

Synthesized and Study the Structural and Morphological Properties of Polyaniline-Cadmium Sulfide Nanocomposite

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Abstract

The nanocrystalline CdS powder was prepared using sol–gel method. The polyaniline were prepared using chemical oxidative polymerization of aniline. The PANI-CdS nanocomposites had been prepared via same method of polyaniline preparation and different concentrations of CdS (10, 20, 30, 40 and 50 wt%) were added. X-ray diffraction shows that the peaks of emeraldine salt polyaniline powder are located at $2\theta = 21.5^\circ$, 25.7° and 28.1° which indicate of polycrystalline polyaniline and the peaks of CdS powder are located at $2\theta = 26.69$, which is indicate of crystalline CdS coincides with hexagonal [002] structure, $2\theta = 47.47$ which is refers to CdS with hexagonal [103] and cubic [220] structures. The crystallite size of PANI and CdS were found to be 7.95 and 12.09 nm respectively. FTIR measurement indicates that there are interaction between polyaniline matrix and CdS nanoparticles. The AFM investigation shows that there is uniform distribution for CdS nanoparticles in the PANI matrix. [DOI: [10.22401/JNUS.20.3.14](https://doi.org/10.22401/JNUS.20.3.14)]

Keywords: Polyaniline, CdS, Polyaniline-Cadmium Sulfide Nanocomposite.

1- Introduction

Recently, the inorganic-polymer hybrid materials on nanometer scale has been receiving significant attention due to their applications in optoelectronic devices [1], [2] and in field effect transistors [3]. The change of the optical, electrical and dielectric properties of polymer requires using inorganic fillers. The goal of the preparation of polymer with inorganic material is obtaining a composite material having behaviors between the polymer and inorganic material. The polyaniline (PANI) is one of the conducting polymers, has significant attention in the preparation of a wide range of materials due to its optical and electrical properties [4]. PANI is commonly used in the previous studies because of its relative ease in preparation, good environmental stability [5], [6] and tunable conductivity [7]. Chemical or electrochemical oxidation methods of aniline monomers can be used for preparation of polyaniline and then processed into films, fibers and composites. The inorganic materials such as ZnS, CdS, and PbS nanoparticles are semiconductor materials which are used in many applications such as solar cells, optoelectronic devices and sensors [8]. CdS is an important II–VI semiconductor compound. It has wide optical band gap about 2.4 eV at room temperature [9]. PANI-CdS

nanocomposites were studied by many researchers [10], [11] and they are focused on electrical conductivity. In this research the structural and morphological properties of PANI-CdS nanocomposites were presented.

2- Materials and Methods

2-1 Synthesis of polyaniline

Chemical oxidative polymerization method was used to prepare polyaniline. Initially 0.1M (0.4 g) aniline and (50 ml) of 1M HCl with distilled water were stirred in a beaker. The beaker was put inside ice bath at (0-4)°C. The glass substrate was dipped in the solution. The oxidizing agent 1.14 g ammonium peroxydisulfate was dissolved in 50 ml of 1M HCl with distilled water. Ammonium peroxydisulfate solution was added drop wise to aniline solution with constant stirring. During polymerization, the color of the mixture was changed from light blue to blue green and finally becomes greenish black. The greenish black color indicates to emeraldine salt polyaniline. This solution was kept overnight. The solution was filtered and then washed two times with HCl and distilled water to remove the impurities. The filtered residual and the substrate were dried in electrical oven at 80 °C for 4 h.

2-2 Synthesis of cadmium sulfide

3.198 mg of cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), 1.824 g of thiourea ($\text{CH}_4\text{N}_2\text{S}$) were dissolved by 40 ml distilled water. The cadmium acetate solution was stirred for 5 minutes, and then the solution of thiourea was added drop wise with constant stirring. After 3.5 h, the solution color becomes yellow and the nanoparticules were precipitate. The stirrer were turn off and the solution was left overnight. The CdS nanoparticles stabilized at the bottom. The solution was filtered and washed several times by distilled water to remove the impurities. The filtered precipitate and the substrate were dried in electrical oven at 70°C for 4 h.

