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Preparation and Characterization of Nanocompocite Conducting Polymers (PANI-DBSA/MWNCT)

Kareema M. Ziadan[1*] Hanaa H. Inayh[2]
1.University of Basrah , College Science ,Department of physics, Basrah-Iraq
2.M.Sc. student,t University of Basrah, ,College Science ,Department of physics, Basrah-Iraq
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Abstract
Nanocomposite conducting polymers ,PANI-DBSA/MWNCT were prepared by adding different weight ratios of c-MWNCT (1,2,3,5) % to Polyaniline (PANI) doped with DBSA(PANI-DBSA). Structural characteristics of nanofibers composites and the formation of functional group were measured by . X-ray diffraction (XRD) and FT-IR spectroscopy. X-Ray Diffraction showed crystalline peaks of the Nanocomposites PANI-DBSA /MWNCT. FT-IR spectra confirmed the change of MWNCT to c-MWNCT by strong acids ,and PANI doped with DBSA. The Morphology and diameters for the nanofibers composites were studied by Atomic Force Microscope (AFM) and scanning electron microscope(SEM). The average diameter for nanofiber composites was about 117 nm (at 1 wt% MWCNT concentration) and 90.47 nm (at 5wt% MWCNT concentration) found from AFM. SEM also show the homogeneous coating of PANI-DBSA onto the MWNCNT indicating that carbon nanotubes were well dispersed in conducting polymer matrix
Keywords: conducting polymer, polyaniline, multi-walled carbon nanotubes, nanocomposites

1. Introduction

In recent years Nanocomposites Conducting polymers have gained great interest for their unique physicochemical properties of these Nanocomposites(Amer N.J.et al 2015 , Javad A. et al 2010) .Since the discovery of carbon nanotubes (CNTs), by Ijima (Ijima S,1991) , have received much attention for their possible use in fabricating new classes of advanced Nanocomposites material, due to their unique structural, optical, mechanical and electronic properties (De Heer, W.A 1995, Neetesh K. 2009). Polyaniline (PANI) is one of the best materials among this class of polymers due to its relatively high conductivity, better stability, low cost synthesis and easier fabrication procedure (Kareema. M. Z.et al 2011, Tariq J. A., 2014, . PANI has also potential uses in synthesizing polymer/ MWCNT composites due to its environmental stability, good processability and changeful control of conductivity both by protonation and charge-transfer doping (Kondawar S. B et al ,2012, Kondawar S. B.et al 2013 . Many researches have been done on PANI/CNTs nanocomposites.one of these reported the morphology and Effect of multiwall carbon nanotubes on optical properties (Ali E.et al 2015), electrical conductivity . (Chakrabority G.2010) and magnetoconductivity of polyaniline (Goutam C.2012). Other studies investigated the application of PANI/CNTs as a sensor (Li.et.al. 2009 , Neetesh K. 2009).

In this research prepared Nanofiber composites. conducting polymers(PANI-DBSA/MWNCT) prepared by chemical polymerization of PANI-DBSA and mixed with different ratio of MWNCT's. The effects of NWMCT on the chemical structure , morphology ,grain size and nanofibers diameters on nanocomposites conducting polymers(PANI-DBSA/MWNCT) also investigated.

