Study of the Structural and optical properties of Pure and Sn doped Polyaniline hydrochloride polymer (PANI) thin films prepared by Spin coating method

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Abstract

In this study the structural and optical properties of pure and Sn doped films polyanilinehydrochloride (PANI) doped by Tin (Sn) with volumetric percentages (3, 6, and 9)%, which prepared by using the spin coating method on substrates of the glass at room temperature. The structural properties of the prepared films were studied by x-ray diffraction technique. The results illustrate amorphous structure .The atomic force microscope (AFM) diagnosis has led the doping process to decrease in the roughness of the surface and the average rate of the square root with the variation in particle size distribution. The study of the optical properties by measuring then absorption and transmission spectra as a function of wavelength (320-910) nm to the pure and doped film of PANI, the results showed that the transmittance decreased with increasing doping due to the increase in the impurity resulted which makes attenuation in the intensity of incident light with a increasing of absorption. The results also showed that the polymer has an indirect allowed energy gap and it decrease with increasing doping because of the doping levels (Sn) inside the optical energy gap.

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Key Words: Polyaniline hydrochloride films, Structural and optical properties, Spin coating.

دراسة الخواص التركيبية والبصرية لأغشية بوليمر أنيلين هيدروكلورايد (PANI) النقية والمشوبة بالقصديروالمحضرة بطريقة الطلاء بالتدوير

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الخلاصة

تم في هذا البحث دراسة الخصائص التركيبية والبصرية لأغشية بولي أنيلين هيدروكلورايدPANI النقية والمشوبة بالقصدير(Sn) وبالنسب الحجمية%(3,6,9)المحضرة بتقنيةالطلاء بالتدوير (spin coating) على ارضيات من الزجاج بدرجة حرارة الغرفة . تم دراسة الخواص التركيبية للأغشية المحضرة النقية والمشوبة عن طريق دراسة حيودالأشعة السينية، أذ أظهرت النتائج ظهور التركيب العشوائي للأغشية المحضرة. كذلك تم استخداماالتشخيص بمجهر القوى الذرية (AFM) فقد أدت عملية التشويب إلىالنقصان في متوسط الجذر التربيعي وخشونة السطح مع تباين في توزيع الحجم الحبيبي بحسب نسب المادة الشائبة.كما تم تشخيص الخصائصالبصريةمن خلال قياس طيفي النفاذية والامتصاصية في مدى الأطوال الموجية (320-910nm)لأغشية PANI النقية والمشوبة ، حيث بينت النتائج ان النفاذية تقل مع زيادة واضحة للامتصاصية مع زيادة نسب الشوائب, وبينت النتائج أيضاً امتلاك البوليمرفجوة طاقة غير مباشرة مسموحةوانها تقل بزيادة نسب التشويب لتكون مستويات لشوائب (Sn) داخل فجوة الطاقة البصرية .

الكلمات المفتاحية : أغشية بولي أنيلين هيدروكلورايد , الخواص التركيبية والبصرية , الطلاء بالتدوير.

1. Introduction

Conducting polymers are known to be compatible with biologicalmolecules and also have the quality to efficiently transfer the electriccharges produced during the biochemical reactions through theirconjugated backbone[1]. In the last few years many conducting polymershave been used with the different prospects for bio sensingapplications[2]. Polyaniline is known to be semi-flexiblerod and has been found to provide the efficient medium for electrontransfer. The chemical and structural flexibility surrounding its aminenitrogen linkages for the immobilization of desired biomolecules hasattracted much efforts towards the various applications in the field ofbiosensing due to its electrochemical, electronic, optical and electro-optical properties[3,4].