2-3 Synthesis of PANI–CdS nanocomposite

The PANI-CdS nanocomposite were prepared with five different percentages of CdS nanoparticles (10, 20, 30, 40 and 50 wt%) in oxidation polymerization method. Initially, 0.87 g aniline prepared in aqueous solution in a beaker with 1M HCl in (94.3 ml) distilled water. The solution was put inside the ice bath at ($0 - 4^\circ\text{C}$) on the stirrer. After that, 2.1 g ammonium peroxydisulfate was dissolved in 94.3 ml of 1M HCl in distilled water. Under the constant stirring the solution of ammonium peroxydisulfate was added drop wise to the solution of aniline. Then, the CdS (10, 20, 30, 40 and 50 wt %) was added and the solution was stirred for 12h. The precipitate was filtered and washed two times by HCl and distilled water. The filtered precipitate and the substrate were dried at 80°C by using electrical oven for 4 hours.

3- Results and Discussions

3-1 X- ray diffraction (XRD)

The X-ray diffraction patterns of emeraldine salt (ES) polyaniline and cadmium sulfide are shown in Fig.(1). The diffraction peaks of ES-PANI powder are located at $2\theta = 21.5^\circ$, 25.7° and 28.1° which indicate of polycrystalline polyaniline [12]. The PANI crystallinity is due to benzenoid and quinoid rings repetition in PANI chains. The broad peak $2\theta = 25.7^\circ$ corresponds to [110] plane of PANI. The XRD of CdS powder show an intense diffraction peak at $2\theta = 26.69^\circ$, which is indicated of CdS coincides with hexagonal [002] structure. There are another two peaks at

$2\theta = 47.47^\circ$ which refers to CdS with hexagonal [103] and cubic [220] structures, and $2\theta = 52.05^\circ$ which is indicated to CdS with hexagonal wurtzite structure corresponds to [112] plane that's refer to polycrystalline CdS. These results are consistent with the CdS standard values which are given in JCPDS no. (80-006). Table (1) explains the PANI and CdS peaks which are appear in XRD of PANI-CdS composites. From this table can be observed the CdS with hexagonal and cubic structures and almost peaks refer to the hexagonal CdS.

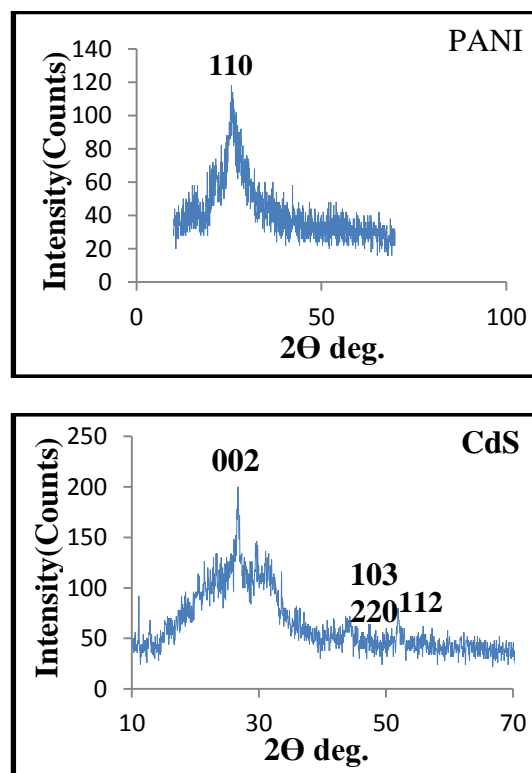


Fig.(1): XRD of PANI and CdS powders.

Table (1)
Shows the diffraction peaks of PANI and CdS in PANI-CdS composites.

