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Organic Solar Cell Based on Conducting Polyaniline (PANi/H_2SO_4): Preparing and Characteristics

AMER N. JARAD Al-DAGHMAN
Department of Physics, Materials Science, Polymer Research Center,
University of Basrah, Basrah, Iraq
E-mail: ameer978nj@yahoo.com

Abstract:

we have been prepared Polyaniline (PANI) used the chemical polymerization by oxidation method at room temperature and studied the effect the dopant (Sulfuric acid) on the structure of the polymer which prepared with molarities of sulfuric acid 1M, the changes taking place were follow-up by the following measurements: HRXRD, FT-IR , UV-Vis and J/V solar cell characterization. The reaction was exothermic, we study the effect of acid on the reaction temperature and reaction time, and found that the reaction time is fixed with ratios of doping was up to 1h , even while the acid had a clear impact on increase in the reaction temperature, which reflected positively on the amount of the product. The analysis of the output polymer composition by using Fourier transformer infrared spectroscopy FT-IR, for doped samples with 1M molarities of sulfuric acid observed change in the intensity of emission opposite the wave number corresponding to each bond, while not any change in the position of the bonds with appearance at peak return to SO_4 compound. By the X-ray, crystalline nature of the polymer revealed that it has the nature of semi-crystalline and with the effect of the acid clear improvement happened to the installation of the crystalline nature of the polymer. The properties of the surface was studied and the calculated of particle size revealed that the compound has micro porous as granular affected with the presence of acid which has positive influence in decreased the particle size from (97.72- 18.16) nm.

Keywords: *Polyaniline, Porous Silicon, Organic Solar cell.*

1. INTRODUCTION

The conducting materials polymer have been of great interest for their applications in new technologies and are considered as materials for the next generation of electronic and optical devices. In view of this, a great deal of attention has been given to their structural, optical and electrical properties. The conductivity of these materials can be controlled by the process of doping which involves the transfer of charges from dopant to polymer [1]. The electrical properties of metals combined with the advantage of polymers such as smaller weight, resistance to corrosion and lower cost [1] hence can be regarded as suitable candidates for the replacement of metals [2]. Polyaniline PANI is one of the most useful of these polymers due to its easy preparation, environmental stability, and low cost of monomer [3, 4]. Its high absorption coefficient in the visible part of the electromagnetic spectrum, high mobility of charge carriers and great stability has made it very attractive to researchers [1]. Polyaniline PANI is unique among conductive polymers in that its electrical properties could be reversibly controlled both by charge transfer doping and by protonation, this makes it a potential material for applications such as chemical sensors, microelectronic devices, etc. It is a good material for applications in photocells, circuit boards, rechargeable batteries, biosensors, corrosion protection materials, and optoelectronic devices. PANI is a phenylene-based polymer having an –NH– group on either side of its phenylene ring. The oxidation and reduction of this polymer takes place on this –NH–group, resulting in various forms due to the number of imine and amine segments on the polyaniline chain structure. The polymer may occur in different redox states with emeraldine base being consider as the most useful form of polyaniline due to its high stability at room temperature [5]. It is insulating, and the only form of polyaniline, which can be doped by acids [6].

Acid doping converts the insulating emeraldine base to the conductive form, of emeraldine salt [7]. This is the most conducting form of polyaniline with conductivity on a semiconductor level of the order of 100 $S{\cdot}cm^{-1}$, many orders of magnitude higher than of conventional polymers ($<10^{-9}$ $S{\cdot}cm^{-1}$). In this study, we synthesized the Polyaniline (PANI) thin films by chemical oxidative polymerization of aniline in the presence of Sulphuric acid using Ammonium peroxydsulfate (APS) as an oxidizing agent. The Aniline and APS solutions were prepared by mixing 0.25M of Aniline and 1.5M of APS in 1M of H_2SO_4 respectively.

