

Organic-inorganic hybrid material: synthesis, characterization for solar cell application

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We report a hybrid system based on conducting polymer-semiconductor from poly(o-toluidine) (POT) doped with camphor sulfonic acid(CSA) and cadmium selenide capped with Tri sodium citrate(CdSe-TSC) by the physical mixing method. The influence of CdSe nanoparticles weight percent on the hybrid thin films have been investigated by means of XRD, FESEM, UV-VIS absorption and photoluminescence spectroscopy (PL) measurements. The main diffraction peaks of POT/CdSe hybrids are analogous to the neat CdSe nanoparticles. The absorption measurement reveals that the interaction between CdSe and POT in the hybrid materials led to the blue shift and broadening of the polaron absorption band. The energy gap has been decreased with an increase in the concentration of CdSe NPs. the PL intensity has been totally quenched when the tow materials are bring to other. The hybrid nanocomposite material and provides useful evidence apropos the optimum use of CdSe nanoparticles in conductive polymer based optoelectronics.

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1. Introduction

Conducting polymers have enormous benefit of being easy to synthesize, with their chemical structure customized to change their physical characteristics, such as their band gap[1]. They display a wide variety of electrical conductivity from metal to insulator (10^{-9} - 10^5) S/cm. Further to their ease of synthesis and lower cost, they are known to have low poisoning effects[2]. Polyaniline (PANI) is an excellent practical application candidate for conducting polymers due to its excellent environmental stability, easy preparation, high temperature resistance and tunable electrical conductivity with different types and dopant concentrations[3]–[5]. The primary drawbacks of this polymer (PANI) are its insolubility and infusibility in prevalent organic solvents. In order to improve the solubility and processibility of the PANi and its synthesized derivatives, alternative methods were developed. Ring- substituted (alkyl and alkoxy) and N-alkyl-substituted PANi have been discovered to be more soluble than unsubstituted PANI[5]. Poly (o-toluidine) (POT) is a derivative of polyaniline, which contains methyl group in its ortho position of the aniline monomer. POT was likely the most commonly studied among the ring-substituted PANI derivatives because it is one of promised polymers used in various area of applications such as light emitted diode, filed effect transistor, schottky diode, solar cell and sensors[6]. Organic structures incorporating semiconductor nanocrystals have been particularly attractive because they enable active devices that combine the diversity of organic materials with the high-performance electronic and optical properties of inorganic NCs[7]. Recently, more and more attention has been paid to conductive polymer-inorganic hybrid materials with distinct combinations of the two parts because they have interesting physical properties and many possible applications in distinct fields[8]. The direct charge transfer (CT) and/or exciton energy transfer occur at the interfaces between the conducting polymers acting as hosts and the NPs acting as dopants; however, the

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transfer mechanisms of the charges and/or exciton dissociation in the conducting polymer-NPs composites are still not completely understood[9]. Hybrid materials have been synthesized by controlling the compositions, structures and morphologies of the components[10]. Proper mixing of inorganic nanoparticles and polymer results in the hybrid nanocomposite material having novel optical and electrical characteristics.

The improvements in the properties of the hybrid materials rely on the degree of dispersion and interaction of nanoparticles within the polymer matrix[11], [12]. The preparation of the hybrid material of POT with inorganic nanoparticles is another potential route to improve the performance of POT and the performance of inorganic nanoparticles too, aiming to obtain the materials with synergetic or complementary behaviors between POT and the inorganic nanoparticles. Among inorganic, Cadmium selenide (CdSe) is semiconductor of excellent optical and photoelectrical properties that make them attractive in solar cell applications[13]. Cadmium selenide (CdSe) NCs were the first applicants used in Bulk Heterojunction solar cells and still own the maximum power conversion efficiency (PCE) compared to other kinds of inorganic nanostructures[14]. CdSe nanoparticles were highly attracted because of their distinguishing catalytic, electrical, electronic and optical properties in addition to their low-cost applications in diverse manufacturing [7]. CdSe have been proven to be decent electron acceptors in mixture with poly(3-hexylthiophene) (P3HT)[15]–[17]. Furthermore, P3HT, specially in regioregular formula, is a costly polymer because of its complicated synthesis method. These disadvantages of the material lead to using the systems with certain environmental features (inert gas mediums) for utilizing the polymer[18]. Thermal stability, easy preparation and using the cost-effective materials and methods are parameters that are important in the field of solar cells so we introduced low cost polymer POT.

