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CHARACTERIZATION OF CdSe/POLYTHIOPHENE NANOCOMPOSITE BY TGA/DTA, XRD, UV-VIS SPECTROSCOPY, SEM-EDXA AND FTIR

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Abstract: We synthesized the Polythiophene by Oxidative Polymerization of Thiophene and then synthesized CdSe/Polythiophene. After this we made a thin film by incorporating this nanocomposite and then studied its characterizations by TGA/DTA (Thermal Analysis), XRD (X-Ray Diffraction), UV-VIS (Ultraviolet-Visible Spectroscopy), SEM-EDXA (Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis), FTIR (Fourier Transform Infrared Spectroscopy).

Keywords: Nanocomposite, thermal analysis, x-ray diffraction, ultraviolet-visible spectroscopy, scanning electron microscopy with energy dispersive X-ray analysis, Fourier transform infrared spectroscopy

1. Introduction

Now-a-days the energy demand over the world increases more and more. Everything what happens in the world is the expression of flow of energy in one of its forms. Mainly there are two types of energy sources; these are conventional and non-conventional energy source. Conventional energy sources include fossil fuels, oil, coal, natural gas, etc., which are running out and not going to long last. These resources are limited and may supply energy for about next 50 to 60 years. Therefore extensive research and development activities are being undertaken to develop efficient, reliable and cost-effective technologies to use non-conventional energy sources such as solar, biomass, wind, sea, geothermal, hydrogen, etc.

Due to day-by-day increase in demand for electricity and fast depleting conventional resources, men have been forced to find an alternative, by which electricity can be produced efficiently and cheaply. Again the source would be non-depleting. Since now-a-days pollution is a great concern, it has been stressed to find alternative, which is non-polluting also. Solar energy is the most important source of energy. It is an inexhaustible and pollution free source. Several technologies have been developed for utilization of solar energy. Photovoltaic devices also known as solar cells convert solar energy to the electricity, which is the most convenient form of energy. For terrestrial applications, along with reliability, the cost of solar cell is important. Hence efforts are being made to produce efficient, reliable and cost-effective solar cells using various types of semiconductors. Presently most successful photovoltaic device is using crystalline silicon. However, the generating cost is very high; hence it cannot be used extensively for terrestrial applications. A method to reduce the cost of solar cell and give good energy conversion efficiency is to utilize nanocomposite semiconductors rather than bulk materials. Hence different nanocomposite thin-film photovoltaic technologies are being developed as a means of substantially reducing the cost of the photovoltaic systems. A solar cell (or photovoltaic cell) is a semiconductor device that converts light into electricity. The most common form of solar cells are based on the photovoltaic effect in which light falling on a two-layer semiconductor device produces a photo-voltage. This voltage is capable of driving current through an external circuit and there by producing useful work. Fundamentally, the device needs to fulfill only two functions: photogeneration of charge carriers (electrons and holes) in a light-absorbing material, and separation of the charge carriers to a conductive contact that will transmit the electricity. The field of research related to solar cells is known as photovoltaic. The research of nanostructure has become a flourishing field in material science. One can obtain smaller, lighter, cheaper and faster devices with greater functionality while using less row materials and consuming less energy by using nanotechnology. Nanotechnology is the almost invisible science of construction on scales of a billionth of a meter. The optical properties of nanocrystals are defined by their size and surface chemistry and they differ drastically from those of the bulk solids. Nanomaterials exhibit highly exotic properties and their industrial demand is steadily increasing.

1.1. Cadmium Selenide (CdSe)

Cadmium selenide is also a solid hexagonal or cubic crystal. It is a direct band gap n-type semiconducting material with a band gap of 1.74 eV at 300K. Its molecular weight is 191.37 g/mol where Cd is 58.74% and Se is 41.26%. Its appearance is dark red colour [1].