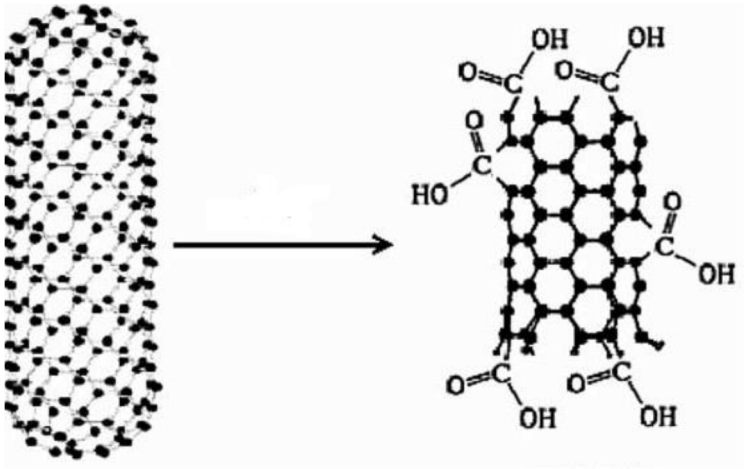
2.Experimental Procedures

2.1preparation of poly PANI-DBSA

Polyaniline doped with dodecylbenzenesulfonic acid (DBSA) was synthesized by the oxidation polymerization of aniline in acidic media DBSA . using a method similar to the research (Kareema. M. Z. et.al.2014).The polymerization of the monomer aniline was initiated by the drop wise addition of the oxidizing agent(ammonium persulphate) in an acidified solution prepared using doubly distilled monomer under constant stirring at (0-5 °c) .The monomer to oxidizing agent ratio was kept as (1:1). After complete addition of the oxidizing agent the reaction mixture was kept under constant stirring for 24hr's , Precipitated polymer was filtered and washed with distilled water until the filtrate was colorless. Finally, the polymer was dried in oven at 70 °c for 12 hr´s .

2.2 Functionalization of MWCNT

Functionalization of Carboxylate Multiwall Nanotubes,(C-MWCNT's involves the generation of -COOH and -OH groups on the surface of MWNCT ,that can improve the solubility and processibility (Neetesh K. et.al.. 2009) . 100mg of NWNCT's (provided by (Alpha chemical) was ultrasonically treated with a 3:1 mixture of concentrated H2SO4 and HNO3 at 50oC for 24 h . After that , MWCNT was collected by filter papers and washed with distilled water. The powder obtained was dried under a vacuum at 60 ^{o}C for 24 h (Javad A.,H et.al. 2010). As a result, the ends and walls of the nanotubes are covered with oxygen containing groups such as carboxylate and hydroxyl groups, as show in figure(1).



MWNCT **C-MWNCT**

Figure 1. Carboxylation of MWNTs(**Tzong-Ming W 2006)**

2.3 preparation of MWNCT/PANI-DBSA

1 mg of POT-DBSA was dissolved in 10 ml of chloroform ($CHCl_3$) with stirring for 4-6 hours. Different weight ratios of c-MWNCT (1,2,3,5) % were added to above solution with stirring for 1 h ,Each ratio used to prepared MWNCT /PANI-DBSA Nanocomposit conducting polymers. Then, thin films of MWNCT /PANI-DBSA Nanocomposites conducting were prepared by using spin coating method on glass substrate. FTIR ,spectrometer ,XRD and AFM used to examined the preparation material.

3. Results and Discussion

3.1FTIR Spectroscopy

Infrared spectroscopy is one of techniques provides useful information about the chemical structure of the molecules and bonding quickly especially those of the organic ones (McMurry J. 2008). Fig.2 shows FT-IR spectra of the PANI-DBSA . The characteristic peaks of PANI at 3118.9 cm^{-1} and 3026. cm-1 related to N-H stretching. The band 2958.8 cm^{-1} is shifted to 2854.65) cm^{-1}) indicates the presence of bond C-H stretching from CH2 [21].The two bands appeared at (1539.20cm^{-1}, and 1498.69cm^{-1}) corresponding to the stretching vibration of the quinoid and benzenoid ring, respectively , while band at 1217.08 and 1118 cm^{-1} may be attributed to the C–N stretching of mode of benzoid unit (Kareema. M. Z. & Wjood T.S.2012) ,Whereas the bands at (1132 cm^{-1}, 1117cm^{-1}, and 1010 cm^{-1}), are the characteristic bands of(C-H) bending vibration. The band at 831.32 cm^{-1} represents the C–C stretching for benzoid unit of polyaniline,((Kareema. M. Z et.al.2012) . Finlay the band at 698 cm^{-1} refers to out of plane C–H vibration (Zelikman E. e 2008) .The bands indicated the doping PANI with DBSA are 582.5, 665.44 cm^{-1} represents to C-S bond of DBSA. As well as the wavenumber of 1037.7 cm^{-1} refer to SO3(Kareema M. Ziadan and Dalal K., 2015) . The band at 2897 cm-1 indicates S=O and C–H stretching of the benzenoid ring in DBSA, these result argument with (] E. Zelikman]. E. 2008, Tze. S. C.2015).

