CdSe reinforced polythiophene nanocomposites as excellent materials for diode applications

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Abstract. In the present work, nano-rods of mixed semiconductors were reinforced to conducting polymers to get their composites. CdSe semiconductor nanoparticles were reinforced into the conducting polymer polythiophene (PTh) at room temperature following an oxidation polymerization method. This method was rapid, cost effective and produced larger yield of polymer. X-ray diffraction (XRD) data of composites revealed that the crystallite size was of the order of 45–47 nm. Field emission scanning electron microscopic (FESEM) analysis showed horizontal cross section of CdSe nanoparticles after they were embedded into the PTh matrix. In the composites phase, the nano-rods of CdSe were seen lying over the PTh matrix. UV-Vis spectral studies showed reduction in the energy band gap from 3.05 eV of native PTh to 2.26 eV of PTh/CdSe nanocomposites. I-V plots of nanocomposites comprising of p-type PTh and n-type CdSe showed similar characteristics as those of the junction diode. The DC conductivity and short circuit current (J_{sc}) of PTh/CdSe nanocomposites indicated drastic changes as compared to those of the pure PTh. Since, I-V plot of nanocomposites phase resembled well with that of a junction diode, the as-synthesized materials has potential to be used in diode applications.

Keywords: polymer nanocomposites, nanoparticles, polythiophene, conductivity, diode

1. Introduction

Polymers are often known for their lower conductivity. Certain polymers, due to the presence of delocalized π -electron systems, show charge mobility and enhanced polarization and called as conducting polymers. The conducting polymers have long chain of conjugated molecules having σ and π bonds [1]. These polymers are light weight, flexible, cost-effective, moderately conducting and easily polarizable [2–4]. Among the family of conducting polymers such as polythiophene (PTh), polyaniline (PANI), polypyrrole (PPy), etc. the PTh has received special attention due to its low production cost, excellent thermal, chemical and environmental stability, high electrical conductivity and facile synthesis [5]. PTh consists of linear chains of thiophene (Th) molecules and exhibits conduction property when electrons are

added or removed from the π -conjugated orbitals via doping [6–14]. PTh has σ and π bonds and is an intrinsically conducting polymer having large π -conjugated structure, flexibility, high conductivity, and ease of doping. A number of derivatives of this conducting polymer have also been reported in literature [15–19].

Semiconductors are materials which show conductivity and their conductivity can be tailored with the addition of either trivalent or pentavalent impurities. Moreover, semiconductors such as CdSe has a band gap that is best suited for materials like nanocomposites. In recent years, photovoltaic devices, solar cells, and junction diodes have been fabricated by judicious combination of p-type conducting polymers and n-type inorganic semiconductor nanoparticles [10]. Due to high electron mobility in inorganic

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semiconductors and charge transfer mechanism in conducting polymers, conducting polymer-inorganic nanocomposites heterojunctions have been used in various applications, such as photovoltaic cells, actuators, electrolytes membrane, solar cells, light emitting diodes, optoelectronics devices [20–22] lithium ion batteries, sensors, and super-capacitors [23–25]. Nanoparticles of CdSe are known to improve the electrical conduction properties of conducting polymers. Their association with conduction polymers provides new materials which possess properties of both of its native constituents. Moreover, some of their properties are so much enhanced that they become superior to polymers and semiconductors. CdSe is an inorganic semiconductor having a direct band gap of 1.74 eV [26, 27]. The quantum dots (QDs) of CdSe are frequently used as inorganic nanosized materials due to their excellent physical, electronic, optical and structural properties [28]. II-IV semiconductor CdSe QDs are inorganic particles having size less than 10 nm. Particles of CdSe are quantum confined because their size is less than the Bohr radius which results in an increased electrical performance of nanoparticles [29, 30]. Acharya *et al.* [31] studied the optical and structural properties of PTh/CdSe nanocomposites and found that the energy band gap of PTh/CdSe nanocomposites is higher than that of the native CdSe. Furthermore, they also measured the electrical properties of as-prepared nanocomposite and published their results elsewhere [32]. AlFannakh *et al.* [33] investigated electrical and kinetic thermal analysis of polyaniline/poly(vinyl alcohol) magnetite nanocomposites film and found enhancements in thermal stability, activation energy and electrical conductivity of PANI/PVA magnetite (Fe_3O_4) nanocomposite as compared to those of the PANI/PVA blends. In the present work, CdSe nanoparticles have been synthesized through solution route and PTh was obtained by polymerization of thiophene. Both of them were mixed to get the CdSe reinforced PTh nanocomposites and their electrical properties have been investigated.