2. EXPERIMENTAL PROCEDURES

Polyaniline was synthesized by chemical polymerization of aniline in the presence of Protonic acid (H_2SO_4) and ammonium peroxydisulphate (APX) as an oxidant agent. For the synthesis, we took 50ml beaker, 1M of sulphuric 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 an acid of (H_2SO_4), 1M acid was drop wise added into the above solution. Both solutions mixed in a round bottomed flask and gentle stirring to polymerize the mixture. The reaction is found to be exothermic. The temperature as a function of time for this reaction through the polymerization processes. The precipitate (PANI) was collected and filtration and washed with three times of 0.2M Hydrochloride and 150 ml of Acetone. After that (PANI) dried in oven vacuum 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 (PANI-ES) was thoroughly grounded in a mortar to obtain very fine particles. Then used HF acid o.1M of to solving PANI powder and prepared the thin films samples.

3. INSTRUMENT AND MEASUREMENTS

X-ray diffraction studies were carried out using high resolution an X-ray diffract meter (Model: PANalytical X pert Pro MRD PW3040). The XRD patterns were recorded in the range of 2θ: $10–70^{o}$ with a step width of 0.02^{o} and a step time 1.25 sec by using ($CuK\alpha$) 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}. 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. Solar cell simulator characteristic, which were study by using IV (Model: Keithley-2400 SOURCE METER). The solar simulator intensity, values were measured by using a solar simulator light source led, power output 100$mW.cm^{-2}$, white light, 100% intensity is adjustable, The lamp had spectral distribution closely matching that of the solar spectrum.

4. RESULTS AND DISCUSSION

Figure. 1 which represents the x-ray diffraction of doped polyaniline (ES) with acid with (H_2SO_4) show tow wide peaks at ($2\theta=22^{o}$,25^{o}). The spectrum of x-rays to film of Polyaniline as the angel at (22^{o}) show diffraction levels parallel in the polymeric chain, the angle at (25^{o}) shows diffraction levels orthogonal these results are identical to the researcher Singla et al [8]. X-ray diffraction of doped polyaniline represents the diffraction of the film of polyaniline when researcher used different of acids to doping polymer and the results was one of the terms of the film of the peaks at angle (22^{o}, 25^{o}), no matter what type of doping. The average crystallite grain size is calculated according to Debye Scherer formula:

$Gs = K\,\lambda/\beta\,\cos\theta$ ……………….. (1)

Where: K is the shape factor (0.9), *Gs* is the average grain size; λ is the wavelength of X-ray radiation use (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 and the semi crystalline nature of the synthesis polymer [9, 10]. The peaks at ($2\theta=22^{o}$, 25^{o}) may also represent the characteristic distance between the ring planes of benzene and quionied rings respectively in adjacent chains [11]. 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.

Table 1. Effect of Protonic acid on Bragg angle and intensity in conducting PANI doped.

Sample	Pos. [2θ °] (degree)	FWHM (degree)	*d*- spacing (Å)	G_s (nm)
PANI-ES (H_2SO_4)	22^0	0.78	3.9	97.72
	25^0	0.98	3.5	18.16

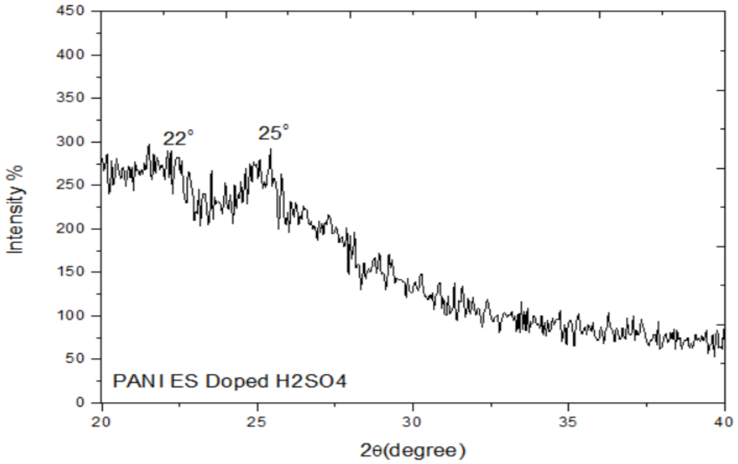

Figure. 1. X-ray diffraction of doped PANI-ES with different acid.