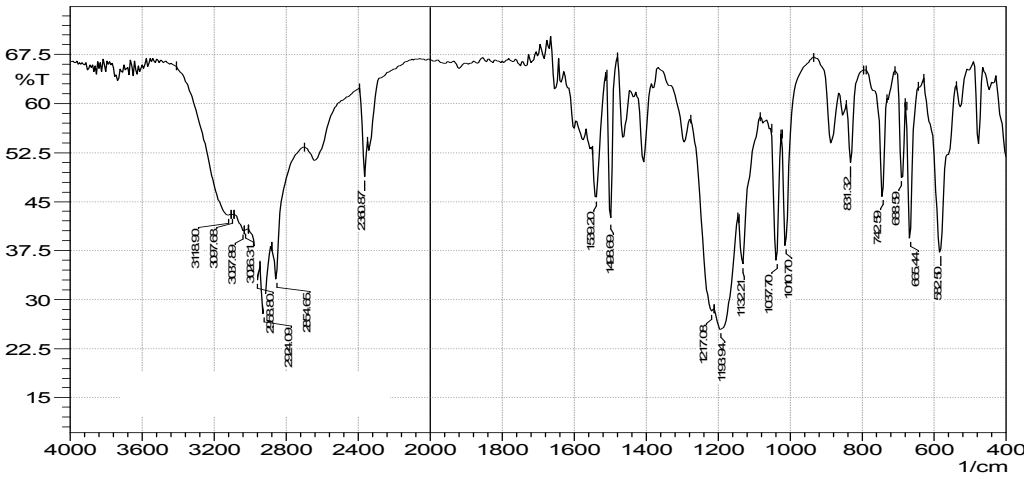


Figure 2. The active groups of PANI-DBSA

figure (3) shows the active groups of Multi-Walled Nano carbontubes (MWNCT). a very broad peak at 3414 cm-$^{-1}$ indicate to groups O-H on the surface of (MWCNT) This is due to presence of moisture. The two peak 1614.42 cm^{-1} and 1481.33 cm^{-1} indicate bonds C = C and C-C in MWNTs due to conjugated C=C bond in MWNTs, respectively(Charkaborty G.Y, S 2010).

Figure (4) shows important group of C-MWCNT' after treatment MWNCTs by strong acids . the new peak arises at 1680 ,1660 cm^{-1} which is correspond to C=O of COOH group (Sun YP, 2001). The peak observed at 1558 cm^{-1} correspond carboxylate ion COO-.The broad peak at 3460.0 cm^{-1} due to OH stretching vibration in -COOH group. From that result conclusion that the carboxylic groups (-COOH) had been attached onto the surface of the MWNCTs successfully after acid treatment H2SO4/HNO3 mixture(Tzong-Ming W.et.al.2006, Hu C.y. et.al.2009 Holzinger M, V.et.al.2001).

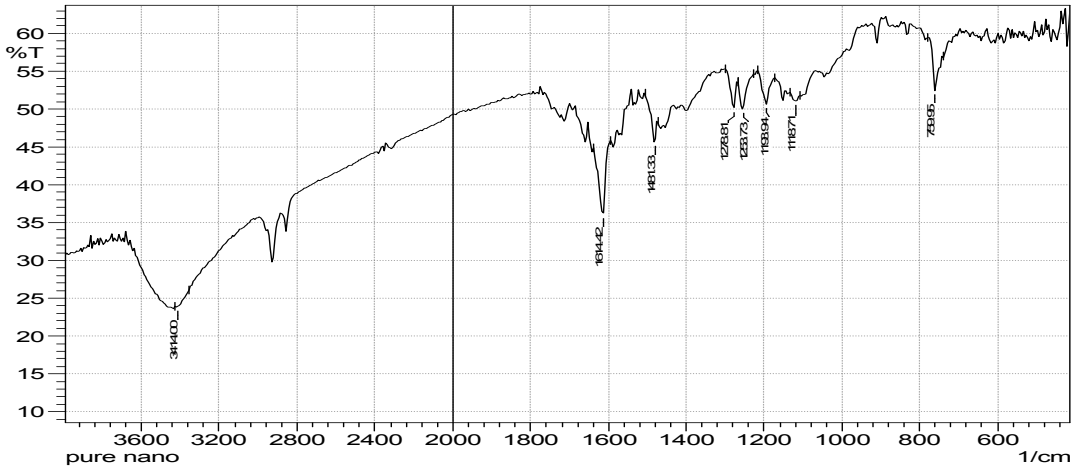


Figure 3. The active groups of (MWCNT)

