

Preparation, characterization and electrical conductivity of doped polyaniline with (HCL and P-TSA)

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Abstract

Polyaniline (PANI) in Emeraldine salt form was prepared by chemical oxidative polymerization of the appropriate monomeric aniline using two different acid doping (Hydrochloric acid (HCL) and P-Toluene sulfonic Acid (PTSA)) respectively. The prepared samples were characterized by Fourier transform- infrared (FT-IR) spectroscopy; Ultraviolet- Visible (UV-VIS) spectroscopy and X-ray diffraction technique (XRD). The FT-IR and UV-VIS spectroscopy results indicate the doping state of PANi (HCL and PTSA). The crystallinity of the samples was studied in detail by X-ray diffraction technique. The (I-V) characteristic of (PANI) at room temperature, it was showed linear curve close to zero bias indicates that the charge transfer is a straight forward consequence of ohmic behavior, indicating that the measurement was performed in a field independent conductivity region. The scanning electron microscopy (SEM) was used to determine the morphology of the as-prepared nanomaterials.

Keywords: conducting polymer, Polyaniline, polymerization, doping.

تحضير وتركيب ودراسة الخصائص الكهربائية للبولي أنيلين المشوب بحامض الهيدروكلوريك والبارا تولوين سلفونك

الخلاصة

تم تحضير البولي أنيلين وشوب مع حوامض (الهيدروكلوريك والبارا تولوين سلفونك اسد) بطريقه الاكسدة الكيميائية. حيث تم دراسة الخصائص الكهربائية للعينات المحضرة و كانت (67 و 16) $(\Omega.cm)^{-1}$ وفجوة الطاقة (3.3 و 3.5) (e.v) للبولي أنيلين المشوب بحامض الهيدروكلوريك و البارا تولوين سلفونك اسد على التوالي. استخدمت تقنية حيود الأشعة السينية ومطيافيه الأشعة المرئية و تحت الحمراء لدراسة الخصائص التركيبية والبصرية وأكدت النتائج حصول عملية التشويب للبولي أنيلين المشوب مع حوامض (الهيدروكلوريك والبارا تولوين سلفونك اسد).
الكلمات المرشدة: البوليمرات الموصله ، بولي أنيلين ، البلمرة ، التشويب (التطعيم) .

INTRODUCTION

Conducting polymers are a special class of organic polymers that have conjugated structure with alternate single (σ) bond and double (π) bonds, the (π) bonds are delocalized polymer network result in enhanced electrical conductivity [1]. Among all the conducting polymers, conducting polyaniline (PANI) is of great attention due to the fact that, unlike inorganic metals and semiconductors, both the synthesis and chemical modification of organic materials offer unlimited possibilities [2]. The conductivity of polyaniline is affected by various factors such as the degree of oxidation of the polymer, the protonation of acid and its percentage, the degree of crystallization and the polymer chain length and the morphology of the polymer, etc. Doping plays an important role in the conducting polymers. Doping is the process which allows electrons to flow through π conjugated system of the conducting polymers due to the formation of conduction bands [3]. Polyaniline which have several properties such that: It ease of preparation, light weight, low cost, better electronic, optical properties, highly stable in air and soluble in various solvents, and good processibility .PANI exists in various forms: leucoemeraldine base (LEB, fully reduced form), emeraldine base (EB, partially oxidized form) and base Pernigraniline (PNB, fully oxidized form. Among the different oxidation states of PANi, the emeraldine salt (ES) is the only one that presents electrical conductivity[4].

Hydrochloric acid (HCL) is a common and well-known inorganic acid doped polyaniline with improved electrical conductivity .On the other hand, other functional dopants like para toluene sulfonic acid (PTSA), Dodecylbenzenesulfonic acid (DBSA), Camphorsulfonic acid (CSA) and naphthalene sulphonic acid, etc have been studied. In this paper, the chemical synthesis and characterization of polyaniline-(HCL and PTSA) are described. Aniline was polymerized with the two different acids by chemical oxidative polymerization using ammonium peroxydisulphate as an oxidizing agent. The polymer samples were characterized by infrared, UV-Vis, XRD and conductivity measurements.

