

Size Effects on the Luminescence Properties of Polymer Nanowires

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Abstract Poly(3-(2-methoxyphenyl)thiophene) (PMP-Th) nanowires were fabricated using porous anodic alumina (PAA) as template through electrochemical polymerization by cyclic voltammetry. The control on the size of nanowires was confirmed by electron microscopy. The results indicated that the luminescence spectra of PMP-Th nanowires in PAA nanochannels were blue-shifted and emission intensity was enhanced compared to the emission of the PMP-Th film. Moreover, the luminescent spectra of PMP-Th nanowires were size dependent, which may result from the change in the degree of confinement of nanowires in PAA. Förster energy transfer from PAA to PMP-Th molecules is considered to be responsible for the enhancement of luminescence from PMP-Th nanowires in PAA. The results show that the emission properties of polymers with nanostructures can be tuned by controlling their size.

Keywords: Polythiophene; Nanowires; Luminescence; Blue-shift.

INTRODUCTION

Conducting polymers are an important subject of intensive research in recent years because of their great potential application in light-emitting diodes, solar cells, field effect transistors, nonlinear optical devices, sensors and so on^[1–5]. Polythiophenes (PThs), as a classic example of conducting polymers, have attracted considerable attention due to their good opto-electronic properties and chemical stability in both the neutral and doped states^[6–8]. In most reports PThs have been described as a red-orange light-emitting materials with low emission efficiency, which impeded the path toward the application in full-color emitting devices^[9, 10]. Although tremendous efforts have been devoted to improve their luminescence property^[11–13], it still remained a big challenge to modify PThs with chemical and physical methods to realize full-color emission and high efficiency. Recently, one dimensional (1D) polymer nanostructures, such as nanowires and nanotubes, have attracted a broad interest due to great effects on the alteration of optical and electronic properties^[14–16], which present us another strategy to solve the full-color challenge of PThs. Nevertheless, to the best of our knowledge, although the fabrications and some electrical properties of PThs-related nanostructures have been intensively reported^[17–19], the effects of the diameter on their optical behavior are still unknown. In this report, we fabricated poly(3-(2-methoxyphenyl)thiophene) (PMP-Th)-a derivative of polythiophenes-nanowires with diameters from 40 nm to 80 nm and investigated systematically their luminescence properties, which may have more promising applications in novel optoelectronic devices.

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EXPERIMENTAL

Materials

3-Bromothiophene (97%), 2-bromoanisole (97%) and dichloro(1,3-bis(diphenylphosphino)propane)Ni(II) were purchased from J&K-Acros Co. (USA). Acetonitrile (HPLC grade) and boron trifluoride diethyl etherate (BFEE) (AR) were supplied by Sinopharm Chemical Reagent Co. Ltd. (China). All the reagents were used as received. Aluminum foil with purity of 99.999% was purchased from Beijing Youyanyijin Co. The 3-(2-methoxyphenyl)thiophene (MP-Th) monomer was synthesized according to the similar procedures as reported in literature^[20].

Fabrication of PAA Membranes with Different Size of Nanochannels

The porous anodic alumina (PAA) was fabricated *via* a typical two-step anodizing electrochemical process^[21]. The high-purity aluminum foils were degreased in acetone and cleaned in a 0.2 mol·L⁻¹ NaOH aqueous solution at 60 °C for 30 min and then were electrochemically polished in a mixture of sulfuric, phosphoric and chromic acids. These pretreated aluminum foils were anodized at a constant voltage in 0.3 mol·L⁻¹ oxalic acid aqueous solution at about 5 °C for 6 h, which generated irregular pores. For a well-defined pore pattern, this porous alumina layer was removed by using an aqueous mixture of phosphoric acid and chromic acid. After being washed with deionized water, the second anodization was performed under identical conditions as the first anodization until a desired thickness (*ca.* 60 μm) was reached. In order to obtain through-hole PAA templates, we put the resulted PAA to a mixed solution of hydrochloric acid and CuCl₂ to dissolve the remaining aluminum. Subsequently, the transparent PAA was pore-widen by a 0.3 mol·L⁻¹ phosphoric acid solution. PAA templates with nanochannels diameters from 40 nm to 80 nm were obtained by changing anodize voltage and pore-opened time. Prior to electropolymerization, a metallic layer (Au) serving as electrode is thermally evaporated onto one side of the PAA membrane.