samples	PANI peaks			Hexagonal CdS peaks			Cubic CdS peaks		
	2θ deg.	hkl	I/I ₀	2θ deg.	hkl	I/I ₀	2θ deg.	hkl	I/I ₀
PANI-CdS (10%)	25.7	110	100	28.1	101	39	28.1	111	39
				43.4	110	13	47	220	11
				50.8	200	11	56.3	311	18
				52.8	201	18	68.7	400	18
				58	202	18			
				66.8	203	21			
PANI-CdS (20%)	25.5	110	100	28.1	101	53	28.1	111	53
				36.3	102	6	32.5	200	15
				36.9	102	4	46.8	220	11
				43.9	110	9	56.1	311	13
				52.9	201	9	59	222	6
				54.3	004	6			
58.2	202	15							
PANI-CdS (30%)	25.4	110	100	26.6	002	13	27.8	111	44
				27.8	101	44	32	200	16
				43.7	110	22			
				51.1	200	22			
				52.5	201	22			
				54.2	004	13			
58.1	202	19							
PANI-CdS (40%)	25.7	110	100	26.8	002	53	28	111	28
				28	101	28	32.9	200	10
				36.4	102	15	55.7	311	13
				51	200	18	58.4	222	20
				52.2	112	18			
				53	201	5			
58.4	202	20							
60.5	104	10							
PANI-CdS (50%)	25	110	19	25	100	19	27.9	111	27
				26.6	002	100	32.5	200	2
				27.9	101	27	46.6	220	8
				44	110	73	59	222	6
				48.1	103	6			
				52.1	112	56			
53.1	201	15							
54.5	004	2							
60.8	104	6							

The crystallite sizes of pure PANI, CdS and PANI-CdS composites are calculated by Scherrer formula:

$$C_s = k\lambda / B \cos\theta \dots\dots\dots (1)$$

Where C_s is crystallite sizes, k is constant and equal to 0.9 and B is full width half

maximum. Table 2 gives the obtained values of crystallite sizes. In general, the crystallite sizes of nanocomposites increase with the increasing in CdS concentration as shown in Fig.(2).

Table (2)
XRD for PANI, CdS nanoparticles and PANI-CdS nanocomposites.

Samples	2θ (deg.)	Plane (hkl)	FWHM (deg.)	Crys. size (nm)	d (Å°)
PANI	25.75	110	1.05	7.95	3.45
CdS	26.69	002	0.925	12.09	3.33
PANI-CdS (10%)	25.72	100	1.25	6.64	3.46
PANI-CdS (20%)	25.54	100	1.158	7.01	3.48
PANI-CdS (30%)	25.45	100	1.176	6.84	3.49
PANI-CdS (40%)	25.75	100	1.885	4.42	3.45
PANI-CdS (50%)	25.05	110	0.50	15.90	3.55

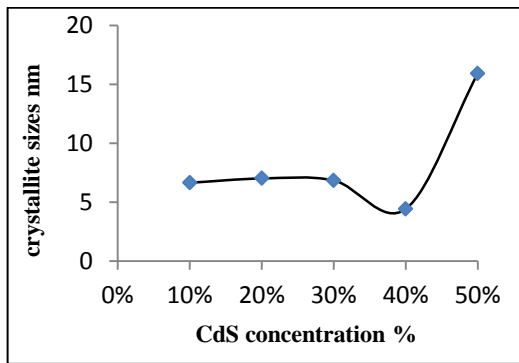


Fig.(2): Shows the change of crystallite sizes with CdS concentration.

The lattice constants equation of hexagonal system was used to calculation the lattice constants of hexagonal CdS and CdS with hexagonal structure in nanocomposites:

$$1/d^2 = 4/3[(h^2+hk+k^2)/a^2] + l^2/c^2 \dots\dots\dots (2)$$

Where d is lattice displacement, a and c are lattice constants and h, k and l are miller indicies. The obtained values of a and c are consistent with the values of a and c that's given in JCPDS no. (80-006). The stress S along a axis and the stress along c axis ϵ were also calculated using Eq. 3 and Eq. 4 respectively.

$$S = [(a-a_0) / a_0] * 100\% \dots\dots\dots (3)$$

$$\epsilon = [(c-c_0) / c_0] * 100\% \dots\dots\dots (4)$$

Where S is stress along a axis, ϵ is the stress along c axis, a_0 and c_0 are standard lattice constants. The obtained values of a, c, S and ϵ are shown in Table (3).

Table (3)

The lattice constants, stress along the a and c axes values of hexagonal CdS in PANI-CdS nanocomposites.