Experimental Procedure

Materials

Aniline (MERCK Schecharde) and ammonium persulphate (APS as an oxidant) and P-toluene sulphonic acid(dopant, PTSA) were procured from CDH, India ,and all with (AR)grade. Deionized water used throughout the studies. Figure (1) shows the preparation of polyaniline.

Synthesis of Polyaniline Doped with hydrochloric acid.

Doped polyaniline (PAni-HCl) was chemically synthesized using aniline monomer and ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) as oxidant). A specific amount of aniline was dissolved in aqueous solution of hydrochloric acid (1M), and stirred at (0 –5) °C for 1 h which was achieved by using an ice bath. Then the ammonium persulphate was dissolved in (1M) hydrochloric acid, and then added drop-wise to a stirred solution of aniline to ensure completion of the reaction, the monomer to oxidizing agent ratio was kept at 1:1.35. The precipitated emeraldine salt is filtered and washed with hydrochloric acid until the filtrate is colourless. The precipitate is then washed with ethanol to remove

oligomeric impurities. Finally it is washed with acetone, to remove water content. The precipitate is dried for 4 h at 80 °C. The dried precipitate is then grinding into fine powder to get emeraldine salt. Figure (2) shows the Oxidation of aniline hydrochloride with ammonium peroxodisulfate to yield polyaniline (emeraldine) hydrochloride [5].

Synthesis of Polyaniline Doped with Para toluene sulfonic acid.

Doped Polyaniline (PANI-PTSA) was chemically Synthesis using aniline monomer and ammonium persulfate ((NH₄)₂S₂O₈) as oxidant). A specific amount of (0.25 M) (PTSA) was dissolved in deionized water and stirred at (0 - 5)⁰C for 1 h which was achieved by using an ice bath, Then Aniline was adding drop- wise to the above solution, on the other hand the ammonium persulphate was dissolved in deionized water with stirred at (0 - 5)⁰C for 1 h, and then added drop-wise to a stirred solution of aniline to ensure completion of the reaction, the monomer to oxidizing agent ratio was kept at 1:1.2 . The precipitated is filtered and washed with the same way we have mentioned above. Finally, the precipitate is dried for 4 h at 80 °C. The dried precipitate is then grinding into fine powder to get emeraldine salt.



Figure (1) Show the preparation of Polyaniline

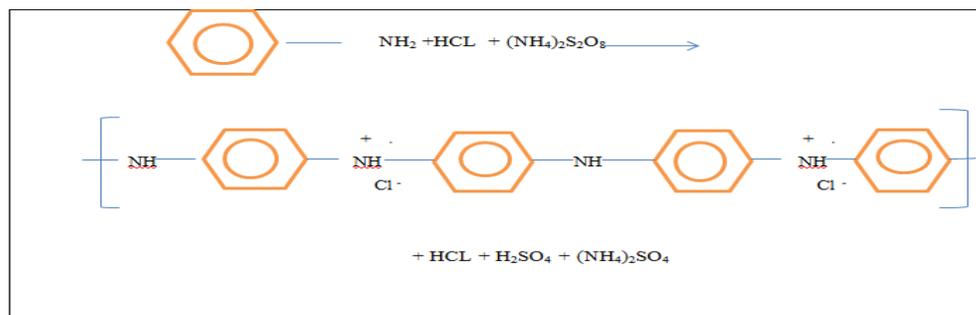


Figure (2) Oxidation of aniline hydrochloride with ammonium peroxodisulfate to yield polyaniline (emeraldine) hydrochloride [5].

Result and Discussion

Infrared Spectroscopy (FT-IR)

The composition of the synthesized PANI were characterized Fourier Transform-infrared Spectroscopy (FTIR) model (SHIMADZU-8400S) is analytical tool measures the molecular vibrations of samples molecules. KBr pellets were prepared to obtain the FT-IR spectra in the range of (4000 – 400) cm^{-1} shown in Fig (3) for polyaniline doped with (HCL and PTSA) respectively.

