Polyaniline-CdSNanocomposite; Synthesis, Structural, Thermal and Spectroscopic Analysis

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Abstract: *Nano particles of CdS compound have been successfully synthesized utilizing coprecipitation technique. Polyaniline has also been synthesized employing chemical oxidative polymerization method. CdS-polyaniline nano-composite was fabricated and characterized. Structural, morphological structure, thermal and spectroscopic examinations were inspected. Spherical particles with average size of order 4.0 and 4.88 nm for CdS and Pani-CdS were perceived respectively. Core shell model for the nanocomposite was suggested and the shell thickness was given. Thermal analysis by TG, DTG DSC and the heat capacitance $C_P$were also conducted over wide range of temperature. In addition FTIR spectroscopy for the CdS, pani and CdS pani nanocomposite were inspected. The investigation confirmed the formation of thermally stable core-shell of pani-CdSnanocomposite.*

Keywords: *CdS, polyaniline, nanocomposite,XRD, EDX,TG, DTG, DSC,C_p and FTIR analysis.*

I.   Introduction

Much attention has been paid for polymers and polymeric materials. Such concern is ascribed to the spread and wide use of such materials in man's life. In addition for the miss use of the polymeric materials environment wasenormously contaminated. Nowadays polymers have been involved in many novel applications besides the ability of recycling such materials to be less harm to mankind. Among these applications, drug release devices [1], drug delivery medium, the fabrication of disposable polymer products, hard tissue replacement [2]. New class of materials composed of polymer and material of nanoparticles, nanocomposite, is emerged. Materials as such have distinctive characterization different from that of the component [3]. Due to its significance Polyaniline, pani, is the most important polymer used in polymeric composites. Pani is a conducting polymer withhigh absorption coefficient in thevisible light, high mobility carriers, of low cost, easily reproducibleand can be readily doped with other dopants [4-5].Chalcogenides,as inorganic semiconductors, are widely doped inpani to form composite. The composite properties are mostly modified whenfiller size is descended whence nanocomposite materials are developed.pani-CdS nanocomposite has been the subject of many research papers [6-7] and has many technological aspects of applications [8-9].

In this study structural, morphological, thermal and spectroscopic investigations will be analyzed at different temperatures.

II.   Experimental

Pani was synthesized via polymerization of aniline in a catalytic acidic medium using chemical oxidative polymerization technique. Constituentsof the composite were added according to the molecular weight and the stoichiometric concentration and thoroughly mixed using magnetic stirrer. For the structural characterizationX-ray diffraction was carried out by **Bruker D8** having CuK_αsource (λ=1.5418 Å). Fourier Transform Infra Red (FTIR) spectroscopy (**Model:JASCO – 6300 JAPAN**) of pani, CdS and pani–CdSnanocomposites were studied in the range of 400–4000 cm^{-1}. Microstructure and Morphological study of powder pani, CdS and pani–CdS nanocomposite were carried out using scanning electron microscopy (**Type JEOL-JSM-5410, from Japan**) operating at 20kV. Finally thermal analysis for the three compounds using (**DSC NETZSCH STA 409 CD Germany)** was carried out in, He atmosphere, to investigate the thermal stability and detect any physical transitions during the heating loop.

III.   Results And Discussion

X-rays diffraction pattern of CdS powder is depicted in Fig.(1a). For the first glance one observe that the pattern includes broad peaks. Such broadening is a sign of very fine powder in range of nano meters. Moreover there are four pronounced peaks at d-spacing values 3.29764 Å, 2.05641 Å, 1.76238 Å, and 1.32178 Å. Such peaks, according to the ICDD (89-0440), were indexed to be (111), (220), (311), and (331) planes respectively. The unit cell is recognized to be cubic with lattice constant evaluated from the (hkl) according to:

$$a = d * (h^2 + k^2 + l^2)^{0.5} \qquad (2)$$

Values of a were calculated for each plane and the average value was found to be about 5.7837 ±.06 Å. Such value seems likely to be consistent with that obtained from the ICDD card and previously reported values [10].

(a)

(b)

