Preparation and characterization of electrospun fibers containing poly(3-hexylthiophene) and poly(3-hexylthiophene)/CdS

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\textbf{A B S T R A C T}

Poly(3-hexylthiophene) (P3HT) and P3HT/cadmium sulfide (CdS) fibers were prepared in order to determine their morphological and structural properties and thermal stability. To our knowledge, this is the first study to investigate electrospun P3HT/CdS fibers. P3HT fibers were manufactured by electrospinning technique by varying process parameters. Because of P3HT electrospinning was not possible, polyethylene oxide (PEO) was mixed with P3HT to increase the viscosity of the solution. It was possible to form non-beaded fibers containing a maximum of 80 wt% P3HT. The fibers were washed with acetonitrile to remove the built-insulator (PEO) and thus improve its electrical properties. P3HT–PEO fibers (before and after washing) were characterized by FTIR technique and confocal microscope to determine the decrease of the insulating material into the fiber and by SEM to determine the size and surface morphology of the fibers. The P3HT–PEO fibers before washing showed morphology with heterogeneous surface features, however after washing the fibers showed morphology similar to ribbons with higher porosity caused by PEO removal. Conjugation length of P3HT molecules into P3HT fibers was obtained with washing time of fibers. P3HT/CdS fibers were prepared by precipitation of CdS on P3HT washed fibers. P3HT/CdS fibers were characterized by FTIR and TGA to determine the presence of CdS in the fibers. The precursors concentration for the precipitation of CdS on the P3HT fibers; influenced in the morphology of CdS deposit.

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1. Introduction

The large surface to volume ratio of the fiber making them suitable to the performance of several optoelectronic devices such as: electrical and optical sensors [1,2], organic photovoltaic cells [3], batteries [4], organic thin film transistors [5] and light-emitting devices [6]. Electrospinning is a facile and effective method for processing solutions into continuous fibers having diameters that can range from a few nanometers to a few micrometers [7,8]. Fibers materials have several advantages over film-based materials in electronic devices: form a continuous charge transport pathway [9], provide enhanced electrical properties [10], and offer a high surface area [7]. Conductive polymer fibers prepared by electrospinning technique, therefore, can contribute to the preparation of high-performance devices.

The poly(3-hexylthiophene) (P3HT) organic semiconductor is widely used in polymer film because of their easy processability in common organic solvents, this property makes them good candidates for the formation of fibers by electrospinning. González et al. [11], prepared P3HT (regioregular) fibers using a solution of P3HT in CHCl\textsubscript{3}, however the presence of beads along the fiber were observed. These beads could result from the simultaneous interplay between solution viscosity and rapid evaporation of the solvent during the electrospinning process. An important parameter in the electrospinning is the viscosity of the solution to assist the formation of fibers, thus Bianco et al. [12], electrospun fibers using blends of polyethylene oxide (PEO) and poly(3-dodecylthiophene) (P3DDT), the fibers obtained were washed with acetonitrile producing dense fibers made only of P3DDT. By another hand, Lee et al. [13], electrospun fibers using...
blends of P3HT and poly(ε-caprolactone) (PCL), the fibers obtained were dipped in trifluoroethylene (TFE), which completely removed PCL while P3HT was kept intact under these conditions. The field effect mobility of pure P3HT fibers was 0.017 cm²V⁻¹s⁻¹ which is acceptable for device fabrication. Laforgue et al. [14], prepared fibers of P3HT (region-random) with PEO. They found that the maximum conductivity of 0.16 ± 0.02 S/cm was obtained for fibers (average diameter about 850–1100 nm) containing above 75 wt% of P3HT. They found that for obtaining perfect non-beaded fibers required a good control of the processing parameters.

A typical photovoltaic cell array consists of two thin films in sandwich form; one of the films is formed by nanoparticles of an inorganic material and another one by an organic polymer. This configuration results in the generation of electrons and holes transported through of the organic and inorganic semiconductors and immediately collected in the electrodes, taking advantage a short trip of electron-hole pair [15]. Saunders [16] mentions that the diffusion length of the excitons is usually between 10 and 20 nm. Therefore the architecture of the photovoltaic cells must consider a wide contact area between the two semiconductors materials, the organic/inorganic composite fibers may be an option.