The FT-IR Spectrum of Polyaniline Doped with hydrochloric acid

In (HCL and PTSA) doped PANI, the major peaks are at around (1511.27 and 1441.81) cm^{-1} are assigned to the stretching vibration of quinoid ring (Q) and benzenoid (B), respectively, thereby indicating the oxidation state of emeraldine salt PANI[6]. The band observed at 1290.47 cm^{-1} is attributed to the stretching of the C – N bonds of secondary aromatic amines and or / displacement of π electrons, induced by acid doping of the polymer [4]. The band at 1144.95 cm^{-1} formed in the acid doping process of polyaniline [7] and described as the electronic-like band, is considered to be a measure of the degree of delocalization of electrons and thus it is characteristic peak of PANI [6]. In addition to the above peaks, the spectrum of the polyaniline around 762.69 cm^{-1} is assigned as due Paradisubstituted aromatic rings indicating polymer formation [8]. Out of plane bending deformation of C–H is observed 590.43 and 561.78 [6].Table (1), summarized the observed absorption bands of PANI prepared by doped with (HCL and PTSA).

Table(1) Show the observed absorption bands of PANI prepared by doped with (HCL and PTSA)

Bands cm^{-1}	Vibrational assignments
1511.27	C=C stretching of quinoid ring (Q)
1441.81	C=C stretching of benzenoid (B)
1290.47	C – N stretching of the secondary aromatic amine
1144.95	NH^+ • PANI is in the doped state
762.69	Paradisubstituted aromatic rings
590.43 and 561.78	C–H out of plane bending vibration

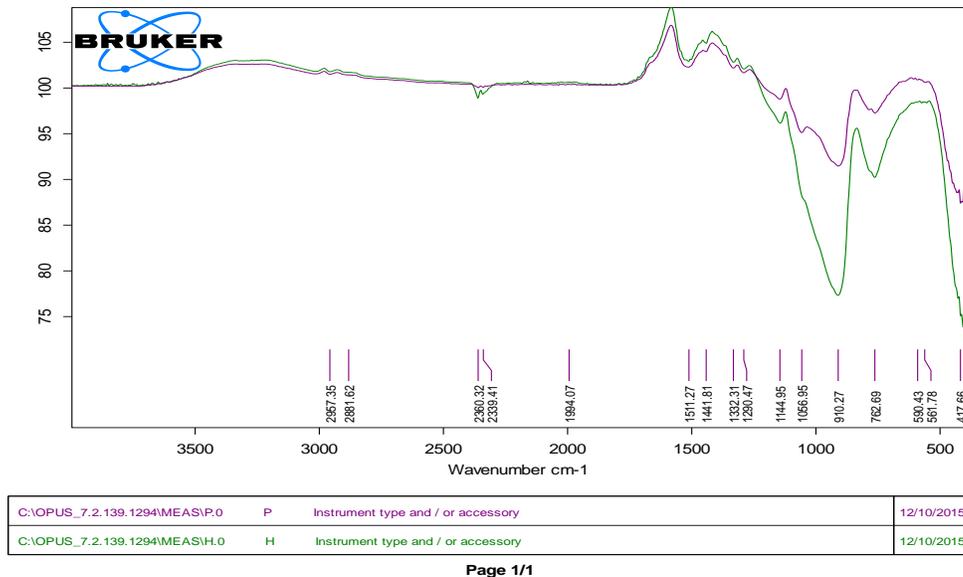


Figure (3) Show the FT-IR Spectrum of Polyaniline Doped with hydrochloric acid and para toluene sulphonic acid

X- ray Diffraction

To investigate the phase analysis of the samples was done by x-ray diffraction (XRD-6000) SHIMADZU, Japan Using with a Cu target ($\lambda = 1.54 \text{ \AA}$) with Current= 30 mA, Voltage = 40 KV and Scanning speed =5 deg/min). The range of the Bragg's angles are taken ($2\theta=10^\circ - 80^\circ$) for the samples. The crystallite size (G.S) of the polycrystalline material can be calculated from the X - Ray spectrum by means of Full Width at Half Maximum (FWHM) method (Scherrer relation) .

$$G.S = 0.9 \lambda / \beta \cos \theta \quad \dots (1)$$

Where:

β is the full – width at half maximum (FWHM) of the XRD peak appearing at the diffraction angle θ , the value of which depends on the crystalline shape, is 0.9 and the grain size obtained from Scherrer equation is (8.9 and 27.6)nm for PANI doped with (HCL and PTSA) respectively.