CdSe in the bulk form is not very interesting. The most interesting form of CdSe is nanoparticles. Much current research on CdSe has focused on nanoparticles. Researchers are concentrating on developing controlled synthesis of CdSe nanoparticles. It has useful properties for optoelectronic devices, laser diodes, nanosensing, biomedical imaging and high efficiency solar cells.

1.2. Polythiophene (PTh)

Polythiophenes are one of the most valuable types of conducting polymers that may be easily modified to afford a variety of useful electrical and physical properties such as solubility, electrical conductivity, mobility and others.

Polythiophenes are the polymerization of thiophenes (a sulphur heterocycle), i.e. a linear chain of thiophene monomers. It possesses lower band gap and better electronic properties. It may give rise also some very useful properties such as increased ionization potential and stability [2, 3]. Polythiophenes usually do not possess metallic type conductivity even in a doped state. Therefore, they are much more commonly used as organic semiconductors. Many of them possess also good luminescent, nonlinear-optical, and other useful optoelectronic properties.

2. Experimental Analysis

All the experimental work has done in Centre for Materials For Electronics Technology(C-MET), Pune, India.

2.1. Synthesis of Polythiophene (PTh) (Oxidative Polymerization of Thiophene)

Here 0.1 M of thiophene was dissolved in 25 ml of acetonitrile or methanol (non-aqueous media) with 1ml of CTAB as surfactant. Then 0.3 M of lithium perchlorate was added as a supporting electrolyte to increase the bath conductivity and also added 0.1 M of ferric chloride as an oxidant to the above stirred solution. Again stirred the above mixture for 2 hours and kept several hours for polymerization. Then the products of black coloured precipitates were collected. These products were washed thoroughly with acetonitrile to remove any residual ferric chloride. These products were dried in a vacuum oven at 70°C for 10 hours to get powder form of polythiophene [3,4].

2.2. Synthesis of CdSe / PTh Nanocomposite

Here first Se metal powders were dissolved in 0.4 M sodium sulphite solution at 60°C under stirring for 4-5 hours and then the undissolved particles were filtered out after the solution cooled to the room temperature. That solution was sodium selenosulphate used as a selenium ion source. Second, 50 ml of methanol, 45 ml of distilled water and 5 ml of CTAB stock solution were added together and then divided into two equal volumes. 0.1 M of thiophene, 0.3 M of lithium perchlorate and 0.1 M of ferric chloride solutions were prepared in one part. Again 0.1 M of cadmium nitrate and the above prepared sodium selenosulphate solutions were prepared in another part. These solutions were mixed slowly under stirring for 1 hour and irradiated 20 KHz frequency for 1 hour in an ultrasonic bath. The products of blackish-brown coloured precipitates were collected and then washed thoroughly with absolute ethanol. The final products were dried in a vacuum oven at 70°C for 10 hours. Finally CdSe/polythiophene nanocomposite powders were collected [5].

2.3. Deposition of Nanocomposite Thin Films (Electrodeposition)

The nanocomposite thin films were galvanostatically deposited on copper substrates. Here 25 ml of n-hexane, 25 ml of distilled water and 1 ml of CTAB were added together and divided into two equal parts. For CdSe/polythiophene film, 0.1 M of sodium selenite was added instead of sodium thiosulphate. These solutions were added together slowly and applied 1.2-1.5 mA current for electrodeposition. After 75 minutes a brown colored uniform film was deposited on the copper substrate. Here copper substrate was connected to the cathode and graphite electrode was used as anode [6].

3. Results and Discussion

Thermal stability, i.e. weight loss/gain with different temperatures of the prepared samples were investigated by using Thermal Analyzer (Mettler Toledo 851e) in dynamic nitrogen atmosphere in the temperature range 30°C to 900°C at 10°C/min. The absorption band edge and band gap energy were recorded by using UV-VIS spectrometer (Spectrophotometer, Jasco V-570). The surface morphology, particle size and elemental composition were determined by using Scanning Electron Microscope with Energy Dispersive X-Ray Analysis (SEM-EDXA, Model XL 30, Philips, Holland).