2. Experimental techniques

2.1. Materials

The chemicals used for the synthesis of nanocomposites were cadmium acetate dihydrate ($(\text{CH}_3\text{COO})_2\text{Cd}\cdot 2\text{H}_2\text{O}$) (98%), selenium (Se) (metal) powder (99%), thiourea (99%), thiophene (99%), ferric chloride (FeCl_3) (96%), chloroform (CHCl_3)

(99.5%), triethanolamine (TEA) (97%) and nitric acid (HNO_3) (71%). All chemicals were procured from Thermo Fisher Scientific India Pvt. Ltd. & Central Drug House, New Delhi, India.

2.2. Synthesis of polythiophene

PTh was synthesized by following an oxidation polymerization method. In a typical experiment, 1.18 M Th was added into 40 ml chloroform to prepare the monomer solution which was further stirred and ultra-sonicated for 10 min. FeCl_3 (0.5 M), used as an oxidant, was added to 40 ml chloroform and stirred for 15 min to produce a clear solution. The prepared oxidant solution was added dropwise into the Th solution for polymerization. The resulting solution was further ultrasonicated at 20 KHz frequency and after completion of the ultrasonication, the solution was kept at 4°C for 6 h to complete the polymerization reaction. After completion of the polymerization process a viscous solution was obtained this was filtered, and washed several times with distilled water and acetone to remove the impurities and un-reacted chemicals. The material so obtained was dark brown in color. After drying it at room temperature for 2 days, the black colored solid material of PTh having 90–95% yield was obtained which was crushed to powder, and stored in airtight glass tubes for subsequent studies.

Mechanism of polymerization of thiophene

The formation of PTh follows an oxidation polymerization mechanism as given below (Equation (1)–(4)):

As shown in Equation (1), thiophene molecule is oxidized by the ferric ion to produce a radical cation ($\text{Th}^{\bullet+}$) which further dimerizes to give a dimer of thiophene ($\text{Th}-\text{Th}$) releasing two protons (Equation (2)). This dimer is further oxidized by ferric ion to form dimer ion- radical of thiophene ($\text{Th}-\text{Th}^{\bullet+}$) which subsequently reacts with thiophene ion-radical to give a trimer ($\text{Th}-\text{Th}-\text{Th}$). In general, the whole mechanism may be presented as given below (Equations (5), (6)):

Thus, these reactions lead to the formation of PTh.

