Structure and optical properties of PANI/MWCNTs nanocomposites thin films prepared by plasma jet polymerization

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Abstract

Polyaniline Multi walled Carbon nanotubes (PANI/MWCNTs) nanocomposite thin films have been prepared by non-equilibrium atmospheric pressure plasma jet on glass substrate with different weight percentage of MWCNTs 1, 2, 3, 4%. The diameter of the MWCNTs was in the range of 8-15 nm and length- 10-50 μm. the nanocomposite thin films were characterized by UV-VIS, XRD, FTIR, and SEM. The optical studies show that the energy band gap of PANI/MWCNTs nanocomposites thin films will be different according to the MWCNTs polyaniline concentration. The XRD pattern indicates that the synthesized PANI/MWCNTs nanocomposite is amorphous. FTIR reveals the presence of MWCNTs nanoparticle embedded into polyaniline. SEM surface images show that the MWCNTs homogenously inside the polyaniline house. It can be concluded that the nanocomposite can be prepared PANI/MWCNTs thin films by plasma jet polymerization and control the optical energy band gap irregulars by controlling the MWCNTs weight concentration.

الخصائص البصرية والتركيبية لأغشية المتراكبات النانوية بولي أنيلين – أنابيب الكاربون النانوية متعددة الجدران المحضرة عن طريق البلمرة ببلازما النفث عند الضغط الجوي

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الخلاصة

حضـرت متراكبـات الأغشـية النانويـة بـولي أنيلـين _ أنابيـب الكـاربون النانويـة متعـددة الجـدران PANI/MWCNT عن طريق البلمرة ببلازما النفث عند الضغط الجوي على قواعد زجاجية مع تراكيز وزنية مختلفة من أنابيب الكـاربون النانوية المتعددة الجدران (1، 2، 3، 4) %. قطر أنابيـب الكـاربون النانويـة متعددة الجـدران المستخدمة كانت في مدى (8-15) نـانو متر وطولهـا مـن 10-50 مـايكرو متـر. أغشـية المتراكبـات النانوية وصفت بواسطة الطيف المرئي والاشعة فوق البنفسجية ، حيود الاشعة السينية ، مطيـاف الاشـعة تحت الحمراء (تحويل فـورير) والمجهر الالكترونـي الماسح. النتـائج البصرية أظهرت بـأن فجـوة الطاقة لأغشية المتراكبـات النانويـة PANI/MWCNT كانت تختلف وفقاً لتراكيز أنابيب الكـاربون النانويـة متعددة الجدران. حيود الأشـعة السينية يشير إلى أن تخليق أغشية متراكبـات PANI/MWCNT هو غير متبلـور (عشوائي). مطياف الأشـعة تحت الحمراء يشير إلى أنه أنابيب الكـاربون النانويـة متعددة الجدران جزأ لايتجزأ في البولي أنيلين. الصورة السطحية للمجهر الالكتروني الماسح أظهرت أن توزيع أنابيب الكاربون النانوية متعددة الجدران ذات توزيـع متجـانس داخـل البـولي أنيلـين. يمكـن الاسـتنتاج بأنـه يمكـن تحضـير أغشـية متراكبـات نانويـة مـن PANI/MWCNT بواسطة بلازما النفث عند الضغط الجوي والتحكم بفجوة الطاقة البصرية عن طريق التحكم بالتراكيز الوزنية لانابيب الكاربون النانوية متعددة الجدران.

Introduction

Carbon nanotubes (CNTs), discovered by Iijima and Ichihashi [1], there was great interest in exploring and exploiting their unique characteristics for various applications[2, 3]. CNTs have been attracted significant interest owing to their application in fabricating new categories of advanced materials in result of their unique structural, mechanical and electronic properties [4]. Conductive polymers got a enormous interest during the last decay because it's excellent electrical conductivity. They have a conjugated structure with alternative σ and π bonds. The π bonds are delocalized throughout the entire polymer network [5, 6]. As expected for theoretical reasons, experimentally introducing CNTs into a polymer matrix improves the electrical conductivity and the mechanical properties of the original polymer matrix [7–10]. Among various conductive polymers polyaniline (PANI) is one of the greatest intensively investigated conducting polymers because it was easy synthesis, well-behaved electrochemistry, good environmental stability, high conductivity [11]. Due to their ability to combine the remarkable properties of CNTs, polymeric composites based on carbon nanotubes (CNTs) are of great interest in both academic and technological areas, properties such as extremely high electrical and thermal conductivity, low density, high tensile strength, and Young's modulus, with the versatility, processability, and mechanical properties of polymers[14]. Recent studies have shown that, besides possibly improving the mechanical and electrical properties of polymers, the formation of polymer/CNT composites is considered a useful approach for incorporating CNTs into polymer-based devices [15]. It is well known that the strong interaction between the aromatic rings of PANI and the graphitic structures of CNT would be a great benefit to the charge transfer interaction between the two components [16].

