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OPTICAL AND MORPHOLOGY OF SELF-ASSEMBLED POLYHEXYLTHIOPHENE (P3HT) NANOWIRES

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ABSTRACT

Poly (3-hexylthiophene-2, 5-diyl) (P3HT) is a well-known p-type semiconductor for electronic and optoelectronic applications with a bandgap of ~ 1.9 eV. It is believed that the nanowire form of the polymer offers better structure, stability, and carrier pathways as an electronic device. In this study, P3HT nanowires were synthesized by aggregation under the dark for 72 h in a partial solvent, toluene. To investigate the change in polymer chain entanglement, spectra of UV-Vis absorption, FTIR and Raman of both P3HT nanowires and amorphous P3HT films were compared and further analysed. The result shows that the optical absorption of P3HT nanowires had blue shifted to higher energy indicating bandgap widening compared to amorphous P3HT. This electronic behaviour change is supported by FTIR and Raman results that implied increasing P3HT conjugation length with nanowire formation. The randomly oriented nanowires had an estimated diameter size of 10 – 20 nm. This improved nanostructure is majorly driven by intermolecular π-π stacking interactions that can produce P3HT film with better performance as charge carrier layer and photon absorber.

1.0 INTRODUCTION

In the last decades, numerous conjugated conducting polymers have been employed for modern electronic devices such as solar cells [1], light-emitting diodes, photovoltaics [2], and field effect transistors (FETs) [3]. The fact that they are organic, mechanically flexible, solution-processable, and with good charge transport attracts a lot of research interest. Due to the delocalization of π-electrons along and between backbones, conjugated polymers such as polyaniline, polypyrrole, and polythiophene possess intriguing electrical and optoelectronic features that are chemically tuneable. The carrier transport occurs both within the polymer rigid backbone chain and between adjacent backbones when the molecules are stacked against each other. Poly (3-hexylthiophene-2, 5-diyl) (P3HT) is a conjugated semiconductor with semi-crystalline properties. Semi-crystalline polymers have a highly ordered molecular structure and low viscosity. As such, these polymers remained at solid state until suitable heat was absorbed [4]. The popularity of P3HT is also because it has good thermal stability compared to other conjugated polymers [5].

Although P3HT semiconductor material can conduct high current, it has apparent limitations in optical absorption that will affect device performance [6-9]. In most applications of heterojunction organic solar cells, P3HT was mixed blend with another n-type semiconductor, typically PCBM as a mostly amorphous state. Therefore, the energy conversion of P3HT was affected by the narrow optical absorption coverage. Maximum light absorption can also be obtained by thicker P3HT film that can result into coherent

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collection of charge following exciton dissociation at the interface. However, this means more material content posing hindrances as electronic devices require minimal thickness and good flexibility. As a p-type charge carrier, low mobility in the interchain π-π stacking direction of P3HT compared to the intrachain polymer chain can become another disadvantage. By fabricating P3HT nanowires or nanofibers, the charge carriers can have higher mobility across the film and lower recombination rates [10]. For this reason, the structuring of the P3HT system was suggested to enhance its optical, electronic and optoelectronic properties [11]. Tuning P3HT into crystalline material can offer the possibility for various application such as transistors, saturable absorbers and photonic materials.

Controlling and optimizing of P3HT structure is important to produce effective organic devices. One method to control P3HT structures is by preparing as functional conductive polymer nanowires. Cao et al (2019) found that the efficiency of the charge carrier could be improved by connecting the long P3HT polymeric chains to crystalline domains [12]. As a result, long and wide P3HT nanowires can be produced. Polymer-based nanowires are basic building blocks for nanoelectronics devices and an important class of one-dimensional nanostructures due to their given flexibility, stretch-ability, and low cost formed via bottom-up fabrication [13]. Several approaches for the synthesis of polymer-based nanowires such as templating using porous alumina, electrospinning, and solution chemistry methods. Previously, Li and his co-workers (2014) produced P3HT nanowires in marginal solvents and fabricated multiple layers using method of spin coating [14]. Tang et al (2019) also reported the fabrication of P3HT nanowires using spin-coating of low-concentration P3HT solution. Under the right conditions, spin coating of organic polymers can produce a uniform distribution that produces good optoelectronic properties [15].

