Synthesis and electrical properties of conductive polyaniline/ SWCNT nanocomposites

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Abstract

The synthesis of conducting polyaniline (PANI) nanocomposites containing various concentrations of functionalized single-walled carbon nanotubes (f-SWCNT) were synthesized by in situ polymerization of aniline monomer. The morphological and electrical properties of pure PANI and PANI/SWCNT nanocomposites were examined by using Fourier transform- infrared spectroscopy (FTIR), and Atomic Force Microscopy (AFM) respectively. The FTIR shows the aniline monomers were polymerized on the surface of SWCNTs, depending on the π-π^* electron interaction between aniline monomers and SWCNTs. AFM analysis showed increasing in the roughness with increasing SWCNT content. The AC, DC electrical conductivities of pure PANI and PANI/SWCNT nanocomposite have been measured in frequency range (50Hz - 600KHz) and in the temperature range from (30 to 160K). The results show the electrical conductivity of the nanocomposite is higher than pure PANI.

Key words

Conductive polyaniline, carbon nanotubes, nanocomposites, electrical properties.

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تحضير ودراسة الخصائص الكهربائية للمتراكبات النانوية البولي انيلين الموصل – انابيب الكاربون النانوية احادية الجدران (PANI/ SWCNTs)

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الخلاصة

تم تحضير المتراكبات النانوية لبولي انيلين الموصل المتضمن تراكيز مختلفة من انابيب الكاربون النانوية الاحادية الجدران المحفزة بواسطة البلمرة الموقعية لمونيمر الانيلين. فُحصِت الخواص التركيبية والكهربائية للبولي انيلين النقي وللمتراكبات النانوية بولي انيلين/ انابيب الكاربون النانوية الاحادية الجدران بواسطة مطياف فورير للأشعة تحت الحمراء ومجهر القوى الذرية على التوالي. اظهر مطياف فورير للأشعة تحت الحمراء بلمرة الانيلين على سطح انابيب الكاربون النانوية احادية الجدران اعتمادا على تفاعل الكترونات $\pi - \pi^*$ بين مونيمر الانيلين وانابيب الكاربون النانوية الاحادية الجدران. بينت تحليلات مجهر القوى الذرية زيادة الخشونة بزيادة محتوى انابيب الكاربون النانوي. قيست التوصيلية الكهربائية المستمرة والمتناوبة للبوليمر النقي وللمتراكبات النانوية ضمن مدى تردد (50Hz – 600 KHz) ضمن مدى درجات حرارة (30 – 160 K). اظهرت النتائج ان التوصيلية الكهربائية المتناوبة للمتراكبات النانوية اعلى من البولي انيلين النقي.

Introduction

Since the discovery of Ijiman [1] the carbon nanotubes (CNT) takes a great attention from researchers and scientist due to their excellent electrical properties. It has a wide range of application such as supercapacitance, devices, Schottky contact, solar cell, gas sensor [2-7]. CNT /polymer composite result a nanocomposite with high electrical conductivity [8, 9]. Polyaniline (PANI) is the most conductive polymer used because it's easy synthesis and good electrical properties so it can use as electronic material [10]. There are three forms of PANI, namely fully oxidized pernigraniline, half-oxidized emeraldine base (EB) and fully reduced leucoemeraldine base (LB). Emeraldine is said to be the most stable form of PANI and also the most conductive form when doped (emeraldine salt) [11]. There are many methods to prepare CNT/PANI nanocomposite, solution processing, melt blending, in situ-polymerization and grafting macromolecules to the CNTs, in situ polymerization is the most used because it enables grafting of polymer molecules on CNT, this lead to a better dispersion coefficient and better interaction between polymer matrix and CNT, where the CNT will enhance the electrical conductivity of PANI since it acts as bridge between conducting domains of PANI [12]. In this paper, in situ fabrication and characterization of SWCNT/PANI nanocomposite with various concentration of functional CNT has been done.

Experimental

1. Material

SWCNT (purity =95%) was supplied by neutrino factory, India. The diameter of the SWCNT was in the range of 1-2 nm and the length 30μm. The aniline (purity 99.99%) was purchased by Hopkin and William Germany. Hydrochloric acid (HCl) was obtained from Samchun Pure Chemical (Korea).