Polyaniline is one of the most promising organicpolymers due to its potential technologicalapplications such as gas sensors, storage batteries ,light emitting diodes (LEDs), corrosion control , electrodes for redox supercapacitors, protectioncoating,electrochromic displays biosensors ,photovoltaic devices, etc. Polyaniline is environ mental stable, well-behaved electro chemistry, and has high electrical conductivity “upondoping”. PANI films can beprepared by different techniques such as ;precipitation polymerization, dispersion polymerization, flash dry deposition, pulsed-plasma polymerization, and electrochemical polymerization[5]. Spin coating has been used for several decades as a method for applying thin films,the advantage of spin coating is its ability to quickly and easily produce very uniform films from a few nanometers to a few microns in thickness[6].Structure of conductive polyaniline hydrochlorideis shown in fig. (1)[7].

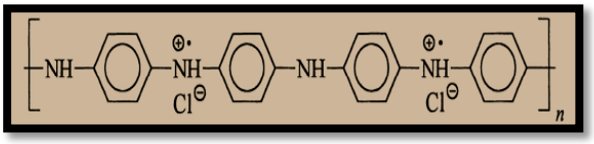


Fig.(1)structure of conductive polyanilinehydrochloride[7].

In this research, pure and Sn doped polyanilinehydrochloride films will be prepared using a spin coating method and study their structural and optical properties.

2. Experimental

The synthesis of conducting polymers(PANI) by chemical synthesis can be done by weight chemical method. It can be done by take aniline hydrochloride as a primary material for preparation. The method of perpetrating represent a case of oxidative polymerization. Where the oxidant can be done by ammonium peroxydisulfate and the polymerization is carried out in acid medium. Now the synthesis of polyaniline included dissolve of (5.18gm) of aniline hydrochloride in (100ml) of distilledwater . Another solution by dissolve (11.42gm) of amoniumperoxydisulfate in (100ml) of distilled water(the aniline hydrochloride and ammoniumperoxydisulfate were supplier from CDH Chemicals Ltd,India).

Both solvents are kept at room temperature for one hour.The mixture is then mixed and move them by magnetic stirrer for 5 minutes,leave the solution for 24 hours and then be filtered and then washed with

(100ml) of (0.2M) of HCl and then (100ml) of acetone,We obtain a dark green precipitation from PANI. The resulting polymer (PANI) is then dried in an oven at (60^{o}C)for 2 hr.(PANI) powder was added to 0.1 M dimethylformamide(DMF) (which also suppliedfrom CDH company)and mixed under constant stirring at room temperature. The weighted calculation of the material were done using equation[8].

$M=1000xW/W_gxV$---------- 1

M: Molecular concentration.

W:Polymer material weight (PANI) (0.75gm).

W_g:Molecular weight(129.59g/mol).

V: The volume of the dissolvent material(50mol).

The polymer material (PANI) was doped with Snand volume percentages (3%, 6% and 9%). Where we took (0.6815gm)tin chloride was taken to obtain the tin material, which was dissolved by (50ml) of distilled water at a concentration of 0.1M. With stirring for (15 - 10) min using a magnetic stirrer after completion the mixing process then the mixture was deposited on glass substrates, type of(Microscope slides)the supplier of the company(China national machinery), dimensions of glass slide is(25.4-76.2)mm and 1mm thickness, preparation of (PANI) thin film using spin coating method, It is manufactured locally manufactured using a mixer (Braun) with a maximum rotation speed (30000rpm / min) ,use tachometer to calibrate the speedand also used variacdevice to determine the appropriate voltages.The speed with which prepared the filmsare(800rpm).table (1) shows the volumetric ratios of the solution for polyaniline hydrochloride and Tin chloride.

Table (1) shows the volume ratios of solution (PANI, $SnCl_2$)

PANI (ml)	**$SnCl_2$ (ml)**	**Ratios of volumetric impurity**
100	0	0%
97	3	3%
94	6	6%
91	9	9%

3. Results and discussion

The structural properties of the prepared films were measured using a type device (XRD- 6000 Shimadzu),the results of the x-ray diffraction for pure andSn doped (PANI) thin films prepared by spin coating method with volumic percentages (3,6,9)% of Tin , is shown in figure (2), the figure shows that the prepared films had a low degree of crystalinaty or other word amorphous structure, the characteristic peak for all prepared thin films where a wide peak appears at ($2\Theta = 23.5^{\circ}$), this is an indicationthat thepolyaniline hydrochloride material is amorphous , this result is consistent with literatures[9].figure (3,a,b,c) represents x-ray diffraction spectroscopy for films polyaniline doped Tin with volumic percentages (3,6,9%),we also note that the x-ray spectrum of the pure film is very fine, with a wide crest at ($2\Theta = 23.5°$) ,the results agree with the results of the studies [10].

