

**P3HT-NANOFIBERS BASED FIELD EFFECT
TRANSISTORS**

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5.1 Introduction

Organic conducting polymers have attracted a great curiosity in the area of research and industrial applications due to their easy synthesis, good solution processibility, good physical and chemical properties and excellent mechanical flexibility [Cui *et al.* (2003), Tiwari *et al.* (2012), Lim *et al.* (2006), Chen *et al.* (2013)].

Nowadays, semiconductor polymer nanofibers have been increasingly investigated due to their high surface to volume ratio and improved charge transfer properties. Nanofiber provides straightforward route for the charge carriers to move end to end directly; therefore, performance of nanofiber based devices get enhanced. A range of techniques such as catalytic synthesis, chemical vapour deposition, dilute polymerization, interfacial polymerization, electrospinning *etc.*, have been already developed for the synthesis of polymer nanofibers [Jo *et al.* (2012), Colangelo *et al.* (2012), Sun *et al.* (2010), Oosterbaan *et al.* (2009)]. These techniques provide controlled growth of polymer nanofibers of proper shape, size, chemical stability, and tensile strength. Amongst the various organic conducting polymers, polyalkylthiophene and its derivatives are most frequently used in several organic thin-film devices and sensors. Regioregular poly(3-hexylthiophene) (P3HT), a member of polyalkylthiophene family, has been extensively studied in organic electronic devices [Babel *et al.* (2005), Cosseddu *et al.* (2012), Pal *et al.* (2010)] due to their good processibility, efficient electronic and optical properties, and high inclination towards crystallization and nanofiber formation [Oosterbaan *et al.* (2009)]. Two approaches which have been generally used for P3HT-nanofiber formation are whisker method and mixed-solvent method [211,218,219 Sun *et*

al. (2010), Kiriya *et al.* (2003), Li *et al.* (2008)]. In the whisker method, a polymer solution is prepared and then super cooled such that polymer molecules get self-assembled and generate nanofibers which are segregated from the super cooled suspension by filtration and centrifugation. Nanofiber morphology and dimensions of the polymer produced with this method are strongly dependent on selection of solvent, polymer molecular weight and their regioregularity, solution concentration, outer interference, and cooling rate [Sun *et al.* (2010), Oosterbaan *et al.* (2009), Zhao *et al.* (2009), Liu *et al.* (2009)]. These issues highly influence the chemical interaction occurring among polymer and solvent and therefore controlled morphology and precise dimensions of polymer nanofibers are a challenging issue. In mixed-solvent technique, a polymer such as P3HT is initially dissolved in a poor solvent (like anisole) by heating and then, this solution is further doped with little amount of a good solvent (like chlorobenzene). Poor solvents assist self-assembling of polymer molecules and the good solvents (used as dopants) control the fiber morphology. Doping of P3HT solution with good solvents changes their morphology as nanofibers and also enhances the crystallinity of thin-film casted by this solution. Therefore, such doping of P3HT provides an electronic device like FET with improved performance than an un-doped P3HT based FET [Sun *et al.* (2010)]. High carrier mobility of $0.06 \text{ cm}^2/\text{Vs}$ has been reported for single fiber P3HT-FET [Merlo *et al.* (2004), Merlo *et al.* (2003)] which is much closer to the mobility $0.25 \text{ cm}^2/\text{Vs}$ found in conventionally constructed P3HT-FET of similar design [Cho *et al.* (2006)]. Recently a research group has reported an excellent mobility of $2 \text{ cm}^2/\text{Vs}$ along with an ON/OFF ratio of 10^5 for an electrospinning P3HT-nanofiber based FET in which the conventional gate oxide (SiO_2) layer has been replaced with polyelectrolyte [Lee *et al.* (2009)].

Organic field effect transistors (OFETs) are generally used as basic building blocks in modern organic electronic devices and applications like radiofrequency identification tags, active-matrix displays, and sensors [Yang *et al.* (2010), Raval *et al.* (2009), Crone *et al.* (2011), Lim *et al.* (2006), Ando *et al.* (2007)]. The progress in OFETs depends on many issues like enhancement in device performance, decrement in fabrication cost and expansion in the area of applications. Solution-processed organic transistors on flexible substrates are smart candidates to fulfill such demands. Solubility nature of polymer semiconductors reduces the device fabrication complexity as well as the cost.