FTIR is one of the most common methods of spectroscopy, we were studying the IR spectroscopy of doped Polyaniline emeraldine salt dopant with Protonic acid such as H_2SO_4, and this is achieved by comparison of the band position and intensities observed in IR spectra with wave numbers for determining functional groups present in Polyaniline. Infrared spectrum can be affected by several factors in the whole region from (400-2000 cm^{-1}) such as the influence of different ambient conditions (humidity, temperature and concentration dopant of the samples preparation). The infrared 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}). Figure. 2 shows the infrared spectrum of the Polyaniline-ES (H_2SO_4) samples. The observed peak for the prepared Polyaniline-ES at room temperature with equal concentration of H_2SO_4, list in Table (2), 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 chloride). While the peak at (1290-1350 cm^{-1}) could be related to the aromatic amine and to, Sulphate compounds which resulting from the dopant acid. 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 quionied rings, respectively. Finally the other bands which located they presence the vibration bands of water molecules in most of the spectra shown by figure (2) correspond to a high of humidity during measurements that were made [12, 13].

Table 2: 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 Benzeniod ring conjugate cycle alkenes band

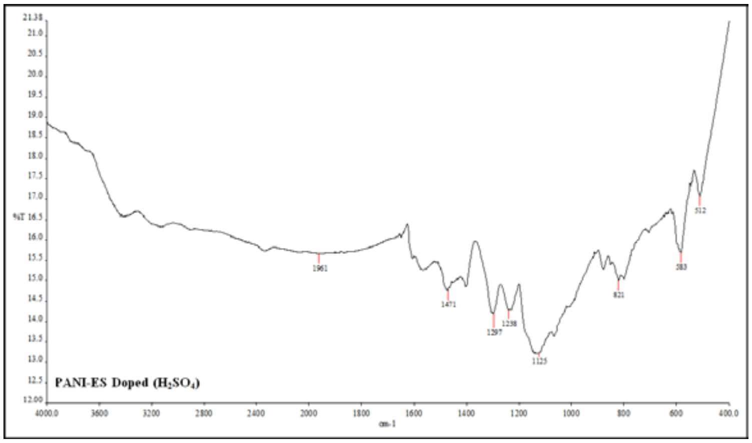

Figure 2. FTIR spectra of PANI-ES doped H_2SO_4.

The absorption spectrum of the polyaniline dopant (ES) films prepared at temperatures (-4 °C) with 1M doping concentration of Protonic acids. At the visible spectrum, which is measured on a Shimadzu UV1700 ultraviolet visible spectrophotometer. Figure. 3 shows three prominent absorption peaks are observed around 300 nm, 400 nm and 800 nm confirming the HCl- doping and H_2SO_4-doping in PANI-ES films [14–16].

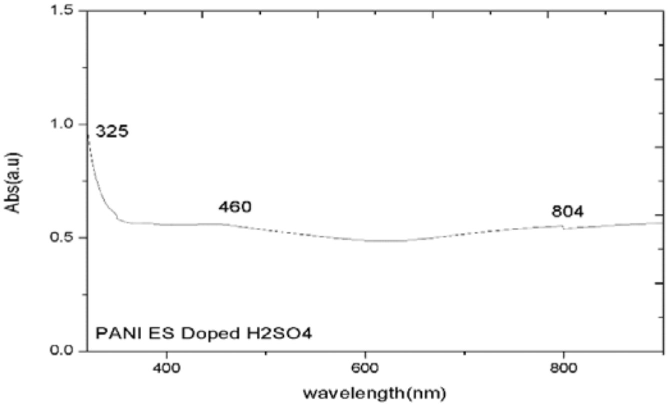

Figure. 3 UV-Vis spectra of PANI-ES doped with 1M (H_2SO_4).

The peaks at (325 nm, 460 nm and 804 nm) for Polyaniline doped with acid H_2SO_4 assigned to: ($\pi \rightarrow \pi^*$) transition, (Polarons→π^*) transition and ($\pi \rightarrow$Polarons) transition, for Polyaniline-ES doping with 1M acid (H_2SO_4) respectively according to Figure. 3. This confirms the Polarons 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 as reported by Stejskal et al. [17]. Moreover, the localized defect states increases largely with decrease in temperature (-4 °C) as reported by Banerjee et al. [18]. Absorption coefficients (α) of these PANI-ES films is maximum at 325 nm for PANI-ES (H_2SO_4) as shown in Table 3. Expected electronic change in all prepared samples of PANI-ES can be theoretical explained by calculating the band gaps from their UV-Vis spectra. The following relation relates the energy (hυ) of the photon to the wavelength λ of UV-Vis radiation [19-21].