Experimental

1- Materials

MWCNT purity 95% was supplied by neutrino factory, USA. The diameter of the MWCNT was in the range of 8 -15 nm and the length 10-50 μm.

2- Synthesis of nanocomposite

PANI/MWCNTS have been prepared by aerosol assisted plasma polymerization. Thin films were prepared by dielectric barrier discharge plasma jet. The thin films were deposited on glass substrates. Pure aniline monomer was used as the organic precursor. Fig. 1 shows schematic diagram for PANI/MWCNTs nanocomposites thin films preparation by non-equilibrium atmospheric pressure plasma jet. PANI / MWCNTS nanocomposite thin films were prepared with different MWCNTS weight concentration 1%, 2%, 3%, 4%. Argon gas with flow rate of 1 l/min passes through the mobilizer which contains a mixture of MWCNTs and aniline. The mixture convert to aerosol, this aerosol was guided by the Ar gas to the plasma jet. The plasma was ignited by using an electric source at a fixed frequency of 28.0 kHz. The plasma was generated downstream to the substrate which was positioned at suitable distance from the plasma torch end. The film deposition was carried out for 5 min under constant carrier gas flow rate and the substrate at room temperature. The substrate moved on the x and y direction mechanically for the purpose of obtaining a

homogeneous films thickness along the substrate area. Test The films thickness was measured using the optical interferometer method. A double – beam UV-VIS-NIR 210A Spectrophotometer was used to measure the absorption spectrum for the prepared thin films in the range of 200-1200 nm. The absorption data with films thickness can be used to calculate the absorption coefficients of the films at different wave length, have been used to determine the energy band gap Eg. FT-IR spectra were recorded by using solid KBr discs and testing all samples by Shimadzu Co. FT-IR 8000 series Fourier transform,

infrared spectrophotometer from wavelength range 400–4000 cm^{-1} under identical conditions. In order to study the structural properties, the structure is analyzed with a SHIMADZU 6000 X-ray diffract meter system which records the intensity as a function of Bragg's angle. The source of radiation is Cu with current 15mA and voltage 30 kV. The scanning angle 2θ is varied in the range of 10 – 80 degree with a speed of 5 deg /min. The morphological surface analysis is carried out employing an SEM From a manufacturing company FEI) Models (Inspect s50).
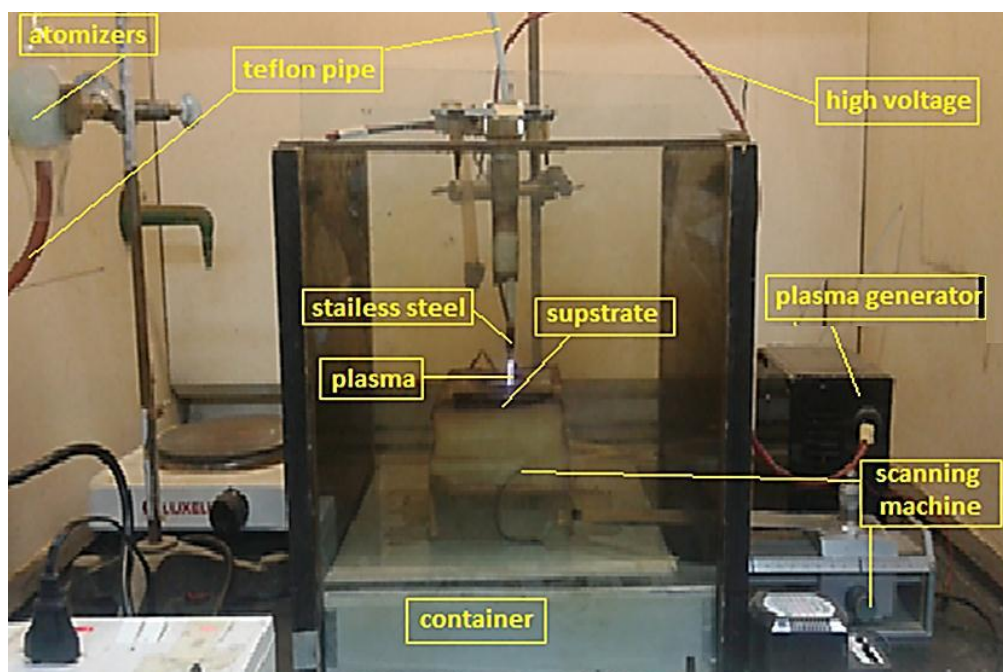

Fig. 1: Schematic diagram for PANI/MWCNTs nanocomposites thin films preparation by non-equilibrium atmospheric pressure plasma jet.