Material	a A ⁰	c A ⁰	S	ϵ
hexagonal CdS	4.12	6.67	-0.29%	-0.68%
PANI-CdS (10%)	4.16	6.67	0.56%	-0.70%
PANI-CdS (20%)	4.11	6.94	-0.59%	3.36%
PANI-CdS (30%)	4.13	6.68	-0.14%	-0.51%
PANI-CdS (40%)	4.12	6.62	-0.37%	-1.42%
PANI-CdS (50%)	4.10	6.69	-0.84%	-0.38%

The lattice constants a and c are changes with CdS concentration, that's shown in the Figures 3.A and B respectively. The stress along a axis behavior is shown in the Fig.(3.C). It's clear from this figure there are a

tension stress for 10% and compression stress for another samples. Fig.(3.D) show the stress along the c axis behavior with CdS concentration .This figure exhibited tension stress for 20% and compression stress for another samples. The stress in nanocomposites may be caused by the difference in the crystal structure of PANI and CdS or may be due to the distribution of cadmium sulfide particles in polyaniline matrix.

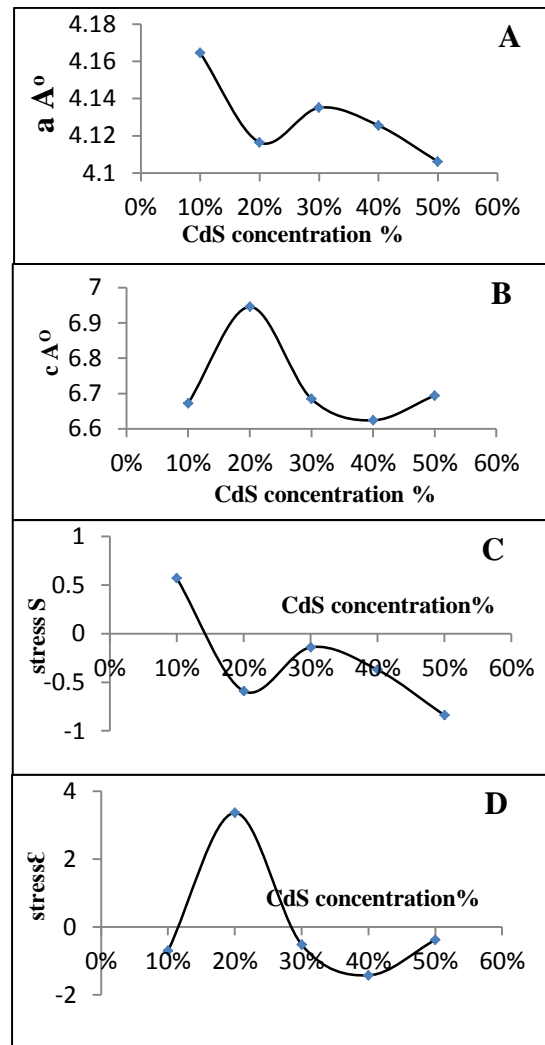


Fig.(3): The change of (A) The lattice constants a (B) The lattice constants c (C) The stress along the a axis (D) The stress along the c axis with CdS concentration.

3-2 Fourier Transform Infrared Spectroscopy (FTIR)

Fig.(4) shows the FTIR spectra of polyaniline. The polyanilin peaks at 3360 cm⁻¹ and 3456 cm⁻¹ are caused by the stretching of N-H bond of aromatic amines, the aromatic of C-H stretching was appeared at 2708 cm⁻¹ [13]. The band at 1587 cm⁻¹ is attributed to

C=N vibration for quionoid [14]. Peak at 1442 cm^{-1} is due to stretching mode of vibration for C=C bond in the benzenoid units of PANI. The stretching mode of C-N bond in the benzenoid units was located at 1134 cm^{-1} and the bands 626 cm^{-1} and 711 cm^{-1} correspond to out of plan C-H bending vibration [13].

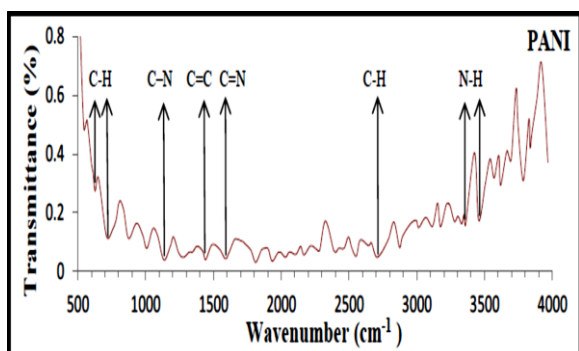


Fig.(4): FTIR spectra of pure PANI nanoparticles.

