

## Study the Characteristics of CdSe\Polythiophene Nanocomposite By TGA/DTA, XRD, UV-VIS Spectroscopy, SEM-EDXA & FTIR

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**Abstract:** In this work 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).

[A K Singh, M Sakil, G S Roy. **Study the Characteristics of CdSe\Polythiophene Nanocomposite By TGA/DTA, XRD, UV-VIS Spectroscopy, SEM-EDXA & FTIR.** *Researcher* 2012; 4(12):16-20]. (ISSN: 1553-9865). <http://www.sciencepub.net/researcher>. 3

**Keywords:** Nanocomposite; Thermal analysis; X-ray diffraction; Ultraviolet-Visible spectroscopy; Fourier transform infrared spectroscopy; Scanning electron microscopy with energy dispersive X-ray analysis.

### 1. Introduction

A nanocomposite is as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material.[1] In the broad sense this definition also include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite differs markedly from that of the component materials. Size limits for these effects have been proposed [2], < 5 nm for catalytic activity, < 20 nm for making a hard magnetic material soft, < 50 nm for refractive index changes, and < 100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement. Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials. Jose-Yacamán et al. [3] investigated the origin of the depth of colour and the resistance to acids and bio-corrosion of Maya blue paint, attributing it to a nanoparticle mechanism. From the mid 1950s nanoscale organo-clays have been used to control flow of polymer solutions (e.g. as paint viscosifiers) or the constitution of gels (e.g. as a thickening substance in cosmetics, keeping the preparations in homogeneous form). By the 1970s polymer/clay composites were the topic of textbooks [4], although the term "nanocomposites" was not in common

use. In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibres (e.g. carbon nanotubes or electrospun fibres). The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement. Ajayan et al. [1] note that with polymer nanocomposites, properties related to local chemistry, degree of thermoset cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix. This large amount of reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macroscale properties of the composite. For example, adding carbon nanotubes improves the electrical and thermal conductivity. Other kinds of nanoparticles may result in enhanced optical properties, dielectric properties, heat resistance or mechanical properties such as stiffness, strength and resistance to wear and damage. In general, the nano reinforcement is dispersed into the matrix during processing. The percentage by weight (called mass fraction) of the nanoparticles introduced can remain very low (on the order of 0.5% to 5%) due to the low filler percolation threshold, especially for the most commonly used non-spherical, high aspect ratio fillers (e.g. nanometer-thin platelets, such as clays, or nanometer-

diameter cylinders, such as carbon nanotubes). In the present way we have synthesized the nanocomposite CdSe/Polythiophene characterized it and then studied its properties through TGA/DTA, XRD, UV-VIS Spectroscopy, SEM-EDXA.

### 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 [5]. 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 [6,7]. 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

The experimental work has been done in Centre for Materials for Electronics Technology (C-MET), Pune.

### 2.1 Synthesis of Polythiophene (PTh)

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 [7, 8].

### 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 [9].

### 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 coloured uniform film deposited on the copper substrate. Here copper substrate was connected to the cathode and graphite electrode was used as anode [10].

## 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<sub>α</sub> radiation (λ=1.5405 Å). The infrared spectra were recorded in the wave number range 400-4000 cm<sup>-1</sup> 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 is due to the solvent evaporation and there is a second weight loss is due to the expulsion of dopant i.e. Cl at 500°C and there is a steady plateau upto 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 CdSe and expulsion of dopant in polythiophene.