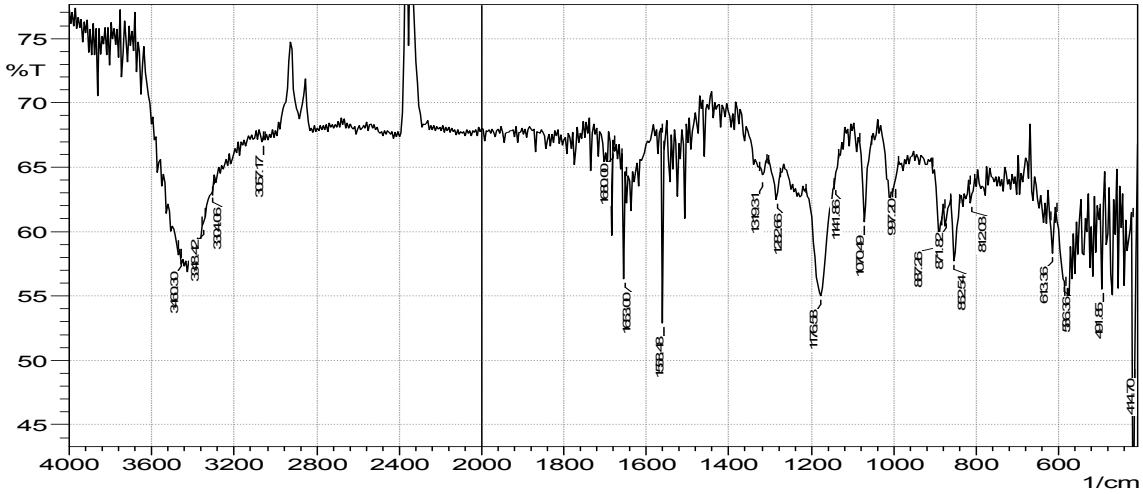


Figure 4. The active groups of (c-MWCNT)

3-2. X-Ray measurement

The Structural information and crystallinity of the PAni doped DBSA (PANI/DBSA) and its composites with different ratio of MWCNTs are show in Fig. 5 . PANI/DBSA exhibits three peaks 18º,20º and ,23º the large peak appear at 20º .These peaks may arise due to regular repetition of aniline. The appearance of these peaks as a result of doping with (DBSA) may be due to the tails (Alkyl DBSA),which are non-uniform and spaced between the main chain of the polymer (Wan M.2004) , may be DBSA works the role of plasticizers that drive the nature of the crystal of the (PANI-DBSA). These resut aregument with researchers (Cullity B.D.2001, Estabraq T. Abdullah 2016,Tariq J. A.2013) . Composites of polyaniline with MWCNTs show similar crystalline behavior of polyaniline at 1% MWNCT. As a MWNCT increses to 3% and 5% ,the larger peak appeared at 23o in comparison with those of polyaniline. This may be due to the incorporation of MWCNTs and ordering of polyaniline along the MWCNT axis (Ero-Phillips, O. 2012).