Phase identification was carried out by X-ray Diffractometer (X-Ray generator, Regaku Miniflex, Japan) employing a scanning rate of 2°/minute in diffraction angle 2θ range from 10° to 80° and CuK$_\alpha$ radiation (λ = 1.5405 Å). The infrared spectra were recorded in the wave number range 400-4000 cm^{-1} by Fourier Transform Infrared Spectrometer (FTIR, Perkin-Elmer, Model Spectrum 2000, USA) by making the pellet of samples in KBr matrix.

3.1. Thermal Analysis (TGA/DTA)

Figure 1 gives the TGA/DTA of polythiophene synthesized by oxidative polymerization of thiophene. It clearly indicates that the initial weight loss due to the solvent evaporation and there is a second weight loss due to the expulsion of dopant, i.e. Cl at 500˚C and there is a steady plateau up to 800˚C. Figure 2 gives the TGA/DTA of CdSe/polythiophene nanocomposite. It clearly indicates that the weight loss after 400˚C is due to decomposition of CdSe and expulsion of dopant in polythiophene.

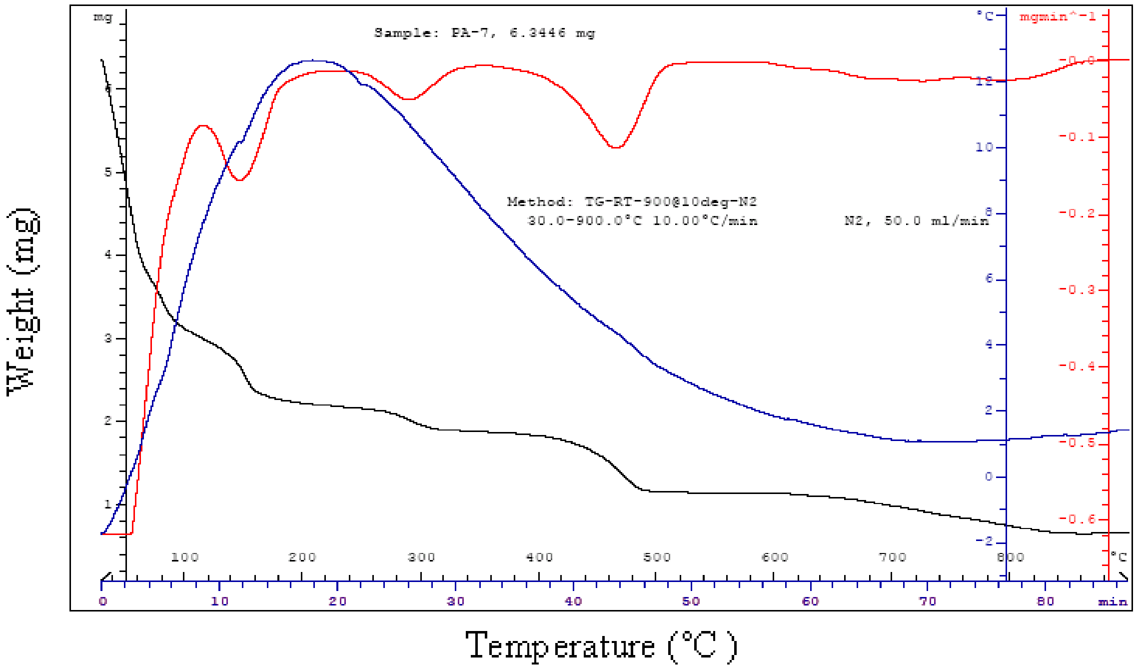


Fig. 1. TGA/DTA of polythiophene.