(c)
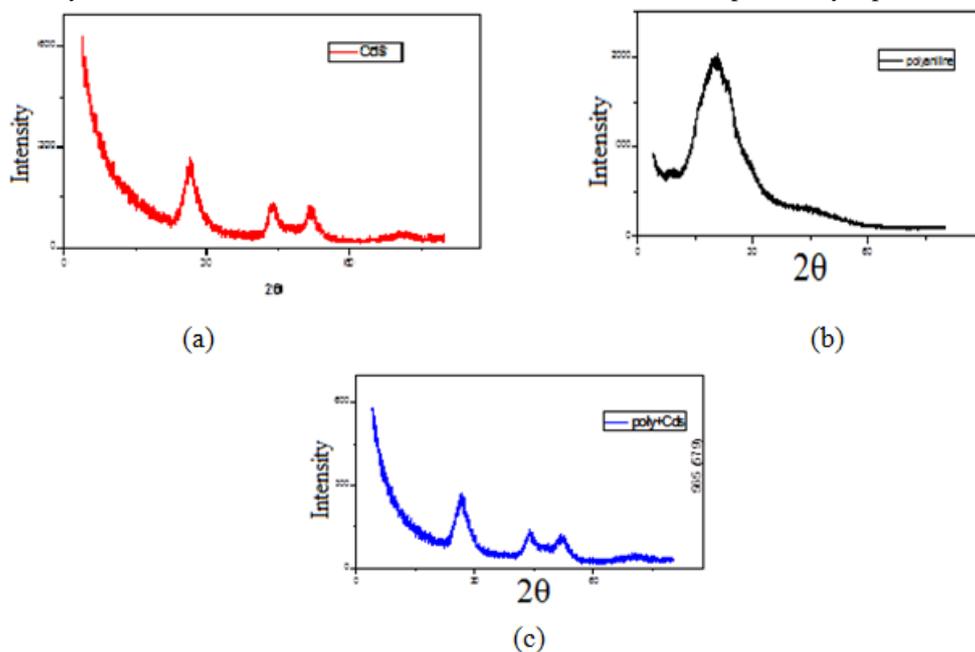
Fig.(1) X-ray diffraction of : a)Pure CdS nanoparticle, b)Pure polyaniline and
c) pani-CdS nanocomposite.

On the other hand the X-ray diffraction pattern of the pure polyaniline is shown in Fig. (1 b). It is clear from the figure and data of [11], that polyaniline has the amorphous state where no peaks were detected except wide broad one at $2\theta=26°$ as shown in Fig.(1 b).

Furthermore the X-ray diffraction pattern for pani--CdSnancomposite is represented in Fig. (1 c). It is clearly shown that peaks of the composite are similar to that of CdS which confirms the formation of cubic nanocrystals enwrap in polyaniline. This also means that CdS is homogeneously distributed in the polyaniline matrix. However a fine increase in the d-spacing is noticed due to the addition of CdS to the polyaniline. Such increase in the d-spacing tends to expand the lattice constant to a=5.8184 ± 0.021 Å. The difference in lattice parameter of pani-CdS composite and CdS is $\Delta a = 0.0347$ Å.

Considering figures (1 b&c), the crystallite size were calculated using 3 independent techniques using Scherrer formula [12], utilizing XPowder program [13] and using Winfit program [14]. Table (1) includes the crystallite size of CdSand pani-CdSnanocomposite. For all the applied techniques it has been found that the crystallite size of CdS is always less than that of polyaniline-CdS nanocomposite. In other words the crystallite size of pani-CdS nanocomposite is always higher than the crystallite size of CdS. Since the X-ray data showed neither alteration in the diffraction pattern nor change in phase, the increase in size is a strong evidence for core-shell formation of pani-CdS in which thin cover of pani envelops the CdS spheres as schematically represented in Fig.(2).Regarding the crystallite size of both pani-CdS and CdS a rough estimation of the average thickness of the pani layer is found to be about ~ 0.35 nm .

Table (1): Crystallite size for the as prepared CdS and pani-CdS composite

|	Debye Eq.	XPowder	Winfit	Average
Pani	----	----	----	
CdS	3 nm	3.15 nm	5.9 nm	4.016
Pani-CdS		3.66 nm	6.1 nm	4.88
Pani layer		0.51 nm	0.2	0.864
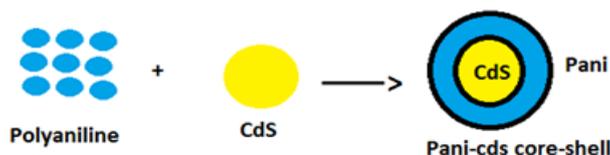
Fig.(2). Schematical representation of Pani-CdS core shell