X- ray Diffraction of Polyaniline Doped with hydrochloric acid.

The X-ray diffraction pattern of PANI in Fig (4), found two diffraction peaks of about 2θ (13.0816° and 27°) .The sharp peak around (27°) is the characteristic peak of PANI.PANI is only partially crystalline with conducting metallic island separated by large amorphous regions [9].

X- ray Diffraction of Polyaniline Doped with PTSA.

The X-ray diffraction pattern of the para-toluene sulphonic acid (PTSA) doped polyaniline (PANI) is shown in Fig (5). It is observed that two bands centered at 2θ (13°

and 28°) are partially crystalline. The sharp peak around (28°) is a characteristic peak indicating that some part of the PANI sub chains becomes rigid and well-ordered due to interchain packing between poly-cation while TSA^- acts as an anion [6].

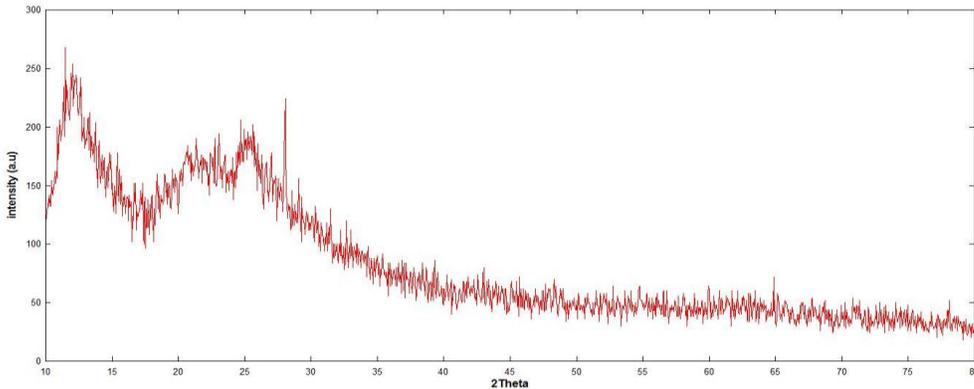


Figure (4) XRD pattern of PANI-(HCL)

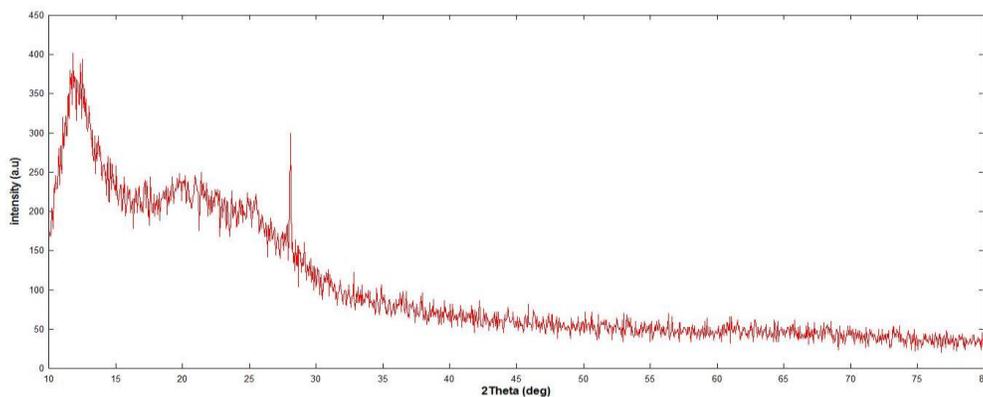


Figure (5) XRD pattern of PANI-(PTSA)

Optical absorption

The UV-Visible spectrum of the polymer was recorded using “(T80+UV\VIS Spectrometer) in the range (200-1100) nm. Electronic absorption of conducting polymers is useful in investigating the oxidation and doping state of the polymer.

The optical absorption spectra of the polyaniline doped with) HCL and p-TSA) is presented in Fig (6 and 7) respectively.

UV- Visible Spectroscopy of Polyaniline Doped with hydrochloric acid

In Fig.5, The absorption curved at 300 nm is due to $\pi \rightarrow \pi^*$. Also it observed two absorption peaks at about 440 and 780 nm assigned to the $\pi \rightarrow$ polaron band and nonbonding(n) $\rightarrow \pi^*$ band transitions for polyaniline, respectively[10]. The energy gap obtained is (3.3)eV.