5.2 Experimental Details

5.2.1 Nanofibers Preparation

Regioregular poly-3-hexylthiophene (RR-P3HT) was synthesized in the laboratory and earlier reported method was adopted for the synthesis [Tiwari *et al.* (2014), Tiwari *et al.* (2014)]. A homogeneous RR-P3HT solution of 1 wt% concentration was prepared in dehydrated toluene via heat treatment, and then after it is cooled to room temperature, the solution was stored for two weeks in a firmly sealed glass container at a constant temperature of 25 °C. Steadily, the P3HT molecules join together due to the driven force of π - π interchain stacking and result in the formation of suspended nanofibers. The solubility of P3HT in various solvents are influenced by their molecular weight; so, a few high molecular weight P3HT molecules have poor solubility in toluene even at room temperature. Therefore, very slow aggregations of P3HT molecules promote the formation of well-stretched nanofibers [Trznadel *et al.* (1998)]. The solution was observed regularly and it was found that a few physical changes occurred such as the changes in viscosity and color of the stored solution. Day by day the color of the solution was changed from dark orange to dark brownish-purple and the viscosity increased due to fiber formation

and with time. After two weeks, the suspended P3HT nanofibers were isolated from the stored suspension by centrifuging the suspension at 6000 rpm for 30 min. The collected solid parts were separated and re-dispersed in dehydrated chloroform immediately before drying. The nanofibers suspension concentration was measured with the help of UV-visible absorption spectra of the P3HT-solutions of known concentrations as shown in Fig. 5.2 (a) & (b), which has been discussed in the later part of this chapter. This nanofiber suspension was further utilized for fabricating the OFETs.

5.2.2 OFET Fabrication

Heavily p-doped silicon chips of area 1 cm^2 covered with thermally grown SiO_2 ($C_{\text{ox}} = 10 \text{ nF/cm}^2$) layer (as gate insulator) of thickness 300 nm were used as base substrates for OFETs. The nanofibers suspension prepared as in section 5.2.1 was mixed properly by using cyclo-mixing equipment and then was spin coated on the substrates. The coating speed was maintained at 1000 rpm for 10 s followed by 3000 rpm for 50 s. The thin-film thickness was measured with the help of DEKTAK 6M Profiler and thickness was found in the range of 50–55 nm. Fiber coated $\text{p}^+\text{-Si/SiO}_2$ substrates were further annealed at $80 \text{ }^\circ\text{C}$. Then, by using nickel shadow mask, the source/drain electrodes of gold were deposited at the top of the spin coated nanofibers thin-film with thermal vapour deposition technique at a vacuum level of 4×10^{-6} torr. The thickness of the electrodes was 40 nm; however, the device dimensions such as channel length and width were maintained to be 20 μm and 2 mm, respectively. The current-voltage characteristics of the fabricated OFETs were measured with Semiconductor Parameter Analyzer at vacuum pressure of 3×10^{-6} torr. The structural morphology and optical characteristics of P3HT and P3HT-nanofibers thin-films were studied by measuring UV-visible absorption spectra (JASCO V-750

spectrophotometer) and atomic force microscopy (AFM) (JEOL SPM5200), respectively.

5.3 Results and Discussion

The nanofibers formation was verified by observation of AFM images and UV-visible absorption spectra of the P3HT and P3HT-nanofibers. A comparison in the UV-visible absorption spectra of P3HT solution and P3HT-nanofibers suspension in chloroform is given in the Fig. 5.1, and it was found that the absorption peak heights and wavelengths for both (P3HT and P3HT-nanofibers) were significantly different. For P3HT solution the absorption peak was detected at the wavelength of approximately 450 nm, and on the other hand, four distinct peaks for P3HT-nanofibers suspension were examined at the wavelengths of 470 nm, 520 nm, 560 nm, and 610 nm respectively [Tiwari *et al.* (2014)], as shown in the Fig. 5.1. These shoulder peaks signify that the nanofibers were formed with aging of the P3HT/toluene solution. The shoulder peaks at 520 nm, 560 nm, and 610 nm were also ascribed in the growth of nanofibers conjugation length owing to improved $\pi - \pi$ stacking of the P3HT molecules in polymer chain [Chen *et al.* (2011), Sun *et al.* (2011)].

