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To cite this article: N I Pratiwi *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **496** 012031

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Synthesis of one-dimensional nanotubes from an organic semiconducting polymer (PDPPBTT) by the centrifuge method

N I Pratiwi, V Fauzia and C Imawan

Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA)
Universitas Indonesia, Depok 16424, Indonesia

Corresponding author: vivi@sci.ui.ac.id

Abstract. The synthesis of the nanostructures of low-band-gap organic semiconducting materials has attracted significant attention as a technique to attain high surface areas. This study aims to synthesize PDPPBTT nanotubes using an anodic aluminum oxide (AAO) template and centrifugation method at three different speeds (3000, 3500, and 4000 rpm). The results show the effect of the rotational speed on the structural, morphological, and optical properties of PDPPBTT nanostructures. The results showed that the use of high rotational speeds resulted in shorter nanotubes with lower absorption intensities but enhanced photoluminescence in comparison with those formed at a lower rotational speed. These results demonstrate an important advancement toward materials that better facilitate light absorption, charge separation, and charge diffusion, and are expected to contribute toward the future development of organic solar cells, light-emitting diodes, and sensors on flexible substrates.

Keywords: PDPPBTT, low band gap, semiconductor, nanotubes, anodic aluminum oxide template, centrifuge method

1. Introduction

Low-band-gap organic semiconducting materials have attracted significant attention owing to their unique properties, such as controllable electrical and optical properties, low cost, flexibility, and ease of synthesis. These polymer-based materials have the potential to be applied in organic optoelectronic devices, such as organic solar cells, light-emitting diodes, and sensors on flexible substrates [1–3]. One such material is PDPPBTT (poly {2,2'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)dithieno[3,2-b]thiophene-5,5'-diyl-alt-thiophene-2,5-diyl}).

Generally, organic semiconductor materials are synthesized as thin films, which have very limited surface areas. Therefore, some researchers have attempted to fabricate the nanostructures organic materials, such as nanotubes, nanoflower and nanorods [4–6]. Such nanostructures are expected to increase the surface area to achieve better light absorption, facilitate charge separation, and provide a shorter distance for charge diffusion. Nanostructures are generally created by either bottom-up or top-down methods. Top-down method is a relatively simple and inexpensive method. It uses a soft or hard template, such as polycarbonate, a silica membrane, or a nanoporous anodic aluminum oxide (AAO) template. The infiltration of the polymer material into the AAO template can be facilitated by spin coating, dip coating, electrodeposition, or centrifugation [6–9].

In this study, PDPPBTT nanotubes were synthesized using an AAO template by centrifugation to facilitate the infiltration method. The objective is to observe the effects of the centrifugation speed on the structural, morphological, and optical properties of the PDPPBTT nanostructures. Till date, no data has been reported on PDPPBTT nanostructures so this study has the potential to provide new insight that can be applied to the future development of organic optoelectronic devices.



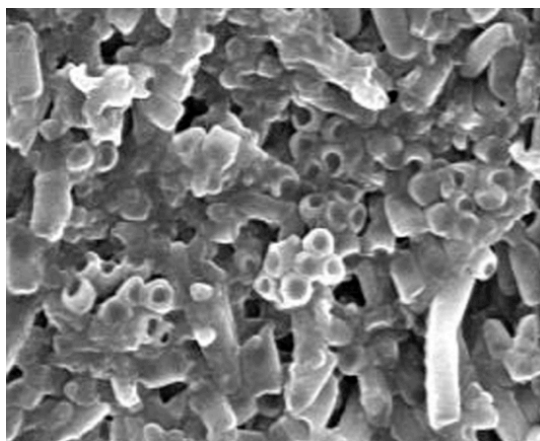


Figure 1. FESEM image of PDPPBTT nanotubes

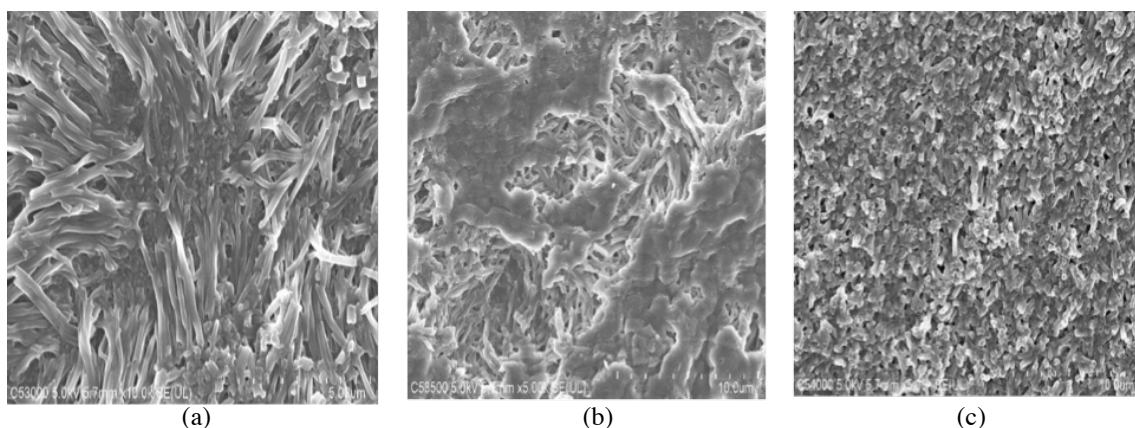


Figure 2. The FESEM images of PDPPBTT nanotubes formed with rotational speeds of (a) 3000 (b) 3500, and (c) 4000 rpm