Results and discussion
A. *FTIR analysis*

The FTIR spectra for pure polyaniline and PANI/MWCNTs nanocomposites thin films with MWCNTs weight concentration 4%. Polymerized by plasma shown in Figs.2 and 3. Fig. 2 shows the FTIR spectra of PANI in the region of 4000–400 cm^{-1} shows peaks at 3433 cm^{-1} N-

H represents the stretching vibration, 2926 cm^{-1} C-H stretching vibration of aromatic ring, 1598 cm^{-1} C=C stretching vibration of quiniod (N=Q=N), 1429 cm^{-1} C=C stretching vibration of bezenoid ring (N=B=N), 1244 cm^{-1} C-N stretching of primary aromatic amines and 1060 cm^{-1} C-H bending vibration.
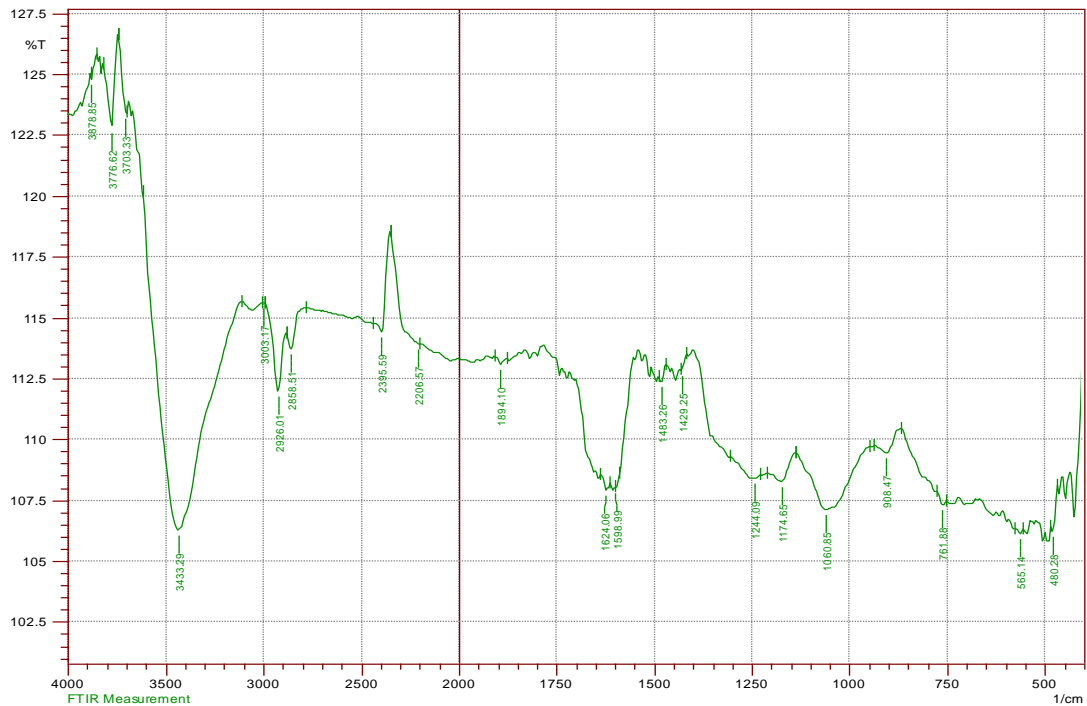
Fig.2: FTIR spectra for pure polyaniline thin film.
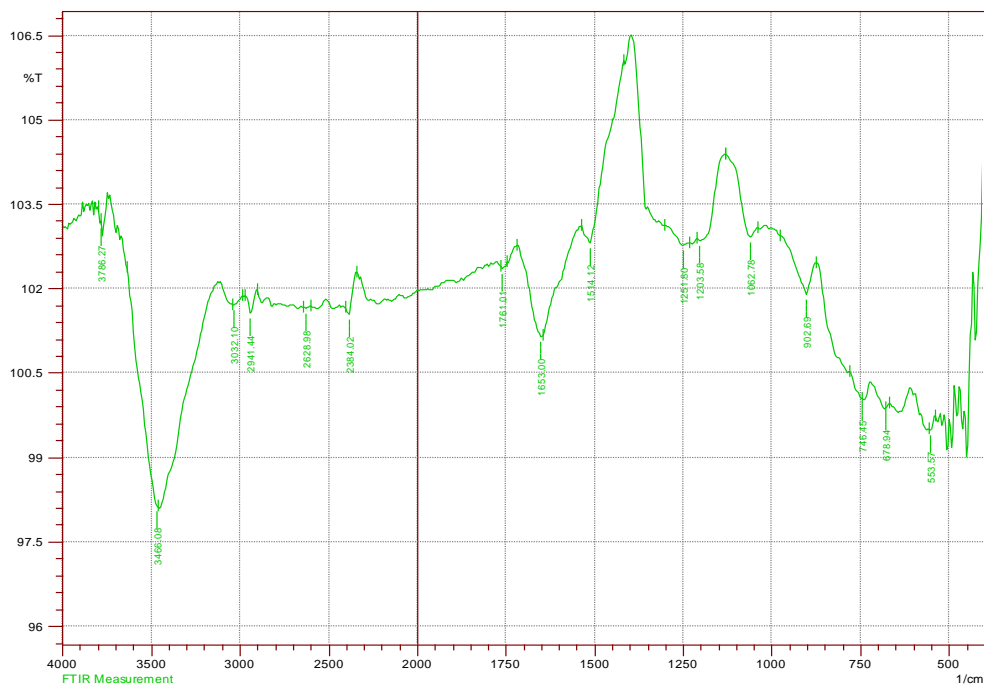