2. Synthesis of PANI

The synthesis procedure for the PANI was followed as described in our previous publication [13]. Oxidation of 0.2M aniline hydrochloride with 0.25M ammonium peroxydisulfate in an acidic medium was the base of preparation PANI. Aniline and ammonium peroxydisulfate were dissolved in 1M HCl aqueous solution separately, both solution were mixed in a rounder and gentle stirring to polymerize the mixture. After polymerization, the mixture is left at rest to the next day PANI precipitate is collected by a filter and washed with 300ml of 0.2M HCl. PANI hydrochloride emeraldine powder is dried in air for 15minuts then in a vacuum oven at 80C° for 4 hours. Fig.1 illustrated the polymerization of aniline and formation of the emeraldine salt.

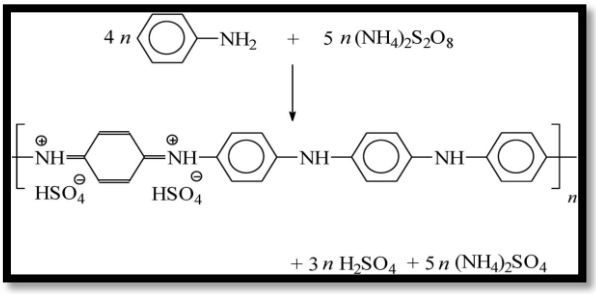


Fig.1: The polymerization of aniline and formation of the emeraldine salt (ES) [13].

3. PANI/SWCNT nanocomposite

The preparation of PANI-SWCNT nanocomposite was performed using in-situ oxidative polymerization by measuring two different quantities of SWCNT (1 and 8) wt% which added to the aniline solution. The prepared PANI-SWCNT was collected on filter papers and washed with 300ml of distilled water and 50ml of acetone. The mixture was dried under the hood for about 20 minute and then in vacuum oven at (80°C) for 4 h, to obtain green-black powder of PANI-SWCNT nanocomposite.

4. Structural analysis

The FT-IR spectroscopy was used to characterize the structure of PANI and PANI-SWCNT composites in the form of powder were tested to analyze the characterization of the composites by Shimadzu. FT-IR was recorded at Shimadzu 8000 series Samples in KBr were analyzed at room temperature. The degree of interaction for PANI and PANI-MWCNT composites powder has been examined by X-ray diffraction by (XRD-6000) model, Shimadzu Co.

5. Morphology analysis

Atomic Force Microscopy (AFM) was used to analyze the surface of all specimens, its type SPM AA3000 Angstrom Advanced Inc., 2008, USA contact mode.

6. Electrical properties

The samples of pure PANI, and PANI/SWCNT nanocomposites were pressed into pellet form under 200bar. The conductivity at room measurement was measured using a programmable AC voltage/current (four probe method). Capacitance C of the investigated samples was measured directly using the automatic RCL meter. The AC conductivity σ_{AC}., was calculated from the following relation

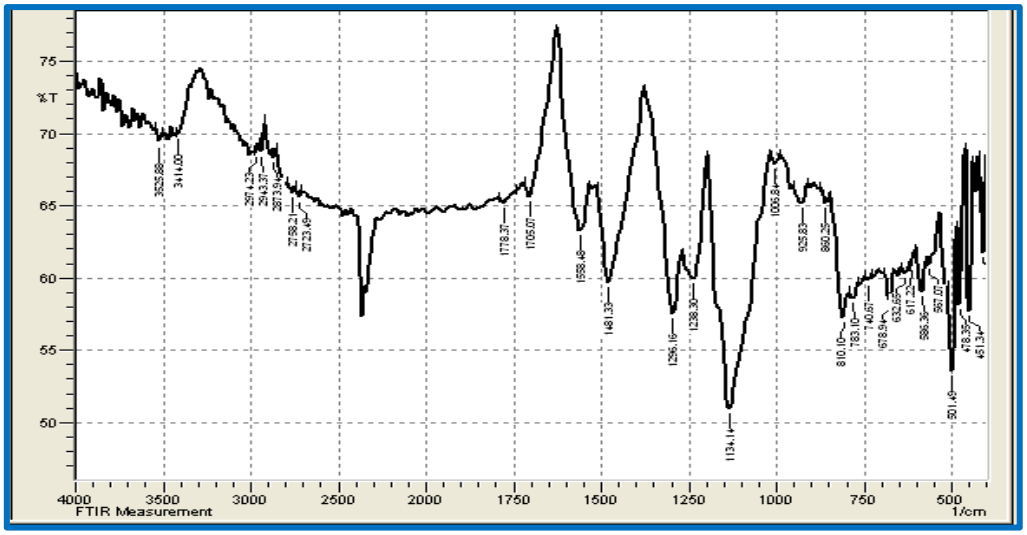
$$\sigma = \frac{t}{RA} \quad (1)$$

R: resistant, A: the area t: thickness.