2. Methods

The commercial semiconducting polymer, PDPPBTT, was obtained from Luminescence Technology Corp. and used without further purification. The nanoporous AAO template with a pore size of 20–200 nm and a thickness of 60 μm was purchased from Whatman Anodisc (Sigma-Aldrich, St. Louis, USA). Prior to the infiltration process, the template was cleaned by sonication in acetone for 15 minutes followed by rinsing in deionized water and dried completely at room temperature. The cleaned AAO template was inserted into a modified centrifuge tube as described previously [6]. PDPPBTT (5 mg) was dissolved in 1 mL of chloroform and 100 μL of this solution was dropped onto the template. The template was then rotated in a centrifuge (Kubota 2420) at either 3000 (1008 g), 3500 (1370 g), or 4000 rpm (1790 g). The PDPPBTT nanostructures were then detached from the AAO templates on copper tape, immersed in 3 M sodium hydroxide for 24 hours, and subsequently rinsed with deionized water.

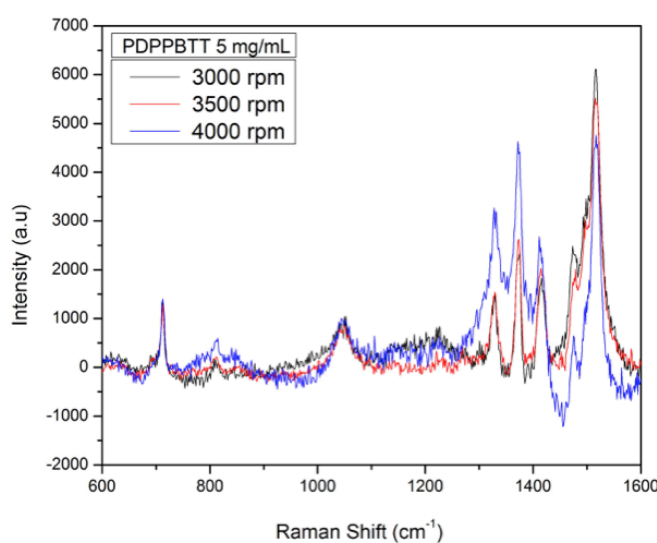
The structural and optical properties were characterized by Raman spectroscopy (Renishaw RE 04), UV-vis spectroscopy (Shimadzu UV-3101 PC), and photoluminescence spectroscopy (Renishaw RE 04). Morphological characterization was conducted using a field-emission scanning electron microscope (FESEM, Hitachi SU-8030).

3. Results and discussion

Figure 1 shows a cross-sectional FESEM image of the PDPPBTT nanostructure formed with a rotational speed of 3000 rpm. It can be seen that the nanotube structure was successfully formed,

Table 1. Vibration modes from the Raman spectra of PDPPBTT nanotubes synthesized with different rotational speeds

Peak	Rotational speeds (rpm)			Vibration modes
	3000	3500	4000	
V1	712	712	710	C–H bending
V2	1150	1149	1147	C–H bending and C=C stretching
V3	1329	1328	1327	C–H bending of BTT
V4	1374	1373	1371	C=C stretching of DPP
V5	1498	1497	1496	C=C stretching/thiophene ring stretching
V6	1516	1516	1515	C–C stretching

**Figure 3.** Raman spectra of PDPPBTT nanotubes prepared with three different rotational speeds

indicating that the polymer solution can infiltrate into the pores and tends to wet the pore wall rather than bind with other PDPPDTT molecules. This implies that the adhesion force between the PDPPBTT molecules and the pore wall is greater than the cohesion force between PDPPBTT molecules. The use of a readily evaporated chloroform solvent promoted the formation of nanotubes instead of nanorods [5,6].

The FESEM images of PDPPBTT nanotubes prepared at three different rotational speeds are shown in figure 2. The nanotubes prepared at 3000 rpm were longer than those prepared at 3500 rpm and 4000 rpm. This can be attributed to the effect of the greater centrifugal force that takes place during centrifugation at a higher rotational speed. For the centrifuge used here [6], a rotational speed of 3000 rpm yields a centrifugal force of 1000.2 mN. This force can easily push a low-concentration polymer solution deep into the pores of the template. However, the use of a higher rotational speed results in a higher centrifugal force of 2000.2 mN, which may be too high and cause the nanotubes to break, resulting in shorter nanotubes [6].

Figure 3 shows the Raman spectra for the three different samples. Six peaks were observed in these spectra. The peaks and the bonds they correspond to are summarized in Table 1. The vibration modes indicate C–H bending, C=C bending, C–H bending in BTT, C=C stretching in DPP, C=C stretching in thiophene, and C–C stretching [10].