Fig.3: FTIR spectra for PANI/MWCNTs nanocomposites thin film with MWCNTs Wight concentration 4%.

The band assignments of the FTIR bands for pure polyaniline, polymerized and PANI/MWCNTs thin films are given in Table 1. It is clear from the table that there is a shift in N–H stretching and C–N stretching bands in the PANI/MWCNTs. The N–H stretch shifts towards high wavenumber. This is an indication that MWCNTs doping causes a change in the structure of the plasma polymerized polyaniline samples.

Table 1: FT-IR spectra for pure polyaniline, and PANI/MWCNTs nanocomposites thin films with MWCNTs Wight concentration 4%.

Band mode	0%	4%
N-H stretching vibration	3433	3466
C-H stretching vibration of aromatic ring	2926	2941
C=C stretching vibration of quinioding (N=Q=N)	1598	1514
C=C stretching vibration of bezenoid ring (N=B=N)	1429	…….
C-N stretching of primary aromatic amines	1244	1251
C-H bending vibration	1060	1062

B - The optical properties

Fig. 4 show the absorption spectra of the pure PANI and PANI/MWCNTs nanocomposites thin films with different MWCNTs weight concentration 1, 2, 3, 4%. as a function of wavelength in the range of 400-1100 nm.
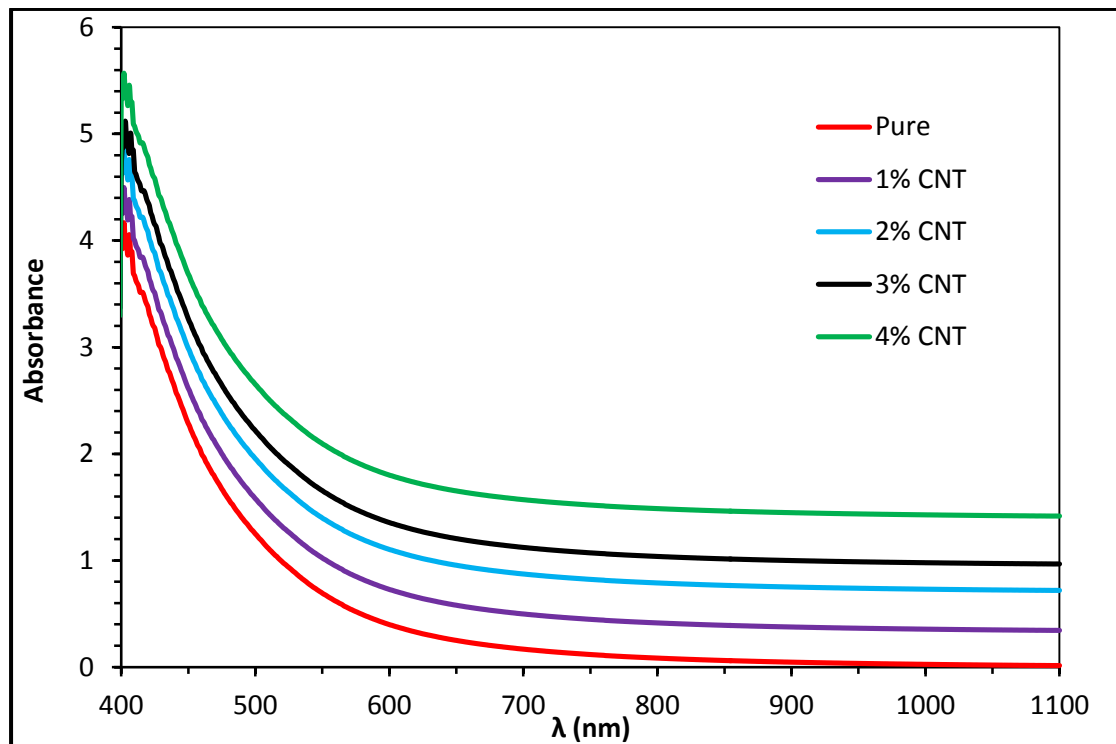