2.3. Synthesis of CdSe nanoparticles

CdSe nanoparticles were prepared by the co-precipitation method as shown in Figure 1. In this method, few drops of HNO_3 were added to 2.53 M of Se metal powder and, thereafter, 20 ml double distilled water was added dropwise into the above mixture. This solution was refluxed at 9°C for 13 h under constant stirring and the solution was filtered and allowed to cool in dark. This was marked as solution 'A'. Another solution 'B' was prepared by mixing 2 M thiourea and 10 ml distilled water by stirring for 30 min. Another solution 'C' was prepared by mixing 1.5 M cadmium acetate and 20 ml distilled water and stirred for 1 h. Thereafter, the solution 'B' was added dropwise into the solution 'C' to get cadmium sulphide. Afterwards, the Se solution, that is solution 'A', was slowly added into the cadmium sulphide solution. On addition of Se solution into the CdS solution, the color of the resulting solution turns milky within 10 second. Soon after few seconds it turns yellow, after few minutes to orange, then to red, and finally it turns dark red. For the synthesis of CdSe nanoparticles, thiourea was used as a stabilizing agent or precursor which increases the stability of the CdSe nanoparticles [34]. In a typical experiment, 3 mL TEA was added to final solution to control the growth of nucleated particles. The pH of the above solution was maintained at 12 by adding aqueous ammonia solution drop by drop. The pH was monitored continuously, and if there was any fluctuation in the pH values, it was adjusted by adding additional amount of aqueous ammonia. The precipitate of CdSe was separated out and centrifuged at

9000 rpm for 10 min. The centrifugation process was repeated 4–5 times and thereafter, the material was isolated and washed several times with distilled water, and finally with acetone. The solid material so obtained was dried in hot air oven at 200°C for 6 h. Then, it was taken out and crushed properly to get powdered CdSe and stored in airtight glass tubes. From the present method 60–70% yield of CdSe was obtained. The reactions involved in the formation of CdSe may be given as below (Equation (7)–(11)):

The above reactions explain the mechanistic formation of CdSe nanoparticles.

2.4. Synthesis of PTh/CdSe nanocomposites

PTh/CdSe nanocomposites were prepared by following an oxidation polymerization method as shown in Figure 2. At first, 1.18 M solution of Th was prepared and 70% of Th solution was irradiated with 20 kHz frequency for ultrasonication. Thereafter, 1.2 g of CdSe nanoparticles were added into the ultrasonicated Th solution, stirred, and again ultrasonicated at 20 kHz frequency to obtain a homogeneous suspension.

Now, FeCl_3 (0.5 M) was dissolved in 40 ml chloroform and stirred to prepare the oxidizing agent solution. This solution was added drop wise into the Th/CdSe solution prepared as above with continuous

Figure 1. Different stages during synthesis of CdSe nanoparticles.

Figure 2. Synthesis of PTh/CdSe nanocomposites.

stirring. The resulting solution was kept at 4°C for 12 h to complete the polymerization process. The material so obtained was dried at room temperature for 2 days till it turns into black. The material obtained was PTh/CdSe nanocomposites which were obtained in larger yield and in lesser time.

The use of ferric chloride provides iron in the solution in addition to the cadmium (Cd) and Se. The ionic radii of Cd, Se and Fe^{3+} ions are in the order of 1.71, 1.22 and 0.6 Å, respectively which reveals that there is a greater probability of association of Cd with Se rather than with iron. The EDAX spectra of the obtained material are shown in Figure 4 which confirms the presence of Cd, Se and Fe in different proportions.

2.5. Fabrication of polymer – nanocomposites pellets

The prepared powders of native PTh and PTh/CdSe nanocomposites were transformed into pellets by subjecting them to a pressure of 2000 lbs/inch² using hydraulic press (Spectra lab model SL-89). The pressure was applied for 20 sec. The as-obtained pellets were subsequently used for their electrical and dielectric measurements.

2.6. Characterization techniques

In order to characterize the as-prepared samples, field emission scanning electron microscopy (FESEM), and energy dispersive X-ray analysis (EDAX) were performed using Carl Zeiss SIGMA 2-12 field emission scanning with electron microscope EDAX λ-METER, Germany. DC conductivity measurements were performed using an electrical probe station (Make: Ecopia, Model: EPS500) and a measuring unit (Make: Keithley, Model: 2450), Cleveland, Ohio, U.S. Dielectric study was done using a HIOKI-3532 LCR Hi-tester, Japan. XRD measurements were per-

formed on Bruker D8-Discover system, UK at Synchrotrons Utilization Section, RRCAT, Indore (MP), India. The radiation used for the measurements was Cu- K_{α} . The wavelength of Cu- K_{α} radiation was $\lambda = 1.5406$ Å. Optical studies were performed on a Shimadzu UV-Vis spectrophotometer (UV-2450), Japan, over the wavelength range 200 to 900 nm.