UV-Visible Spectroscopy of Polyaniline Doped with PTSA

In Fig.6, The absorption at 300 nm is assigned to the $\pi \rightarrow \pi^*$ electronic transition of the phenyl rings in the conducting polymer backbone [6] while the peak at 415 nm is attributed to the localized polarons, the peak at (800 nm) is characterization of protonated polyaniline and confirms the presence of conducting emeraldine salt phase of the polymer. The energy gap obtained is (3.5) eV.

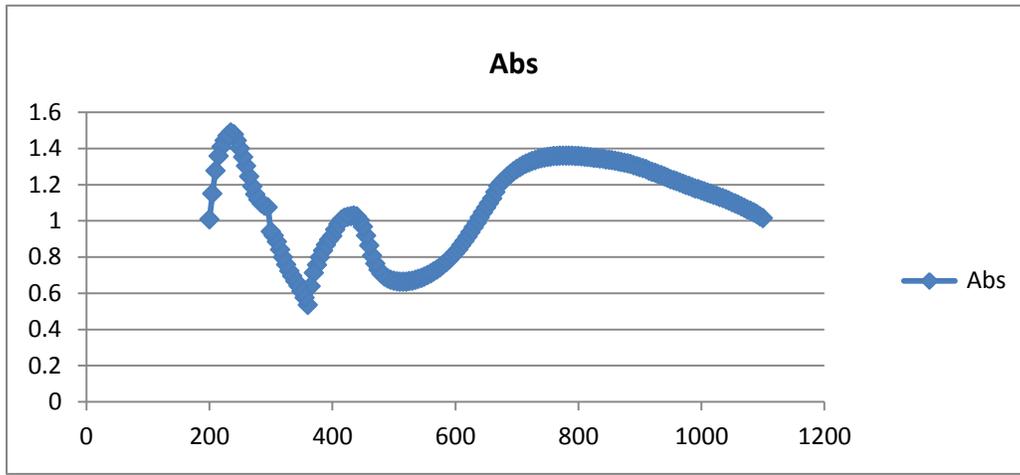


Figure (6) Show UV-V spectra of PANI doped with HCL

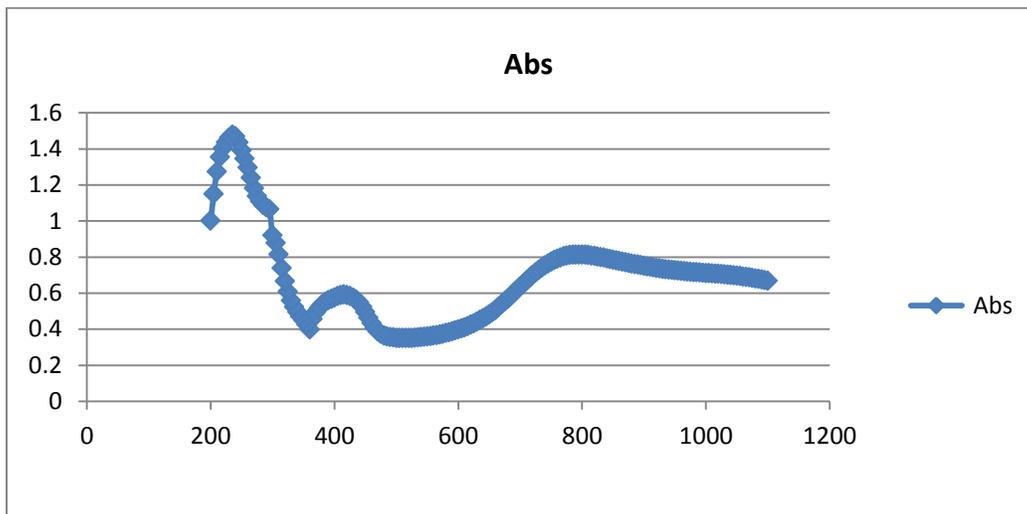


Figure (7) Show UV-V spectra of PANI doped with PTSA

Electrical properties

The I-V characteristics of thin films doped Polyaniline (HCL and PTSA) show in figure (8,9) ,respectively, were recorded at room temperature and are found to be linear that the current increase with increasing voltage, the linear of (I-V) curve close to zero bias indicates that the charge transfer is a straight forward consequence of ohmic behavior (without any breakdown)[1].