Fig. 4: The Absorbance spectra of the Pure PANI and PANI/MWCNTs nanocomposites thin films with different MWCNTs Wight concentration 1, 2, 3, 4 %wt.

From Fig. 4, it can see that peak height increases for all samples, and the absorption band shifts towards longer wavelengths with increasing the weight percentage of MWCNTs. The adding of different amounts of MWCNT material to PANI does not change the chemical structure of the polymer material but new physical mixture is formed. that peak height increases attributed to increasing the number of carries charges which cause to increase the absorbance and this cause more absorption for the incident light by free electrons. When the wavelength decreases at the neighborhood of the fundamental absorption edge, the interaction

between incident photon and material will occur, and the photons will be absorbed. Fig. 5 shows the relationship between the absorption coefficient and wavelength of the pure PANI and PANI/MWCNTs nanocomposites thin films with different MWCNTs weight concentration 1, 2, 3, 4%. as a function of wavelength. And Table 2 shows the PANI/MWCNTs nanocomposites thin films preparation conditions.
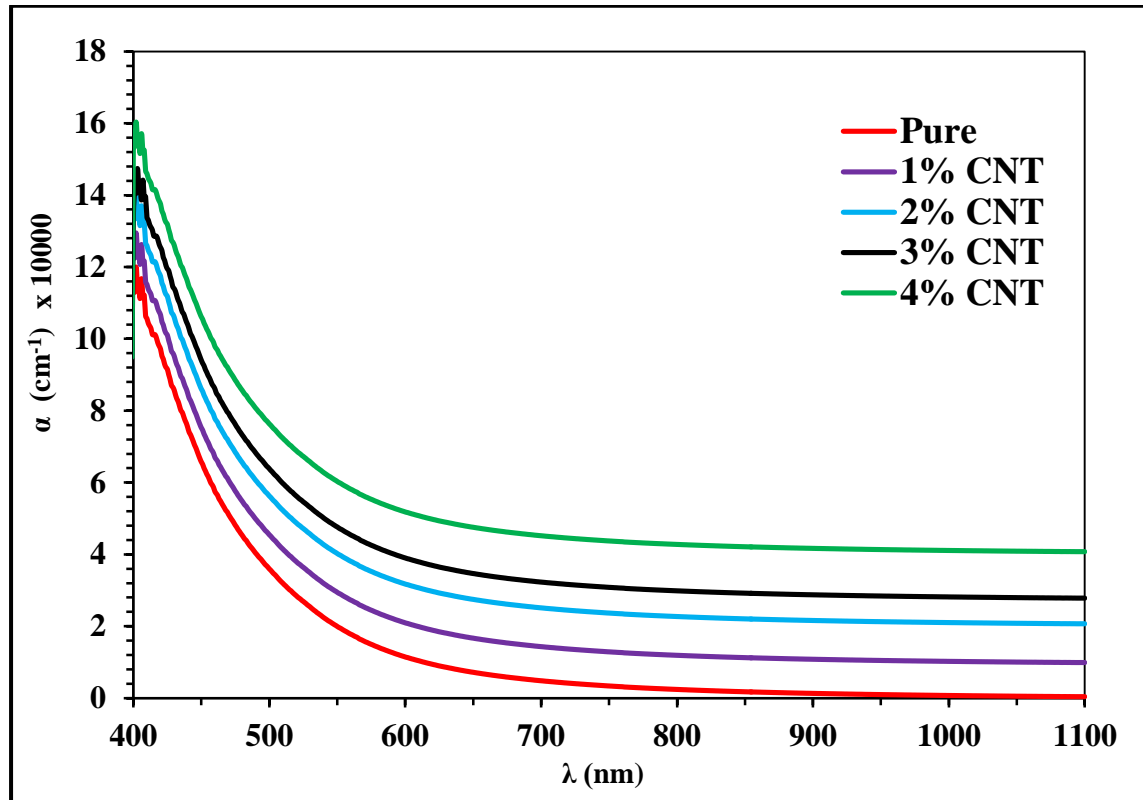

Fig. 5: Absorption coefficient of the pure PANI and PANI/MWCNTs.