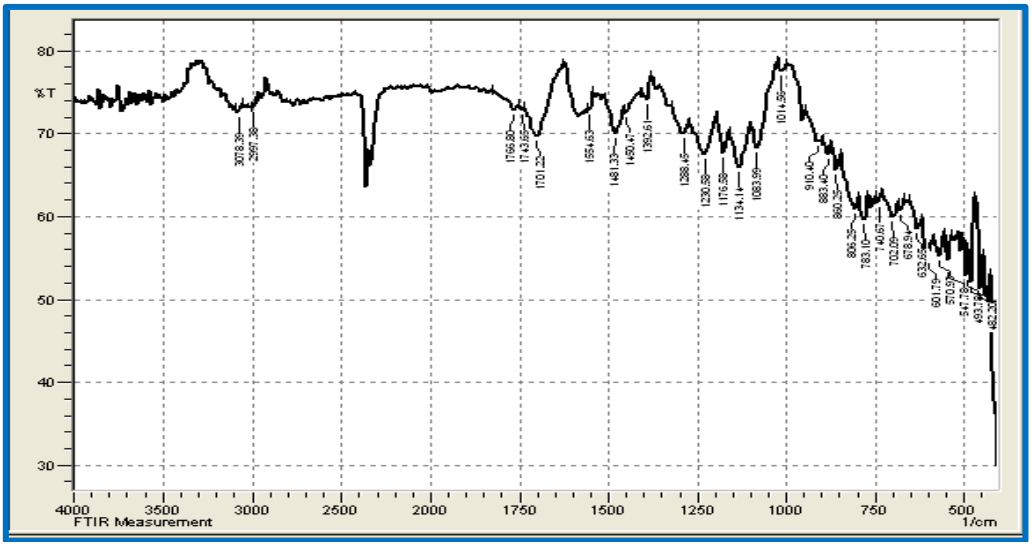
Results and discussions

1.Characterization

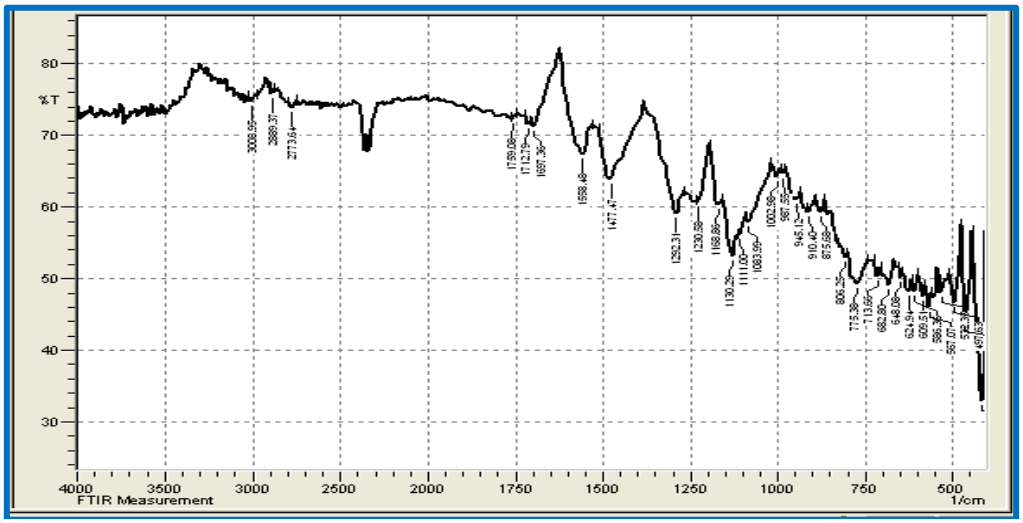
Fig. 2 shows the spectrum of FTIR for pure PANI and PANI/SWCNT nanocomposites. For pure PANI. Fig.(2a) shows the characteristic peaks at 800 cm^{-1} N-H out of plane bending absorption, 970 cm^{-1} C=C bending, 1134.14cm^{-1} C=N imines bending, 1296cm^{-1} C-N stretching mode for benzoid ring N=Q=N, 1481.33cm^{-1} C=C benzenoid ring stretching N=B=N, 1558.48 cm^{-1} C=C stretching modes for quinoid, a broad peak at 3340 cm^{-1} O-H stretching, intermolecular bonding, and small peaks from 3525 to 4000 cm^{-1} vibration band of O-H. In Figs. (2b, 2c) no new absorption peaks observed, this gives identical peaks of PANI with decreasing in peaks intensity, this shows the strong interaction between PANI chain and surface of SWCNT [16].



