

Study of the Properties of Nanocomposite Cadmium Sulphide (CdS)\Polythiophene(PTH) By TGA/DTA, XRD, UV-VIS Spectroscopy, SEM-EDXA and FTIR

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Abstract: In this work we have synthesized the Polythiophene by Oxidative Polymerization of Thiophene and then CdS\Polythiophene nanocomposite. After this we made a thin film by incorporating this nanocomposite and 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).

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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-Yacaman *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 CdS/Polythiophene characterized it and then studied its properties through TGA/DTA, XRD, UV-VIS Spectroscopy, SEM-EDXA and FTIR. Earlier we have studied the properties of nanocrystalline CdS by Sonochemical Route (Accepted by International Journal of Nanoscience and Nanotechnology).

2. Experimental work.

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

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 the above mixture was stirred 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 [5,6].

2.2 Synthesis of CdS / PTh Nanocomposite:

In a typical procedure, 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, 0.1 M of EDTA and 0.1 M of sodium thiosulphate solutions were prepared in another part. Then these solutions were mixed slowly with constant stirring for 1 hour and irradiated at 20 KHz frequency for 1 hour in an ultrasonic bath. The products of brown coloured precipitates were collected and then washed thoroughly with ethanol. The final products were dried in a vacuum oven at 70°C for 10 hours and ground to get CdS/polythiophene nanocomposite powder.

2.3 Preparation of Thin Film (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 CdS/polythiophene film, 0.1 M of thiophene and 0.3 M of lithium perchlorate were added in one of the above solution and 0.1 M of cadmium nitrate, 0.1 M of EDTA and 0.1 M of sodium thiosulphate were added in another solution under constant stirring. These

solutions were added together slowly and applied 1.2-1.5 mA current for electrodeposition. After 75 minutes a brown coloured uniform film was deposited on the copper substrate. Here copper substrate was connected to the cathode and graphite electrode was used as anode [7].

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°C/minute in diffraction angle 2θ range from 10°C to 80°C and CuK α radiation ($\lambda=1.5405 \text{ \AA}$). 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 exhibits the TGA/DTA of CdS/polythiophene nanocomposite. It shows that the initial weight loss is due to the solvent evaporation, the second weight loss is due to phase change. After 400°C, there is loss of weight due to expulsion of dopant and there after the minimum weight loss is due to the degradation of CdS and polythiophene.

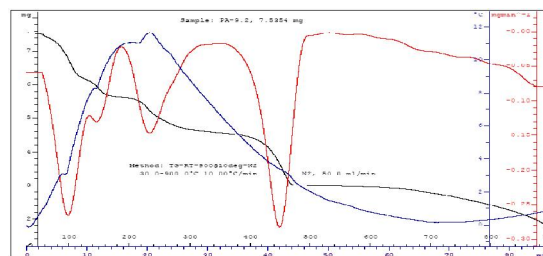


Figure 1: TGA/DTA of CdS / Polythiophene nanocomposite

3.2 X-Ray Diffraction Analysis:

Figure-2 shows the XRD pattern of CdS/polythiophene nanocomposite. Here the more diffraction peaks are due to the presence of polythiophene in CdS/polythiophene nanocomposite. It confirms the successful polymerization of thiophene monomer and the formation of nanocomposite material.

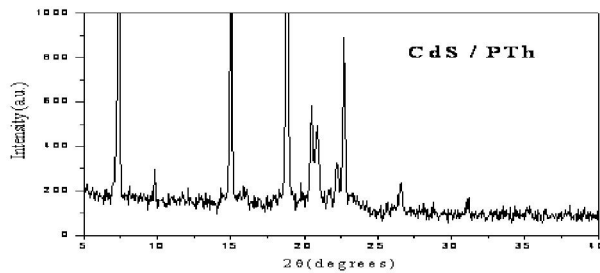


Figure 2: XRD pattern of CdS / Polythiophene nanocomposite

3.3 Ultraviolet–Visible(UV-VIS) Spectroscopy:

Figure-3 shows the UV-VIS reflectance spectrum of CdS/polythiophene nanocomposite. From the spectrum the absorption band edge of CdS/polythiophene nanocomposite is around 730nm, which corresponds to the band gap energy $E_g = 1.7$ eV.