The absorption coefficient of PANI/MWCNTs nanocomposites thin films increased with increasing of MWCNTs concentration. At low wavelength, this means that the energy of incident photon is enough to move the electron from the valence band to the conduction band.

Fig. 6 the obtained results showed that the energy band gap (E_g) decreased with increase of the (MWCNTs) concentration. Because (CNT) have higher electrical conductivity than PANI.
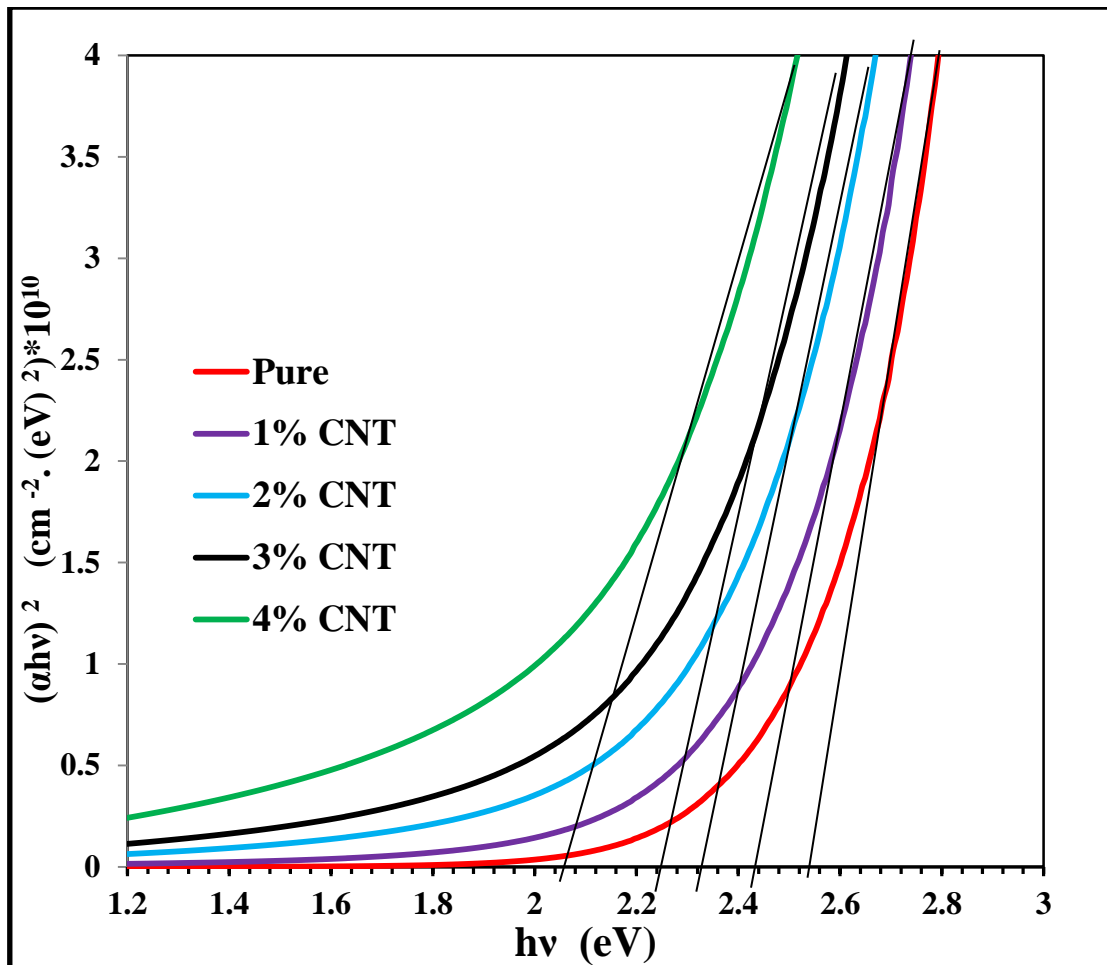
Fig. 6: Direct energy gap of the pure PANI and PANI/MWCNTs nanocomposites.

