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Synthesis , characterization and electrical properties of conductive polyaniline/ functionalized MWCNT nanocomposites

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Abstract

by in situ polymerization of aniline monomer, conducting polyaniline (PANI) nanocomposites containing various concentrations of carboxylic acid functionalized multi-walled carbon nanotubes (f-MWCNT) were synthesized. The morphological and electrical properties of pure PANI and PANI /MWCNT nanocomposites were examined by using Fourier transform- infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Atomic Force Microscopy (AFM) respectively. FTIR spectra shows that the carboxylic acid groups formed at the both ends of the sidewalls of the MWCNTs. The aniline monomers were polymerized on the surface of MWCNTs, depending on the π-π^* electron interaction between aniline monomers and MWCNTs and hydrogen bonding into interaction between the amino groups of aniline monomers and carboxylic acid group of f-MWCNT. The AC, DC, electrical conductivities of pure PANI and PANI/MWCNT nanocomposite have been measured in frequency range (10Hz-100KHz) and in the temperature range from (30 to 160 C°). the results shows the electrical conductivity of the nanocomposite is higher than pure PANI. AC conductivity at low frequencies is independent of frequencies and increased by increasing the MWCNTs concentration.

Key Words: conductive polyaniline , multi-walled carbon nanotubes , nanocomposites , electrical properties and XRD.

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 [2]. It have a wide range of application such as supercapacitance[3], devices[4], schottky contact [5], solar cell [6],gas sensor [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 MWCNT/PANI nanocomposite with various concentration of functional CNT has been done.

Experimental

1. Material

MWCNTs (purity =95%) was supplied by neutrino factory, India. The diameter of the MWCNTs was in the range of (10-20) nm and the length 30 nm. 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 preparation 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 300 mL of 0.2M HCl. PANI hydrochloride emeraldine powder is dried in air for 15 minuts then in a vacuum oven at 80°C for 4 hours. Figure (1) illustrated the polymerization of aniline and formation of the emeraldine salt.

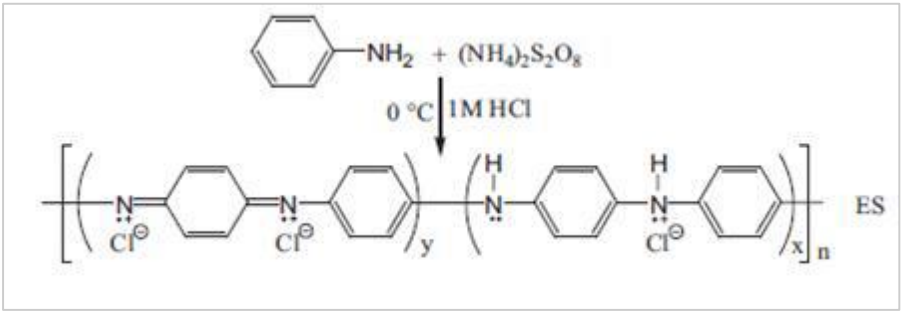


Fig.(1) The polymerization of aniline and formation of the emeraldine salt (ES).

3. *Functionalization of MWCNT*

A solution of Sulfuric acid (6M H2SO4) and Nitric acid (6M HNO3) in 3:1 ratio, and was taken stirred for 10 minute. Then MWCNT was added to the solution, after then the solution was putted on the electromagnetic stirrer for 4 hours at 50°C. After centrifuge the MWCNT, it was collected in filter papers and washed with 300 mL of distilled water, and then it entered electrical oven at 50°C for 4 hours to avoid any effect of moisture absorption [14]. The results of this process shows figure (2) .

Fig. (2): Carboxylation of MWNTs [15]

4. PANI/MWCNT Composite

The synthesis of PANI-MWCNT nanocomposite was performed using in-situ oxidative polymerization by measuring two different quantities of MWCNT (1 and 8)wt% which added to the aniline solution, and then it of PANI preparation shown above. The prepared PANI-MWCNT was collected on filter papers and washed with 300ml of distilled water and 50 ml 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-MWCNT nanocomposite.

5. Structural Analysis

The FT-IR spectroscopy and X-ray diffraction were used to characterize the structure of PANI and PANI-MWCNT 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.