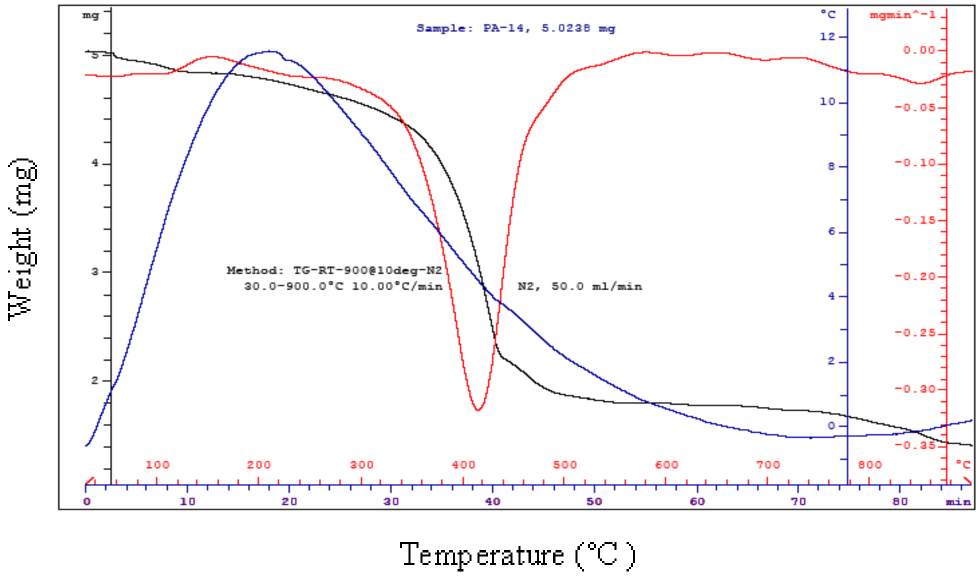


Fig. 2. TGA/DTA of CdSe/Polythiophene nanocomposite.

3.2. X-Ray Diffraction (XRD) Analysis

Figure 3 shows the XRD pattern of CdSe/polythiophene nanocomposite. Here also some extra diffraction peaks are due to the presence of polythiophene in CdSe/polythiophene nanocomposite.

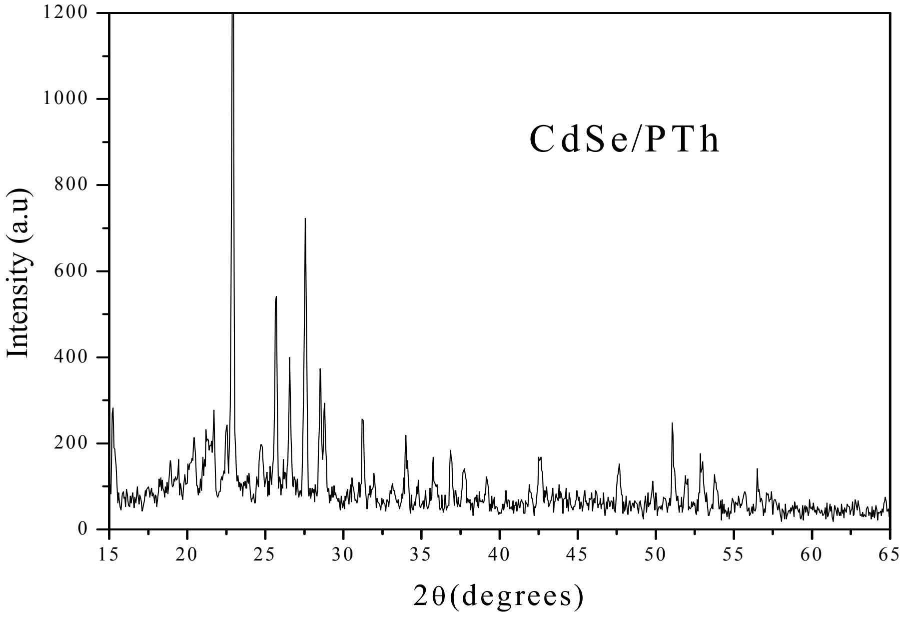


Fig. 3. XRD pattern of CdSe / Polythiophene nanocomposite.