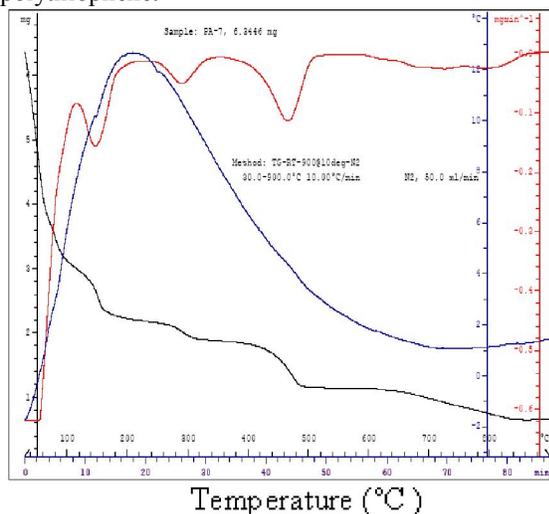


Figure 1: TGA/DTA of polythiophene

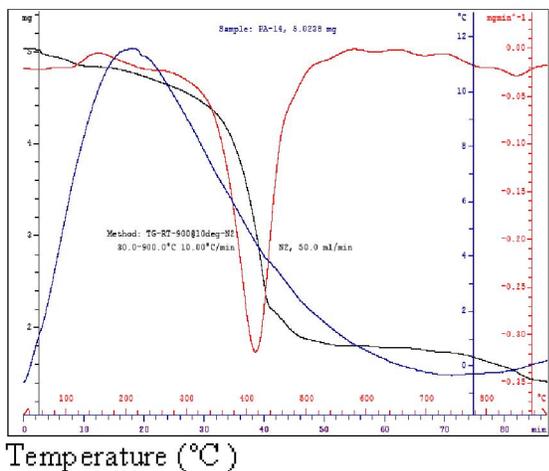


Figure 2: TGA/DTA of CdSe / Polythiophene nanocomposite

### 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.

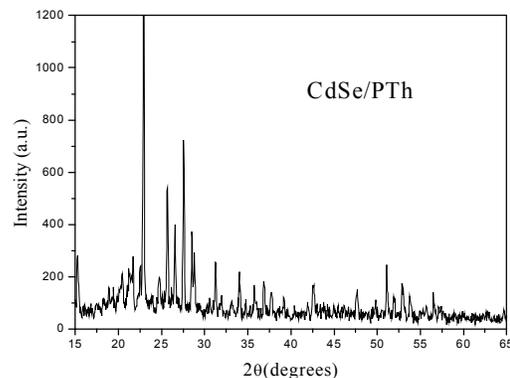


Figure 3: XRD pattern of CdSe / Polythiophene nanocomposite

### 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 750nm, 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.

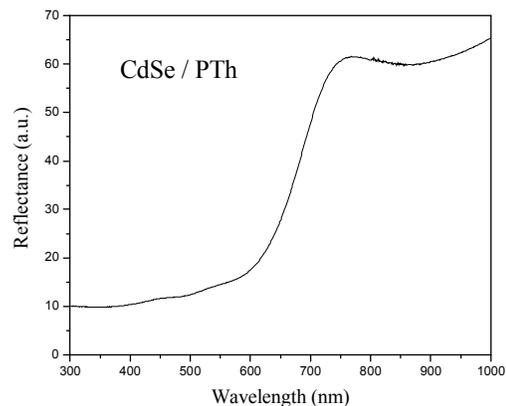
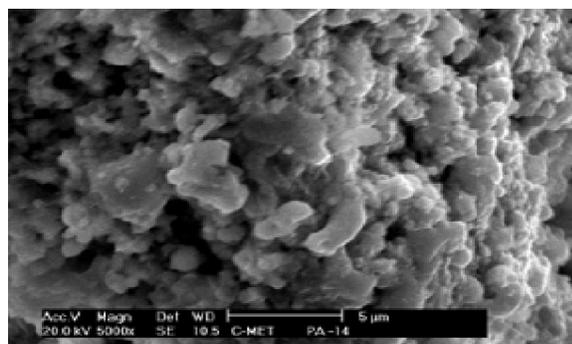


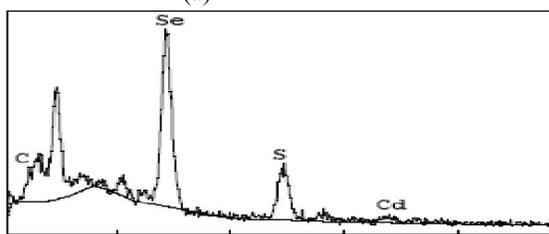
Figure 4: UV-VIS spectrum of CdSe / Polythiophene nanocomposite

### 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)

Figure 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<sup>-1</sup>) of polythiophene prepared by oxidative polymerization. The major peaks at 626.41 cm<sup>-1</sup>, 1088.42 cm<sup>-1</sup>, 1633.89 cm<sup>-1</sup> and 3418.93 cm<sup>-1</sup> 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<sup>-1</sup>) of CdSe/polythiophene nanocomposite. The peaks at 626.33 cm<sup>-1</sup>, 1124.27 cm<sup>-1</sup>, 1635.94 cm<sup>-1</sup>, 2355.68 cm<sup>-1</sup> and 3434.87 cm<sup>-1</sup> are due to the existence of different bonds in both CdSe and polythiophene in the nanocomposite.

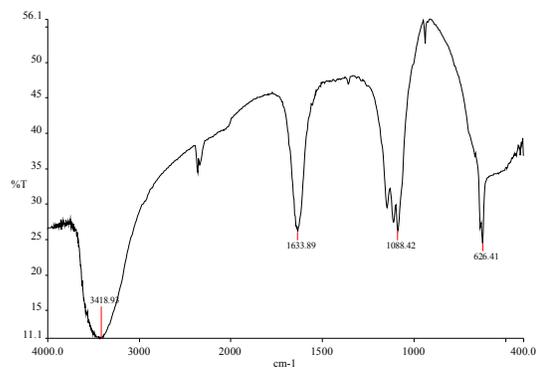


Figure 6: FTIR spectrum of Polythiophene

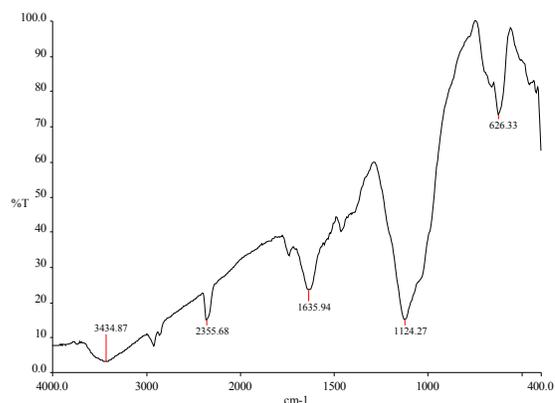


Figure 7: FTIR spectrum of CdSe/Polythiophene nanocomposite

### 3.6 Electrical Characterization of Thin Films:

The resistivity measurements were carried out for the as-deposited and annealed hybrid thin films. The above table 1 shows the electrical resistivity of as prepared and thermal 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 Se vacancies [11].

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 an hour.	Surface resistance 5.3 KΩ
		Bulk resistance 1.8 KΩ

#### 4. Conclusion

In conclusion, it is summarized CdSe/polythiophene nanocomposites are successfully synthesized in room temperature and pressure. In TGA/DTA, we have shown that a small percentage of weight loss of nanocomposites at 400°C-500°C mainly due to 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 due to the existence of peaks of both inorganic and organic materials.

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10/6/2012