levels of the PANi-ES.

The polaron band formation in the band gap of polymer upon of protonic acid doping. It is clear that the absorption increases appreciably with decrease in the temperature of reaction polymerization medium. This is due to the fact that decrease in temperature of reaction, increases in molecular weight of polymer which leads to increase the absorption [14]. The absorption coefficients (α) of PANi-ES films at 322, 325nm for PANi doped HCl as show in Table 2. The expected electronic changes in the samples of PANi-ES can be explained by theoretical calculating the band gap from their UV-Vis spectra. The energy h υ of the photon is related to the wavelength λ of UV radiation by the following relation [15, 16].

$$\Delta E = h\nu = E(HOMO) - E(LUMO) = Eg = 1240/\lambda(nm) \text{ .... } (1)$$

Where: h is Planck's constant ν frequency of light and c velocity of light.

The calculated band gap for each case is reported in Table 1.

Table 2: Optical properties of PANi-ES doped HCl sample.

Polymer	Wavelength λ_{max}(nm)	Abs Coefficient $\alpha x10^5(cm^{-1})$	E_g=E_{HOMO}-E_{LUMO}) (eV)
PANi-ES/ HCl	322	1.2	3.85

For PANi-ES/HCl with 1 M doping concentration, the absorption coefficient (α) as1.2×10^5 cm^{-1} good value for along with increase in band gap (Eg) 3.8 eV at same temperature. Already, the effect of doping concentration on optical absorption of PANi-ES films at a constant temperature of film preparation [17].

Fig. 5, shows the FTIR spectra of PANi-ES/HCl sample prepared at temperature -4 °C with 1M dopant concentration. The spectra recorded in wave number rang 400- 2000 cm^{-1}. FTIR properties can distinguish between the benzenoid and quionied rings in rang 1350-1960 cm^{-1} region of the spectrum. It is clear from the figure that temperature of thin film has effective changed the molecular media of PANi-ES than the dopant concentration. The peaks around (801 cm^{-1},1303 cm^{-1},1474 cm^{-1}, and 1560 cm^{-1}) of all spectra correspond to PANi-ES [18]. The peak around 1243 cm^{-1} corresponds to the electrically conductive state of doped polymer PANi-ES [19]. Decrease in temperature of film prepared will shift few peaks toward lower wave number region (1134cm^{-1}, 1296 cm^{-1}, and 1589 cm^{-1}) along with increase in intensity of the peaks. This due to increase in the degree of polymerization of PANi-HCl with decrease in dopant concentration of PANi-HCl show less variation in the intensity of peaks. This shows that the degree of polymerization is very highly pronounced for PANi-HCl sample prepared at low temperature. Table 3; show the list of observed peaks with their corresponding functional groups.

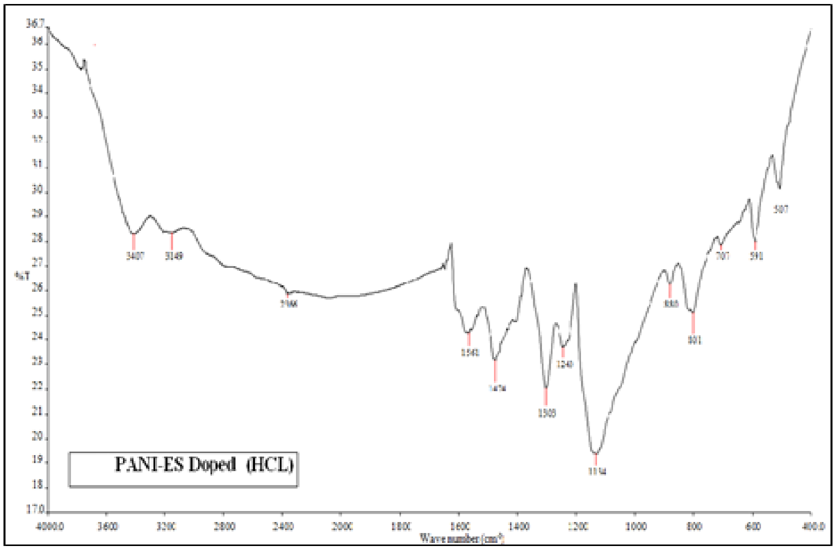

Fig. 4. FTIR spectra of PANi-ES Doped HCl.