DC-electrical resistivity of polyaniline doped with both acids is found by the equation:
 $\rho =R A/ L$... (2)

Where:

(ρ) is the resistivity ($\Omega.cm$), R is the resistance (Ω), A (cm^2) is the cross section of the film, L is the distance between electrodes (cm).

The conductivity of the films is found by the equation:

$\sigma = 1/$... (3)

Where

(σ) represent the conductivity ($\Omega.cm$)⁻¹

The values of electrical conductivities of doped thin films PANi (HCL and PTSA) are 67($\Omega.cm$)⁻¹ and 16($\Omega.cm$)⁻¹, respectively.

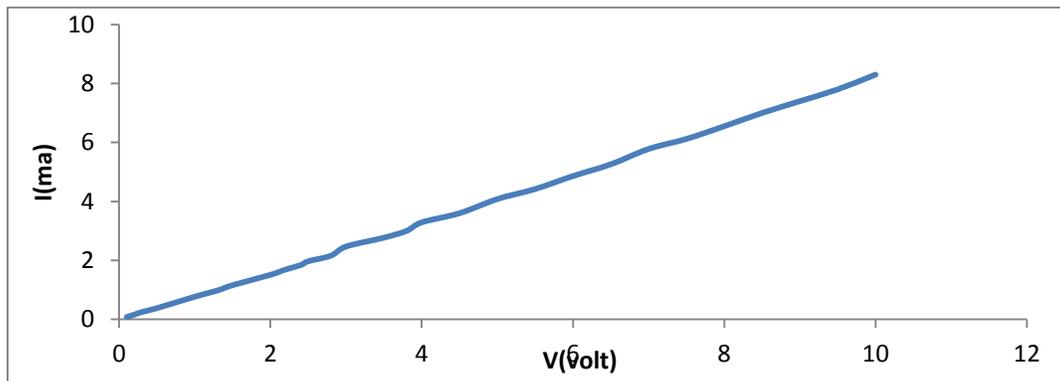


Figure (8) Aniline doped with HCL

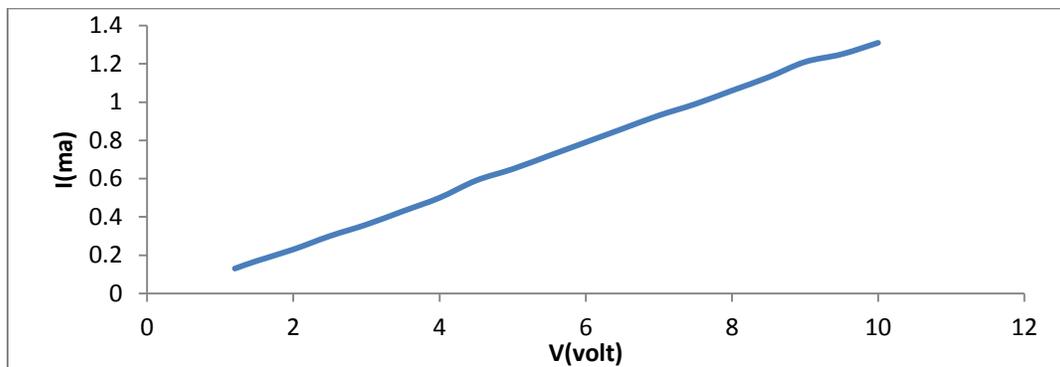


Figure (9) Aniline doped with PTSA

Scanning Electron Microscopy

Fig (10) shows the surface morphologies of the PANi-HCL and appears as uniformly growth of PANi Particles and interlocking between them. While Fig (11) shows that the particles in PANi-PTSA are larger than PANi-HCL and non-uniform in their size distribution and contain porous.