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

The XRD spectra of native PTh, pure CdSe and PTh/CdSe nanocomposites are shown in Figure 3. The XRD spectra of native PTh shows a broad diffraction peak at $2\theta = 17.47^\circ$ corresponding to (001) plane which is associated with π - π stacking structure in PTh chains and suggests for its partially amorphous nature. The similar observation has also been reported by Najar *et al.* [22]. XRD spectra of native CdSe represent diffraction peaks at 2θ values of 25, 42, 45 and 49° , respectively. The planes corresponding to these

Figure 3. XRD spectra of native PTh, pure CdSe, and PTh/CdSe nanocomposites.

peaks are (111, 220, 311), and (103), respectively. The (111, 220, 311) peaks correspond to cubic phase whereas the (103) plan corresponds to hexagonal phase. These peaks match well with those of JCPDS file (Card No. 19-0191, 77-2307 and 65-2891). The XRD spectra of composites show peaks at 26, 41 and 49°, indexed as (111, 220, 311), respectively, corresponding to cubic phases whereas peaks at 2θ values 22, 30, 36, 42, 49 and 52° indexed as (100, 101, 102, 110, 103, 112) correspond to hexagonal phase. All these peaks match well with the JCPDS card no. 77-2306, 77-2307, 65-2891. In the XRD spectra of the composite several extra peaks are observed at 2θ values 31, 32, 34, 45° indexed as (220, 104, 311, 400), respectively which show the presence of iron (Fe) in composites. The entire iron peaks match well with the JCPDS card no. 98-000-0064, 74-0748, 39-1346, 01-089-8103 [31–33]. Fe present in composites, due to FeCl₃, was used as a polymerization initiator. The prominent peak (001) in PTh is broad and represents its partially amorphous nature [35, 36]. On doping with CdSe the peak becomes sharp and changes to polycrystalline. The lattice constants of CdSe in PTh/CdSe nanocomposites were found to be $a = 6.1$ Å for cubic phase, $a = 3.936$ Å, and $c = 6.634$ Å for its hexagonal phase.

The crystallite size of nanocomposites was calculated using Debye Scherer's formula (Equation (12)) [37, 38]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (12)$$

where D is the crystallite size; K is the Scherer's constant (0.9); λ is the wavelength of radiation used (1.5406 Å); θ is the Bragg's angle and β is the full

width of half maximum (FWHM) measured in radian. Since PTh is amorphous in nature, the particle size was not calculated. The crystallite size of pure CdSe was calculated from its XRD spectra and found to be about 3.0 nm. The average crystallite size of the nanocomposite, when CdSe was added in to the PTh matrix, was calculated to be 47 nm for cubic phase and 45 nm for hexagonal phase [39]. The value of crystallite size, lattice parameters, miller indices, prominent peaks and other structural parameters of the present material has been measured and calculated and the results are summarized in Table 1.

The XRD results indicate that amorphous nature of native PTh changes into semi crystalline when CdSe was reinforced into the PTh matrix [40].

3.2. Field emission scanning electron microscope (FESEM) analysis

Surface morphology of native PTh and PTh/CdSe nanocomposites are shown in Figure 4 and 5, respectively. The surface morphology of native PTh can be seen in Figure 4. It is clear from the images that the PTh particles are perfectly spherical in shape having different dimensions. Some of the particles have nanometer size, whereas some of them are in micrometer range. In fact, both the micrographs reveal that the morphology of the particles seem spherical in shape and are well separated from each other having dimension in the range of 500 nm to 1 μm. When CdSe nanoparticles are added into the PTh matrix, the spherical morphology gets distorted, as clear from the Figure 5. Horizontal cross sections of CdSe nanoparticles which are arranged in parallel manner are clearly visible. Hexagonal rods like structures are formed on the PTh matrix surface. Similar spherical

Table 1. XRD data of native PTh, CdSe and PTh/CdSe nanocomposites.