The important question which we are attempting to address in this paper is whether the integrate of CdSe nanoparticles into a polymer matrix effects any noticeable enhancement of its properties.

2. Experimental

2.1. Material preparation

CdSe NPs. have been synthesized using tri sodium citrate as a capping agent using a green chemical route by eluding the toxic capping agents. The detailed experimental process and results was reported elsewhere[19]. Except that the final synthesized product centrifuged at 3000 rpm for 10 min and washed two times (5 min) in ethanol and two times with acetone then one time with distilled water.

POT-CSA has been synthesized by chemical polymerization according to our paper [20]

POT/CdSe hybrid material was prepared by the dispersions of TSC capped CdSe NPs in POT-CSA polymer. POT-CSA mixed with different loading of CdSe-TSC NPs (H1 25 %, H2 50 %, H3 75 %) and milled by a mortar. Mixing was dissolved in formic acid solution. The mixing kept on a magnetic stirrer for 10 hours until the solvent evaporated. Again, the powder milled by a mortar and re-dispersed in 10 ml formic acid. Moreover, drop-cast onto a 2 x 2 cm² glass substrate that was pre-cleaned sequentially by ultrasonication in acetone, methanol and deionized-water. The drop-cast solution was rapidly dried in a vacuum oven at room temperature to form a uniform POT/CdSe hybrid film; the film thickness was 1000 nm, which was measured by FESEM as a cross section. The POT-CSA film without CdSe was also prepared in the same technique. Details of the hybrid samples used in different studies are shown in Table 1.

Table 1. Hybrid thin film details.

S.	Sample names	Compositions in weight ratio
POT/CdSe	H1	75:25
POT/CdSe	H2	50:50

POT/CdSe	H3	75:25
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2.2. Characterization

Patterns of X-ray diffraction were achieved via D2 phaser from bruker company, crystal monochromator ($\lambda=1.5481\text{nm}$), the 2θ range used was from 10 to 70° . The TEM images were achieved with a “JEOL JEM. 2010 electron microscopy” working at 200000 V. The thin films’ surface morphology had been verified by using C.SPM model A.A3000 AFM fund from Angstrom Company and FESEM model MIRA3 from TESCAN Company. Spectra of absorption have been collected by (Shimadzu 1800)UV-Vis spectrophotometer. Photoluminescence (PL) spectrum of our thin film is record in visible region on a luminescence spectrophotometer LS-03 (Perkin Elmer Instruments).

3. Results and discussions

Figure 1a shows a common (TEM) image of such CdSe nanoparticles. The morphology exhibits spherical in shape with an average diameter about 45 nm and no aggregation were observed. Figure 1b displays the optical absorption spectrum of CdSe-TSC NPs. from this figure the optical band gap equal to 2.25 eV.

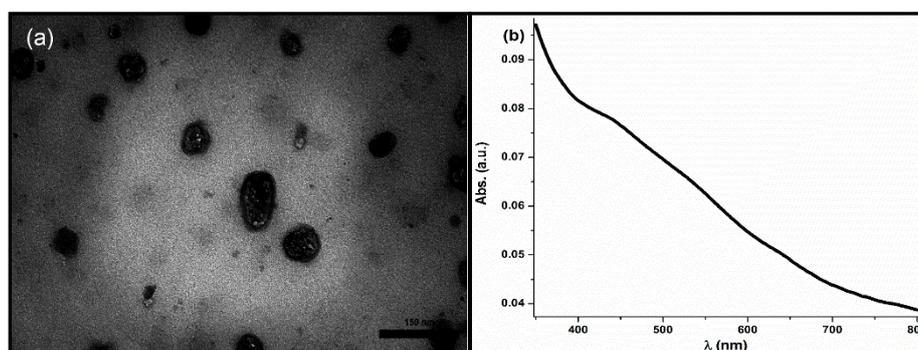


Fig. 1. (a) TEM images and (b) UV-vis absorption spectra of CdSe Nanoparticles.