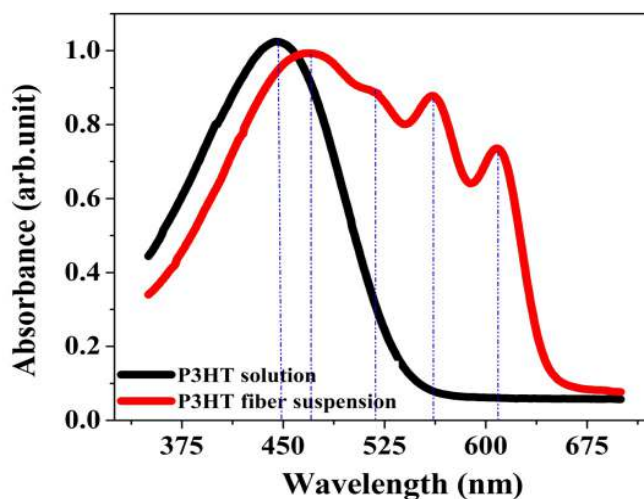


Fig. 5.1 UV-visible absorption spectra for P3HT solution and P3HT-nanofibers suspension in chloroform

Red-shifted and intense absorption wavelengths observed for P3HT-nanofibers suspension demonstrates the generation of nanofibers of extended conjugate length. The nanofibers exhibit good crystallinity, and poor solubility. Peak at 470 nm (as shown in absorption spectra of P3HT-nanofibers suspension) is probably associated to the solution peak which is slightly red-shifted as compared to the absorption peak for P3HT solution ($\lambda \sim 450$ nm) and it may be because that the collected nanofibers were of high molecular weight and possess longer pi-conjugation length. Thus, re-dispersed chloroform solution shows a little longer wavelength as a partially re-dissolved part. The fiber formation by the aging of solution is a kind of recrystallization process in which relatively low molecular weight P3HT molecules may fail to get solidified. The suspended solids (nanofibers) were segregated from the dissolved part by the centrifugation and decantation processes. The formation of P3HT-nanofibers was also confirmed by thin-film morphology studied through AFM measurement which is discussed later in detail.

The concentration of P3HT-nanofibers dispersed in the chloroform and used for OFET fabrication was estimated by the calculation of molar absorption coefficient of the P3HT/chloroform solution. In order to calculate the P3HT fiber concentration, firstly a solution of P3HT of concentration 0.1 wt% was prepared in chloroform. From this solution, different samples, each of 10 mg weight was taken and diluted 50, 100, 200 and 500 folds with chloroform to prepare several different concentrations of P3HT solutions and were then heated for 1 min by using hot drier before measuring the UV-visible absorption spectra for each solution sample. The UV-visible absorption spectra of each prepared P3HT solution of different concentration are shown in the Fig. 5.2 (a), which shows the absorption peak height increases with increasing P3HT concentration. A plot between the absorption peak height at the wavelength of 450 nm and P3HT concentrations is shown in the Fig. 5.2 (b). The peak heights at 450 nm provide a fine

linear relationship with the diluted P3HT concentrations. This fact indicates that the slope provides the molar absorption coefficient of P3HT solution, which was found to be $24 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ [Tiwari *et al.* (2014)]. This linearity also offers the concentration of a diluted P3HT solution having a similar absorption spectrum. Further, from the homogeneous P3HT-nanofibers suspension (used for device coating) a little amount (5 mg) was taken and diluted 100-folds with chloroform, and then heated till nanofibers got dissolved completely and appeared as P3HT solution. Corresponding to the absorption peak obtained for the dissolved fibers solution from Fig. 5.2 (a), the concentration of P3HT nanofibers used for device fabrication was determined from Fig. 5.2 (b) (blue line) by just using the line fitting parameters and the value was estimated around 0.1 wt % [Tiwari *et al.* (2014)].