Parameters	Pure PTh	Pure CdSe	PTh/CdSe nanocomposites
Crystal structure	Partially amorphous	Cubic and hexagonal	Cubic and hexagonal
Prominent peak at 2θ [°]	17.47	25 (Cubic) 49 (Hexagonal)	22 (Cubic) 42, 52 (Hexagonal)
Inter-planer spacing, d [Å]	3.956	3.48 (Cubic) 1.822 (Hexagonal)	3.93 (Cubic) 2.12, 1.732 (Hexagonal)
FWHM, β [°]	0.21	2.783 (Cubic) 1.826 (Hexagonal)	0.145 (Cubic) 0.423, 0.169 (Hexagonal)
Miller indices $[h k l]$	[001]	[111] (Cubic) [103] (Hexagonal)	[100] (Cubic) [110], [112] (Hexagonal)
Crystallite size [nm]	–	3 (Cubic) 5 (Hexagonal)	47 (Cubic) 45 (Hexagonal)
Lattice parameter, a [Å]	–	$a = 6$ (Cubic) $a = 3.936$ & $c = 6.634$ (Hexagonal)	$a = 6.1$ (Cubic) $a = 3.936$ & $c = 6.634$ (Hexagonal)

Figure 4. FESEM images of pure PTh particles with magnification (a) $1 \cdot 10^{-6}$, (b) $1 \cdot 10^{-6}$.

Figure 5. FESEM images of PTh/CdSe nanocomposites with magnifications (a) $1 \cdot 10^{-6}$, (b) $1 \cdot 10^{-6}$.

morphology of PTh particles have also been reported by Pourabbas *et al.* [41].

3.3. Elemental compositional study (EDAX)

Elemental compositional study of native PTh and PTh/CdSe nanocomposites were also performed and the results obtained are shown in Figure 6, respectively. EDAX spectra of native PTh shows the presence of elements C, O, S, Cl, and Fe. Carbon and sulphur show the presence of PTh whereas Cl and Fe are present since FeCl_3 was used as an oxidative polymerization initiator and CHCl_3 as a solvent. EDAX spectra of PTh/CdSe nanocomposites confirm the presence of C, O, Se, S, Cl, Cd, and Fe. Similarly, Cd and Se confirm the presence of CdSe in the PTh matrix.

Khanmohammadi *et al.* [5] have reported the presence of Fe in addition to Mn, O, S, C and Cl in the EDAX spectra of PTh/ MnO_2 nanocomposites. Ozkazanc [10] also reported EDAX spectra of PTh

with different doping [%] of zirconium (Zr). EDAX spectra show Fe (21.12) and Zr (0.650) [wt%]. The authors also used FeCl_3 as an oxidant for the polymerization purpose. Similar type of EDAX spectra were also observed in the present study.

3.4. D.C. electrical measurements

3.4.1. Current-voltage plots

Electrical measurements of native PTh and PTh/CdSe nanocomposites were conducted using the two probe method. Current-voltage characteristics of PTh bulk (pellet) at room temperature are shown in Figure 7a. The potential was varied from 0 to 5 V and -5 to 0 V, respectively so as to cover both the forward and the reverse bias. It was observed that the I-V characteristics of PTh are almost symmetrical with respect to Y-axis. It can be seen that in the beginning, the current increases linearly with the applied voltage but at later stage of the applied voltage, the increase in current turns non-linear. This non-linear increase of

Figure 6. (a) EDAX spectral analysis of pure PTh, (b) EDAX spectral analysis of PTh/CdSe nanocomposites.

current with applied voltage can be related to the conduction mechanism in PTh [22]. In PTh, the conduction is carried out by free charge carriers ‘polarons and bipolarons’. The number of polarons and bipolarons increases with the increase in applied voltage. This increase in charge carriers increases the current through the sample. Similar I-V plots of PTh at different temperatures have also been reported by Tiwari *et al.* [42].

