EFFECT OF DOPING BY STRONGER IONS SALT ON THE MICROSTRUCTURE OF CONDUCTIVE POLYANILINE-ES: STRUCTURE AND PROPERTIES

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Samples of polyaniline (emeraldine salt) were prepared with different protonic acid dopant, namely hydrochloride acid and sulfuric acid. Easiest chemical method for the preparation a conducting polymer of Polyaniline (PANI-ES) emeraldien salt has been reported in this paper. This polymer microstructure are characterized and analyzed with, HR-XRD diffraction, Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM), and UV-vis spectroscopy. Polyaniline (PANI-ES) exhibit amorphous structure confirmed that from XRD diffraction pattern and FESEM analysis study, the formation 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.

1. Introduction

The conducting polymers are highly conjugated *p*-electron systems that display unusual electronic properties such as low ionization potentials and high electron chemical affinities. Many researches are now focused on studying conducting polymers such as polyacetylene, polythiophene, polypyrrole, and polyaniline among others [1]. Polyaniline (PANI) be found in a variety of types 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 [2,3]. The emeraldine base (PANI-EB) can be change to conducting by adding some of a protonation acid dopant.

After protonation doping, there will be separation of bipolaron to state of two polarons, where a bipolaron form will be to accomplish. 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.

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Fig.1. Protonic acid media doping of Polyaniline (PANI-ES).

The efficiently polymerization procedure of aniline is accomplished only in acidic medium, where aniline exists as an anilin cation. A variety of inorganic and organic acids at different concentrations have been used in the preparation of PANI ; the resulting PANI-ES, protonated with various acids, differs in solubility, conductivity [6].

The changes in physicochemical properties of PANI that occur in response to various external exciting are useful in more applications [7]. Many of these applications are based on the electro active properties of PANI such as bio-electronics, polymer-modified electrodes [8]. The choice of physical properties of PANI suitable for specific applications is thus of fundamental importance [3]. The main objective of the present study is to determine the effects of dopant salt ions on the microstructure of PANI-ES.

ln this work, a systematically inquiry on the oxidative chemical polymerization of aniline is made as simple as possible by novelty and easy in situ chemical method at low temperature, which results in good quality, uniform, 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.

2. Chemical Materials:

We have used the following chemical materials for synthesis the Polyaniline.

All chemicals materials used here were of the highest purity available, which their supplier companies and the purpose for used were listed in Table (1).

Table 1. Chemicals materials employed and their supplier companies.

No.	Chemical Materials	Molecular weight (g/mol)	The Origin Company	The purpose for used
1-	Aniline hydrochloric ($C_6H_5NH_2.HCl$)	93.13	Merck Schuchardt, Germany	As a monomer
2-	Ammonium Persulphate ($(NH_4)_2S_2O_8$)	228.20	Merck KGaA, Germany	Used as initiator (Oxidant agent)
3-	Hydrochloride Acid (HCL)	36.46	BRIGHTCHEM, Pinang, Malaysia	Used as doping active
4-	Sulphuric Acid (H_2SO_4)	98.08	QReC, Asia, Selangor, Malaysia	Used as protonic acid
5-	Hydro Formic Acid (HF)	20.0	QReC, Asia, Selangor, Malaysia	Used as a solvent
6-	Acetone (C_3H_6O)	58.08	QReC, Asia, Selangor, Malaysia	Used for purification

3. Instruments and measurements:

X-ray diffraction studies were carried out using high resolution an X-ray diffracto-meter (Model: PANalytical X pert Pro MRD PW3040). The XRD patterns were recorded in the range of 2θ : 20–60° with a step width of 0.02^o and a step time 1.25 sec by using (CuKα) radiation (λ=1.5406A^o). The XRD patterns were analyzed by matching the observed peaks with the standard pattern provided by a JCPDS file.

Fourier Transform Infrared (FTIR) 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 Nova NanoSEM 450) operating at 20 kV. UV-vis the spectra of the samples, which were recorded on a Shimadzu -1800 UV-vis spectrophotometer.

4. Chemical Synthesis of Polyaniline (Emeraldine-Salt):

Polyaniline was synthesized by chemical polymerization of aniline in the presence of hydrochloric acid (HCl) and a sulfuric acid (H_2SO_4) as a reaction stimulating, and ammonium peroxydisulphate (APX) as an oxidant. For the synthesis, we took 50ml beaker, 1.0M of protonic acid medium, and 0.2M of aniline solution were added into a 250ml beaker equipped with a Teflon coated magnetic stirrer at about 0-4°C temperature (ice-bath). Then 0.25 M ammonium peroxydisulphate in aqueous medium combined with a equal molarities acid of (HCl) and (H_2SO_4), 1M acid was drop wise added into the above solution. Both solutions are mixed in a round bottomed flask and slight stirring to polymerize the mixture. The reaction is found to be exothermic.