6. 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.

7. Electrical Properties

The samples of pure PANI, and PANI/MWCNT composites 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, dielectric loss (ε") and tangent (tanδ) of the investigated samples were measured directly using the automatic RCL meter. The AC conductivity σ_{AC}

Results and Discussion

1.Characterization

FTIR: figure (3) shows the spectrum of FTIR for pure PANI, functionalized MWCNT and PANI/MWCNT composites. For pure PANI, fig. a, the characteristic peaks are observed 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. From fig. b, the following beaks indicates the successful oxidation into carboxylated carbon nanotubes [16] The beaks at 1388 and 1570.6cm^{-1} are correspond to O-H vibration bending and carbonyl, respectively. A small intensive peak at 1689cm^{-1} is correspond to the C=O stretching vibration mode, which represent the formation of the carboxylic groups. A broad peak at 3433cm^{-1} correspond to O-H stretching vibration in –COOH group. therefore, the carboxylic groups (-COOH) was considered to be attached on the surface of the MWCNT successfully as a result of the acid treatment. The weak peak at 2885$cm^{-1}$is correspond to the –CH stretch mode. The peak intensity of PANI-MWCNT nanocomposite spectra decreases which indicate the strong interaction between PANI chain and the surface of MWCNT.

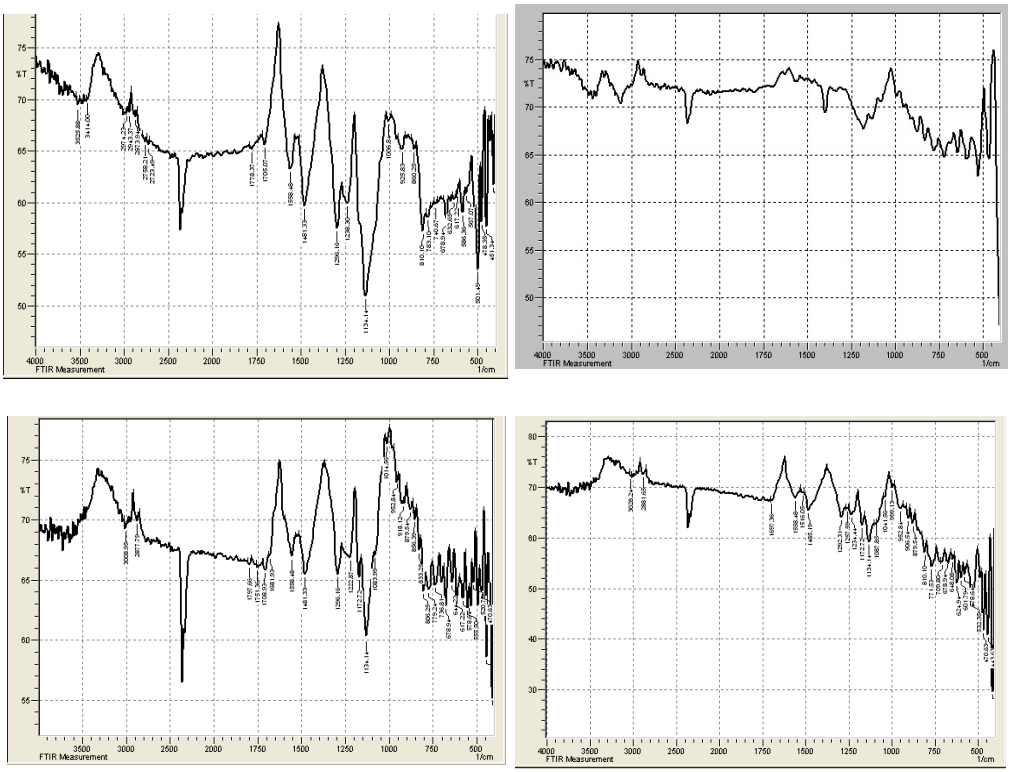


Figure (3)FTIR spectra of pure PANI, f-MWCNT and PANI-CNT .