In this paper we prepared P3HT and P3HT/cadmium sulfide (CdS) fibers using PEO in order to determine their morphological and structural properties and thermal stability. To our knowledge, this is the first study to investigate electrospun P3HT/CdS fibers. We used the lowest percentage of insulating material necessary to obtain optimal fibers in order to improve the properties of the fibers. P3HT–PEO and P3HT–PEO/CdS fibers (before and after washing with acetonitrile) were characterized by FTIR technique and confocal fluorescence microscope to determine the decrease of the insulating material into the fiber, by SEM to determine the size and surface morphology of the fibers and EDX analysis was carried out for determining the elemental content. Finally the fibers were characterized by Thermogravimetric analysis (TGA) for determining the thermal stability.

2. Experimental

2.1. Synthesis of P3HT

P3HT was chemically synthesized using FeCl₃ as an oxidant at 0 °C under inert atmosphere [17,18]. 0.0167 mol of distilled 3-hexylthiophene dissolved in anhydrous CHCl₃ was slowly added to FeCl₃ (0.025 mol) previously dissolved in anhydrous CHCl₃. The reaction mixture was stirred for 24 h. The product was precipitated in methanol, filtered and carefully washed with methanol, hydrochloric acid (10 mol%), acetone, NH₄OH (10 mol%), ethylenediaminetetraacetic acid (EDTA, 1 mol%) and distilled water. The final P3HT product showed Mn = 62365, Mw (g/mol) = 256,454; PDI = 4.4 estimated by GPC in THF using polystyrene as standard. P3HT showed 88% of HT dyads determined by H¹ RMN.

2.2. Synthesis of CdS

CdS was synthesized at room temperature using Na₂S (Fermont) and Cadmium Acetate (Cd (OOCCH₃)₂·2H₂O) (Alfa Aesar, 99.999 %) as precursors at 25 °C (room temperature), the particles size of CdS was 3 nm and showed an optical band-gap between 2.44 and 2.54 eV. [19].

![SEM images of P3HT–PEO fibers (20 wt% PEO and 80 wt% P3HT): (a) and (b) before washing, (d) and (e) after Soxhlet washing for 1 h with acetonitrile, (c) and (f) fibers diameter distributions, before and after washing, respectively.](image-url)
2.3. Electrospinning of P3HT/PEO fibers

PEO (Mw = 1,000,000, Sigma–Aldrich) and chloroform (Sigma–Aldrich) were used to form the electrospinning solution. The electrospinning solution was prepared by dissolving P3HT and PEO in chloroform. Solution in chloroform of P3HT was stirred for 15 min, then was added PEO and the solution was stirred for 20 min until the solution was homogeneous.

A syringe was filled with the polymer solution of P3HT/PEO and it was placed in an injection pump (NEW ERA NE-300 model) connected to a voltage source (CZE1000R Spellman). The fibers were deposited on an aluminum collector plate of 25 cm2.

The appropriate parameters for producing fibers with good morphological properties were determined. Likewise the minimum amount of PEO necessary for fiber formation was determined. The optimal polymer solution concentration for obtaining fibers with fewer insulator phase (PEO) was 80 wt% P3HT and 20 wt% PEO. The range of the electrospinning optimal parameters was: concentration solute (P3HT–PEO) in solvent 2.3–3.2 wt%, applied voltage = 9–13 kV, flow rate = 2.8–3.3 ml/h, Distance needle tip and collector = 21–25 cm.

Acetonitrile (99%, Sigma–Aldrich) was used to wash the P3HT–PEO fibers and thus eliminate the PEO. Washing with acetonitrile was carried out by Soxhlet extraction. Washing of the fibers was carried out at different times (5, 30 and 60 min) in order to determine the optimum washing time, the optimal washing time was 60 min.