Microstructure and morphology analysis

In order to inspect the surface morphology of both CdS and polyaniline; samples were examined by SEM. Fig. (3 a, b and c) represent Scanning Electron Micrographs (SEM) of CdS, polyaniline and pani-CdS respectively. It can be seen that CdS has some sort of conglomeration with few nano sized particles having spherical morphology. On the other hand the SEM of polyaniline is shown in Fig.(3 b). It shows the surface morphology with highly agglomerated irregular shape which reflects the amorphous state of the obtained pani. For the SEM of pani-CdS shown in Fig.(3 c), the morphologyof the composite now has spherical shape and the amorphous state of the polyaniline is developed to be of enwrapped spheres. Such results of the SEM, seems to be in concord with that revealed from the X-ray results and formation of core shell.
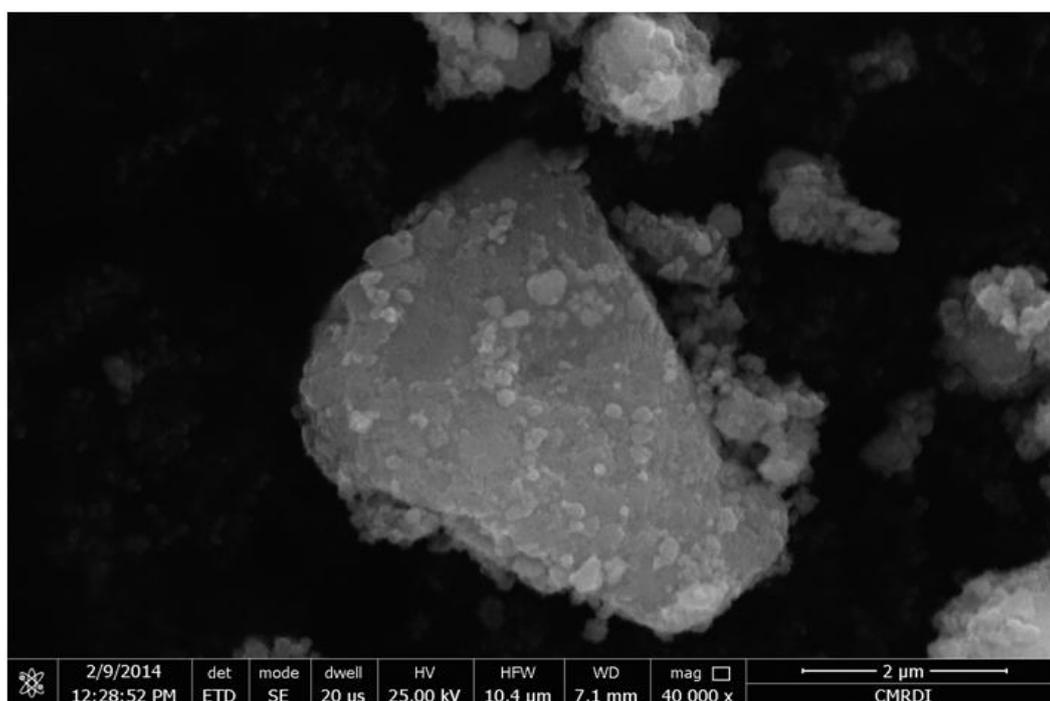
Fig.(3 a):SEM micrograph of pure CdS
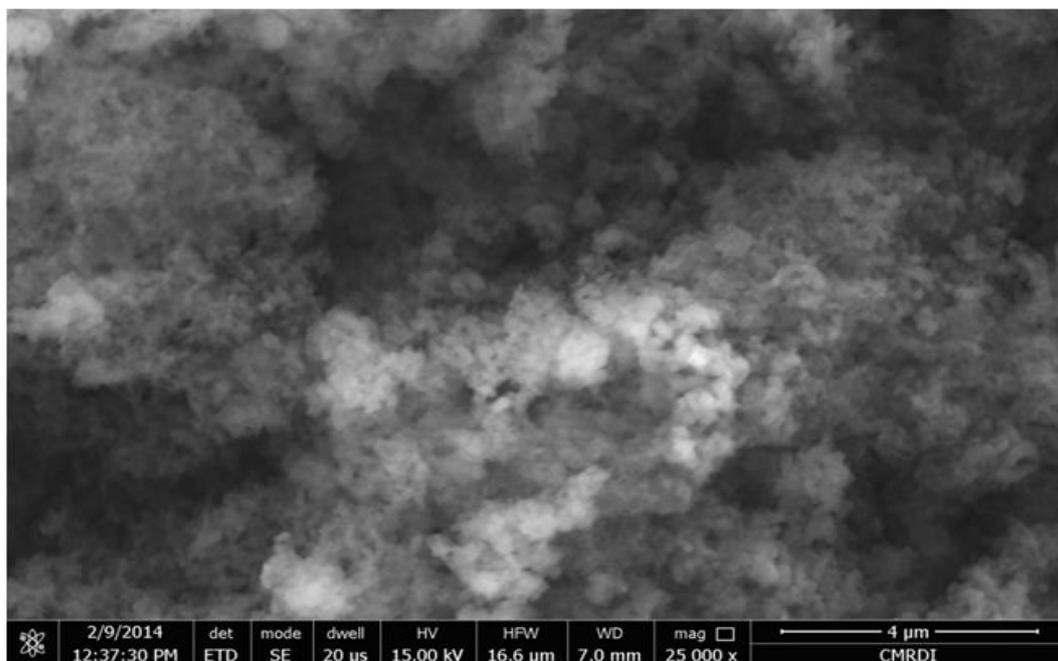
Fig.(3 b):SEM micrograph of pure Pani
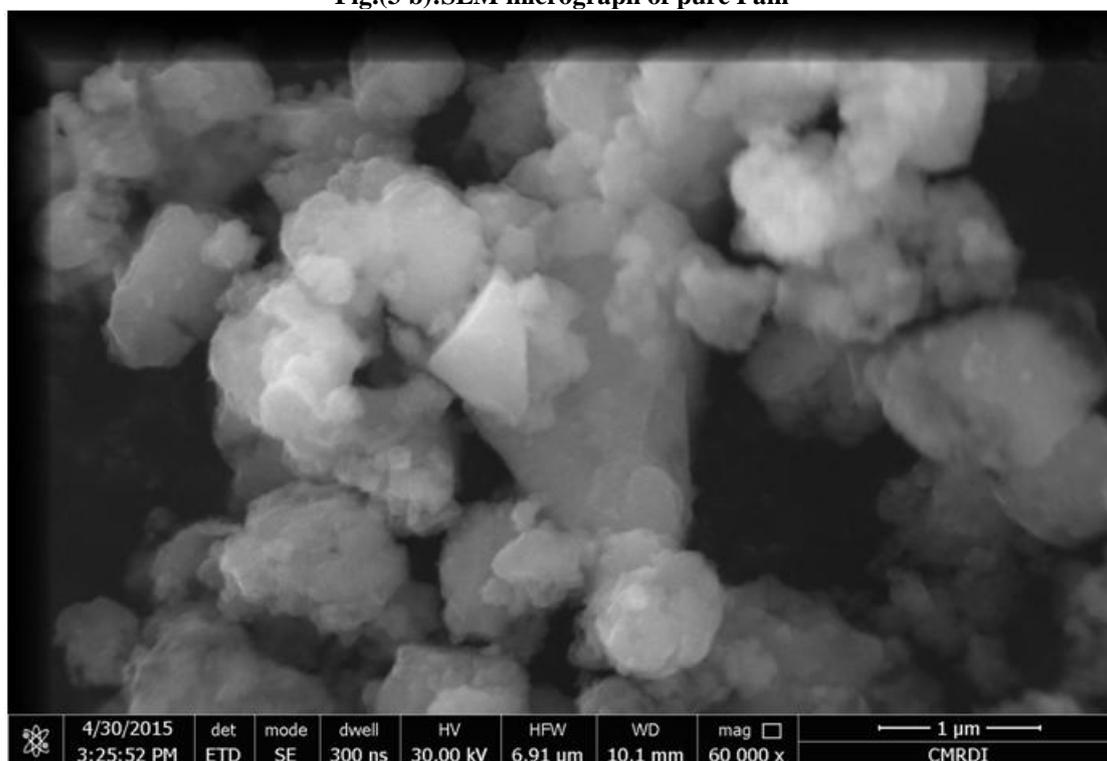
Fig.(3 c):SEM micrograph of Pani-CdS nanocomposite