The mixture was left to rest to overnight. The precipitate (PANI) was collected, filtration and washed with three times of 0.2M HCl and 150 ml of Acetone. After that (PANI) was dried in air for 1h and then 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. Then used o.1M of Hydrofluoric acid as a solving powder and prepared the thin films samples. Table (2). Illustrating the reaction steps.

Table 2: illustration the reaction steps

Step(1)	Step(2)	Step(3)	Step(4)
Setup system of interaction with condenser	The vacuum flask used to purification Polyaniline and initial drying of the sample by using rotary.	PANI powder was dried in vacuum oven about (80°C) for 6h to achieve moisture free polyaniline.	Calculate the weight of product after the drying annealing

5. Results and Discussion

5.1 Structural Analysis:

Fig. 2(a),(b) which represents the x-ray diffraction of doped (PANI-ES) with different acid (HCl and H_2SO_4) show tow wide peaks at ($2\theta=22^o$,25°).

The spectrum of x-rays to film of Polyaniline as the angel at (22^0) show diffraction levels parallel in the polymeric chain , while the angle at (25^0) shows diffraction levels orthogonal, these results are identical to the researcher Singla et al [9].

X-ray diffraction of doped polyaniline represents the diffraction of the film polyaniline when researcher used different types of acids to doping polymer and the results was one of the terms of the film of the peaks at same angle , no matter what type of doping.

The average crystallite grain size Gs is calculated according to Debye Scherer equation:

$$Gs=K \ \lambda/\beta \ Cos \ \theta \tag{1}$$

Where: K is the shape factor (0.9), Gs is the average grain size; λ is the wavelength of X-ray radiation used (1.5406Å); β is the full width at half maximum, θ is the diffraction angle. The pattern of thin film polymer PANI-ES that shows structure by the study of XRD peaks confirmed amorphous structure and semi-crystalline nature of the preparation polymer [10,11]. The peaks at ($2\theta=22^o$, 25°) may also represent the characteristic distance between the ring planes of benzene and quionied rings respectively in adjacent chains [12]. The characteristic wide of the observed peaks refer to that the films are nano crystalline. Table (3) X-ray parameter of polymer PANI-ES acid dopant.

Table3. Effect of acidic media on grain size and Bragg angle in PANI-ES.

Polymer	Pos. [$2\theta^o$] (degree)	FWHM (degree)	d- spacing (Å)	Gs (nm)
PANI-ES (HCL)	22^0	0.59	3.9	14.3
	25^0	0.78	3.2	11.5
PANI-ES (H_2SO_4)	22^0	0.78	3.9	10.8
	25^0	0.98	3.5	8
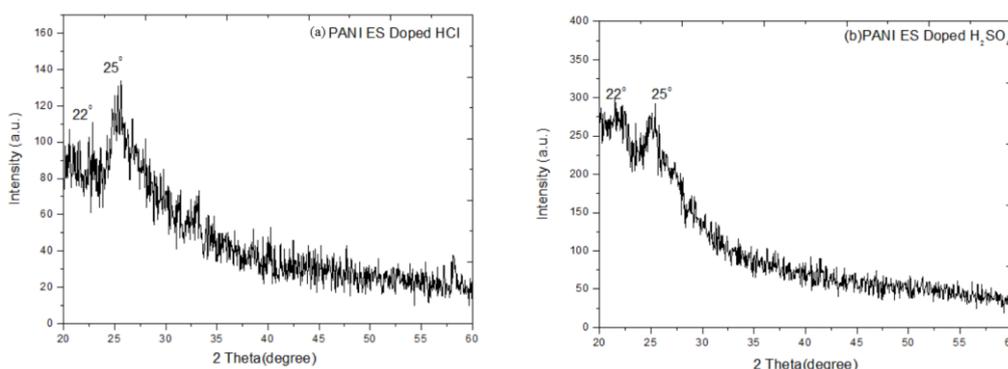
Fig. 2X-ray diffraction of doped PANI-ES with different acid:
(a)HCl; (b)H_2SO_4.