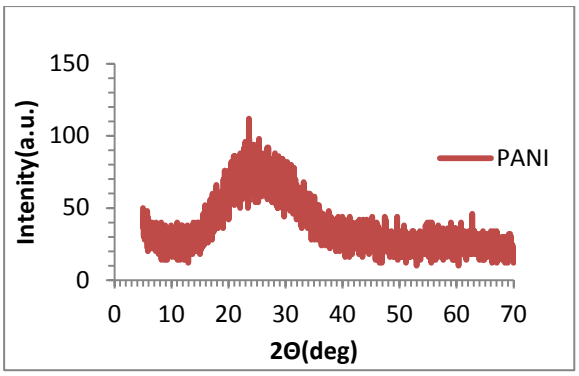


Figure (2) shows the x-ray diffraction of a pure polyaniline

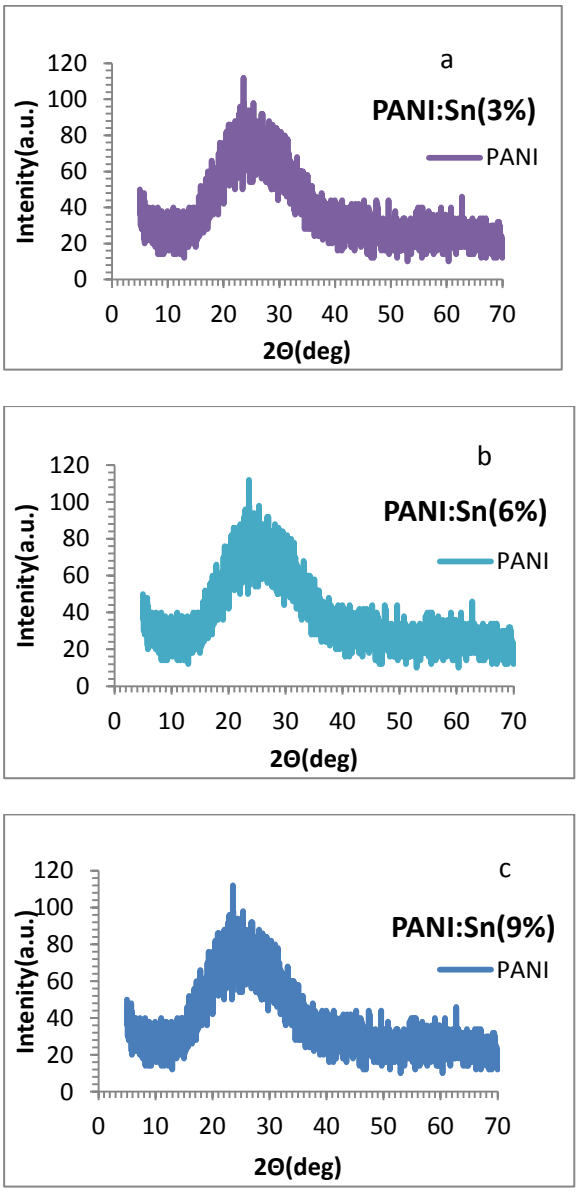
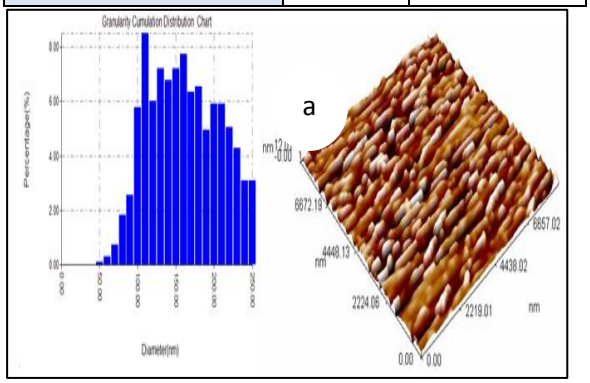