Elemental analysis

For elemental analysis of the prepared nano particles CdS, EDX spectroscopy was achieved. Figure (4) depicts the elemental mapping of CdS. According to the figure the examined particles comprise the constituents of the CdS compound. The stoichiometry of the obtained powder according to the EDX weight % and atomic % are tabulated in table (1) compared with the nominal and chemical formula. According to data of table (1) there is no elemental impurities were detected except about 3 wt% of Oxygen. Such Oxygen percentage may be associated with some oxidation during the preparation process. However this percentage is not noticeable in the X-ray diffraction pattern. In addition the chemical formula is quite close from the stoichiometric formula
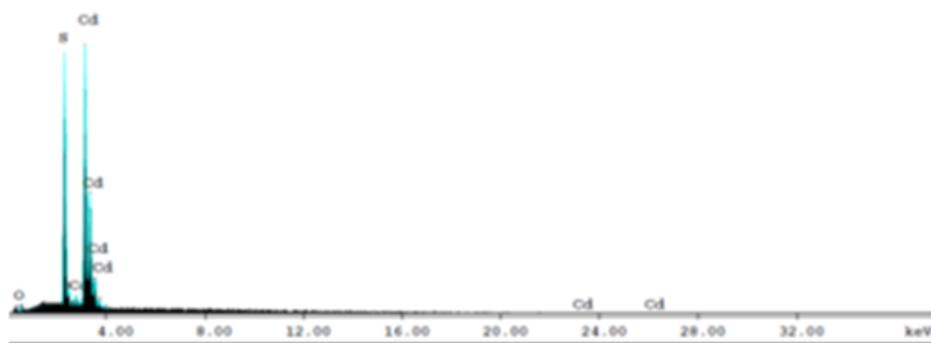
Fig.(4): EDX spectrum of as prepared CdS nanoparticles

Table (2): EDX Elemental analysis and chemical formula

Element	Weight%	Atomic%	Molecular weight
O (K)	3.20	12.81	
S (K)	22.43	44.80	32.066
Cd (L)	74.37	42.38	112.411
Total	96.8	87.18	
Chemical formula	Cd.945 S	Cd.945 S	
Stoichiometric formula	CdS	CdS	