In this research, P3HT nanowires film fabricated by drop casting low concentration P3HT solution as suggested from ref. Zhao et al (2017) were employed to study carbon-carbon interactions between the P3HT molecules in the nanowire state [16]. The discussion entailed optical and structural changes observed in this P3HT transformation. The difference in their UV-Vis, FTIR, and Raman characteristics will help future researchers control P3HT amorphous and crystalline states during device fabrication.

2.0 METHODS AND MATERIAL

Regio-regular P3HT, of molecular weight, M_w ~50000–100000 with 99 % purity and toluene (anhydrous, 99 % purity) purchased from Sigma-Aldrich were used without any prior treatments. P3HT nanowires was produced using dissolution of P3HT in toluene solvent with 1: 200 weight ratios. Toluene was chosen because of its high boiling point and low solubility parameters, 110.6 °C and 18.3 °C respectively. The solution was then stirred at 75 °C for 4 hours. The obtained solution was kept in the dark box for 72 hours to allow P3HT aggregation or swelling into the nanowires itself. Self-assembly must occur in the dark since the P3HT is susceptible to light absorption. After 72 hours, 50 µL of P3HT nanowires solution was then dropped onto a clean quartz substrate and dried at room temperature. P3HT nanowires thin film were characterized to confirm the presence of nanowires. On the other hand, amorphous P3HT film was processed from a different P3HT solution made using a 1:2 weight ratio of P3HT and tetrahydrofuran. The solution was stirred at 50 °C for 24 hours prior to spin coating on a glass substrate at 500 rpm in 3 seconds. The stability of the film was observed for 24 hours before characterization.

UV-Vis-NIR spectrophotometer from Perkin Elmer UV, Winlab was used to investigate the absorption of P3HT nanowires. The information of the present functional group was determined using Fourier transform infrared (FTIR) spectroscopy. The spectra were analysed at 650 – 4000 cm^{-1} range. Raman spectroscopy with excitation line 633 nm was used to study interaction at the conjugation chain. The surface morphology of P3HT nanowires was observed using field emission scanning electron microscopy (FESEM; Zess Gemini). The size of nanowires was calculated at 50 K magnifications.

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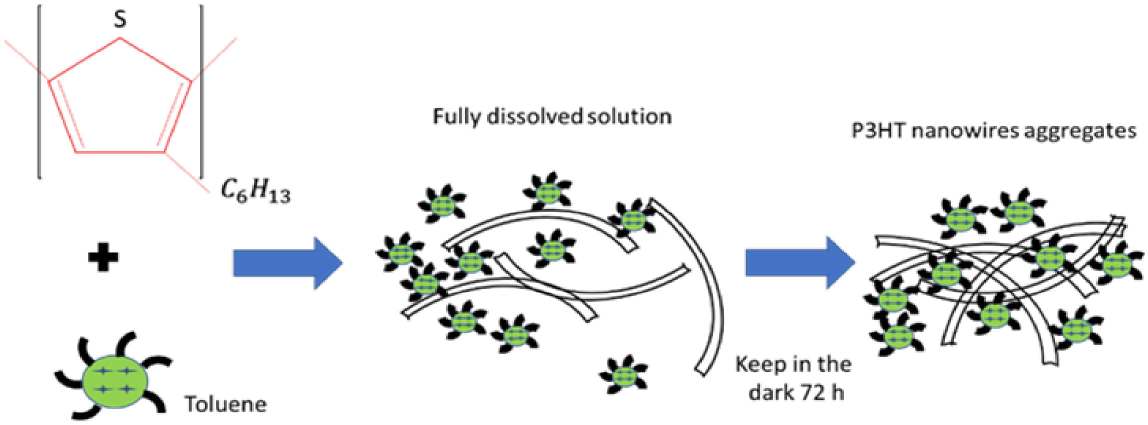