a



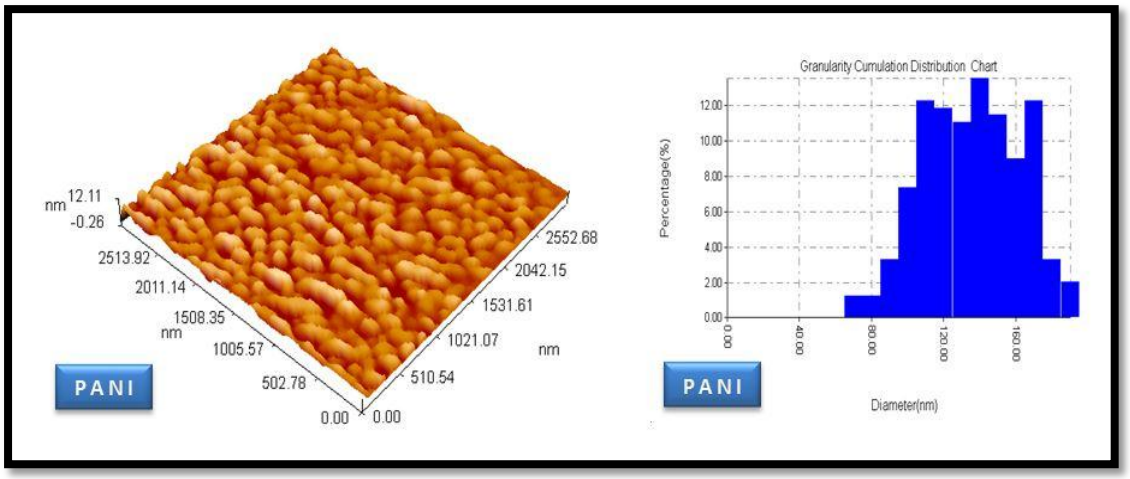
b



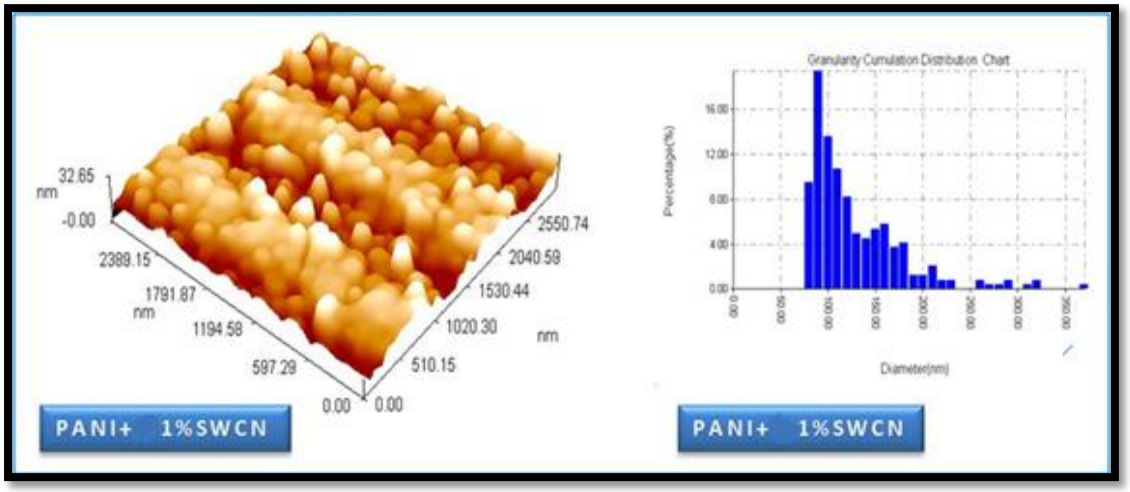
c

Fig.2: FTIR spectra of a- pure PANI, b- 1%wt and c-8%wt of PANI-SWCNT nanocomposite.