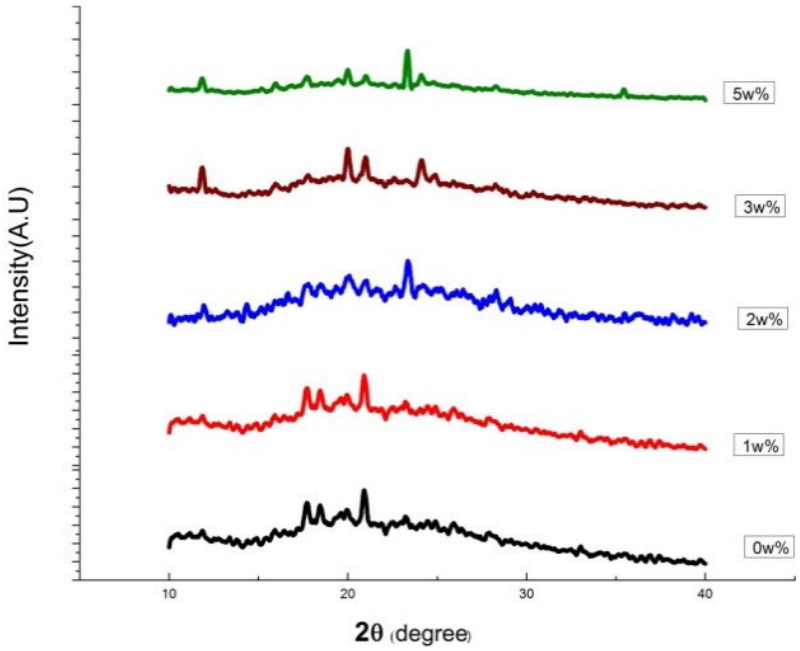


figure 5 . The XRD of PANI-DBSA / c-MWCNT

The d- spacing values were calculated using Bragg's equation(Jeno Sólyom, ,(2007). :

$$2d \sin \Theta = n \lambda \quad (1)$$

The d- spacing characteristic distance between the ring planes of benzene ring in adjacent chains or the close contact distance between the two adjacent chains (Cullity B.D. and S.R. Stock, (2001).The results are tabulated in Table I. The average grain size (GS) of the composite material can be calculated from Scherrer relation (Cullity B.D 2001):

$$GS = \frac{\lambda B}{\Delta\theta \cos\theta} \quad (2)$$

where $\Delta\Theta$ is the full – width at half maximum(FWHM) of the XRD peak appearing at the diffraction angle Θ, B Scherrer constant, usually assume ~ 1

The average grain size(G.S.) fluctuated. The lower crystallite size showed at 3% MWNCE ratio is about (58 nm) , and the other fluctuated between (89-58). The results of average grain size (GS.) are tabulated also in Table (1). And argument with (Tariq J.A.2013,Kareema M.Z.& Dalal K.T.2015)

Table 1. The effect of MWNCT ratio on the structure parameters of PANI.DBSA/MWNCTNano fiber composite .

Polymers	2Θ	d-spacing(A o)	FWHM(2Th)	G(nm)
PANI-DBSA (0%)	23.3	3.81767	0.0590	71.66
PANA-DBSA/1% MWCNTs	21.0499	4.22053	0.1378	61.41
PANA-DBSA/2% MWCNTs	23.38	3.8044	0.1181	71.9
PANA-DBSA/3% MWCNTs	20.98	4.233	0.059	53.66
PANA-DBSA/5% MWCNTs	23.3	3.81428	0.0984	86.33

3-3. The Morphology of material

The morphology, of conducting polymers ,PANI-DBSA and the other sets of PANI –DBSA / MWNCT Nanocomposite, were examined using AFM images . The weight ratio of MWNCT in PANI-DBSA (0wt%, 1wt%, 2 wt%, 3 wt%, and 5% are shown in Figure 6. The image size of PANI-DBSA is(2454.47 nm X 2391.97nm) and the roughness about 1.83nm,that was nearly smooth . The histograms diameters distributions of the above samples are shown in Figures.7 . Alignment Rod nanofiber of PANI-DBSA and PANI –DBSA / MWNCT Nanocomposite are seen in AFM images. The roughness increases as the weight ratio of MWNCT from 1.83-15.2) nm, as show in figures 6&7. It is also observed that the average diameter of nanofiber PANI-DBSA/MWCNT composite changed from (81nm – 118nm) . This suggests that the PANI-DBSA was on the surface of the MWCNTs and forms columnar and pellet-type growths (Tzong-M. W.2005) .Also from Figs. 6 it is possible to observe that uniaxial aligned nanofibers were obtained in all composite under the same conditions .However, the 3 wt% concentration appears to have the best alignment. Figure 8. show SEM images of c - MWCNT and PANI-DBSA/3%MWCNT nanocomposites ,the SEM show the diameter of c-MWCT increased (from(5-10) nm for MWNCT) to (20-40)nm after treatment with strong acids. the PANI-MWCNT composite shows the homogeneous coating of PANI-DBSA onto the MWNCNT indicating that carbon nanotubes were well dispersed in polymer matrix. however the diameter of the PANI-DBSA/MWNCT was estimated to be in the range 50–80 nm.. This result confirm by the atomic force microscope AFM and argument with other research's(E. Zelikman E.2010, Suckeveriene R. Y 2011).