The current-voltage characteristics of PTh/CdSe nanocomposite at room temperature are shown in Figure 7b. Since PTh is a p-type material and CdSe is n-type, the pellets of PTh/CdSe nanocomposites are expected to behave like P-N diode. In order to have forward bias, the one face of composite material pellet was made positive with respect to its other face. At lower voltage, the current rises due to the motion of polaron and electrons or holes. This results

Figure 7. (a) I-V characteristics of pure PTh, (b) I-V characteristics PTh/CdSe nanocomposites.

in minimization of the width of depletion layer at the interface in between the pellet and the contact probe. In the reverse bias, width of the depletion layer increases due to high barrier potential. Here the current is just because of minority charge carriers which produce small current [18, 22, 43]. Similar electrical conduction in CdS/polyaniline heterojunction has also been reported by Patidar *et al.* [40] and Singh *et al.* [44] respectively.

3.4.2. DC conductivity plot

DC conductivity plots of native PTh and its nanocomposites PTh/CdSe are shown in Figure 8. It is clear from the plots that the DC conductivity initially decreases rapidly with increasing potential and finally attains a constant value. The initial decrease in conductivity can be related to the mutual interaction between the charge carriers which enhances the resistivity. At higher potential, however, the induced electric field causes the net force to become operative and hence the conductivity attains a constant value. In composites, the order of conductivity is greater in comparison to that in the native PTh which is expected also because of the presence of semiconductor CdSe. On comparing the EDAX spectra of pure PTh and its composite with CdSe, it is clear that the impurities of Fe, Cl, S, C and oxygen which are present in pure PTh are also present in the composite. The extra elements which are present in the composite are Cd and Se, whose presence is reflected in EDAX results. Therefore, the enhanced conductivity in the composite phase might be due to the presence of Cd and Se. The nature of variation of conductivity in both the materials remains same as similar mechanism of conduction is operative in composite

materials. The increased hindrance in the composite puts obstacles in the charge transfer to inter and intra chains through hopping process. Finally, at higher potential the DC conductivity becomes constant with respect to the applied voltage. Kaneto *et al.* [45] also reported variation in DC conductivity with temperature. Nasrollahzadeh *et al.* [46] have reported an enhancement in electrical conductivity of PTh-carbon nanocomposites with increasing temperature in comparison to pure PTh.

The DC conductivity of composites was calculated using the formula reported in the literature [47, 48]. It is observed that when CdSe is mixed with PTh matrix, the DC conductivity increases from 10^{-9} to $10^{-7} \text{ S} \cdot \text{cm}^{-1}$. The observed order of conductivity in composite phases lies in the range of conductivity of semiconducting ions like Cd and Se. Thus, it can be inferred that the increased conductivity is due to the presence of Cd and Se ions [49–51]. The conductivity and resistivity are related by the relation (Equation (13)):

$$\sigma = \frac{1}{\rho} \quad (13)$$

where ρ is the resistivity of the material defined by the formula [48] given below (Equation (14)):

$$\rho = \left(\frac{V}{I}\right)\left(\frac{A}{l}\right) \quad (14)$$

where A is the surface area and l is the thickness of the pallet [48]. The enhanced DC conductivity of PTh/CdSe in comparison to that of the native PTh shows that the nanocomposites may be used for device fabrication that may be suitable for energy storage such as in batteries and diodes. Kamat and Chandraprabha have also reported the DC conductivity of PTh at different potentials [18, 44, 52].