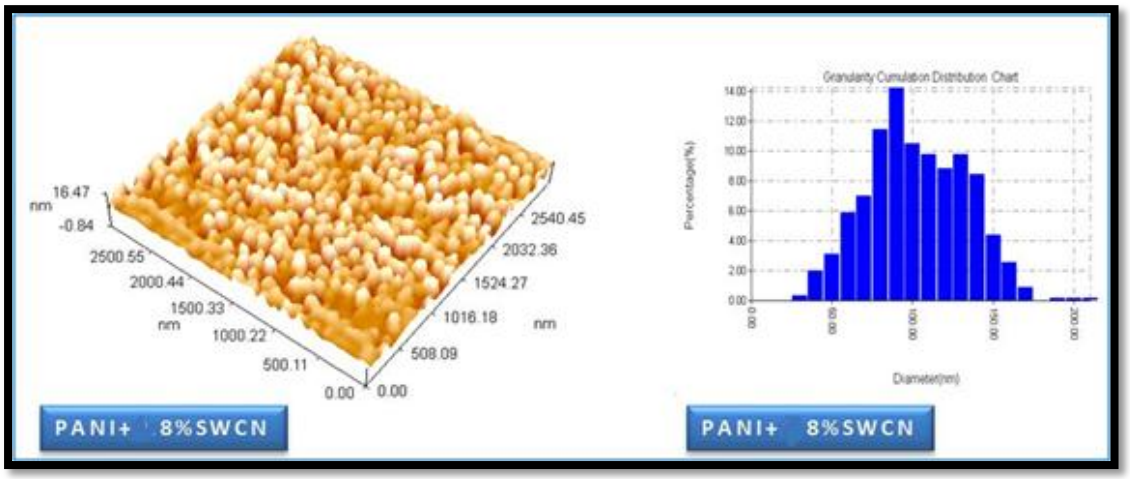
Figs. (3a, 3b, 3c) AFM measurements for pure PANI and PANI/SWCNT nanocomposites. These analyses clarified the increasing of the roughness with increasing the SWCNT contents, as well as, the average of a particle sizes, which illustrated in Table1.



a



b



c

Fig.3: AFM analysis for a-pure PANI b-1wt% and b-8wt% PANI/SWCNT nanocomposite.

Sample	Average Diameter crystalline (nm)	RMS roughness (nm)	Peak-peak (nm)
PANI	130.67	1.12	10
PANI+1%SWCNT	123.81	2.34	18.2
PANI+8%SWCNT	97.72	2.57	17

DC-electrical conductivity

Fig. 4 shows the temperature dependence of DC-conductivity in the temp. Range (30-160)K for pure PANI and PANI/SWCNT nanocomposites. The figure shows as the concentration of SWCNT increase in the PANI matrix the conductivity increase. This can be attributed to the charge transfer process between PANI and CNT. The conductivity for all samples decreases with increasing temperature. The sample gives a nearly straight line which indicates that all samples have single activation energy for the temp. range. Arhenus eqn. was used to calculate the activation behavior

$$\sigma_{DC}=\sigma_{\circ} \exp(-E/2KT) \quad (2)$$

where K: Boltzmann constant, E: activation energy, T: temperature, σ_{DC}: DC conductivity, $\sigma_{\circ}$: conductivity. Table 1 shows the values of activation energy.

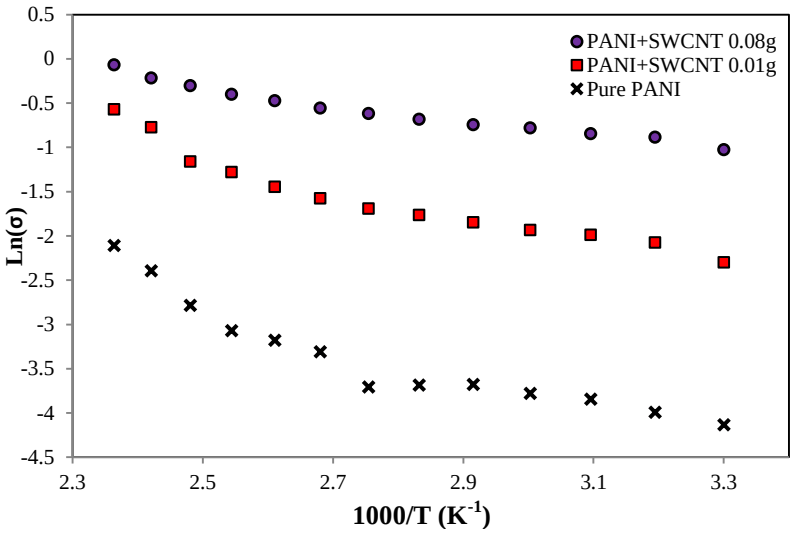


Fig.4: DC conductivity vs temperature of pure PANI and PANI/SWCNT nanocomposites.