Figure 1. P3HT nanowires preparation

3.0 RESULTS AND DISCUSSION

For start, it was observed that the colour of the P3HT solution changed after the polymers self-assembled into nanowires. The P3HT mixed toluene solution was observed as dark brown, as shown in Figure 2. However, after the stirring process was finished, the colour changed to yellowish-brown colour. The colour of the P3HT solution after 72 hours was dark purple indicating P3HT had successfully assembled into a nanowires state. This solution was then used to make the thin film through the drop-casting method. After 24 hours dried at room temperature, the dark purple colour is still retained in the film. The physical comparison between the nanowires and amorphous polymeric thin films is shown in Figure 3. In comparison, the colour of amorphous P3HT film was observed as dark brown colour. The colour differences of films indicated that both P3HT have different morphologies.

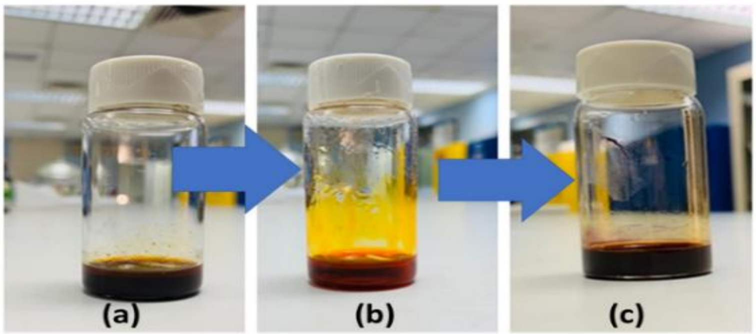

Figure 2. (a) P3HT solution before stirring; (b) P3HT solution after stirring; (c) P3HT solution after keep in the dark box

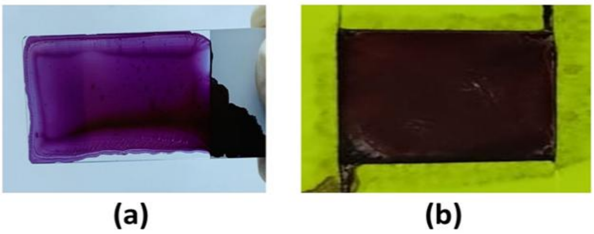

Figure 3. Images of (a) drop casted P3HT nanowires; (b) spin coated amorphous P3HT film

The investigation is followed by UV-Vis absorption spectra analysis of amorphous P3HT and P3HT nanowires films. As conjugated polymers, three distinct peaks were observed in the amorphous P3HT spectrum, the peaks are located at 530 nm, 575 nm, and 615 nm referring to π-π^* electronic band transitions of the polymer as reported from other literature as well [17-18]. Similar peaks were observed in the P3HT nanowires spectrum but with different intensity ratios that can be the result of changes in the density of states distribution (DoS) of the system. The intensity of the 530 nm peak seen in the P3HT nanowire spectrum is higher than amorphous P3HT and can be interpreted as densely packed molecules

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present in P3HT nanowires in accordance with Beer-Lambert Law [18]. We also highlighted the apparent blue shift of the optical absorption band edge in the P3HT nanowire because of the bandgap widening. The study of difference in molecular states in P3HT molecules could be further confirmed using XPS spectroscopy.