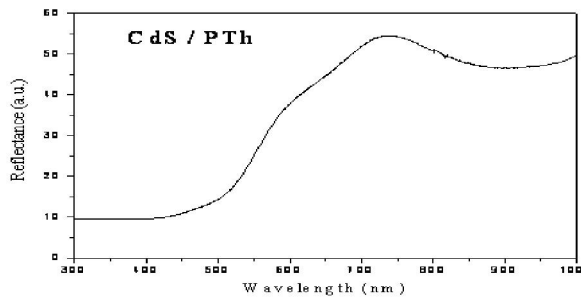


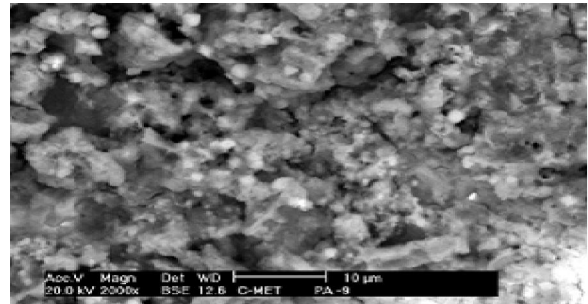
Figure 3: UV-VIS spectrum of CdS / Polythiophene nanocomposite

3.4 Scanning Electron Microscopy With Energy Dispersive X-Ray Analysis (SEM-EDXA):

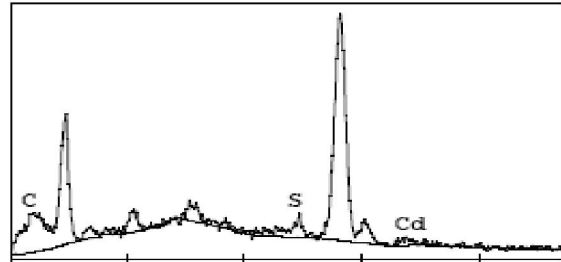
Figure 4 (a) is the SEM image of CdS/polythiophene nanocomposite. This SEM image clearly indicates that the CdS nanoparticles were immersed and well separated in polythiophene matrix. Figure 4 (b) is the EDX spectrum of CdS/polythiophene nanocomposite. Table-1 gives the element composition of CdS/polythiophene nanocomposite. This shows that the prepared nanocomposites are stoichiometric in composition.

Table-1: (EDX element composition table of (c) CdS/PTh)

EDAX ZAF Quantification Element Normalized		
Element	Wt %	At %
C K	82.51	95.70
S K	6.86	2.98
CdL	10.64	1.32
Total	100.00	100.00



(a)



(b)

Figure 4: SEM image of (a) CdS/PTh nanocomposite EDX spectra of (b) CdS/PTh nanocomposite

3.5 Fourier Transform Infrared Spectroscopy:

Figure 5 shows the FTIR spectrum in the frequency range (400–4000 cm^{-1}) of CdS/polythiophene nanocomposite. The major peaks at 630.29 cm^{-1} , 1089.82 cm^{-1} , 1374.73 cm^{-1} , 1634.48 cm^{-1} and 3380.52 cm^{-1} are due to the presence of different bonds in both CdS and polythiophene in the nanocomposite.

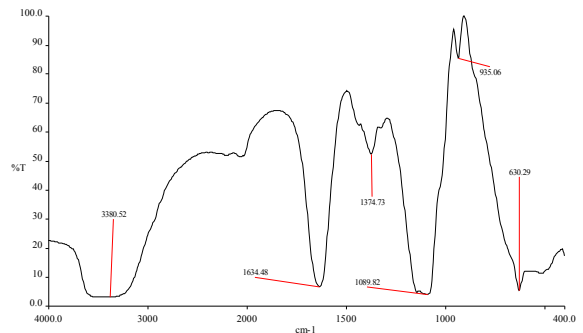


Figure 5: FTIR spectrum of CdS/Polythiophene nanocomposite

3.6 Electrical Characterization of Thin film

The resistivity measurements were carried out for the as-deposited and annealed hybrid thin films. The table-2 shows the electrical resistivity of as prepared and thermal annealed CdS/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 vacancie [8].

Table - 2

Thin Films	Condition	Electrical resistivity
Electrodeposited polythiophene / CdS thin film	As prepared	Surface resistance 29 K Ω
		Bulk resistance 11 K Ω
	Heated 200°C for half an hour.	Surface resistance 4.6 K Ω
		Bulk resistance 1.5 K Ω

4. Conclusion

In conclusion, it is summarized that CdS/polythiophene nanocomposite is 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 CdS/polythiophene nanocomposite is of 1.7 eV. This indicates, the as prepared CdS in the resulting polymer matrix shows quantum size effect. 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. The SEM images of nanocrystals and nanocomposites are shows that, they are ideal materials having particle sizes < 200 nm. The EDX spectra showing that the powders are stoichiometric compositions. In FTIR, it confirms that the successful polymerization of thiophene and the formation of CdS/polythiophene nanocomposite due to the existence of peaks of both

inorganic and organic materials We observed that, the electrical conductivity of as-prepared films have less conductivity than thermal annealed films. This is because of the increase in grain sizes of the materials and becomes more crystalline.

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