These results show that an increase in the rotational speed causes a peak shift toward shorter wave number (downward), indicating that the rotational speed affects the bonds between the molecules of PDPPBTT. Moreover, the greater rotational speeds resulted in higher peak intensities at 1329 and 1374 cm^{-1} and lower peak intensities at 1498 and 1516 cm^{-1} . This may be related to the FESEM observation that higher rotational speeds yield shorter nanotubes.

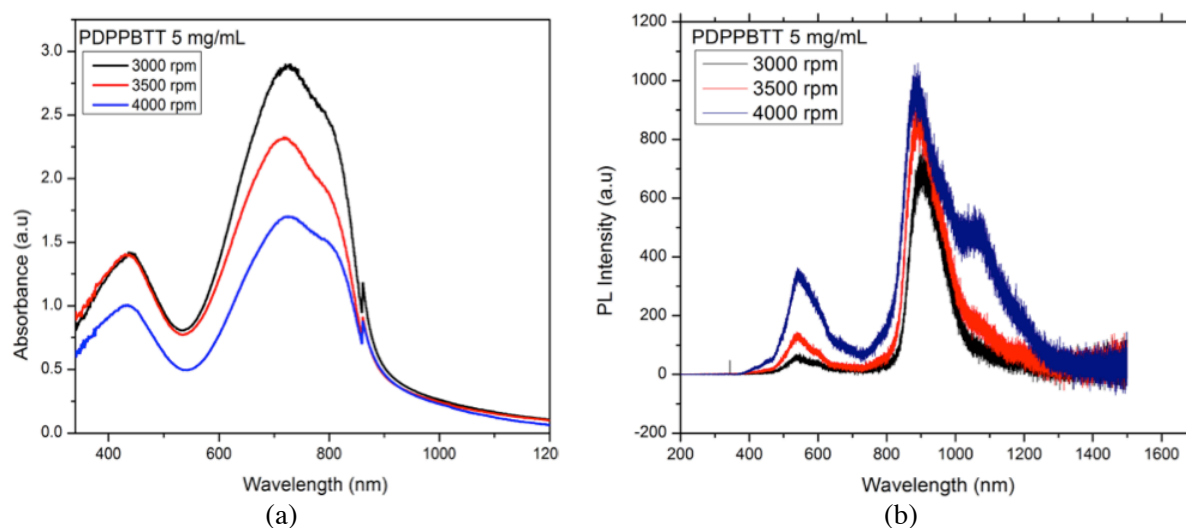


Figure 4. (a) UV-Vis Absorption spectra and (b) photoluminescence spectra of PDPPBTT nanotubes prepared with three different rotational speeds

The UV-vis absorption spectra of the PDPPBTT nanotubes prepared with different rotational speeds are shown in figure 4a. The main absorption peak of PDPPBTT was located at 419 nm; this corresponds to the absorbance of DPP due to excitation from the π band to the π^* band [4,11] and another peak at 729 nm corresponding to the absorbance of BTT [12]. The results indicate that the samples prepared at higher rotational speeds have lower absorption intensities. This may be because longer nanotube structure can absorb light more effectively. Alternatively, the high level of coplanarity and more effective intra-molecular charge transfer from the donor unit, BTT, to the acceptor unit, DPP, may increase the conjugation length and, thus, increase the absorption intensity [13].

Figure 4b shows the photoluminescence spectra of the PDPPBTT nanotubes prepared at different rotational speeds. The spectra exhibit two emission peaks, i.e., one at a wavelength of 540 nm and another in the infrared region at 890 nm. These peaks result from the radiative transitions when the material absorbs light at wavelengths of 419 and 729 nm, respectively, as shown in absorption spectra in figure 4a. Moreover, greater rotational speeds enhance the photoluminescence intensity in contrast to the absorption intensity, which was decreased at the greater rotational speeds. The mechanism leading to this effect is not clearly understood based on the information available. However, we hypothesize that the observation that high absorption intensity is not always accompanied by high radiative transitions indicates that there are non-radiative transitions occurring in the PDPPBTT nanotubes prepared at higher rotational speeds.

4. Conclusions

In this study, low-band-gap semiconducting PDPPBTT nanotubes were successfully synthesized with a nanoporous AAO template via the centrifuge method at three different rotational speeds (3000, 3500, and 4000 rpm). The results show that an increase in the rotational speed results in longer nanotubes with Raman peaks shifted toward shorter wave numbers, reduced absorption intensity, and enhanced photoluminescence intensity. All samples exhibited the two typical absorption peaks at 419 and 729 nm and emission peaks at 540 and 890 nm. However, the reason for the opposing effects of the rotational speed on the absorption and photoluminescence intensities is not clearly understood yet. We hypothesize that the longer PDPPBTT nanotubes absorb the light more effectively but that this absorption is not accompanied by high radiative transitions. This phenomenon should be further investigated in future studies.

Acknowledgements

The authors would like to thank Einago (www.einago.com) for the English language review.

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