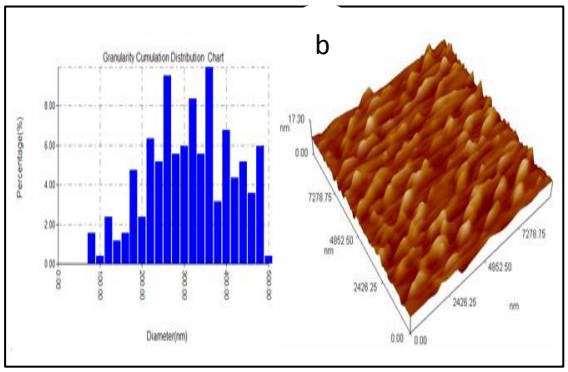
Figure (3) shows the x-ray diffractionfor polyaniline doped by Tin (Sn) with volumic percentages (3,6,9)%

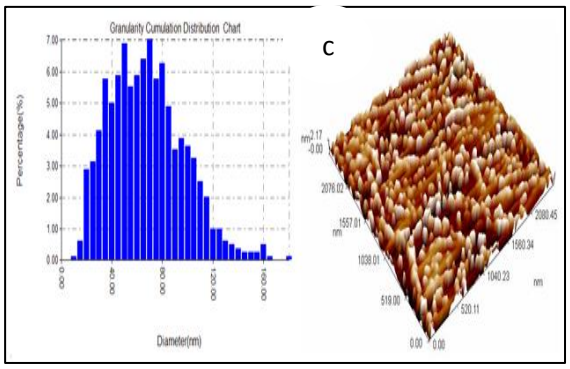
Fig. (4) shows the AFM images of thin films of pure andSn doped (PANI) thin films deposited by spin coating on glass substrates,using a type device(SPM AA3000). The measured root means square (RMS) and the average roughness values obtained from AFM measurements have been decreases with the increase of dopant volumic ratio from (0,3,6,9)% (3.27 to 0.669 nm) and from (2.78 to 0.57 nm) respectively these results are recorded in the table (2), these result was in good agreement with literature [11],through the results listed in the table(2) for films (PANI) pure and doped by Tin(Sn) the average square root values (root mean square) and the average surface roughness (roughness average) change when doping .Figure (5, a, b, c,d) show images of AFM results with three dimensions of pure and Tin-prepared for films with ratios (3,6,9)% , the decrease in the rate of surface roughness at when doping can be attributed to the difference in the kinetics of the atom atoms with the atoms of the host material,the forms included curves mentioned size distribution of crystalline granules nano-metric for the structure of crystalline pure and doping of the films, which change according to the size of the particle distribution ratios of the material dopant ,the results agree with the results of the studies[12,13].

Table (2) mean square root mean and roughness of pure and dopingPANI films

Compound	Root mean square (nm)	Roughness average (nm)
PANI	3.27	2.78
PANI:3%Sn	1.63	1.26
PANI:6%Sn	0.603	0.52
PANI:9%Sn	0.669	0.57







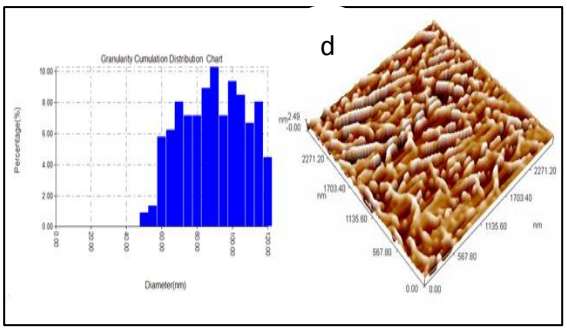
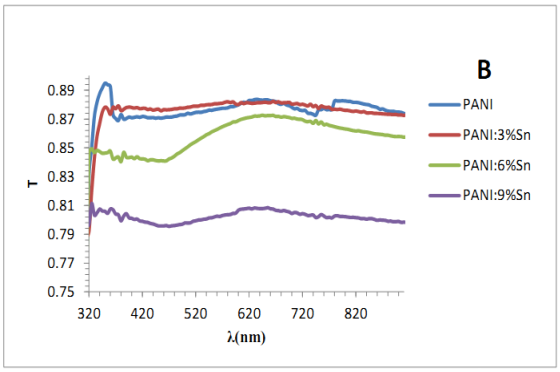