2.4. Synthesis of P3HT–CdS fibers

In order to see the effect of the concentration of the precursor solutions in the precipitation of CdS on P3HT fibers, 2 different synthesis were tested for obtaining P3HT–CdS fibers: cadmium acetate (3 and 5 mg) with Na2S (2.9 and 4.9 mg), respectively. Two solutions in 2 ml of methanol were prepared: Na2S (solution 1) and cadmium acetate (solution 2). Both solutions were stirred by 30 min. P3HT–PEO fibers were added to the solution 1 and stirring was continued for 10 min. Subsequently the solution 2 is added to solution 1 slowly, a change in color from transparent to yellow was observed immediately, indicating the formation of CdS. This solution was stirred for 30 min. Now we will use the following nomenclature: Sample A was prepared with less concentrated solutions of the precursors and sample B was prepared with more concentrated solutions of the precursors. The P3HT–PEO/CdS fibers were Soxhlet washing with acetonitrile by 1 h.

2.5. Characterization

P3HT and P3HT–CdS fibers were characterized by SEM (Hitachi SE-SEM 5500) equipped with an EDX analysis system for determining the morphology and elemental content. To analyze the diameter was used an image processor (Image J) software. The fluorescence confocal microscope (Zeiss Axiovert 200 LSM 510, HeNe Laser excitation of 633 nm, 10% power) was also used to confirm the decrease of PEO phase in the fibers PEO–P3HT.

The presence of PEO phase in the PEO–P3HT fibers before and after washing with acetonitrile was characterized by FTIR Spectrometer (FT-IR ATR Platinum BRUKER), the sample was compressed into a tablet for analysis.

The thermal stability and decomposition temperature of the fibers were obtained by thermal gravimetric analysis (TGA TA Q500); the samples were heated at 10 °C/min rate under nitrogen atmosphere.

3. Results and discussion

3.1. Morphology of P3HT/PEO fibers

Fig. 1a shows the P3HT/PEO fibers morphology before of washing, the fibers showed a size of 1.4 to 2.8 μm, non-beaded fibers were obtained. A greater amplification (Fig. 1b) shows very heterogeneous surface features on the fibers surface, according to Lafouge et al. [14] these results were believed to be related to superior phase separation in the polymer blends. They said that P3HT was surrounded by PEO in the structures, and tended to agglomerate and form irregular nodules. Besides, it seemed that the interactions with the solvent play an important role in the phase separation process, as it was significantly enhanced when the relative humidity was increased from 23 to 39% [14]. In our case the relative humidity was even greater (RH = 45% in laboratory), which would benefit these heterogeneous surface features. The fibers size (diameter) distribution was calculated by the Image J software (Fig. 1c).

The fibers were washed with acetonitrile to remove the insulating polymer (PEO). The washed fibers morphology is shown in Fig. 1d and e, the fibers showed a higher porosity caused by PEO removal. The fibers average diameter was mainly about 2.0–7.0 μm (Fig. 1f), the fibers width was higher than in the unwashed fibers. Removing of PEO phase of the fibers was given, which probably caused hollow fibers of P3HT phase, resulting in morphology similar to ribbons.

![Fig. 2. Fluorescent confocal images of P3HT–PEO fibers: (a) before washing with acetonitrile (b) after washing.](image-url)
Fig. 2 shows images of the P3HT/PEO fibers obtained in the confocal fluorescence microscope before and after washing with acetonitrile (Fig. 2a and b, respectively). P3HT–PEO fibers (Fig. 2a) show a cylindrical shape due to the insulating material (PEO) that gives body to the fiber. The fluorescent material correspond to P3HT (due to π–π∗ transition (360–680 nm)) and the black color material (no fluorescence) correspond to the insulating material of the fiber (Fig. 2a), only fluorescent points on the fibers were observed. After washing the fibers with acetonitrile, morphology like ribbons was observed, the ribbons showed a higher fluorescence (with fluorescence coming from all the fiber volume) due to the greater amount of visible P3HT by the PEO extraction out of the fibers. Bianco et al. [12] observed a similar morphology after washing the fibers P3DDT/PEO.

Chan et al. [20] observed the ribbon-like morphology in electros spun P3HT fibers, they mentioned that is due to accelerated evaporation and solidification at the surface of the polymer solution jet during spinning. Differences in solidification rates between the surface and interior of solution jet forced the collapse of the solid surface layer onto the solution rich interior, thus the development of flat or ribbon-like fibers. In our case we observe this form of ribbon-like morphology due that to PEO removal is initiated at the outside of the fiber and finally the innermost part of the fiber causing the contraction of the fiber.