5.2 Microstructure Analysis of Polyaniline-ES

As shown in the FESEM images of Fig. 3(a),(b) the PANI-ES samples with different dopants acid exhibit varying microstructures. Variation in microstructure leads to different of properties of the samples. The addition of acid dopants improved the polymer lattice, which leads

to the ionization of sites in the chains. The defects in the chain due to the dopant ions provide more of the mobility of the charge carriers on which conduction depends [13]. Fig (3a) shows the doped PANI-ES with acid HCl showing fine spongy formation fused together. Fig (3b) shows a micro porous pattern of semi-globular microstructures for the PANI-ES dopant with H_2SO_4.

The highly porosity nature of the material and the clump spherical morphology was confirmed with a FE-SEM study. The orientation of structures and morphology of samples at the macroscopic level affects the mobility of charge carriers and, thus, influences conductivity of polymer [13].
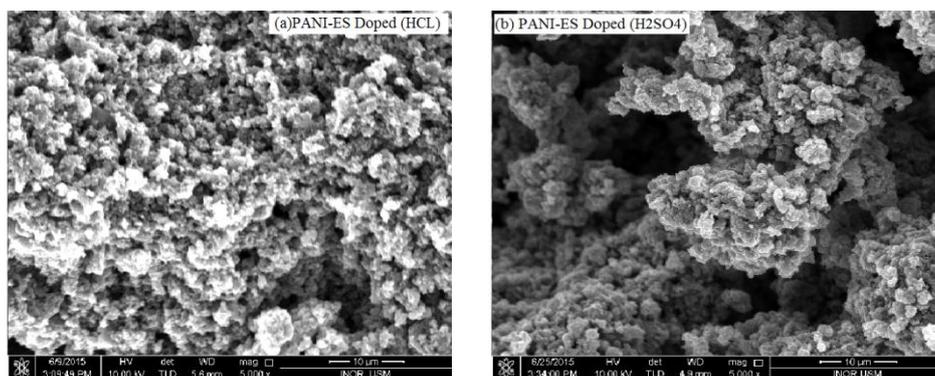
Fig 3FESEM morphology of doped Polyaniline-ES.
(a)HCl; (b)H_2SO_4.

5.3 FT-IR Spectrum Analysis

FTIR is one of the most common methods of spectroscopy, we were studying the IR spectroscopy of doped Polyaniline emeraldine salt dopant with different of protonic acid such as HCl and H_2SO_4, and this is achieved by comparison of the bands position and intensities observed in IR spectra with wave numbers for determining functional groups present in Polyaniline. Infrared spectrum can be influenced by several factors in the whole region from (400-4000 cm^{-1}) such as the influence of different medium conditions (humidity, temperature and concentration dopant of the samples preparation).

The FTIR spectrum of the samples prepared study at room temperature with equal concentrations of acidic, where the percentage of transmittance is plotted as a function of wave number (cm^{-1}). The characteristic of FTIR can distinguish between benzenoid rings and quioniod rings in the rang (1350-1960 cm^{-1}) region of the spectrum. This region of the spectrum is very important to distinguish and diagnostics the polymer in cases of doped [14,15]. Fig. 4(a). Shows the FTIR spectra of PANI-ES (HCl) sample prepared at temperature 0 °C with 1M dopant concentration. The spectra recorded in wave number rang (400- 4000 cm^{-1}). It is obvious from the figure that temperature of thin film has effectively changed the molecular medium 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 as reported by earlier workers [16,17]. The peak around 1243 cm^{-1} corresponds to the electrically conductive state of doped polymer PANI-ES [18]. At low temperature of samples prepared will shift few peaks toward lower wave number region (1134-1100 cm^{-1}, 1303-1296 cm^{-1}, and 1589-1560 cm^{-1}) along with increase in intensity of the peaks. This may be 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 and only slight shift in the peaks positions.

This shows that the degree of polymerization is very highly pronounced for PANI-HCl samples prepared at low temperature. Table 4(a); show the list of observed peaks with their corresponding functional groups.
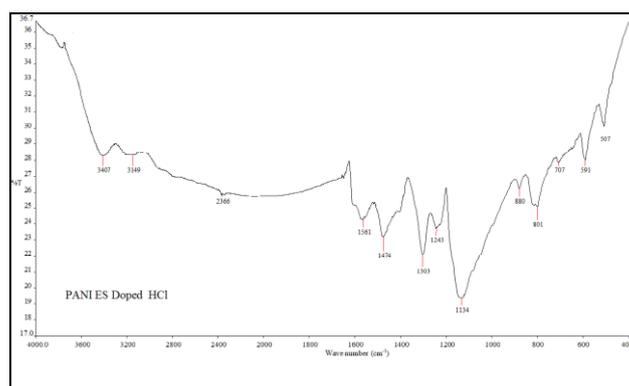
(a)
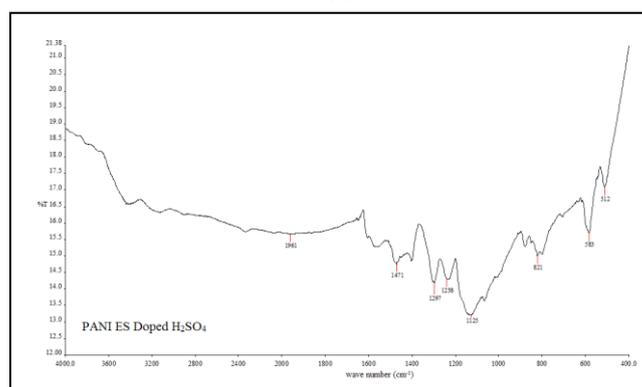
(b)