Figure (5,a,b,c,d) images of atomic force microscope (3D) AFM andstatistical distribution scheme of Particle size rates of a-PANIb -PANI:3%Snc -PANI:6%Sn d-PANI:9%Sn

The optical transmittance spectrum was studied in the range of wavelengths (320-910)nm for pure and doped PANI,using a type device(UV-Visible 1800),we observe a decrease in the optical transmission values when the rate of Sn is increased. Absorbance is increasingthis may be due to tin levels inside the energy gap leading to increased absorption and reduced transmission, these results when compared with the published results show that they are highly consistent and as shown in published research[14],as shown in figure (6).



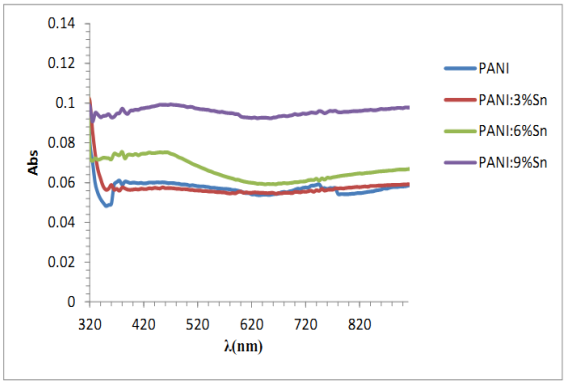


Figure (6): transmission and absorption spectrum as a function of the wavelength of pure and Tin-doping PANI films.

Also calculated the value of the indirect allowed energy gap for the transfer is draw between $(\alpha h\upsilon)^{1/2}$as a photon energy function (hυ),as low energy gap values in the case of increasing the ratiodoping of films prepared of pure and Sn doped ,so as to be doping levels (Sn) inside the optical energy gap.These results when compared with the published results are found to be highly consistent, as shown in published research [15], as shown in Table (3), as shown in figure (7).

Table (3) indirect energy gap values(PANI) pure and doping tin

Material	Ratio doped %	Eg(eV)
PANI	**0**	**3.8**
PANI:Sn	**3**	**3.68**
PANI:Sn	**6**	**3.34**
PANI:Sn	**9**	**3.22**

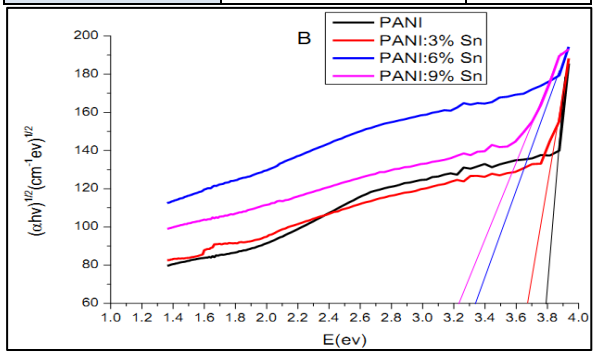


Figure (7) the indirect allowedenergy gapto films PANI pure and tin doping

4. Conclusion

According to the results of atomic force microscope (AFM) diagnosis , the doping process decrease in the roughness of the surface and the average rate of the square root with the variation in particle size distribution,alsoobserve from the results of optical measurements that indirect electronic transmission is allowed and the value of the optical energy gap decreases by increasing the doping ratio of all prepared films.

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