This behavior can be attributed to the fact that in heterogeneous composites, the electrical conduction depends on defect and impurities due to the formation of defects created during the blending and the interaction between the polymer chains and the formation of some bonds [17-19].

Table 2: The experimental condition for the preparation of Pure PANI and PANI/MWCNTs nanocomposites thin film by plasma polymerization.

Sample Name	Gas flow (L/min)	Distance	Thicknesses (nm)	Eg (eV)
Pure polyaniline	1	1.3	190	2.55
MWCNT 1%	1	1.3	210	2.44
MWCNT 2%	1	1.3	207	2.35
MWCNT 3%	1	1.3	227	2.27
MWCNT 4%	1	1.3	230	2.08

C. *Structural characterization*

Fig. 7a shows the X-ray diffraction for pure polyaniline and Fig.7b the X-ray diffraction for PANI/MWCNTs nanocomposites thin films with 4%. MWCNTs weight concentration. From the x-ray diffraction pattern it is clearly indicated that the thin films have an

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amorphous structure. Plasma polymer has short chains of building units and a high degree of cross-linking. Plasma polymers are usually amorphous in nature.
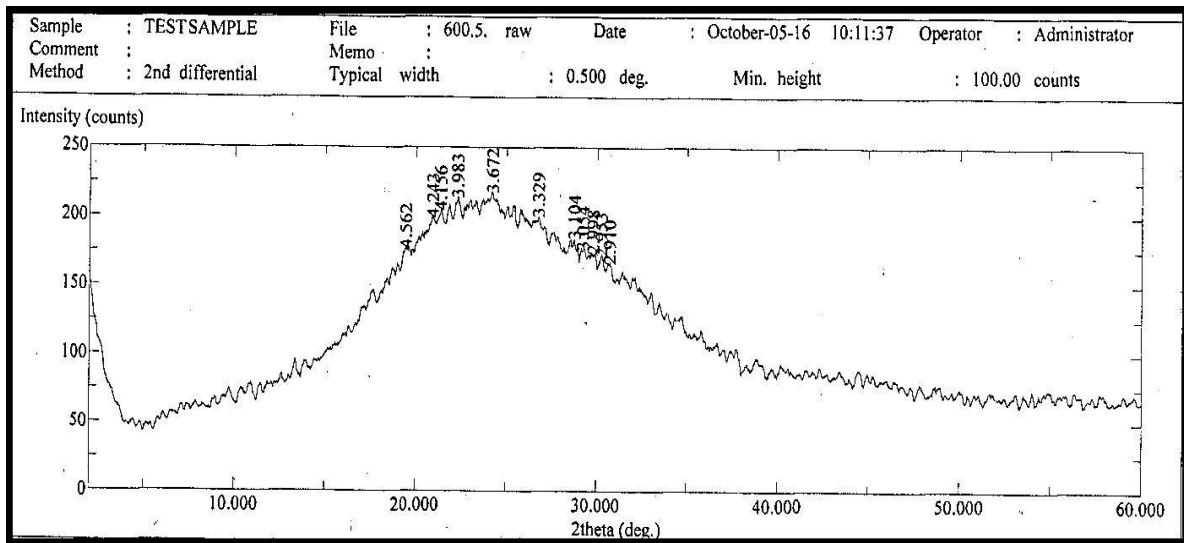

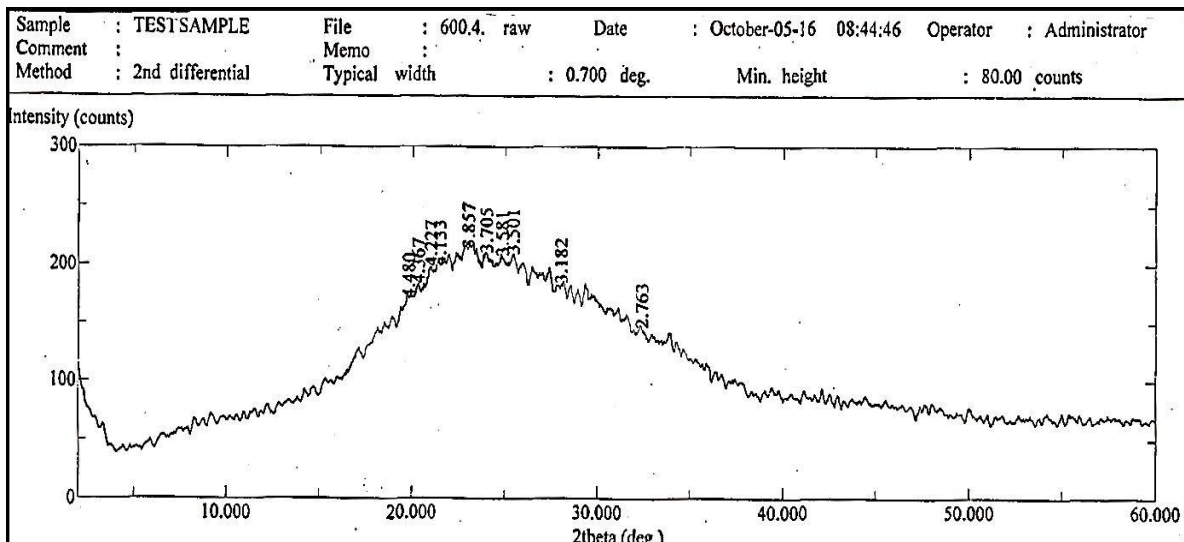**Fig. 7a: XRD for pure polyaniline thin films.**