$$\Delta E = h\nu = E(HOMO) - E(LUMO) = Eg = 1240/\lambda(nm) \text{ ....} (2)$$

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

For PANI-H_2SO_4 films with 1 M doping concentration, absorption coefficient (α), in PANI-H_2SO_4 (0.8×10^5 cm^{-1}) for along with increase in band gap (Eg) to 3.8 eV with same temperature. Already, the effect of doping concentration on optical absorption of PANI-ES films at a constant temperature of film preparation [22, 23]. It is observed from the spectra Figure. 3 films prepared at (-4 °C) temperature alone show weak peak around 800,804 nm irrespective of the doping concentration which may be due to the decrease in localized defect states in the Polarons band**.**

The (J-V) property of PANI-H_2SO_4 as shown in Figure 4. The device was with the thickness 285nm, same illumination and the same power intensity $100mW.cm^{-2}$. The V_{oc}, FF, and η are recorded at Table 4. The efficiency η of the PANI doped with H_2SO_4 0.26% is good value. It can be clarified that PANI-H_2SO_4 have more prominent excitation states than that of PANI pure [24]. Likewise, the series resistance R_s and R_{sh} are little in structure device organic solar cell. From the table one can consider that the structure (PSi/PANI- H_2SO_4) is the best one among other devices.

Table 4: The (J-V) parameter for PANI doped, PANI-H_2SO_4.

Sample	Voc (mV)	Jsc ($mA.cm^{-2}$)	V_{max} (mV)	J_{max} ($mA.cm^{-2}$)	P_{max} ($mW.cm^{-2}$)	FF	η (%)
PANI-ES (H_2SO_4)	773	$3.3x10^{-3}$	520	$1.2x10^{-3}$	$1.6x10^{-3}$	0.48	0.26

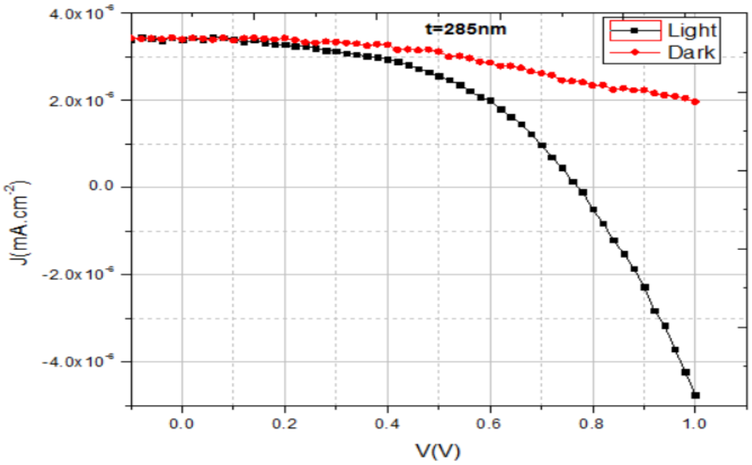

Figure 4. J/V for PANI-H_2SO_4 solar cell with light illuminator intensity 100mW.cm^{-2}.

5. CONCLUSION

As new chemical synthesis method has been developed to produce PANI-ES a directly by one-step and environmentally friendly simple, chipper, easy method. This may be helpful for commercially synthesis of polyaniline. Study of physical and chemical characteristics with more of techniques such as HRXRD, FT-IR, and UV-Vis spectroscopy, it can be proved that Polyaniline has microstructure and chemical stability. The Polymerization reaction of Polyaniline was exothermic reaction.

The diagnosis of X-rays indicated that the Polyaniline has an amorphous semi-crystal structure; however, the effect of acid caused an increase in the properties of crystallinity and an unusual decreasing in grain size of the polymer. The FTIR confirmed the internal structure of the polymer with the presence of protonic acid, the position of the bonds has not changed. The optical characteristic confirmed preparation of microstructure polymer, wide optical band gap energy and low resistivity of doped PANI-ES thin film. An organic solar cell fabricated from the conductive polymer deposited on porosity silicon wafers. The efficiency of solar cell increased when used organic solvent as HF to 0.26 % for PANI-Sulphuric acid.

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