3.3. Ultraviolet-Visible Spectroscopy (UV-VIS)

Figure 4 shows the UV-VIS reflectance spectrum of CdSe/polythiophene nanocomposite. From the spectrum the absorption band edge of CdSe/polythiophene nanocomposite is around 750 nm, which corresponds to the band gap energy E_g =1.65 eV. From these figures one can see that the absorption bands are in the green-red wavelength region.

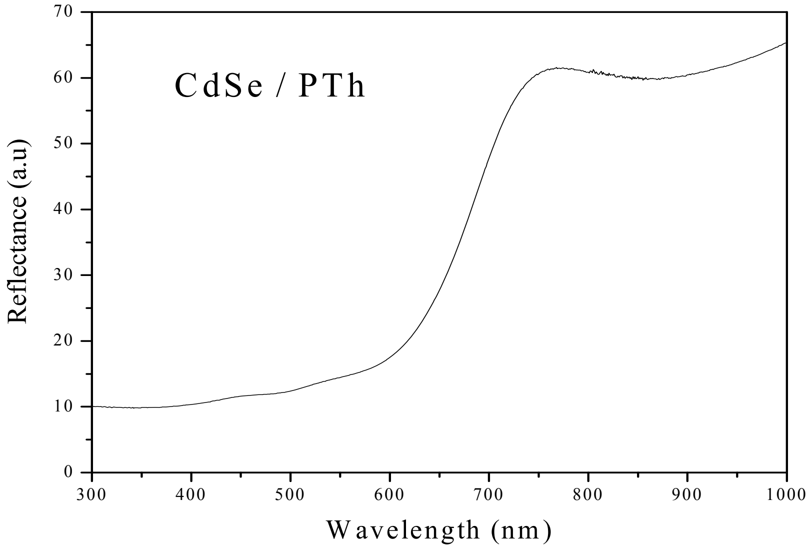
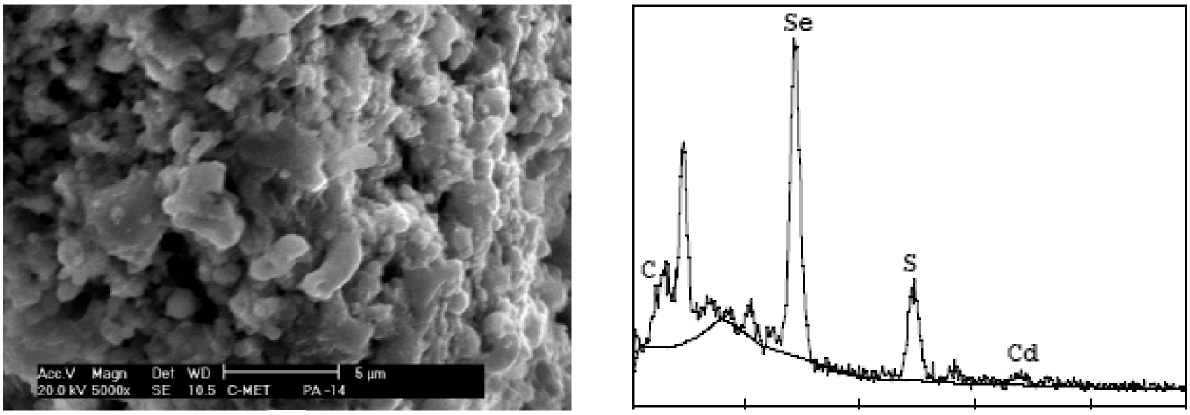


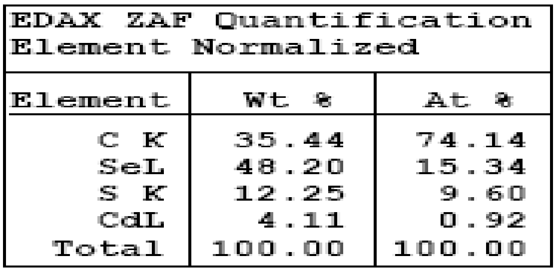
Fig. 4. UV-VIS spectrum of CdSe / Polythiophene nanocomposite.