Table 3: FTIR peaks in the PANi-ES doped HCl sample.

Wave number(cm^{-1})	Assigned Functional groups
507	C-Cl aromatics out of plane band

801	C-Cl aromatics out of plane band
1134	Vibration of (–NH*=) structure
1243	Stretching of (C-N*) polaron structure
1296	C-N stretch of Benzenoid ring
1474	C-C stretch of Benzenoid ring (N-B-N)
1589	C=C stretch of Quinoid ring (N=Q=N)
2366	C-H stretching band
3407	N-H stretching band

FESEM scanning images as shown in the Fig. 5, the PANi-ES sample with varying dopants acid exhibit varying microstructures. The addition of acid dopants improved the polymer lattice, which leads to the ionization of sites in the chains of polymer. The defects in the chain due to the dopant ions provide more of the mobility of the charge carriers on which conduction depends [20]. Fig. 5, (a, b) image at 5 µm, 10 µm shows a micro porous pattern of globular microstructures for the PANi-ES doped with HCl. The orientation of structures and morphology of samples at the macroscopic level affects the mobility of charge carriers and, the conductivity of polymer [20]. The highly porosity nature of the material and the clumped spherical morphology was confirmed with a FESEM study.

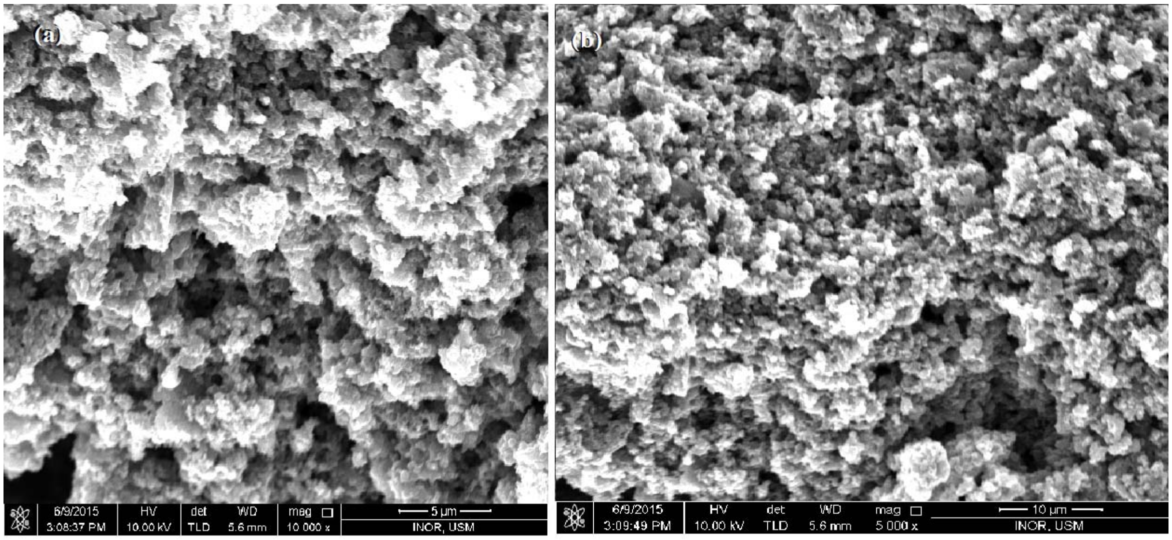

Fig 5. FESEM morphology of doped Polyaniline-ES at (5 µm and 10 µm).

V. Conclusion

Polyaniline synthesis by chemical oxidative method has been developed to produce PANi-ES as conductive polymer. Study of physical and chemical properties with more of techniques such as: XRD, FT-IR, FESEM and UV-vis spectroscopy, it can be proved that Polyaniline has microstructure and chemical stability. X-rays analysis indicated that the Polyaniline has an amorphous nature; however the effect of acid caused an increase in the crystalline of polymer. The results of FE-SEM exhibit that the particle size of polymer within the micro scale and with the presence of protonic acid. The diagnosis of the FT-IR spectra confirmed the internal structure of the polymer, and the position of the bonds has not changed. Optical techniques confirmed preparation of microstructure polymer. The wide band gap and low resistivity of doped PANi-ES thin film. The optical properties show that it can even acts as an organic semiconductor. By this one can expect a good results in the field of photovoltaic and optoelectronic device.

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