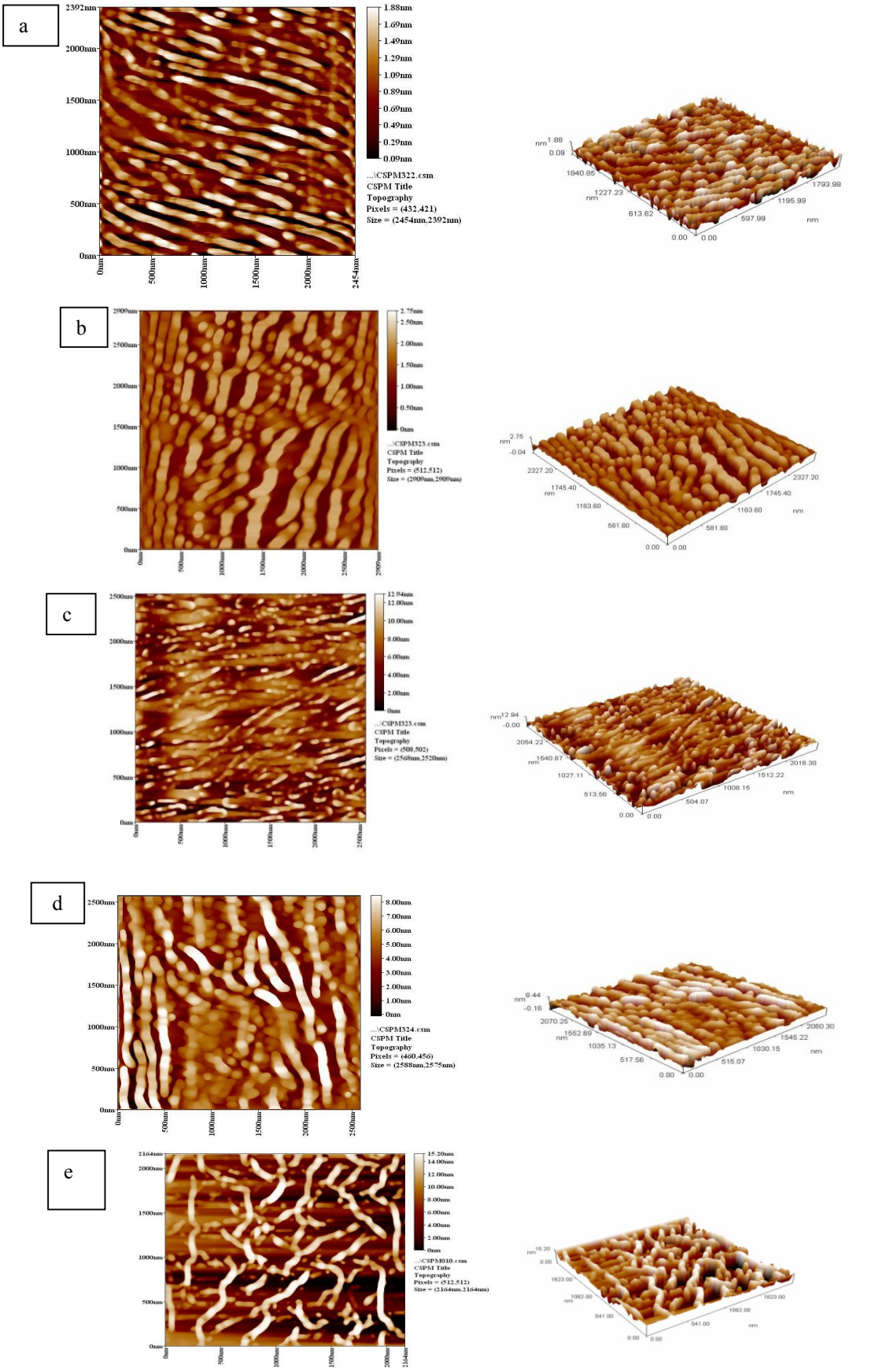


figure 6. AFM morphology for of (a) PANI-DBSA ,(b) 1%, (c) 2%, (d) 3%, and (e) 5 wt % MWNT in PANI-DBSA as a MWNCT/PANI-DBSA composites