Fig. FTIR spectra of (a)PANI-ES Doped HCl.(b) Doped H$_2$SO$_4$.

The observed peak for the prepared Polyaniline-ES at room temperature with equal concentration of H$_2$SO$_4$, list in Table 4(b), shows the main transmission band of the PANI. The observed peak at (512,850 cm^{-1}) is a measure of the amount of chlorine which was returned to the used monomer (aniline hydrochloride). While the peak at (1290-1350 cm^{-1}) could be related to the aromatic amine and to sulphate compounds which resulting from the dopant acidic. As well as, for the peak at (1380, 1475cm^{-1}) can be attributed to a case of sulphate groups attached to the aromatic ring in addition to alcohol as products. The most important characteristic bands installed Polyaniline is the band observed at a wavelength of 1650 cm^{-1} and the band at 1961cm^{-1}, which represents the benzeniod and quinoid rings, respectively. Finally the other bands which located they presence the vibration bands of water molecules in most of the spectra shown by figure 4(b) correspond to a high of humidity during measurements that were made [15].

Table 4(a): List of the FTIR peaks in the PANI-ES (HCl) sample.

Wave number(cm^{-1})	Assigned Functional groups
507-700	C-Cl aromatics out of plane band [15]
801-890	C-Cl aromatics out of plane band
900-1134	Vibration of (–NH*=) structure [14]
1243	Stretching of (C-N*) polaron structure [14]
1296-1303	C-N stretch of Benzenoid ring
1474	C-C stretch of Benzenoid ring (N-B-N)
1560-1589	C=C stretch of Quinoid ring (N=Q=N)
2366	C-H stretching band
3100-3407	N-H stretching band

Table 4(b): List of the FTIR peaks in the PANI-ES (H_2SO_4) sample.

Wave number(cm^{-1})	Assigned Functional groups
500-850	C-Cl compound stretching band
1020-1125	C-N Benzene derivative amine stretching band
1200-1297	C-N amine stretching strong band
1299-1350	S=O Sulphur stretching band strong
1380-1475	S=O Sulphur Chloride, stretching band
1650-1961	C=N Benzenoid ring conjugate cycle alkenes band

5.4 Optical Absorption studies:

Absorption spectrum of the PANI-ES dopant films prepared at temperatures (0-4°C) with 1M doping concentration of protonic acids. At the visible spectrum, which is measured on a Shimadzu UV1700 ultraviolet visible spectro-photometer shows in Fig. 5(a,b) three prominent absorption peaks are observed around 300 nm, 400 nm and 800 nm confirming the HCl,H_2SO_4 doping in PANI-ES films[19–21].
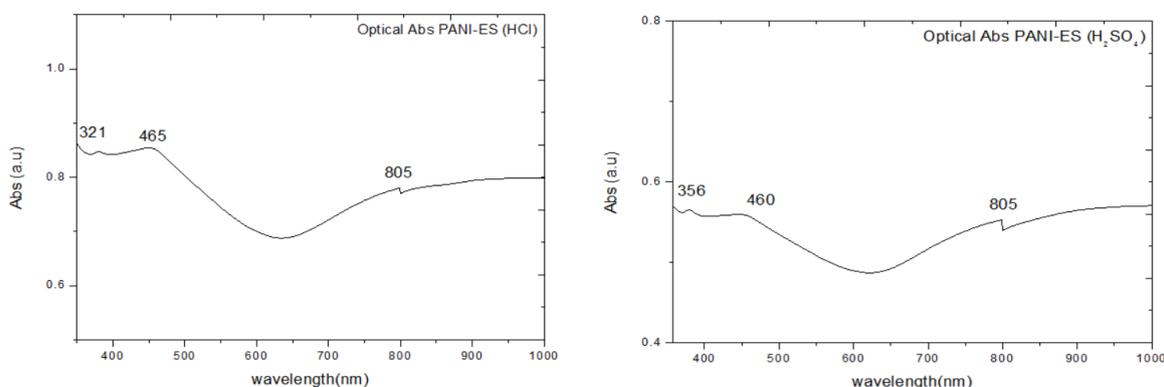
Fig. 5 UV-vis spectra of PANI-ES Doped with 1M (a)HCl; (b)H_2SO_4.