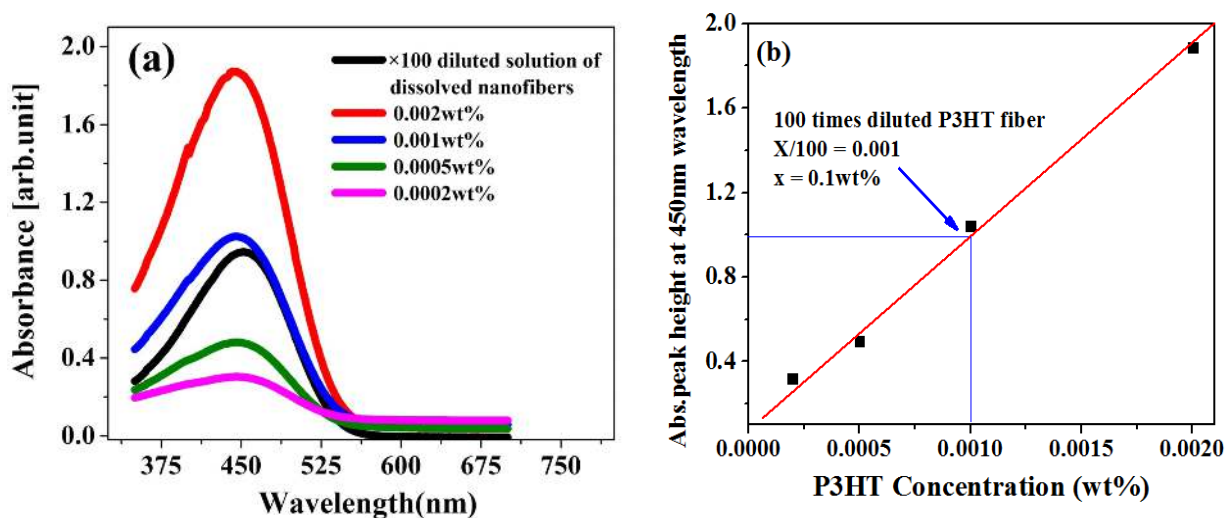


Fig. 5.2 (a) UV-visible absorption spectra of P3HT solutions of different concentrations, (b) Absorption peak height (at $\lambda = 450 \text{ nm}$) versus P3HT concentration (wt%)

Here, it may be noted that the change in the spectral shape might involve a possibility of misestimating the concentration, but it is enough for clarifying the state in the nanofiber dispersion as a coarse approximation in this study.

The surface morphology of P3HT and P3HT-nanofibers based thin-film were examined by using AFM measurement, and the measurements were done for the scanning area of $5\ \mu\text{m}\times 5\ \mu\text{m}$ and $1\ \mu\text{m}\times 1\ \mu\text{m}$, as shown in Fig 5.3.