3.4. Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDXA)

Figure 5 (a) gives the SEM image of CdSe/polythiophene nanocomposite. This SEM image clearly indicates that the CdSe nanoparticles were immersed in the polythiophene matrix. Figure 5 (b) is the EDX spectrum of CdSe/polythiophene nanocomposite. Table 5 (c) gives the element composition of CdSe/polythiophene nanocomposite.



(a) (b)



EDAX ZAF Quantification
Element Normalized

Element	Wt %	At %
C K	35.44	74.14
SeL	48.20	15.34
S K	12.25	9.60
CdL	4.11	0.92
Total	100.00	100.00

(c)

Fig. 5. SEM image of (a) CdSe/PTh nanocomposite EDX spectra of (b) CdSe/PTh nanocomposite EDX element composition table of (c) CdSe/PTh.

3.5. Fourier Transform Infrared Spectroscopy

Figure 6 gives the FTIR spectrum in the frequency range (400–4000 cm^{-1}) of polythiophene prepared by oxidative polymerization. The major peaks at 626.41 cm^{-1}, 1088.42 cm^{-1}, 1633.89 cm^{-1} and 3418.93 cm^{-1} are due to the presence of C=C, C-S, C-C and C-H bonds in polythiophene, respectively. This is similar to the standard FTIR spectrum of polythiophene and totally different from that of monomer thiophene, which confirms the successful polymerization of thiophene monomer and the formation of polythiophene. Figure 7 gives the FTIR spectrum in the frequency range (400–4000 cm^{-1}) of CdSe/polythiophene nanocomposite. The peaks at 626.33 cm^{-1}, 1124.27 cm^{-1}, 1635.94 cm^{-1}, 2355.68 cm^{-1} and 3434.87 cm^{-1} are due to the existence of different bonds in both CdSe and polythiophene in the nanocomposite.