The morphologic analysis by AFM for PANI/MWCNT nanocomposites that prepared by polymerization clarified the increasing of the roughness with increasing the MWCNT contents. As well as, the average of a particle sizes increased with an increasing of MWCNT except the PANI+0.2%MWCNT. figures (4a) and (4b) shows the increasing in the roughness and particle size with the increasing MWCNT contents.

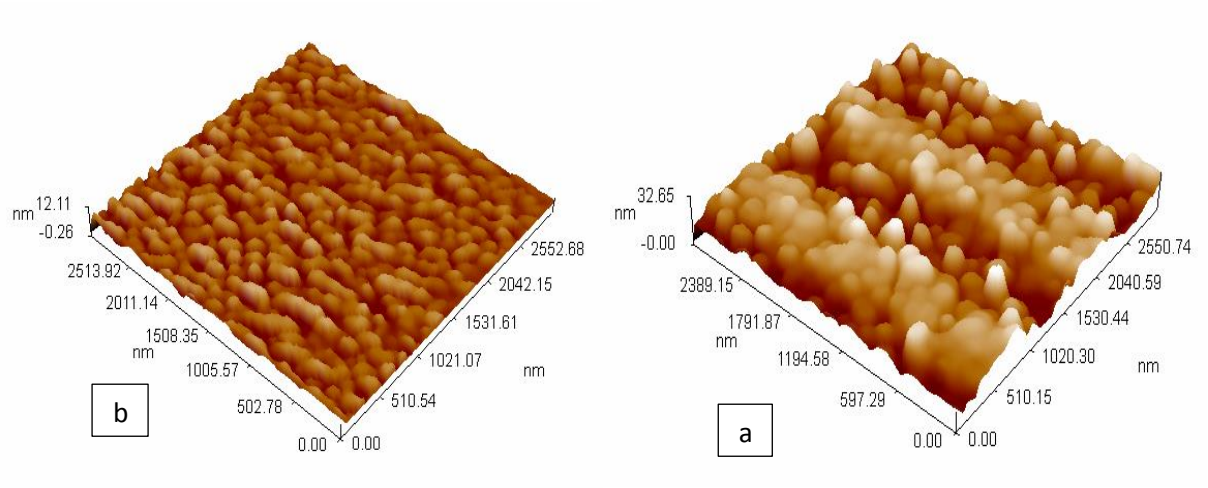


Fig (4). (AFM) images shows the increasing in the roughness and particle size with the increasing MWCNT contents .

DC-Electrical Conductivity

Figure shows the temperature dependence of DC-conductivity in the temp. range(5) for pure PANI and PANI/MWCNT nanocomposites. The figure shows as the concentration of MWCNT increase in the PANI matrix the conductivity increase. This can be attributed to the charge transfer process between PANI and MWCNT. 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 eq. was used to calculate the activation behavior