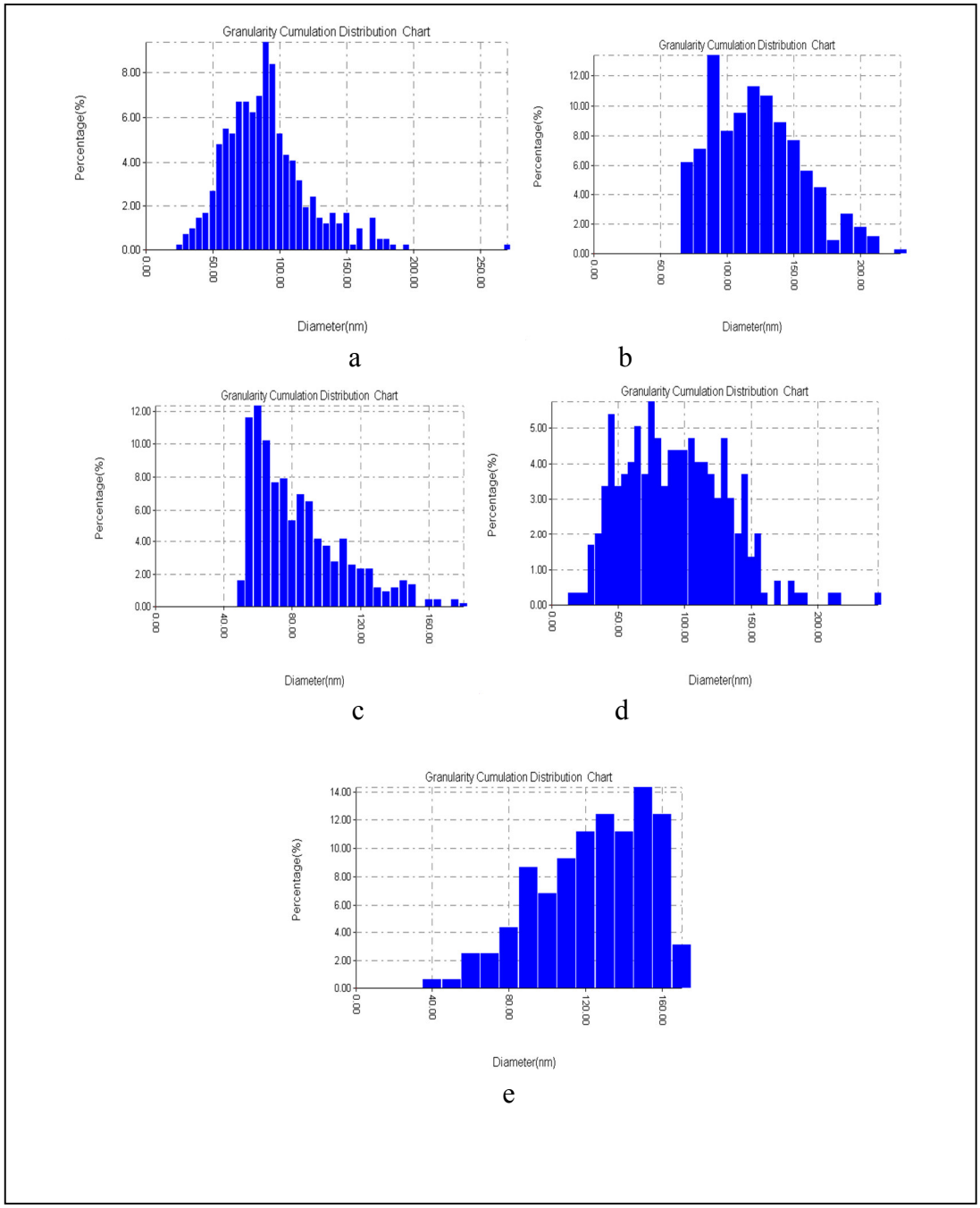


Figure 7. Size distribution of diameters for (a) PANI-DBSA (b) 1%, (c) 2%, (d) 3%, and (e) 5 % MWNT in PANI-DBSA as a MWNCT/PANI-DBSA