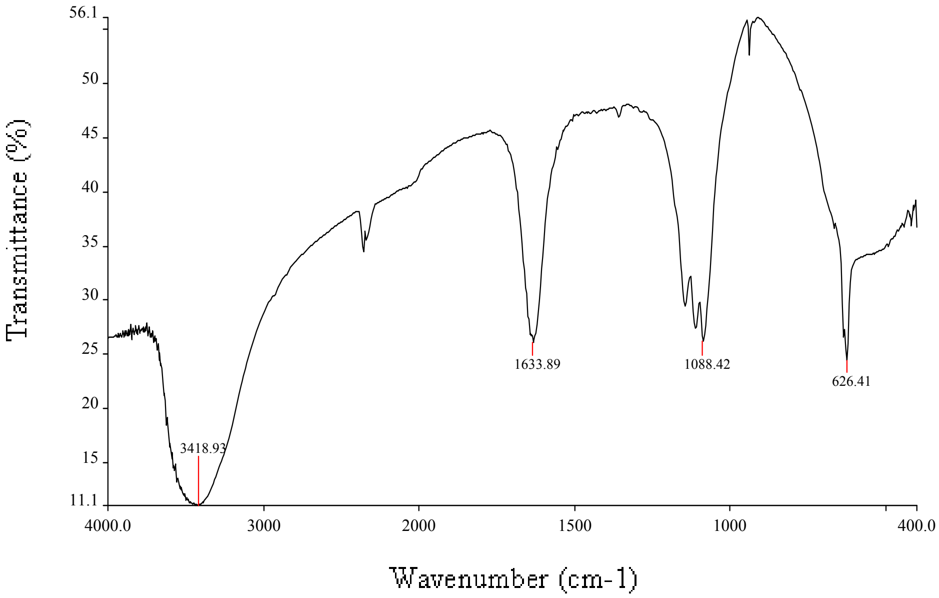


Fig. 6. FTIR spectrum of Polythiophene**.**

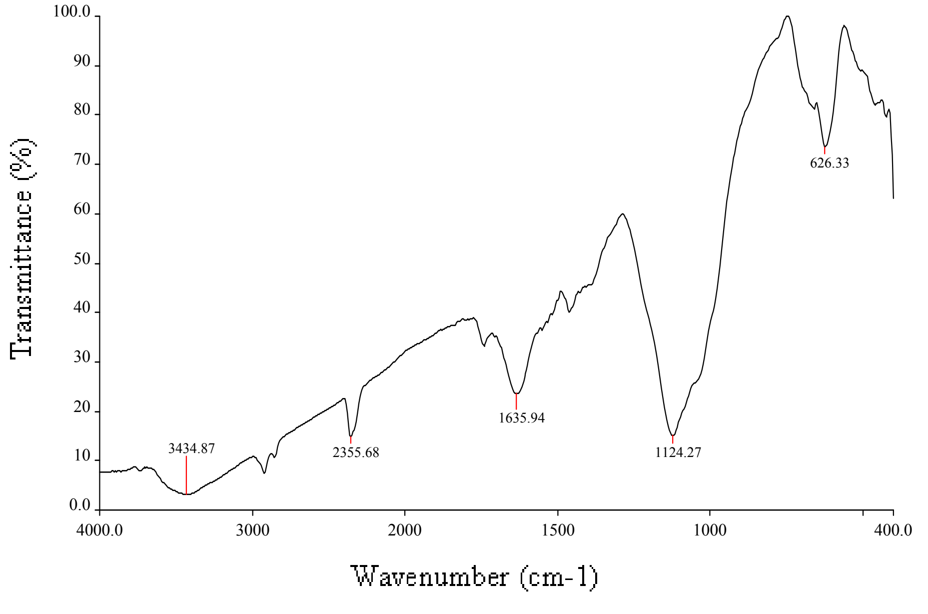


Fig. 7. FTIR spectrum of CdSe/Polythiophene nanocomposite.

3.6. Electrical Characterization of Thin Films

Table 1. Electrical characterization of thin films.

Thin Films	Condition	Electrical resistivity
Electrodeposited polythiophene / CdSe thin film	As-prepared	Surface resistance 34 KΩ
		Bulk resistance 15 KΩ
	Heated 200°C for half a hour.	Surface resistance 5.3 KΩ
		Bulk resistance 1.8 KΩ

The resistivity measurements were carried out for the as-deposited and annealed hybrid thin films. The Table 1 shows the electrical resistivity of as prepared and annealed CdSe/polythiophene nanocomposite hybrid thin films. The decrease in resistivity after thermal annealing may be due to the increase in effective grain size and also to the formation of S and Se vacancies [7].

4. Conclusion

In conclusion, it is summarized that CdSe/polythiophene nanocomposites are successfully synthesized at room temperature and pressure. In TGA/DTA we have shown that a small percentage of weight loss of nanocomposites at 400°C-500°C is mainly due to the presence of dopants. From UV-VIS spectroscopy, the band gap energy of CdSe/polythiophene nanocomposites is 1.65 eV.

The SEM images of nanocomposite shows that they are ideal materials having particle sizes < 200 nm. The EDX spectra showing that the powders are stoichiometric compositions. In XRD the broadening of peaks indicates the inorganic components are in nanometer scale. Some extra peaks in nanocomposites may be assignable to the dopants. In FTIR, it confirms that the successful polymerization of thiophene and the formation of CdSe/polythiophene nanocomposite take place leading to the existence of peaks of both inorganic and organic materials.

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