Thermal analysis:

In order to elucidate the thermal stability, perceive the interior interactions between composite components and thermodynamic kinetics of both CdS, polyaniline and pani-CdS, thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) measurements were carried out. The studied temperature was in range between 300 and 1000 K with 10 °C/ min heating rate and He gas atmosphere. Figures (5 a, b and c) displayetypical thermographs of CdS. Polyaniline and pani-CdS naoncomposite. For the TG, one can observe that CdS nanocrystals are thermally stable over the whole range of temperature except a step of mass loss of about 2%through the temperature range between 180 to 220 C°. The weight loss in this rang of temperature may be attributed to moisture and water evaporation[15].In the DTG curve the change of slope in TG curve is strongly pronounced as an endothermic peak. A minimum in DTG is observed at about 230 °C. Such temperature is called onset of thermal degradation Td.Table 3 includesthe

Table (3): Onset temperature T$_d$ of thermal degradation.

| Compound	CdS	Pani	Pani-CdS
DTG Onset temperature T$_d$°C	225	525	90, 240
DSC Onset temperature T$_d$ °C	196.9		55.7, 173.1

onset temperature T$_d$ of CdS nanoparticles. The width of the minimum is about 100 °C. CdS nanoparticles seem likely to be strongly stable over the range from 180 up to 700 °C. The DSC curve of CdS nanoparticles does not show any thermal abnormality over the studied range of temperature from room temperature up to 700 °C. Accordingly CdS nanoparticles have neither phase changes nor glass transition.

Regarding Fig.(5 b) for the TG, DTG and DSC curves of the pure pani, one can see that it is reasonably stable in the temperature range from room temperature up to about 480°C. Degradation of pani starts just above 480 °C where about 30% weight loss was occurred. From the DTG curve the onset temperature of thermal degradation is about 525°C as shown in Fig (5 b) and table (3). Despite the polyaniline, from X-ray analysis is in amorphous state the DSC curve does not show any sort of crystallization transition along the studied range of temperature. In terms of pani-CdS nanocomposite the TG shows two steps of weight loss of about 2 % and 15 % for the lower temperature step and the higher temperature step respectively. From the DTG curve of pani-CdSnanocomposite two minima were detected at about 80°C and 240 °C for the two steps shown in the TG curve. The corresponding T$_d$is shown in table (3). These two steps were ascribed to water and moisture. Comparing the above series of curves for pure CdS, pure polyaniline and pani-CdSnanocomposite one can see that the thermal behavior of the composite is associated with the CdS core and the shell has no effect. This confirms the formation of core shell from Pani-CdS nanocrystals as described before.
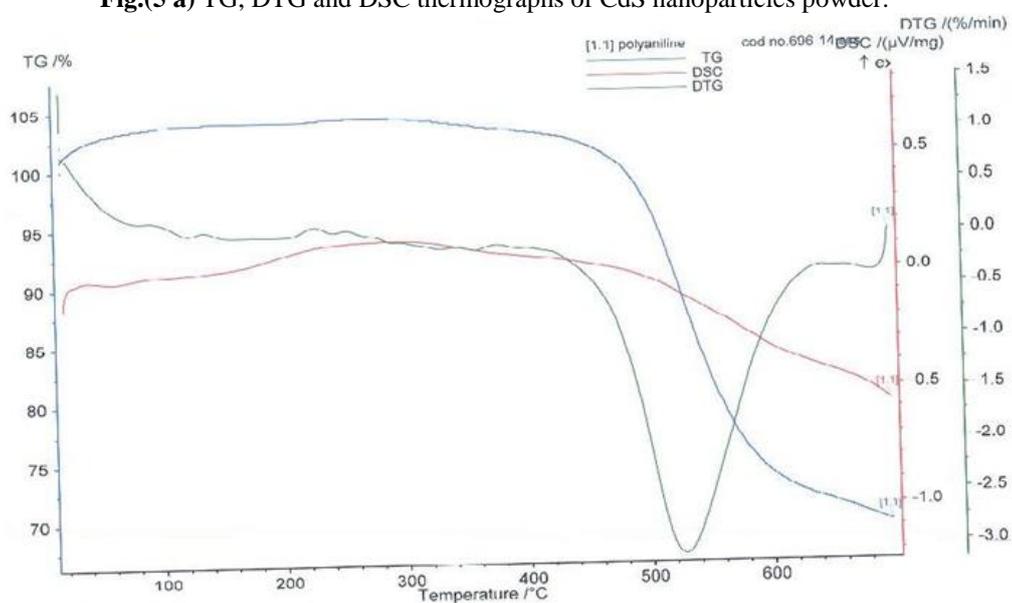
Toconceive the variation of the internal energy of the studied materials, the heat capacitance C$_p$ was estimated in terms of the DSC data where:
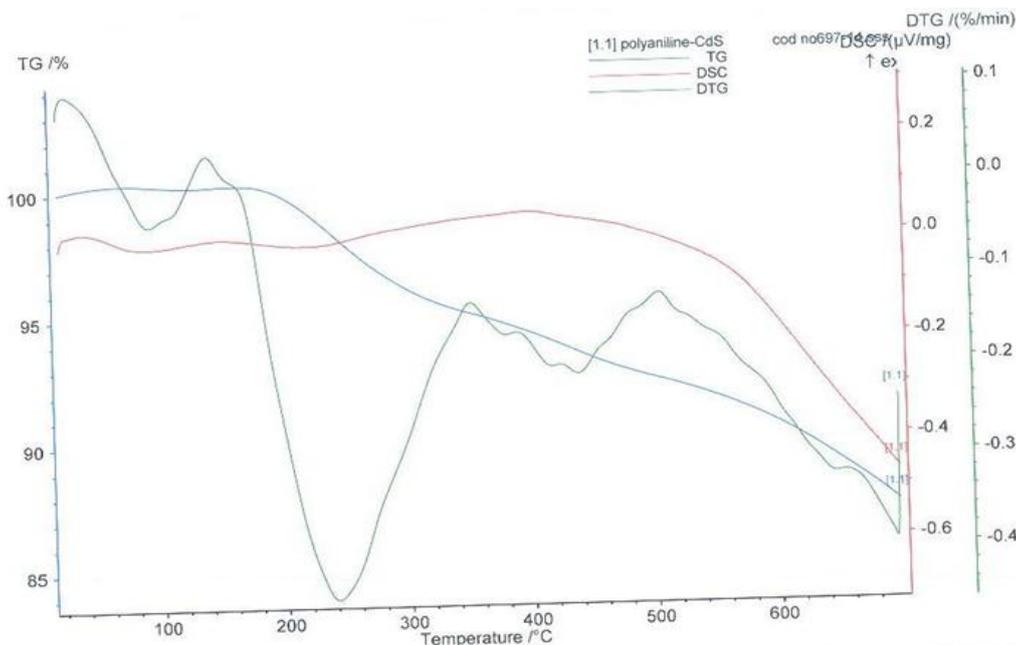
$C_p = Q / [m T]$