FTIR spectra of nano CdS are shown in Fig.(5). The peak at 3429 cm^{-1} is assigned to the stretching vibrations of O-H bond for water molecules [13]. The peaks at 2133 cm^{-1} , 2104 cm^{-1} are due to bending vibrations of water molecules [7]. At 1743 cm^{-1} this is due to C=O stretching vibrations which is may be caused by carboxylic group of cadmium acetate is used in reaction [13]. The band at 1645 , 1546 , 1533 and 1516 cm^{-1} are due to NH₂ bending vibrations which may be due to residue thiourea is used in reaction[13].The medium to strong bands of Cd-S stretching appears at 412 cm^{-1} and 650 cm^{-1} [15].

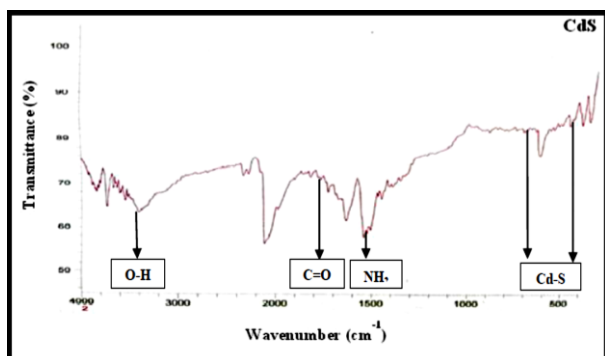


Fig.(5): FTIR spectra of pure CdS nanoparticles.

Fig.(6): presents FTIR spectra of PANI-CdS nanocomposites with five percentages of CdS (10%-50%). This figure exhibits the peaks of PANI and CdS together, that's due to

the interaction between them, those peaks are shown in the Table (4).