Figure 2 illustrated the properties of POT-CSA. For FESEM analysis, suspensions POT-CSA in Formic acid was deposited onto glass substrates. The resulting POT-CSA film was dried in oven at 80 C for 30 minutes. The morphology of the films, displays a dense, uniform and homogenous. Although the mean diameter of POT-CSA nanoparticles is 80 nm, from Figure 2a it can be clearly seen that there are few POT-CSA nanoparticles having size greater than 100 nm. These large POT-CSA particles settle fast and hence could facilitate aggregation. The surface morphology of the POT-CSA thin film was investigated by AFM, as shown in Figure 2b. The smooth surface texture was observed in the deposited thin film. The thin film with average roughness is less than 2 nm. the average diameter of the particles which has been projected from the AFM image is equivalent to 70 nm.

The optical absorption spectrum is shown in Figure 2c. POT-CSA exhibits two characteristic absorption peaks in between ~ 400 nm and 826 nm wavelength, which attributes for to $\pi - \pi^*$ transition and π -polaron transition respectively. The optical band gap energy (E_g) can be obtained by plotting $(\alpha h\nu)^2$ versus $(h\nu)$ in figure 2d and extrapolating the linear portion of $(\alpha h\nu)^2$ to zero. In our case, the allowed direct transition optical gap was found to be 3.1 eV.

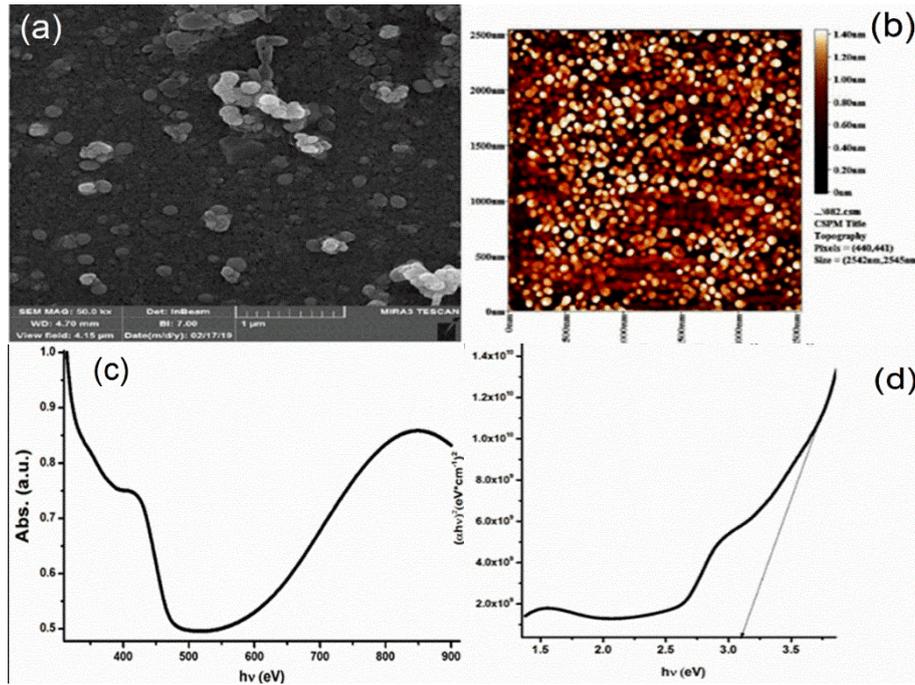


Fig. 2. (a) FESEM image, (b) 2D AFM image (c) UV-vis absorption spectra and (d) energy gap of POT-CSA thin film

Figure 3 shows the XRD patterns of POT/CdSe with different amounts of CdSe. From the figure 3 we can see that crystallinity of hybrids increase with increasing the amount of CdSe NPs. in the crystal pattern of H1 film, the observed $2\theta=25.64^\circ$ are consistent with the cubic structure of CdSe (JCPDS 19-0191). The two peaks at $2\theta = 23.6^\circ$ and 29.77° in the crystal pattern fit to POT-CSA and CSA doped POT, respectively[21]. Therefore the presence of these tow peaks in the XRD pattern of H1 film indicates the effect of POT on structural properties of POT/CdSe hybrid material. The strength of these two peaks is found to be decreasing with decreasing of POT in hybrid thin films. After increasing the CdSe nanoparticles in H2 and H3 hybrid thin films, the cubic crystal of CdSe structure is obtained giving rise of diffraction peaks at 25.64° , 42.74° and 49.48° which corresponding to (111), (220) and (311) planes, respectively. [19]. This indicates that the presence of the crystal structure of CdSe in the hybrid thin films which is not modified due to the presence of POT polymer.