whereQ is the applied thermal energy to mass m to increase its temperature T °C.
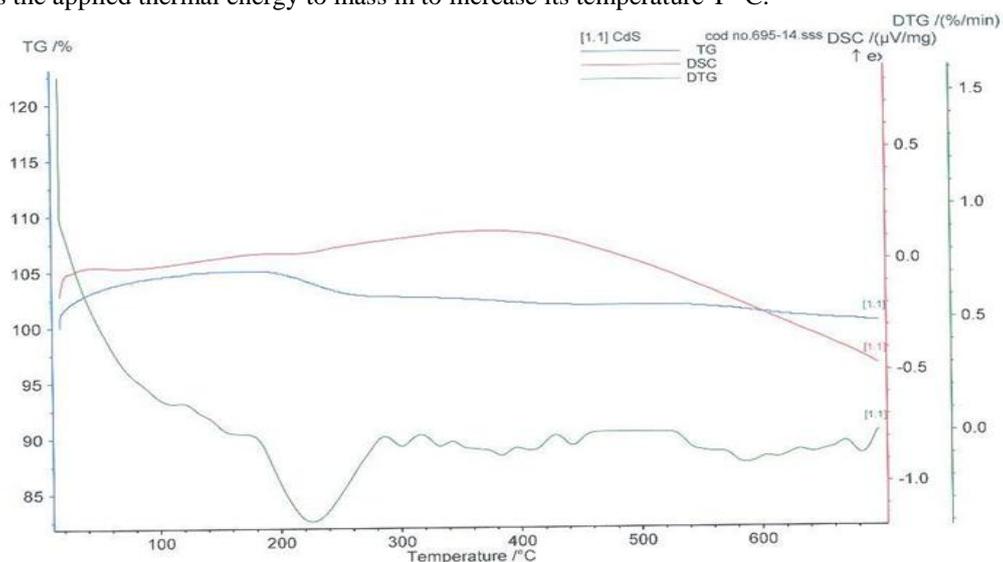
Fig.(5 a) TG, DTG and DSC thermographs of CdS nanoparticles powder.


Fig.(5 b) TG, DTG and DSC thermographs of pani.

Fig.(5 c) TG, DTG and DSC thermographs of Pani-CdS nanocomposite.

The above equation can be written as;

$$C_p = (dQ / dt) /[m\ dT/dt]$$

wheredQ / dt is heat flow and dT/dt is rate of heating.