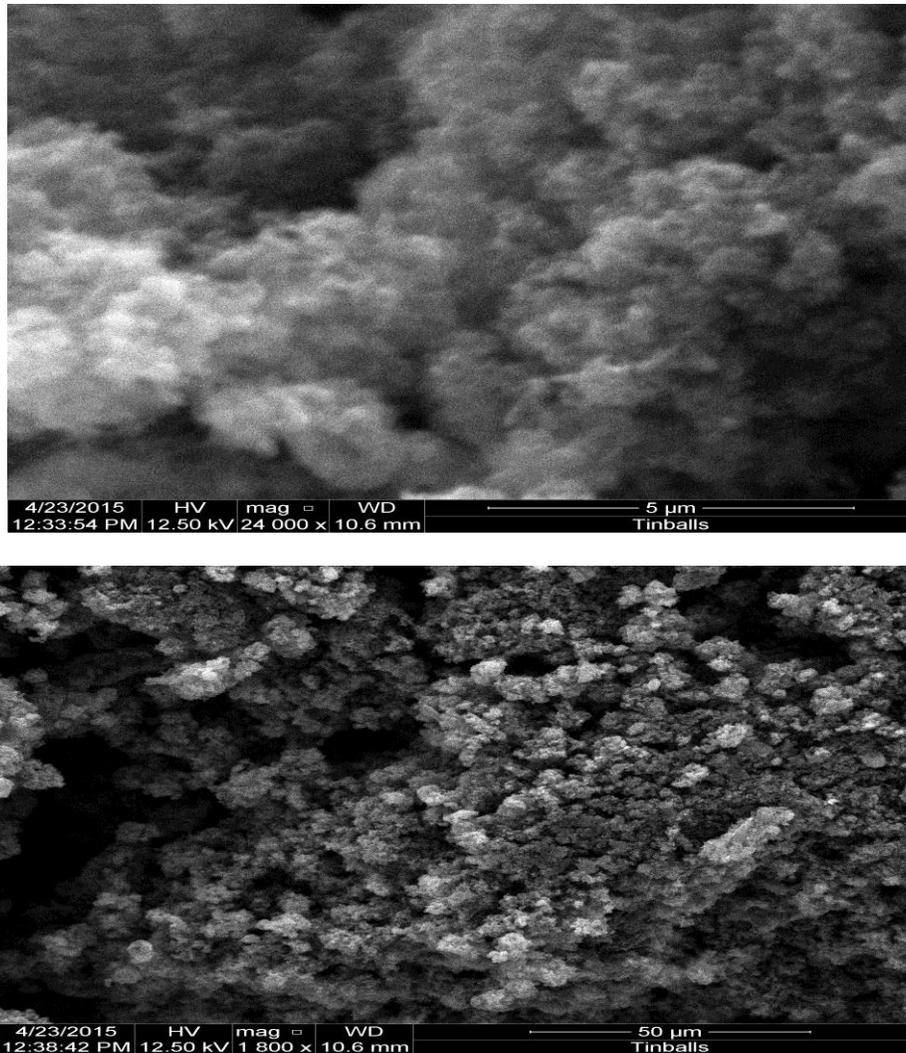


Figure (10) Scanning electron micrographs images of patterned microstructures of PANI-HCL