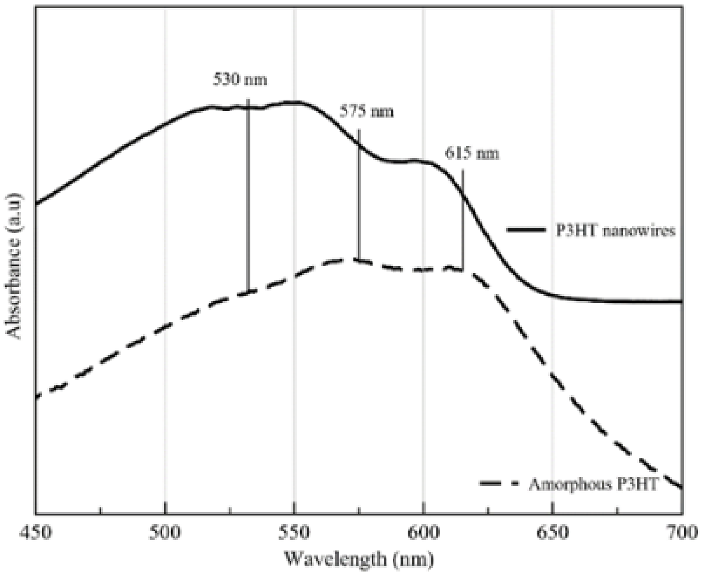

Figure 4. UV-Vis spectra of amorphous P3HT and P3HT nanowires

On the other hand, FTIR spectra of amorphous P3HT and P3HT nanowire films are presented in Figure 5(a). A region of low wavenumber is to be known as a fingerprint of a material. Both transmission spectra show fundamental peaks at 756 cm^{-1} and 864 cm^{-1} belonging to C - H and C - S of the thiophene ring, respectively. There is no shift or new vibration mode present implying that there is no contaminant or molecular structure change after P3HT assembled into nanowires. However, in higher wavenumber, it was observed that two peaks located at 1181 cm^{-1} and 1082 cm^{-1} diminished in the P3HT nanowires film spectrum might be because of the thiophene nanowire formation [19]. These peaks belonged to the C – O vibrational bond diminished in P3HT nanowires indicating that P3HT nanowires were not oxidized and might be more stable than amorphous P3HT. They can be used as one of the indicators that nanowires have formed in film. We also found there are peak shifts at ranges 2880 – 3004 cm^{-1} due to the deformation of the alkyl side chain [20-21]. Polymers with alkyl side chains have face-on orientation and any modifications in molecular stacking will result in the reorientation of long side chains [21].

Since the crystalline phase of P3HT originated from the π-π interactions, both in the plane backbone (intrachain) and (intermolecular) stacking direction of the polymer conjugation length, the study of P3HT crystallinity especially for P3HT nanowires must be strongly supported by Raman spectra shown in Fig. 5 (b). Raman spectrum of P3HT nanowire presents sharp intensities compared to a rather broad spectrum of amorphous P3HT cantered at both C = C symmetric located at 1445 cm^{-1} and the C–C stretching at 1380 cm^{-1} referring to the vibrational modes of thiophene ring [2]. The peaks were not observed in the FTIR, it is a complementary analysis. Interestingly, it was seen that in P3HT nanowires spectra, the intensity of these strong peaks decreased and shifted to a lower wavenumber. The Raman intensity is relatable to the density of non-symmetrical molecules in the film. There is also possibility that this change is the result of increasing of P3HT conjugation length as nanowires that is becoming longer compared to amorphous film [2].