Substituting for the heat flow by the DSC then theheat capacitance C_p can be estimated against temperature. Fig. (6) represents the temperature dependence of the heat capacitance of CdS, pani and pani-CdSnanocomposite. According to Fig.(6) the heat capacitance of pani-CdSnanocomposite is close to that of CdS nano particles at room temperature. However as the temperature increase the divergence between pani-CdSand CdS increase. As the temperature increase the heat capacitance of both CdS and pani-CdScontinuously increase. Such trend indicates the domination of CdS on the internal energy of the composite.
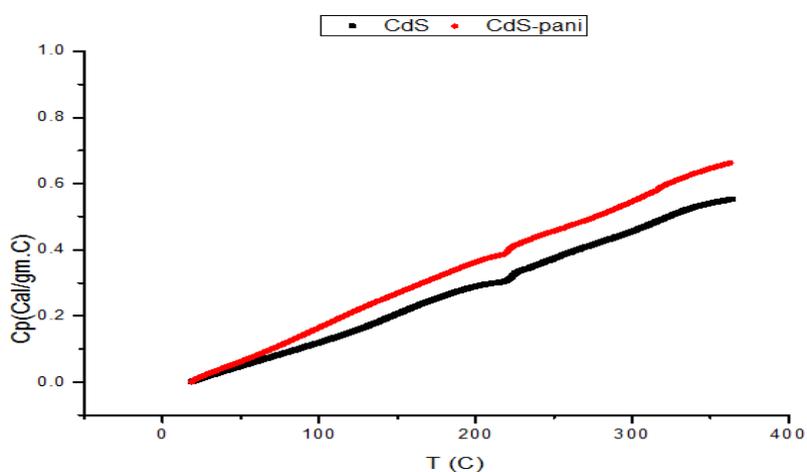

**Fig.(6)** Heat capacitance against temperature

Fourier Transform Infra-red spectroscopy (FTIR)

FTIR spectra of CdS, polyaniline and Pani-CdS nanocomposite are displayed in Fig. (7 a,b and c) from 500 cm^{-1} to 4000cm-1.Comparing theabsorptionpeaks, of the abovecompounds in Fig. (6), it can be said that the peaks of Pani-CdS nanocomposite is a modification of the spectrum of the polyaniline due to embedding CdS .This approves the CdS polymerization and formation of core-shell model.Table (4) includes thebonds corresponding to each wave number. Similar bands have been observed by others but at shifted wave numbers
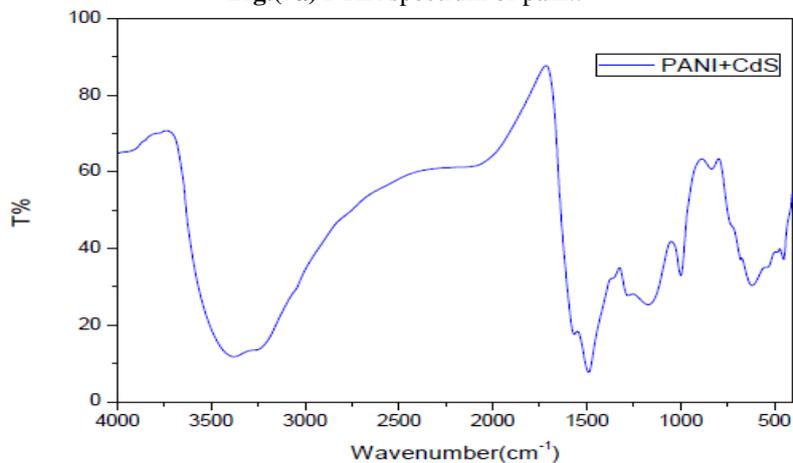
[16-17]. This might be due to difference in crystal structure of CdS either cubic or hexagonal and method of pani preparation.
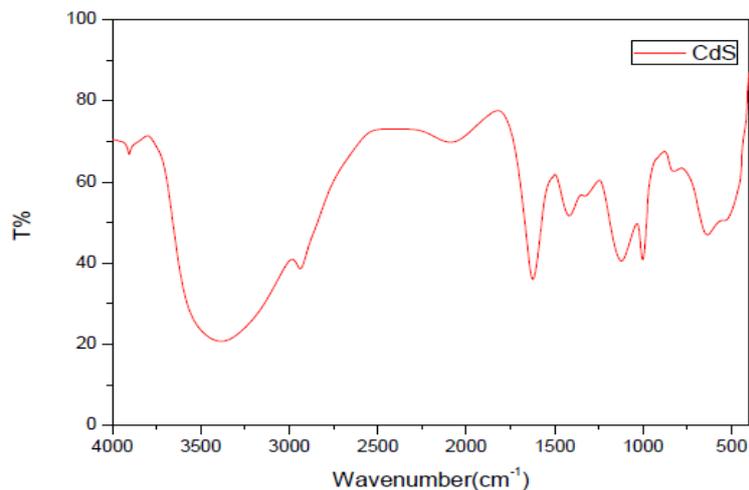
Fig.(7a) FTIR spectrum of CdS.
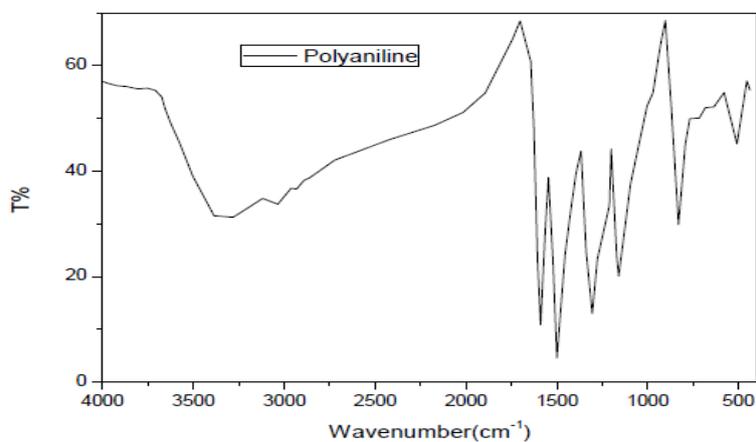
Fig.(7a) FTIR spectrum of pani..