Table 1: The values of activation energy.

Sample	E_{a1} (eV)	Range (K)	E_{a2} (eV)	Range (K)	σ_{RT} ($\Omega^{-1}.cm^{-1}$)
Pure PANI	0.112	303-393	0.471	393-423	1.60E-02
1wt% SWCNT	0.102	303-393	0.359	393-423	1.00E-01
8wt% SWCNT	0.065	303-393	0.156	393-423	3.57E-01

A.C electrical conductivity

The measuring electrical conductivity ($\sigma_{a.c}$) as a function of the frequency of the alternating electric field within the range (10Hz-100KHz),

From Fig.5, the electrical conductivity (σ_{ac}) increased with slightly increasing frequency for all the samples and this is due to the space charge polarization at low frequencies, as well as the movement of charge carriers mediated jump operations (Hopping Process) Low increase in electrical conductivity are at high frequencies due to electronic polarization [17].

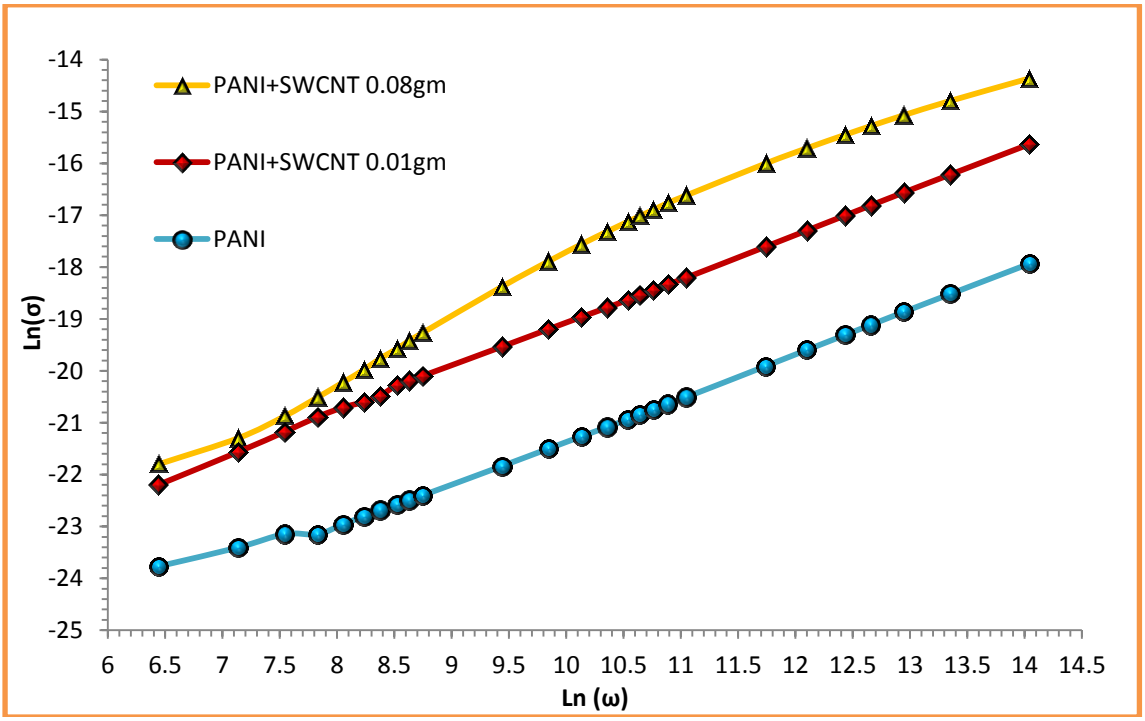


Fig 5: Ln(σ) as a function of frequency change Ln (ω) for pure PANI and PANI / SWCNT nanocomposite.

Conclusions

A PANI/SWCNT nanocomposites has been synthesis successfully by in situ polymerization of aniline monomer. The FTIR, described the strong interaction between PANI and CNT. AFM showed increasing in the roughness with increasing CNT concentration. The nanocomposites showed an increase in the electrical conductivity over pure PANI because the SWCNT serves as a 'conducting bridge' between PANI conducting domains, and that leads to increase in the effective path.

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