Fig. 7b: for PANI/MWCNTs nanocomposites thin films with MWCNTs wight concentration 4%.

D. *Surface morphology*

Fig. 8 using scanning Electron Microscopy (SEM) image for the PANI/MWCNTs nanocomposite thin films. This image show homogeneous distribution of MWCNTs. The homogeneous distribution of MWCNTs was due to the aniline in situ plasma polymerization. Also there are little agglomeration.
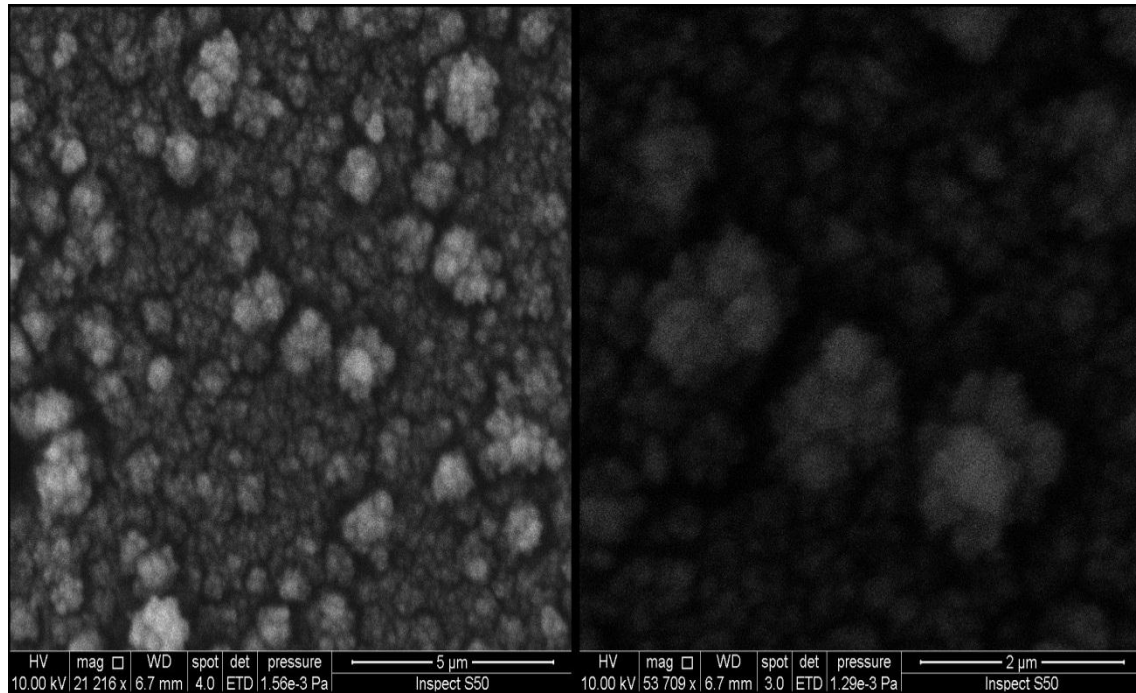
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Fig.8: SEM image for PANI/MWCNTs nanocomposites thin films with MWCNTs wight concentration 4%.

Conclusions

It can be calculated from this work the possibility of preparation of PANI/MWCNTs nanocomposite thin film where the carbon nanotube uniformly distributed within the volume of the thin films. The energy direct allowed band gap of the prepared thin films can be controlled by changing the concentration of carbon nanotubes where the energy band gap decrease with increasing carbon nanotubes concentration. Structure is amorphous of PANI/MWCNT with homogenous distribution of nanocomposite.

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