3.2. FTIR study of P3HT–PEO fibers

To confirm that the PEO had been removed from the fibers, these were characterized by FTIR. Fig. 3 shows the FTIR spectra of P3HT/PEO fibers before and after Soxhlet wash with acetonitrile, additionally PEO and P3HT spectra are shown for comparison. The PEO spectrum showed the following characteristic bands: 1460 and 1342 CH2 asymmetric bending, 1278 CH2 twist, 1093 cm−1 C−O−C asymmetric stretch, 945 CH3 rock, C−O−C stretch, 841 CH2 asymmetric rocking [21,22]. Also P3HT showed the characteristic bands (722 cm−1 methyl rock, 820 cm−1 C−H out of plane, 1114 cm−1 C−S stretching, the peaks at 1510 and 1460 cm−1 corresponds to thiophene ring C=C stretching vibration, asymmetric and symmetric, respectively). The peak at 1377 cm−1 is due to methyl bending. Three bands at 2954, 2920 and 2852 cm−1 assigned to the asymmetric C−H stretching vibrations of CH3− moieties, −CH2− moieties, and symmetric C−H stretching vibration in −CH2− moieties, respectively [23,24].

The FTIR spectra showed that the P3HT–PEO fibers exhibited the characteristic bands of P3HT and PEO, the spectrum is just a superposition of the spectra of the simple polymers. However, when the fibers were washed with acetonitrile, the bands corresponding to PEO are greatly diminished or eliminated with wash time (1460, 1359, 1342, 1278, 1240, 1144, 1093, 1059, 960, 944, 876 y 841 cm−1), which confirmed that observed in confocal microscopy. FTIR spectra indicated that the minimum time required to remove the PEO was 1 h.

The FTIR spectra also indicated the conjugation length of the P3HT polymer chain. The conjugation length is based on the results of the intensities ratio of the symmetric ring stretch at 1456 cm−1 to the asymmetric ring stretch at 1510 cm−1 (l sym/l asym) [25]. Longer conjugation length in the polymer backbone results in smaller l sym/l asym ratio. The l sym/l asym ratio for random P3HT film and the P3HT/PEO fibers at different Soxhlet washing time is shown in Table 1. This ratio was higher for the P3HT/PEO fibers no washing (5.1) than for P3HT film (3.1), probably the presence of PEO during the formation of the fibers did not allow a good arrangement of P3HT chains. However when the P3HT/PEO fibers were washed for 5 min the l sym/l asym ratio increases until 9.6, indicating that a higher disorder of the P3HT molecules was given; after this ratio diminished with higher washing time until 3.2 at 1 h of washing. These results showed the benefit of washing with acetonitrile to increase the conjugation length of P3HT into the fibers.

The conjugation length of P3HT fibers without PEO (washing for 1 h) was almost similar than that of P3HT films, indicating a ordering similar of the chains into the films and into the fibers washing.

3.3. Morphology of P3HT/CdS fibers

P3HT fibers were coated by CdS chemical precipitation. Fig. 4a shows that for the case of carried out the CdS precipitation with less concentrated solutions of the precursors, the P3HT–PEO fibers were coated homogenously with CdS nanoparticles, the pores of the fibers were covered by CdS. However when the CdS precipitation was carried out with solutions more concentrated of the precursors (Fig. 4c), a heterogeneous coating (in form of crusts) onto the fibers was formed, the fibers showed some uncoated areas. Probably the less concentrated solutions of the precursors allowed the CdS deposition within the pores of the fibers which led to a more homogeneous coating on the fibers. EDX analysis confirmed the CdS content on the fibers (Fig. 4b and c).