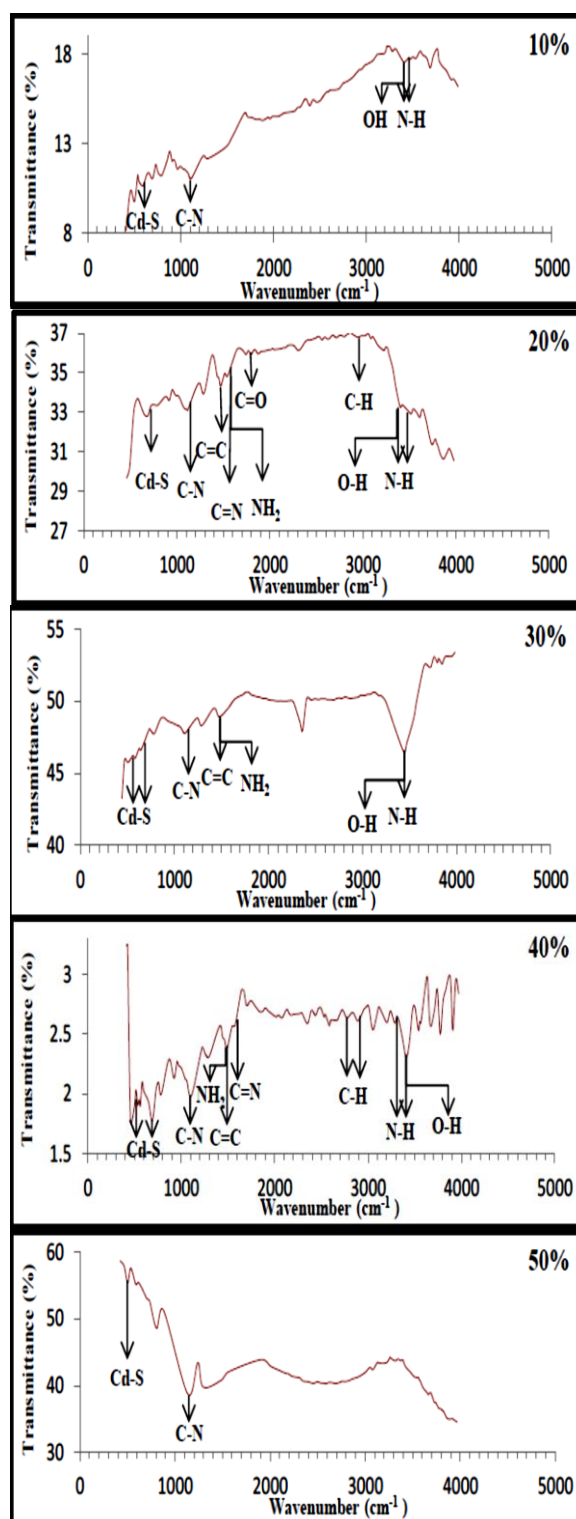


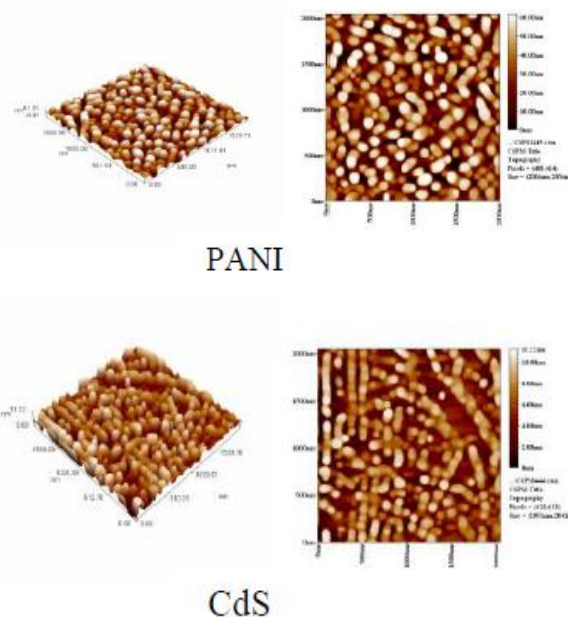
Fig.(6): FTIR spectra of PANI-CdS nanocomposite.

Table (4)
FTIR peaks of PANI-CdS nanocomposite.

Materials	Chemical bonds	The bands locations cm^{-1}				
		10%	20%	30%	40%	50%
PANI bonds	N-H stretching of aromatic amines	3400, 3415	3400, 3423	3437	3284, 3408	3315
	aromatic C-H stretching	2708	2945	-----	2773, 2885	-----
	C=N vibration for quionoid	-----	1544	-----	1575	-----
	C=C stretching mode of vibration for the benzenoid units	-----	1471	1475	1489	-----
	C-N stretching mode of benzenoid ring	1112	1114	1114	1109	1134
CdS bonds	OH stretching vibrations of water molecules	3400	3400	3437	3408	-----
	bending vibrations of water molecules	-----	-----	-----	2079	-----
	C=O stretching vibrations which is may be caused by carboxylic group	-----	1741	-----	1735	-----
	NH ₂ bending vibrations which may be due to residue thiourea	-----	1544	1475	1489	-----
	Cd-S stretching	597	688	514, 642	499, 580, 690	501, 586

3-3 Atomic Force Microscopy (AFM)

Among the important factors which are effect on the optical and electrical properties in application to sensing devices is morphology. The 3D and 2D AFM images of the pure PANI, pure CdS and PANI-CdS nanocomposite with five percentages of CdS (10, 20, 30, 40 and 50 wt%) are shown in Fig.(7). From this figure the PANI nanoparticles are uniform in the array and the grains with spherical structure on crystalline axis. The distribution of CdS is regular with oval arrangement and the roughness of CdS surface is relatively lower compared with PANI. The images of PANI-CdS nanocomposites show that there are interconnect among PANI and CdS nanoparticles and the distribution of CdS nanoparticles is uniform into the PANI matrix.