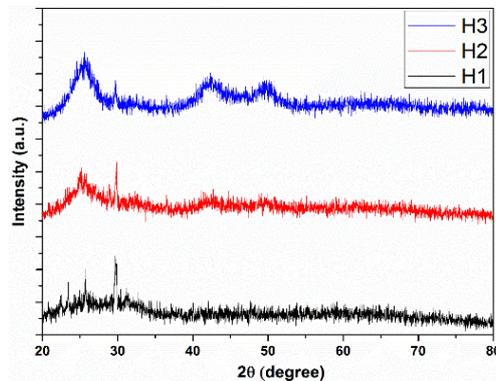


Fig. 3. X-ray diffraction patterns of hybrid films H1 (25% CdSe), H2 (50% CdSe) and H3 (75% CdSe).

The morphology of the prepared hybrid films was illustrated by FESEM. The FESEM photograph of POT/CdSe hybrid films was demonstrated in Figure 4. As can be seen from the figure, nanoparticles diffuse homogeneously in hybrid films of low concentrations, H1 and H2 with the preference homogeneity of a membrane of H2. the interface between POT and CdSe nanoparticles is sufficiently attractive to prevent of micro phase separation between them, this interaction speed up the properties of charge transport (electrons hopping) through the polymer[22].

By comparing the shape and size of the shown nanoparticles, it was clear that the CdSe nanoparticles were near the top of the hybrid films were gray while the POT-CSA nanoparticles were bright. Micro graphs demonstrate that the surface of film turns into denser with the increasing quantity of nanoparticles in the hybrid films.

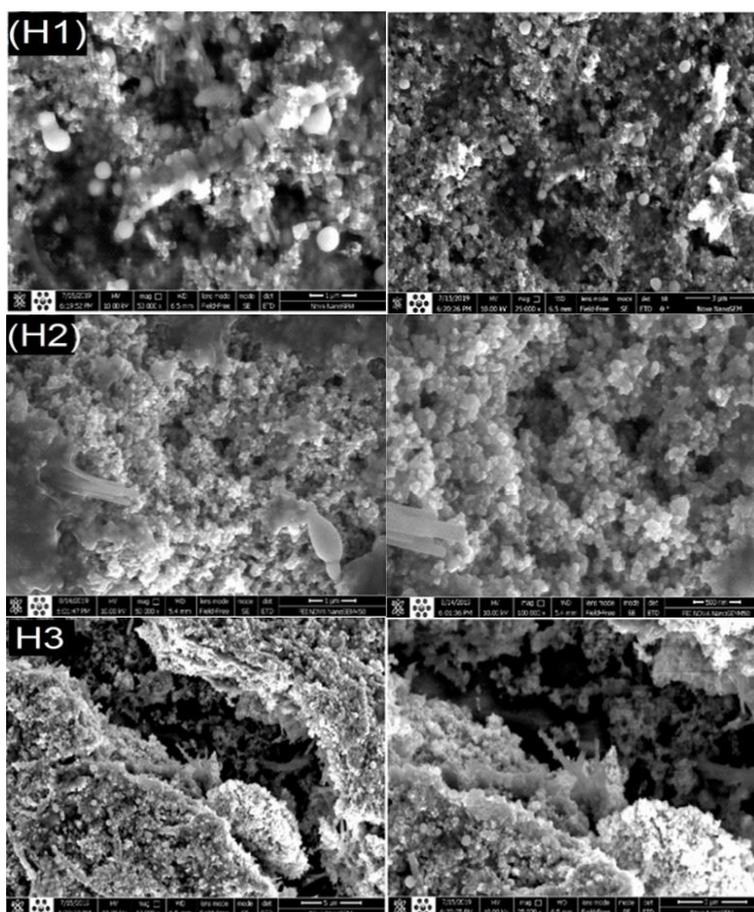


Fig. 4. FESEM images of hybrid films H1 (25% CdSe), H2 (50% CdSe) and H3 (75% CdSe).