3.4.3. Current density analysis

The variation in current density for native PTh and PTh/CdSe nanocomposites in forward bias (0–5 V) are shown in Figure 9. It is clear from the figure that the current density in the native PTh and composites increases with increasing voltage in the forward bias which might be due to the internal charge transfer and inter molecular interaction between the polaron-polaron, polaron-bipolaron and polaron-free charge carriers, as reported by Kamat *et al.* [52] and Singh *et al.* [54]. In the reverse (–5 to 0 V) bias also, the current density in the native PTh and PTh/CdSe

Figure 8. DC Conductivity vs. voltage of native PTh and PTh/CdSe nanocomposites.

Figure 9. (a) J - V plot of native PTh, (b) J - V plot of pPTh/CdSe nanocomposites.

nanocomposites increases which might be due to migration of polarons and minor charge carriers of CdSe. The short circuit current (J_{sc}) increases from 10^{-5} to $3.5 \cdot 10^{-3} \mu\text{A} \cdot \text{cm}^{-2}$ when CdSe was reinforced into the PTh matrix. This might be due to the increased PTh/CdSe interface area and improved conduction path for charge extraction. Because of the enhancement in short circuit current (J_{sc}) in the nanocomposites phase, the nanocomposites may be used for fabrication of energy storage devices and in various potential applications in electronic industries [23, 53, 55]. Seidler and his co-workers [56], have reported that the current density of poly(3-alkylthiophene) (P3HT) film increases with increasing voltage which might be due to intra-chain charge transfer, intermolecular interaction, π -conjugation length etc. They have also measured short circuit current (J_{sc}) of (P3HT) between 8 to $10 \text{ mA} \cdot \text{cm}^{-2}$ for the fabrication of photovoltaic solar cell. Vijeth *et al.* [57], have fabricated PTh/ Al_2O_3 nanocomposites based asymmetric supercapacitor (ASC) as an anode electrode and charcoal as a cathode electrode and also measured its maximum current density for ASC device application. Nasrollahzadeh *et al.* [46], have studied structural, electrochemical and electrical analysis of polythiophene-carbon nanocomposite materials for fuel cell applications. They have also

measured the current density using cyclic voltamogram method. The reported average current density was of the order of $10^{-3} \text{ mA} \cdot \text{cm}^{-2}$. The electrical parameters of pure PTh and its nanocomposites have been measured and calculated and the results are summarized in Table 2.

3.5. UV-Visible spectroscopic analysis

The optical properties of pure PTh and PTh/CdSe nanocomposites were analyzed by UV-visible spectroscopy as shown in Figures 10 and 11, respectively. Figure 10 shows the strong absorption peak at 240 nm for native polythiophene might be due to π - π^* transition of the conjugated structure of thiophene unit. This strong absorption peak is slightly shifted towards higher wavelength side (260 nm), well within the UV region, in the case of PTh/CdSe nanocomposites. The absorption spectra show broad-

Figure 10. Absorption spectra of pure PTh and PTh/CdSe nanocomposites.

Table 2. Electrical parameters of pure PTh and PTh /CdSe nanocomposites.

Electrical parameters	Pure PTh	PTh/CdSe nanocomposites
Current	$4.5 \cdot 10^{-11} [10^{-2} \text{ nA}]$	$2.5 \cdot 10^{-8} [10^{-2} \mu\text{A}]$
DC conductivity	$10^{-9} \text{ S} \cdot \text{cm}^{-1}$	$10^{-7} \text{ S} \cdot \text{cm}^{-1}$
Short circuit current	$10^{-5} \mu\text{A} \cdot \text{cm}^{-2}$	$3.5 \cdot 10^{-3} \text{ mA} \cdot \text{cm}^{-2}$

Figure 11. (a) Tauc plot of pure PTh, (b) Tauc plot of PTh/CdSe nanocomposites.

ening whose edge can be seen to be shifted towards higher wavelength side, when CdSe(S) nanoparticles are reinforced into the PTh matrix. This spectral shift might be caused by the presence of CdSe (S) particles in the PTh matrix when PTh/CdSe(S) nanocomposites are formed, as reported by Vijet *et al.* [37] and Kamat *et al.* [52].