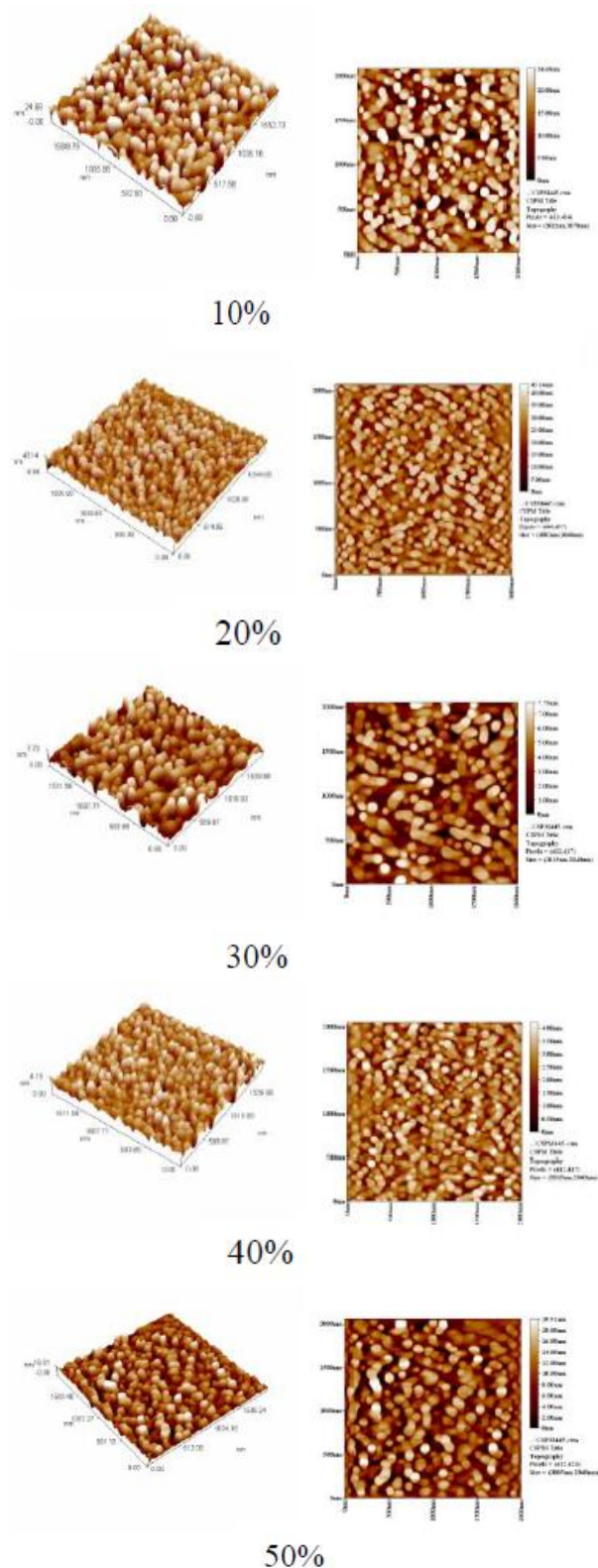


Fig.(7): The 3D and 2D AFM images of the PANI nanoparticles, CdS nanoparticles and PANI-CdS nanocomposites.

The values of roughness and average grain size are shown in Table (5). From this table can be observed that the average grain size estimated from AFM measurement larger than grain size obtained by XRD, that's refer to that

grains are aggregation of many crystals and the XRD gives the size of crystals while the AFM gives the size of grains.

Table (5)

Shows the AFM data of the samples.

Sample	Average grain size (nm)	Roughness (nm)	Root Mean Square (nm)
PANI	99.40	14.5	16.8
CdS	99.40	2.19	2.56
PANI-CdS (10%)	90.07	5.26	6.25
PANI-CdS (20%)	76.66	5.95	7.17
PANI-CdS (30%)	105.22	1.49	1.77
PANI-CdS (40%)	70.55	0.599	0.748
PANI-CdS (50%)	78.34	3.73	4.54

4. Conclusion

PANI, CdS nanoparticles and PANI-CdS nanocomposites were synthesized via simple methods to study their structural and morphological properties. From the X-Ray diffraction pattern of PANI-CdS nanocomposites can be observed the peaks of PANI and CdS were appeared together that's refer to the interconnection between them and the difference in crystallite structure of PANI and CdS lead to stress in the nanocomposites. FTIR indicate that there is interaction between PANI matrix and CdS nanoparticles. There is uniform distribution of CdS nanoparticles in PANI matrix and there are interconnect among them that's obtund from AFM measurements.

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