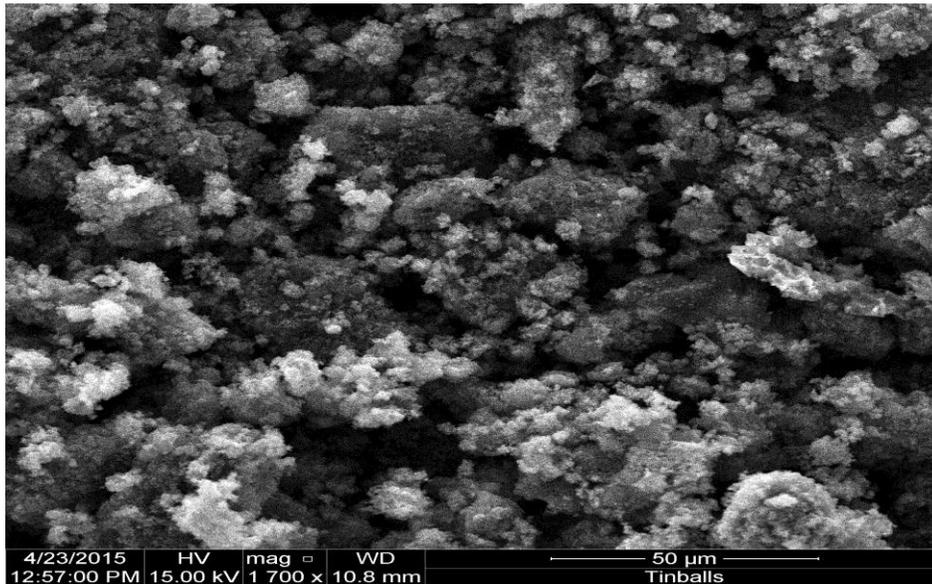
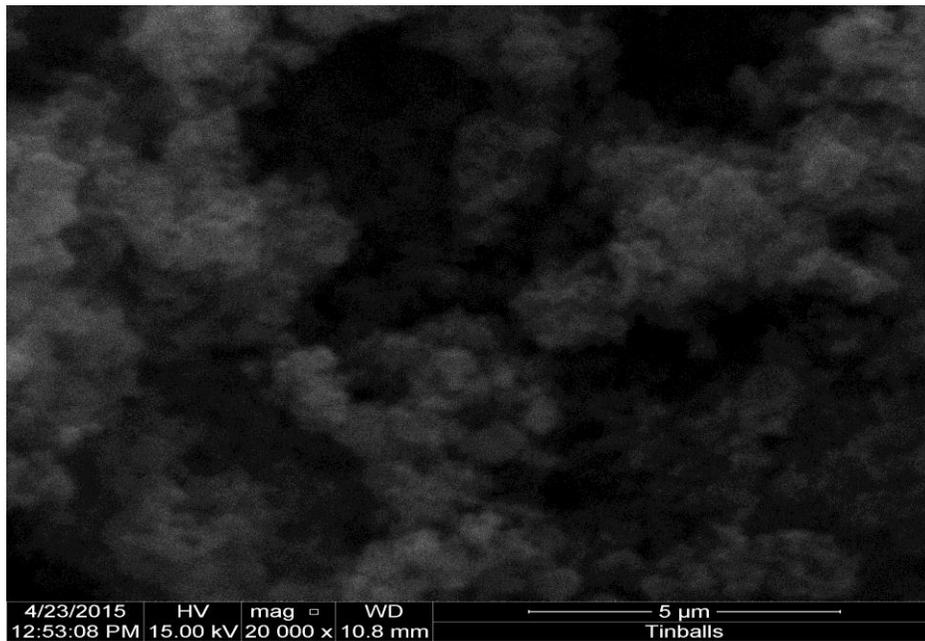


Figure (11) Scanning electron micrographs images of patterned microstructures of PANI -PTSA

Conclusions

Polyaniline material was successfully synthesized by chemical oxidative polymerization of aniline using Ammonium persulphate (APS) which was regarded as the optimal oxidant for polyaniline because of its high yield. UV-Visible, FTIR, XRD and SEM show the effective structural modification. UV-Visible spectra in all doped PANi showed peak around (440 and 415)nm in PANi(HCL and PTSA) respectively is attributed to the localized polarons, which is the characteristic of the protonated polyaniline, no peak appear at (600)nm for (EB) and observed peaks around (790-800)nm in PANi(HCL and PTSA) respectively confirmed the presence of dopant in the emeraldine salt (conducting). The intensity observed upon doping PANi- HCL is higher than PANi-PTSA indicates the increased oxidation state than doped PTSA, thus it is expected that HCL doping should possess higher conductivity than PTSA and this is consistent with the conductivity measurement that show the polyaniline synthesized in HCL acid medium is greater than that of the polyaniline synthesized in of PTSA acid medium, and this occur because the oxidation and doping degree of the polyaniline doped with HCL acid is greater than that of doped with PTSA. The obtained result of energy gap for PANi-PTSA is higher than PANi-HCL. The characteristic peak in FTIR spectra are in good agreement with the reported peaks in literature where observed in the protonated polyaniline representing the conducting emeraldine salt phase of the polymer. The X-ray diffraction pattern obtained shows that the intensity in PTSA is higher than found in HCL it is maybe occur because of the structure of PTSA and thus the crystallinity is higher than HCL.

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