3.4. FTIR study of P3HT/CdS fibers

Fig. 5 shows the FTIR spectra of P3HT/CdS fibers synthetized with 2 different concentrations of the precursor solutions (sample A and sample B). FTIR study shows the CdS incorporating on the P3HT fibers (Fig. 5). P3HT/CdS (sample A) fibers showed a higher content of CdS by the presence of the bands in 621, 1106 and 1007 cm−1, present in the CdS compound (Fig. 5). However P3HT/CdS (B) fiber showed a higher content of PEO in comparison with P3HT/CdS (A) fibers (Fig. 5). P3HT/CdS (B) showed small bands at 840, 960, 1057, 1148, 1279, 1342 and 1360 cm−1 assigned to PEO. Both P3HT/CdS fibers were washed for 1 h by Soxhlet method, probably the CdS deposit (in crusts form) on the P3HT–PEO fibers hindered removing PEO. CdS coating like crusts is denser than the

![FTIR spectra of P3HT, PEO and P3HT–PEO fibers before and after Soxhlet washing; in the frequency range of 800–1600 cm−1.](image)

Table 1

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<th>l sym/l asym</th>
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<tr>
<td>Film P3HT</td>
<td>3.1</td>
</tr>
<tr>
<td>P3HT–PEO fibers no washing</td>
<td>5.1</td>
</tr>
<tr>
<td>P3HT–PEO fibers washing for 5 min</td>
<td>9.6</td>
</tr>
<tr>
<td>P3HT–PEO fibers washing for 30 min</td>
<td>4.2</td>
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<tr>
<td>P3HT–PEO fibers washing for 1 h</td>
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porous thin films of CdS, through a porous thin film can be given more easily penetration of solvent molecules.

3.5. Thermal characterization of P3HT, PEO and P3HT/CdS fibers

The maximum decomposition temperature of PEO was given at 391 °C and for P3HT at 494 °C (Fig. 6). P3HT/CdS fibers showed a thermal stability until 300 °C approximately and 2 maximum decomposition temperatures at 392 and 474 °C for the case of P3HT/CdS fibers prepared with precursor solutions less concentrated (sample A) and at 395 and 479 °C for more concentrated precursor solutions (sample B), assigned to decomposition of PEO and P3HT, respectively. Both samples of P3HT/CdS fibers showed presence of PEO because of fibers were washed until after of the CdS precipitation on the fibers. The sample B showed a higher PEO concentration into the fiber, it is according with FTIR spectra. Furthermore, the sample A showed a higher content of CdS, because weight loss obtained after carried out the decomposition of P3HT, this was greater that in the sample B, which corroborated the FTIR analysis.

4. Conclusions

P3HT–PEO non-beaded fibers with 80 wt% of P3HT were prepared by the technique of electrospinning, the fiber size was of 1.4 to 2.8 μm. PEO was removed by Soxhlet extraction with acetonitrile by 1 h. The P3HT–PEO fibers before washing showed morphology with heterogeneous surface features, however after washing the fibers showed a morphology similar to ribbons with higher porosity caused by PEO removal. A heterogeneous surface is suitable for improving the interaction of CdS nanoparticles on the fibers. The confocal fluorescence microscope and FTIR spectroscopy corroborated the remotion of PEO, the washed fibers showed increased fluorescence and the disappearance of the FTIR peaks corresponding to PEO, respectively. Conjugation length of P3HT molecules into P3HT–PEO fibers was benefited with washing time of the fibers, indicating a better ordering of the chains in the washed fibers, which benefit the conductivity of the material. The conjugation length of P3HT fibers without PEO (washing for 1 h) was similar that of P3HT films. Electrospun P3HT–PEO fibers coated with CdS nanoparticles were prepared. A lower concentration of the precursor solutions for depositing CdS on P3HT–PEO fibers was more suitable for obtaining a more homogeneous coating. FTIR and TGA analysis showed the CdS incorporating on the P3HT fibers, the concentration of the precursor solutions influences in the PEO and CdS content into the composite fibers after washing.

Fig. 4. SEM images of P3HT–PEO fibers coated with CdS after washing: (a) CdS precipitation with less concentrated solutions of the precursors and (c) CdS precipitation was carried out with solutions more concentrated of the precursors; (b) and (d) EDX analysis, respectively.

Fig. 5. FTIR spectra of P3HT–PEO/CdS fibers after washing prepared with 2 different concentration of precursor solutions (sample A and B). PEO, P3HT and CdS spectra were added for comparison.
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