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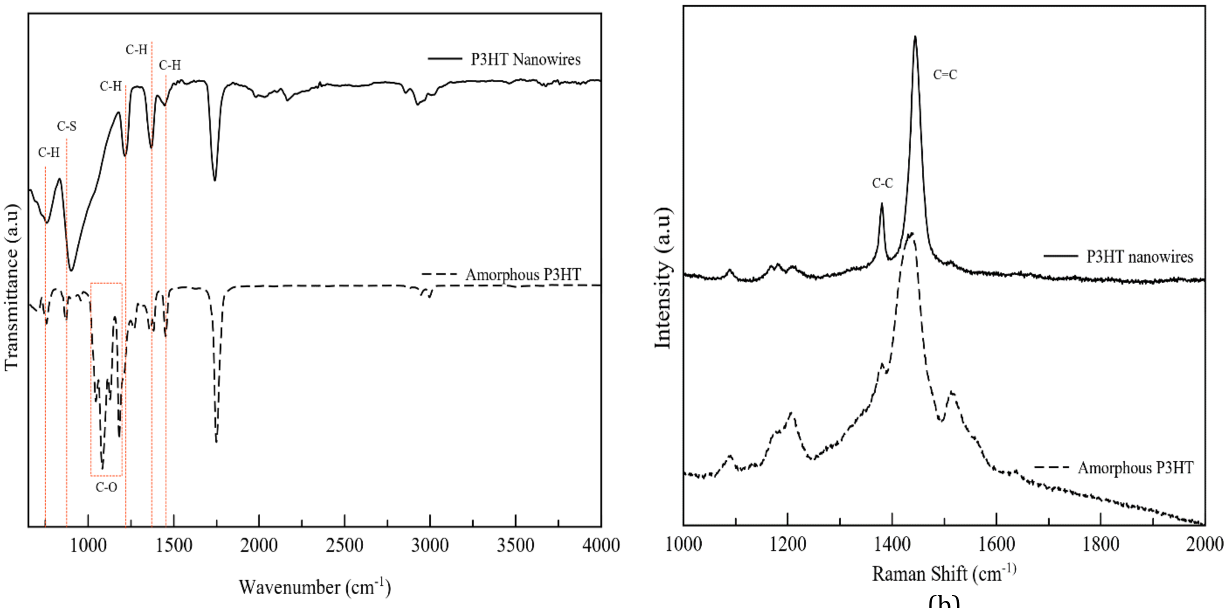
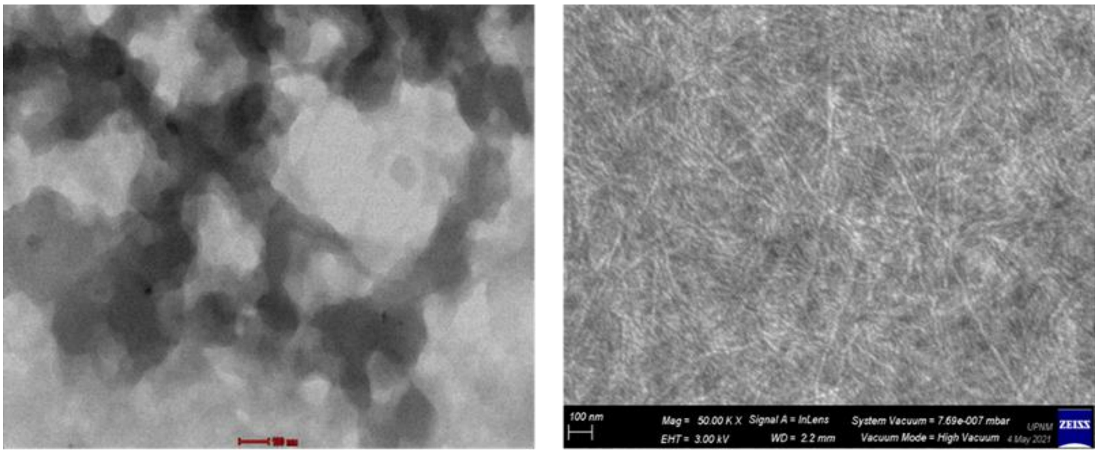


(a) (b)

Figure 5. Comparison of (a) FTIR spectra on amorphous P3HT and P3HT nanowires; (b) Raman spectra on amorphous P3HT and P3HT nanowires

Figure 6 shows electron images of amorphous P3HT and P3HT nanowire films. As the HR-TEM image of the amorphous P3HT shows the polymer appeared as sheets with no specific shape that represent non-crystalline P3HT, P3HT nanowires were observed as closely packed wires that uniformly covered the entire substrate. The 50 K magnification with 100 nm scale image demonstrated that the shape of P3HT nanowires was likely to be tubular or cylindrical with an average diameter of P3HT nanowires around 10 - 20 nm. The nanowires are also randomly oriented consistent with other observations of P3HT nanowires fabricated using chemical methods [22]. This morphology shows that we have successfully fabricated P3HT nanowires using toluene solvent aggregation in the dark.



(a) (b)

Figure 6. The comparison images between (a) amorphous P3HT taken by HR-TEM; (b) P3HT nanowires taken by FESEM

Finally, the P3HT nanowires film deposited on the ITO electrode has been tested for its resistivity measurement. The result of current-voltage measurement done using two probe measurements using DMM6500 Keithley multimeter of bare ITO substrate and ITO/P3HT nanowires film are shown in Figure 7. The measurement was done from 0 V to 5 V and repeated 10 times. The current across the films increased with voltage. The current measured from ITO/P3HT nanowire film dropped to 6.83×10^{-8} A from 7.33×10^{-8} A in bare ITO. This indicated P3HT nanowires produced resistance on the ITO film. The

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gradient of the graph can be defined as total resistance in the substrate. It is calculated that the resistance of bare ITO is $7.188 \times 10^{-7}\ \Omega$ while the resistance of ITO/P3HT nanowires film is $7.679 \times 10^{-7}\ \Omega$. The configuration of P3HT nanowires deposited on anode contact ITO was not optimized for conductivity measurement as such did not allow good electron conduction to be measured from the semiconducting layer due to high ITO work function and heterogeneous deposition of the P3HT layer. The small increase in resistance of ITO/P3HT implied that P3HT acts as another resistive element on ITO.