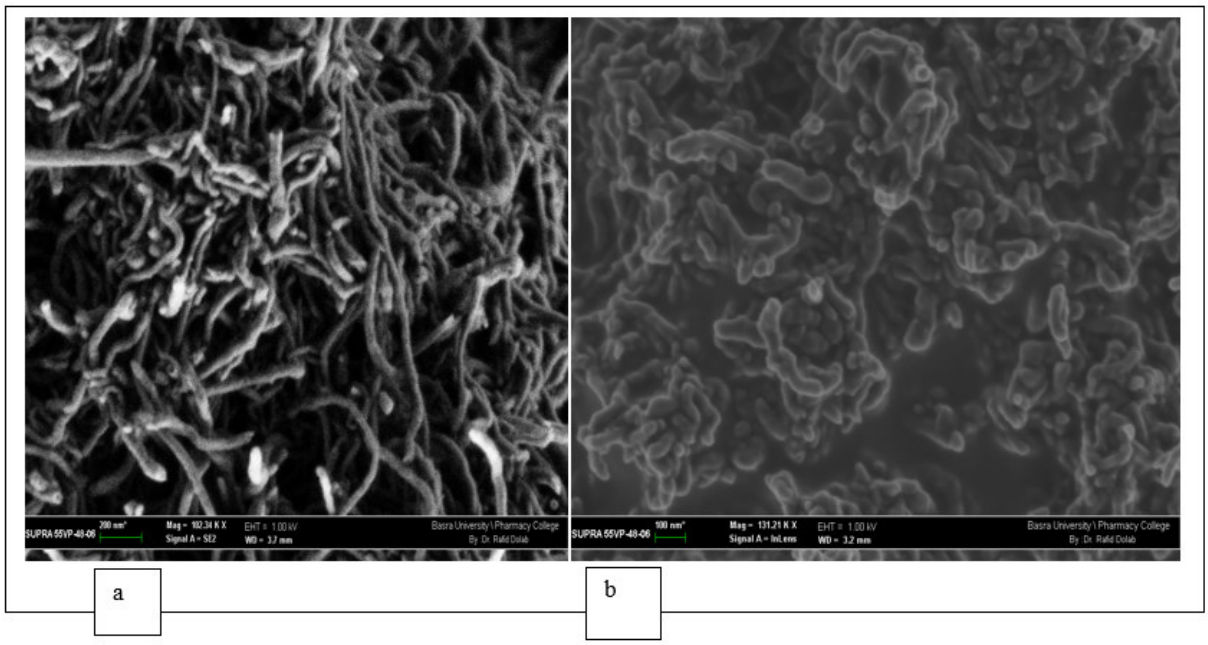


Figure 8. SEM images of nanofibers a.C-MWNCT , b. PANI-DBSA/ 3% MWNCT

4. Conclussion

PANI-DBSA/MWNCNT nanocomposite was successfully synthesized by an out-situ chemical polymerization .the preparation materials characterized by FTIR, XRD,AFM and SEM . The effect of weight ratios concentrations on the , functional group, crystallinity, and a nonfibers diameters, of PANI-DBSA/MWNCT nanofibers were investigated. .show the effective structural modification and confirm the coating of PANI layer on the MWNCNT surface. the diameter of c-MWCT increased from(5-10) nm ,for MWNCT) ,to (20-40) nm after treatment with strong acids .Also the diameter of the PANI-DBSA/MWNCT was estimated to be in the range 50–80 nm..

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Prof. **Dr. Kareema Majeed Ziadan** Is received her Ph.D. degree from University of Basra, College of Science, Physics Department, Basra, Iraq. 1997
Field of interest : Electronic application of Conducting polymers and semiconductor ,her research , interests include: Solid state physics -Electronic application of Conducting polymers , semiconductor, and solar cell, Head of group of material science. Professor . at 2002, member in scientific committee in teragreen conference 2011, member in scientific committee in teragreen conference 2012,, member in scientific committee in TMREES14 conference 2014, member in scientific committee in TMREES15 conference 2015.

Hanaa Hashim Ainia :M.Sc. student in University of Basrah, College of Science, Physics Department