HOMO stands for ‘Highest Occupied Molecular Orbital’ and LUMO stands for ‘Lowest Unoccupied Molecular Orbital’. LUMO is higher in energy than that of the HOMO. The HOMO-LUMO gap is that where the most likely excitation can occur. The HOMO-LUMO gap is determined by the HOMO of the donor and the LUMO of the acceptor. Amna *et al.* [17] and Facchetti [55] have, has reported theoretically calculated the band gap of P3HT (Polythiophene family) for the LUMO level in the range of 3–4.7 eV and for HOMO level of the order of 4–5.5 eV. HOMO-LUMO gap strongly depends on the degree of electron delocalization. HOMO-LUMO gap for the PTh and PTh/CdSe nanocomposites, can be obtained from absorption maxima and absorption onset, respectively.

The energy band gap (E_g) was calculated from the absorption spectra using the Tauc relationship (Equation (15)):

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (15)$$

where A is a constant, α is the absorption coefficient, $h\nu$ is the photon energy, (E_g) is the optical band gap of the material and an exponent n , which depends on the type of transition. The n may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct,

Table 3. Pure PTh and PTh/CdSe nanocomposites.

	Equation	Parameters	Numerical values	Standard error
Pure PTh	$y = a + bx$	Intercept	–14.57453	0.06905
		Slope	6.86833	0.02822
PTh/CdSe	$y = a + bx$	Intercept	–118.2135	0.92242
		Slope	38.46637	0.26191

allowed indirect, forbidden direct and forbidden indirect transitions, respectively [29, 58, 59].

Figure 11 shows the plots of $(\alpha h\nu)^2$ vs. $h\nu$ for native PTh and PTh/CdSe nanocomposites, respectively. Linear fit by extrapolating the linear portion over the set of data (X–Y) are shown in inset. The characteristic parameters of the tangent line drawn in the linear fit are summarized in Table 3.

Using the above equation given in Table 3, the intercept and gradient were calculated. The value of intercept gives the energy band gap. By extrapolating the linear portion the band gap was calculated to be 3.05 eV for PTh, and 2.26 eV for composite, respectively. The reduction in energy band gap of PTh/CdSe composite may lead to an increased conductivity which is a desirable property for employing the material in optical, optoelectronics, LED devices etc.

4. Conclusions

The present work deals with the synthesis of conducting polymer (PTh), semiconductor (CdSe), and their nanocomposite materials which deserve to be proposed for diode applications. This application is the reflection of CdSe nano-rods reinforced PTh nanocomposites by virtue of which the conductivity of the material is enhanced. For developing electronic

devices such as diodes, semiconductor nanoparticles of CdSe are reinforced into PTh matrix by oxidation polymerization method using ferric chloride (FeCl_3) as a polymerization initiator. This method rapidly produces larger yields of polymer nanocomposites and is cost effective also. FESEM images confirm the presence of CdSe in PTh matrix. The EDAX data show the elemental composition of CdSe and PTh in the composites. Composite material shows a reduction in the energy band gap which is an indication of increased conductivity. Short circuit current in the nanocomposites is found to be higher than that of the native PTh. I-V characteristics of PTh/CdSe show an ohmic behavior at lower potential, while at higher potentials it responds like an organic-inorganic heterojunction diode. The electrical measurements show that when CdSe nano-rods are reinforced into PTh nanocomposites, it behaves like a junction diode. Short circuit current and DC conductivity of such heterojunction are also increased in the composite phase in comparison to that in those of pure PTh. DC conductivity of organic-inorganic, PTh/CdSe nanocomposites resembles with that of the heterojunction diode characteristics. These findings open up the possibility of its possible use as junction diode, protective devices, electronic devices, memory devices and designing energy storage devices in the device applications.

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