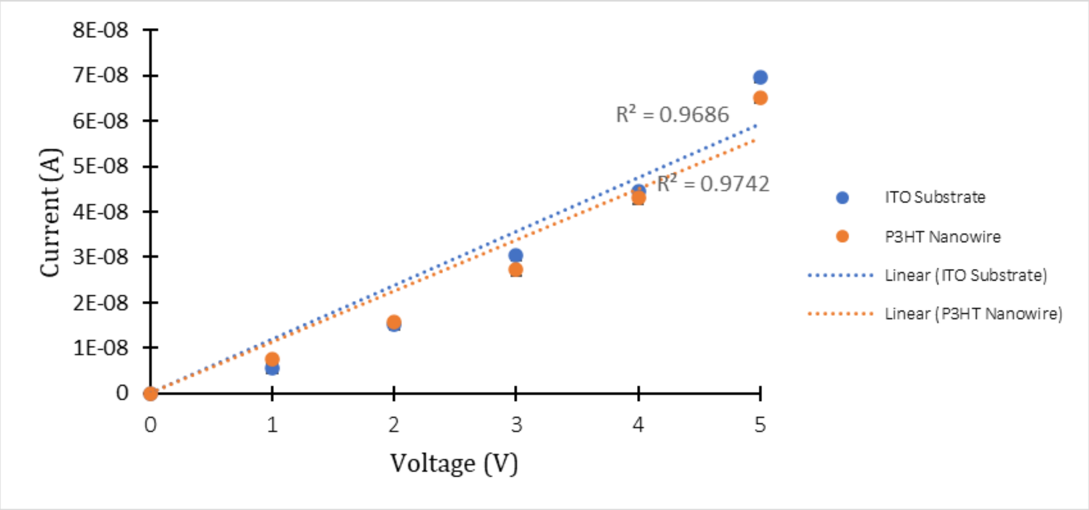

Figure 7. The I-V graph of ITO substrate and ITO/P3HT nanowires film

4.0 CONCLUSIONS

Solution-synthesized P3HT nanowire film was successfully fabricated using drop cast technique on substrates. The colour changed from dark orange to dark purple indicating P3HT nanowires have formed. The P3HT nanowires formation consists of densely packed P3HT molecules as observed from UV-Vis characterization and the average diameter of P3HT nanowires was measured to be 10 – 20 nm as seen from the FESEM images. FTIR and Raman spectra obtained show the crystalline structure of P3HT nanowires has longer conjugation length consistent with other observations. In this study, deposited P3HT nanowires increased the resistance across the ITO film of amount $7.679 \times 10^{-7}\ \Omega$. The small increase in resistance and bandgap widening by ITO/P3HT nanowires show the nanowires structure can give better charge carrier pathway in material and produced maximum light absorption for application such as solar cell. Furthermore, this is a more viable and economical way of synthesis P3HT film material compared to spin coating of amorphous P3HT where high material waste will be produced.

5.0 CONFLICT OF INTEREST

The authors declare no conflicts of interest.

6.0 AUTHORS CONTRIBUTION

Ahmad Poad, N. (Methodology; Formal analysis; Data curation; Investigation; Resources; Software; Visualisation; Writing - original draft)
Abdul Halim, N. (Investigation; Resources; Writing - review & editing)
Sa'aya, N. S. S. (Methodology; Formal analysis)
Ngah Demon, S. Z. (Conceptualisation; Validation; Formal analysis; Data curation; Writing - review & editing; Funding acquisition; Project administration; Supervision)

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