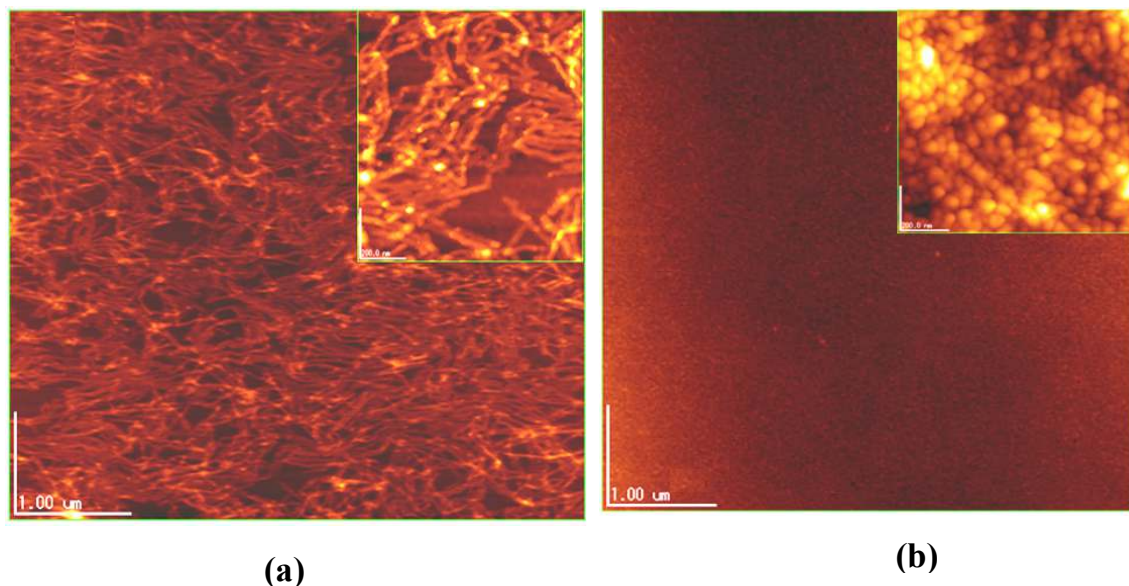


Fig. 5.3 AFM pictures of the spin coated thin-film prepared by (a) P3HT-nanofibers suspension, (b) P3HT solution. The scan film area dimension is $5\ \mu\text{m}\times 5\ \mu\text{m}$; inset scan area dimension is $1\ \mu\text{m}\times 1\ \mu\text{m}$

The morphology of both P3HT and P3HT-nanofibers films appeared significantly different. The spherical shape P3HT molecules in the range of 15 to 20 nm diameter were observed for the spin coated P3HT film, as shown in the Fig. 5.3 (b). On the other hand, nanofibers were clearly observed in the spin coated P3HT-nanofibers thin-film. The length and diameter of the nanofibers formed were estimated to be in the range of 200 to 400 nm and 8 to 10 nm respectively, as shown in Fig. 5.3 (a). Some extent of fiber orientation in the P3HT-nanofibers thin-film was also observed which may be owing to the centrifugal force acting over the substrate during coating. This fiber orientation could also be due to the annealing process which might promote settling in the nanofibers.

However, if P3HT-nanofibers film is annealed at high temperature such as at 120 °C, then fiber got melted and disappeared [Tiwari *et al.* (2014), Tiwari *et al.* (2014)].

Electrical characteristics of the fabricated P3HT-nanofibers based FET are shown in the Fig. 5.4. The output characteristics (I_{DS} versus V_{DS} , at fixed V_{GS}) is shown in Fig. 5.4(a) and the transfer characteristic (I_{DS} versus V_{GS} , at fixed V_{DS}) is shown in Fig. 5.4(b). Initially when V_{DS} across OFET was increased, I_{DS} increased linearly with respect to the V_{DS} , however, after “pinch off” condition I_{DS} got saturated and became independent of V_{DS} . These electrical characteristics demonstrate normally-ON type p-channel behavior of the fabricated transistor. The electrical property and performance of an organic transistor is highly influenced by the active channel thin-film morphology, orientation of the molecules in the film, microstructures, thin-film smoothness as well as the thickness of the organic film [Sakamoto *et al.* (2011)].