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

K: Boltzman constant

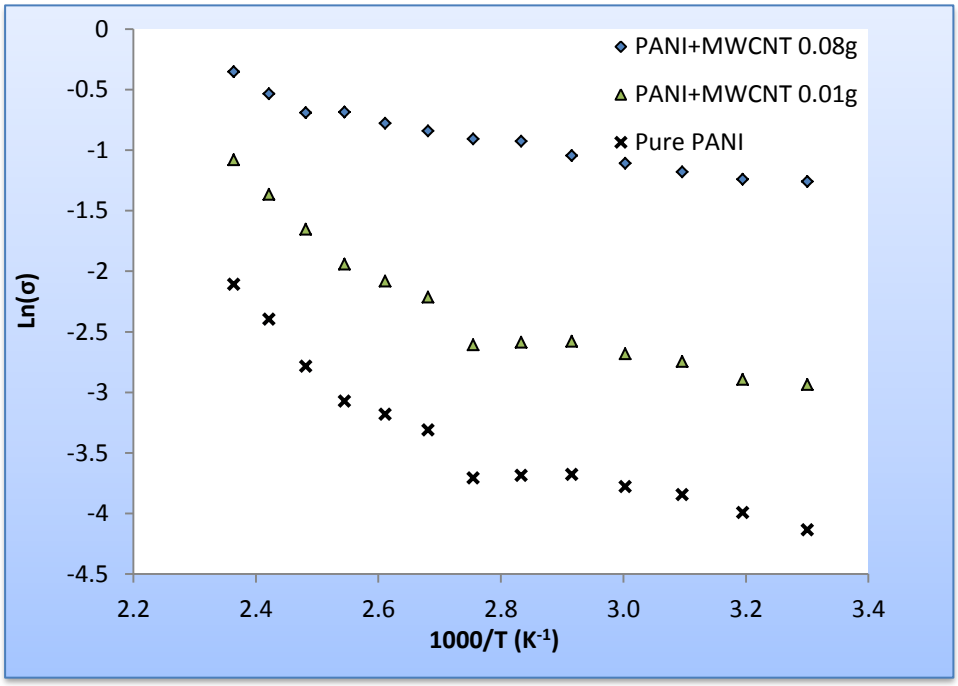
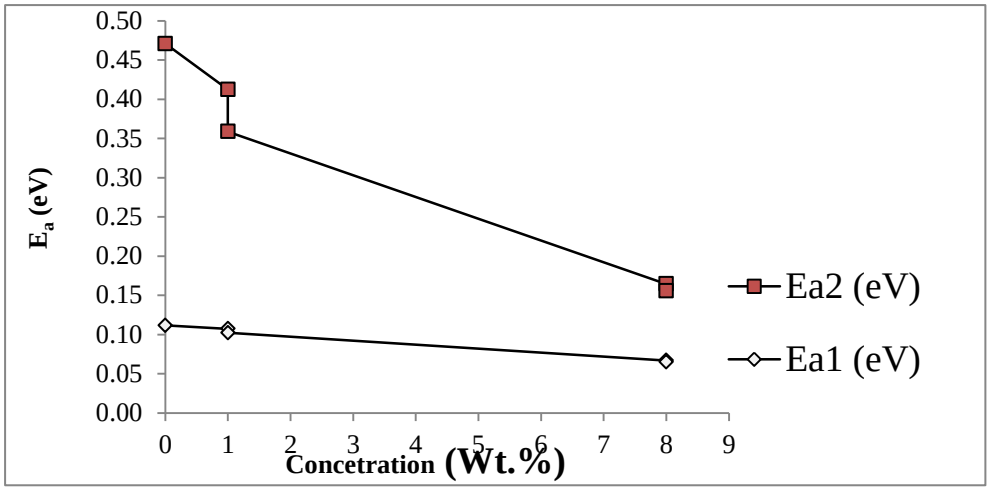


Figure (5) . Plot of d.c. conductivity vs temperature of PANI–PANI/MWCNT composites.



Fig(6) . Variation of DC activation energies for PANI films with CNTs dopant ratio

Table(1) presents the value of activation energy calculated from fig (6).

Eu (%)	E_{a1} (eV)	Range (K)	E_{a2} (eV)	Range (K)	σ_{RT} ($\Omega^{-1}.cm^{-1}$)
0	0.112	303-393	0.471	393-423	1.60E-02
0.1	0.107	303-393	0.412	393-423	5.31E-02
0.8	0.067	303-393	0.164	393-423	2.84E-01

The A.C Electrical Conductivity (σa.c)

The measuring electrical conductivity (σa.c) as a function of the frequency of the alternating electric field Within the range (10Hz-100KHz), As it has been measuring electrical conductivity (σa.c) using the equation (44-2) and shape (7) representing the relationship between Ln (σ) as a function of frequency change Ln (ω) (the composites Polymeric PANI, before vaccination (MWCNT) and representing the relationship between Ln (σ) as a function to change the frequency Ln (ω) the polymeric compsites PANI, after vaccination with different concentrations of (MWCNT).

$$\sigma(\omega)=A_o\ \omega^S \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Whare:

Ao; Constant little dependence on temperature.

ω : Angular frequency .

S : Lacey factor depends on the frequency and its value .