Fig.(7c) FTIR spectrum of Pani-CdS nanocomposite.

Table (4) FTIR characteristic peaks of CdS, pani and Pani-CdS nanocomposite.

Pani	CdS	CdS-pani	Group
3385		3396	N-H stretching
1595		1562	C-C Quinone
1495		1488	C-C Benzene
1294		1288	C-N Quinone
1163		1172	Aromatic C-H in plane bending
821		830	Aromatic C-H out of plane bending
	835		Cd-S stretch strong
	645	609	Cd-S stretch medium

IV. Conclusion

Nanocomposite of Pani-CdS was fabricated and characterized using the coprecipitation and polymerization techniques. The structural investigation proved that the insertion of CdS in polyaniline modifies the latter structure. Accordinglythe adhesion of pani on CdS surface of cubic structure tends to reshape the pani amorphous structure to have cubic structure for the produced Pani-CdS nanocomposite. Core-shell model was suggested for the Pani-CdS nanocomposite where CdS as core with cover of pani layer as shell. The shell thickness was estimated to be about 0. 86nm.The core-shell model of Pani-CdS nanocomposite has been confirmed by the thermal study where the heat capacitance of the composite has similar trend as that of the CdS nano crystals. Also the FTIR spectroscopic analysis proved that the bonds of pani are modified due to the addition of CdS nanoparticles.

References

[1]. R.C.Barthus, L.M.Lira and S.I.C.de Torresi, J.Braz. Chem. Soc. 19, 360, (2008).
[2]. K.Janaki, S.Elamathi, D.Sangeetha, trends Biomater. Artif.Organs.22,169(2008).
[3]. J. B. Bhaiswar, M. Y. Salunkhe, S. P. Dongre, International Journal of Scientific and Research Publications, Volume 3, Issue 1, January (2013).
[4]. Jordan, J., Jacob, K.I., Tannenbaum, R., Sharaf, M.A.,Jasiuk, I. Mater.Sci. Eng.A, 393, 1(2005).
[5]. Berta, M., Lindsay, C., Pans, G., Camino,G,Polym. Degrad. Stabil., 91, 1179(2009).
[6]. XiaofengLu,Youhai Yu, Liang Chen, HuapingMao,WanjinZhang,Yen Wei, Chem.Commun., 1522 (2004).
[7]. X. Y. Ma, G. X. Lu, B. J. Yang, Applied Surface Science, 187, 235(2002).
[8]. E. A Ponzio,T.M. Benedetti, R.M.Torresi, ElectrochimicaActa, 52, 4419(2007).
[9]. N.Singh, M.KulkarniS.Lonkar, A.Viswanath, P.Khanna, Metal-Organic and Nano-Metal Chemistry, 37, 153 (2007).
[10]. M.Zhao, X.Wu, C.Cai,The Journal of Physical Chemistry C, 113, 4987(2009).
[11]. K. He, M.Li, L.Guo, International Journal of Hydrogen Energy, 37, 755(2012).
[12]. B.D.Cullity, Elements of X-ray Diffraction, Addison-Wesley (1978).
[13]. WWW.XPowder.com.
[14]. WWW.geol.uni-erlangen.de.
[15]. N. Qutub, S. Sabir, Int. J. Nanosci. Nanotechnol., 8, 111(2 012).
[16]. B.T. Raut, P.R. Godse, S.G. Pawar, M.A. Chougule, D.K. Bandgar, Shashwati Sen, V.B. Patil, J. Physics and Chem of Solids,74,236 (2013).
[17]. M.V. Kulkarni, A.K. Viswanath, R. Marimuthu, J. Polym. Sci., Part A: Polym.Chem.42, 2043(2004).