The peaks at (321 nm, 465 nm and 805 nm) for Polyaniline doped with acid HCl and (356 nm, 460 nm and 805 nm) for doped with acid H_2SO_4 are assigned to: ($\pi\rightarrow\pi^*$) transition, (polaron$\rightarrow\pi^*$) transition and ($\pi\rightarrow$polaron) transition, for Polyaniline-ES doping with 1M acid (HCl, H_2SO_4) respectively according to Fig. 6(a,b).
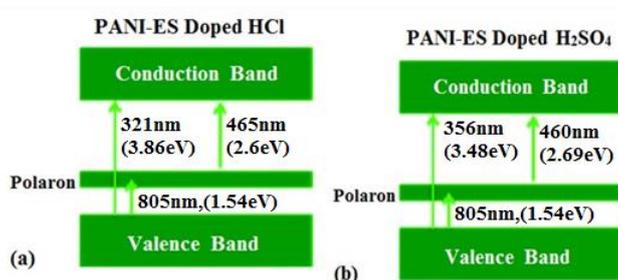
Fig. 6 Diagram of the optical transitions and energy levels in PANI-ES. (a)HCl; (b)H_2SO_4.

This confirm 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 medium. This is due to the fact that decrease in temperature of reaction medium, increases the degree of polymerization which leads to increase in molecular weight of the polymer

which in turn leads to increase the absorption [22]. Moreover, the localized defect states increases to a greater extent with decrease in temperature (0-4 °C) [23]. Absorption coefficients (α) of these PANI-ES films is maximum at 321,356 nm for PANI-ES (HCl, H_2SO_4) as shown in Table 5. Expected electronic change in all prepared samples of PANI-ES can be theoretical explained by calculating the band gap from their UV-vis spectra. The energy $h\nu$ of the photon is related to the wavelength λ of UV-vis radiation by the following relation [24-26].

$$\Delta E = h\nu = E(HOMO) - E(LUMO) = Eg = 1240/\lambda(nm) \qquad (2)$$

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 5.

Table 5: Optical properties of PANI-ES sample.

Polymer	Wavelength λ_{max}(nm)	Abs Coefficient $\alpha x10^5$(cm^{-1})	$E_g=E_{HOMO}-E_{LUMO}$) (eV)
PANI-ES (HCl)	321	1.2	3.86
PANI-ES (H_2SO_4)	356	0.8	3.48

For PANI-HCl and PANI-H_2SO_4 films with 1M doping concentration, absorption coefficient (α), in PANI-ES-HCl (1.2×10^5 cm^{-1}) greater than PANI-ES-H_2SO_4 (0.8×10^5 cm^{-1}) for along with increase in band gap (Eg) from 3.86 eV to 3.48 eV with at same temperature. Already, the effect of doping concentration on optical absorption of PANI-ES films at a constant temperature of film preparation [26,27]. It is observed from the spectra Fig. 5(a,b) films prepared at (0-4°C) temperature alone show weak peak around 805 nm irrespective of the doping concentration which may be due to the decrease in localized defect states in the polaron band.

6. Conclusions

In conclusions, a direct by one step and environmentally friendly simple, chipper, easy and new chemical synthesis method has been developed to produce PANI-ES.
This may be helpful for commercially synthesis of polyaniline. Study of physical and chemical characteristics with more of techniques such as:
HRXRD, FT-IR, FESEM and UV-vis spectroscopy, it can be proved that Polyaniline has microstructure and chemical stability.
The Polymerization reaction of Polyaniline in oxidative chemical method was exothermic reaction. The conditions reaction of temperature and time of polymerization is directly proportional to the amount of protonic acid which used to doping polymer. The diagnosis of X-rays indicated that the Polyaniline has an amorphous nature (Semi-crystalline) structure; however the effect of acid caused an increase in the properties of crystalline and a unusual decreasing in grain size of the polymer.
The diagnostic results of FE-SEM indicated that the particle size of the polymer within the micro-scale and with the presence of acid. The diagnosis of the FT-IR Confirmed the internal structure of the polymer. with the presence of acid, the position of the bonds has not changed. The optical techniques confirmed preparation of microstructure polymer,
wide optical band gap and low resistivity of doped PANI-ES thin film.

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