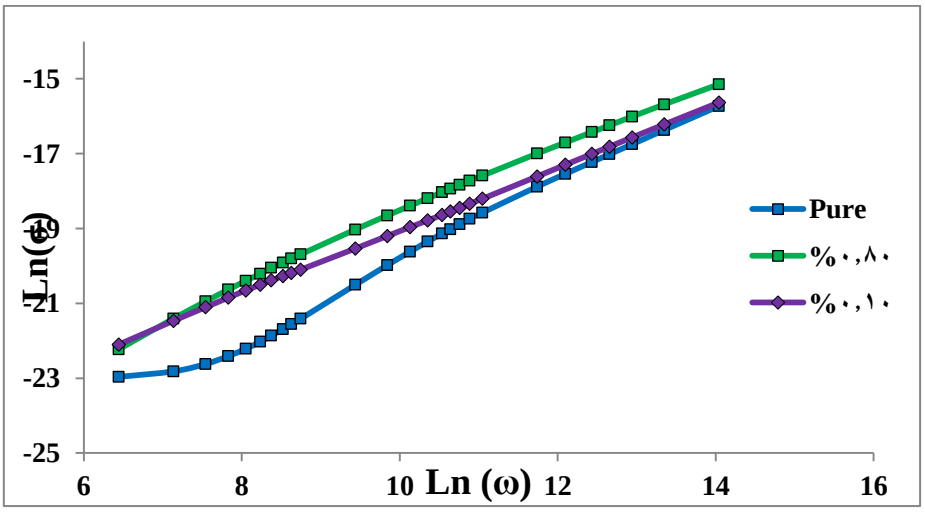


Fig (7). Represents the relationship between Ln(σ) as a function of frequency change Ln (ω) blamed for polymer composites (PANI , PANI / MWCNT) .

note from the figure above that the electrical conductivity (σa.c) increased with 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 and carrier shipment leaving jump operations (Hopping Process) [17]. We also note that the electrical conductivity increases with vaccination (MWCNT) [18]. The increase in electrical conductivity alternating increased emphasis consistent with the researcher [19]. Increased electrical conductivity alternating (σa.c) compared to a decrease factor exponential (S) increase of the proportion of vaccination.

Conclusions

A PANI/MWCNT nanocomposites has been synthesis successfully by in situ polymerization of aniline monomer in the present on MWCNT with different concentrations. The FTIR, described the strong interaction between PANI and CNT. The nanocomposites showed an increase in the electrical conductivity over pure PANI. That is because the functionalized MWNTs serves as a 'conducting bridge' between PANI conducting domains, and that leads to increase in the effective path.

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تحضير وتشخيص ودراسة الخصائص الكهربائية للمتراكبات النانوية البولي انيلين الموصل – انابيب الكاربون النانوية (PANI / f–MWCNTs)

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الخلاصة

تم تحضير متراكبات البولي انيلين النانوية الموصل (PANI) بواسطة البلمرة الموقعية (in situ polymerization) لمونيمر الانيلين مع تراكيز مختلفة من انابيب الكاربون النانوية المتعددة الجدران ذات الجذور الحرة (f–MWCNT) . حيث تم دراسة الخواص التركيبية والكهربائية للمتراكبات النانوية (Pure PANI , PANI/MWCNT) على التوالي . بواسطة مطياف فورير للأشعة تحت الحمراء (FTIR) ومجهر القوى الذرية (AFM) و حيود الاشعة السينية (XRD). حيث بين مطياف (FTIR) ان مجموعة الحامض الكاربوكسيلي (Carboxylic acid) بانحياز امامي عند كلا نهايتيها لجوانب (MWCNT) . حيث تمت بلمرة الانيلين على سطوح (MWCNT) وبالاعتماد على الكترونات التفاعل $\pi - \pi^*$ من مونيمرات الانيلين و (MWCNT) وآصرة الهيدروجين داخل التفاعل بين مجموعة الانيلين ومجموعة حامض الكاربوكسيلي للأنابيب النانوية ذات الجذور الحرة (f–MWCNT) . التوصيلية الكهربائية (A.C , D.C) للمتراكبات النانوية (PANI , PANI/MWCNT). تم قياسها ضمن مدى تردد من (10Hz – 100 KHz) في درجات حرارة (30 – 160 C°) واظهرت النتائج ان التوصيلية الكهربائية (A.C) عند الترددات المنخفضة تزداد بزيادة تركيز (MWCNT).