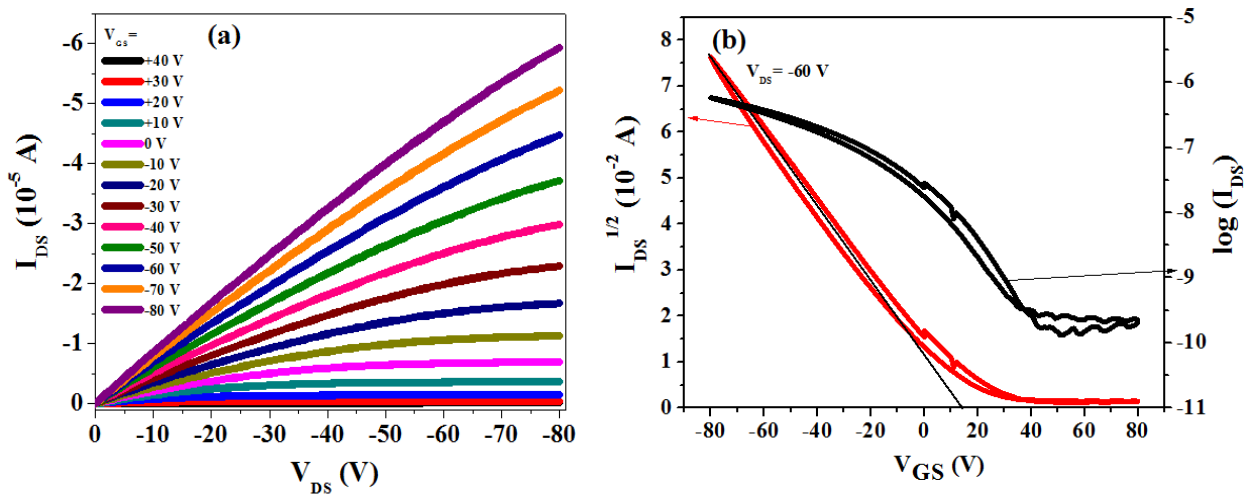


Fig. 5.4 The I-V characteristics of the fabricated P3HT-nanofibers based OFET (a) Output Characteristics, (b) Transfer Characteristics

The essential parameters related to the OFET performance such as field effect-mobility, threshold voltage, ON/OFF ratio, transconductance and sub-threshold slope were calculated from the transfer characteristics (as described in previous chapters) and

the values determined were $0.90 \times 10^{-2} \text{ cm}^2/\text{Vs}$, 13 V, $10^{3.5}$, 6.57×10^{-6} and 12 V/dec, respectively. A comparison in the performance parameters of P3HT solution and P3HT-nanofibers based FETs is given in the Table 5.1.

Table 5.1 Comparison between performance parameters of P3HT solution and P3HT-nanofibers based FETs

Active channel material	ON/OFF ratio	V_{TH} (V)	μ_{sat} ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	SS (V/dec)	g_m (S)
P3HT FET	$10^{2.5}$	5	2.01×10^{-4}	12	18×10^{-9}
P3HT-nanofiber FET	$10^{3.5}$	13	0.90×10^{-2}	10	6.57×10^{-6}

It was observed that the fiber (0.1 wt%) based OFET showed much better performance than the P3HT (0.2 wt%) based FET. So, it was concluded that P3HT-nanofibers based FET has two benefits over the P3HT solution based FET. Firstly, it gives much higher performance and secondly, it requires less material consumption for channel fabrication as compared to P3HT FETs.

It is obvious that the grain boundaries in the organic semiconducting thin-film always decrease their charge carrier transport property. However, in case of fiber based thin-film, every nanofiber acts as a domain for charge transport, and hence, the transport property of the film gets improved [Tiwari *et al.* (2014)].

In the above discussion, it is already mentioned that the spin coated nanofiber films showed some extent of fiber arrangement due to the centrifugal force. These arranged fibers may provide straight lane between the two electrodes (source and drain) for point to point charge carrier transport which drastically improves the electrical property of the film [Bielecka *et al.* (2011)]. But, unfortunately, here only a few fibers may get aligned

in the channel, although many of them were dispersed randomly. So, the carrier movement takes place in several directions by following the nanofibers directions [Kiriya *et al.* (2011)]. Therefore, the fibers alignment is an important issue; so, it is the next important objective of future research work in order to further improve the performance of organic transistors.

5.4 Conclusions

In this chapter, P3HT-nanofibers were prepared in the laboratory and were further used for OFET fabrication. The nanofibers suspension concentration and their thin-film morphology were studied by measuring UV-visible absorption spectra and AFM. P3HT-nanofibers based OFETs were fabricated in the same way as described in the previous chapters. Electrical performance and active channel thin-film microstructure of P3HT-nanofibers based OFET were compared against P3HT based OFET performance and their channel thin-film morphology. It was found that P3HT-nanofibers based transistors showed much improved performance compared to P3HT based FETs. The field-effect mobility of nanofibers based transistor was about 45 times higher than the mobility of P3HT based FET. The other key performance parameters such as V_{TH} , ON/OFF current ratio, sub-threshold slope and transconductance were also improved, and these improvements were due to the improved transport property of the P3HT-nanofiber based active channel film.