Figure 5 illustrates optical absorption in the range from 300 to 800 nm. We have detected a reduction in absorption band intensity as the concentration of CdSe NPs in hybrid films was increased. a comparable behavior for composite Pani-CdSe films has been reported[23]. A significant inter-molecular interface between the chains polymer and the nanoparticles is indicated by presence of peak around (420-450) nm[22]. The peak matching to π - π^* electronic transition looks extended and redshifted with the growing of nanoparticles quantity, indicative of accumulation of polymeric chain or the result of relatively long conjugated chains [11].

The blue shift of polaron band absorption is noted. This may be attributable to the interaction between CdSe and POT, which cause easy charge transfer from POT to CdSe [24,25]. Also, the broadening of this absorption band confirms the presence of highly delocalized electrons in the polymer chain caused by the exist of CdSe nanoparticles[26].

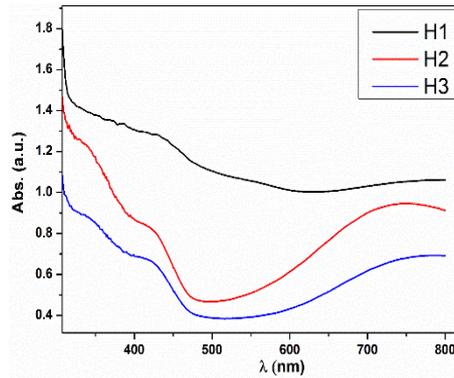


Fig. 5. UV-Vis spectrum of of hybrid films H1 (25% CdSe), H2 (50% CdSe) and H3 (75% CdSe).

The values of optical energy gap (E_g) of POT-CSA mixing different concentration of CdSe-TSC determined by Tauc equation [27]. Figure 6 illustrated the plot of $(\alpha h\nu)^2$ vs. $h\nu$ for POT/CdSe hybrid thin films. The E_g values are determined by extrapolating the straight line portion in the figure. The energy gap decreases with an increase in the rate of CdSe NPs, that might be due to decrease in the disarrangement of the hybrid structure and rise in the defect states density[28].

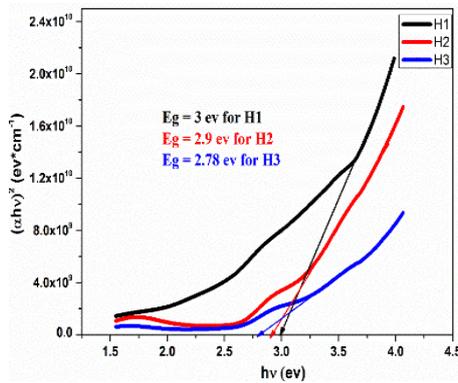


Fig. 6. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for hybrid thin films.

The PL spectra of CdSe nanoparticles and POT-CSA nanoparticles recorded at room temperature with excitation wavelength equal to 350 nm and 300 nm, respectively, were shown in figure 7. Totally quenching in the PL intensity of hybrid films was detected. The total quenching of PL refer that excited electrons have been decayed through non-radiative transitions which could be due to an considerable transfer of charge and energy from polymer to CdSe nanoparticles[29].

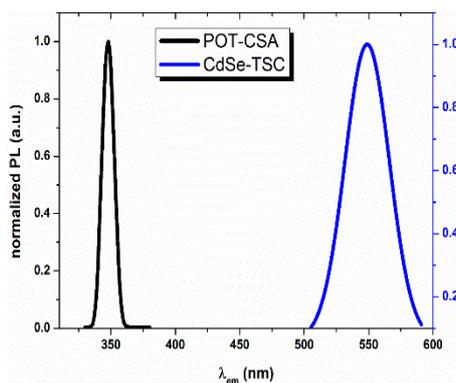


Fig. 7. PL spectra of POT-CSA and CdSe nanoparticles.

4. Conclusions

We have studied the structure, optical and morphological properties of hybrid material POT/CdSe prepared by varying the content of TSC-capped CdSe. Blends of CdSe and POT have been prepared from a solution via drop casting method. XRD studies of these hybrid materials indicate an increase in crystallinity after increasing of CdSe. The optical studies show that the incorporation nanoparticles affect the properties of the hybrid due to electronic interaction between the polymer and the nanoparticles. the POT/CdSe hybrid nanocomposite material is a promising material in bulk heterojunction solar cell applications.

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