Fabrication of PMP-Th Nanowires

The PMP-Th nanowires were fabricated through electrochemical polymerization method in a three-electrode Teflon cell on a LK98BII microcomputer-based electrochemical system (LANLIKE, China), where the Au layer coated PAA served as the working electrode, a glassy carbon electrode as the counter electrode, and an Ag/AgCl electrode used as the reference electrode. The electrolyte used in PMP-Th electrodeposition consists of 10 mmol·L⁻¹ MP-Th in a mixed solution of acetonitrile and BFEE (*V/V* = 1:2). Before electropolymerization all solutions were de-aerated by dry N₂ bubbling and ultrasonically treated successively. During the experiments, the cell was maintained at a slight N₂ overpressure. The PMP-Th nanowires were fabricated by cyclic voltammetry from 0 to 1.20 V (versus Ag/AgCl) with a scan rate of 0.05 V/s at room temperature. After electropolymerization, the membrane had a yellow-red color indicating the existence of PMP-Th. The reference PMP-Th film was polymerized under the same conditions, except that a Pt sheet was used as the working electrode. For the UV-Vis absorption measurement, the PMP-Th film was electropolymerized on an indium tin oxide (ITO)-coated glass electrode. All the samples were prepared by consuming the same total amount of charge in the reaction cell. After the completion of electropolymerization, every sample was rinsed with ethanol and then dried under vacuum at 60 °C for 24 h.

Characterizations

The morphology of all the samples was characterized by a field-emission scanning electron microscope (SEM, Jeol JSM-6700F) and a transmission electron microscope (TEM, Hitachi H-800); UV-Vis absorption spectral studies were carried out in transmission mode by keeping the samples at an angle of 90° to the incident beam on a Shimadzu DUV-3700 spectrophotometer. Photoluminescence (PL) spectra and the corresponding excitation spectra were measured in the reflection geometry by positioning the samples at an angle of 45° to the incident radiation on a Jobin Yvon FLUOROLOG-3-TAU steady-state fluorescence spectrophotometer. Before the spectra measurements of PMP-Th nanowires in PAA, the Au layer was removed by abrasive paper and cleaned with ethanol. All the measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Morphology Characterization

Figures 1(a) and 1(b) show the bottom surface and cross-section morphology of the PMP-Th nanowires in PAA membrane with 60 nm nanochannels after removing the Au layer as representative. It can be noticed that almost every pore is stuffed by PMP-Th nanowires. Representative SEM images of 80 nm and 40 nm nanowires arrays after partial removal of the PAA in NaOH aqueous solution are shown in Figs. 1(c) and 1(d). These results demonstrate the PMP-Th nanowires have been formed in the PAA nanochannels successfully. TEM images of free nanowires after the PAA completely dissolved are shown in Fig. 2. We can see the average diameter of nanowires range from 40 nm to 80 nm, which are close to the corresponding PAA's pore diameter. All the above results indicate that the precise controlling of the nanowire diameters can be realized. The length of nanowires can be controlled by the integrated charge passed through the cell. If sufficient charge is passed through the cell, nanowires can grow as long as the thickness of the template.

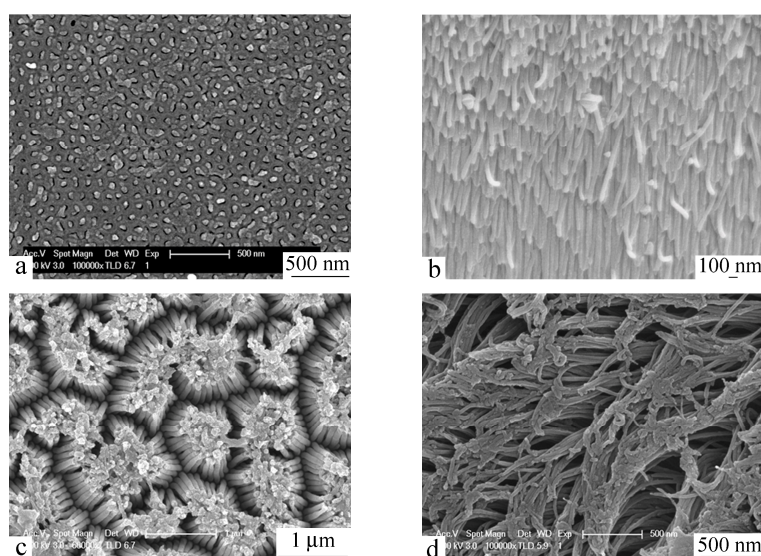


Fig. 1 SEM images of (a) the bottom surface of PMP-Th nanowires in PAA with 60 nm nanochannels, and (b) the corresponding cross-section, (c) PMP-Th nanowire arrays with diameter of 80 nm and (d) PMP-Th nanowire arrays with diameter of 40 nm

UV-Vis Absorption Spectra Results

Figure 3 shows the UV-Vis absorption spectra of PMP-Th nanowires in PAA membrane with various nanochannel diameters. It is obvious that PMP-Th nanowires in PAA membrane have an absorption peak in the region of 400–450 nm, which further confirms the existence of conjugated PMP-Th chains in the channels of PAA. Whereas for PAA, its spectrum shows no absorption peaks in this wavelength range. Apparently the absorption peaks of PMP-Th nanowires in PAA originate from the π - π^* transition of PMP-Th molecules. Subtracting the contribution of PAA, the absorption spectra of PMP-Th nanowires are similar to that of the PMP-Th thin film as shown in Fig. 3. This implies that PMP-Th nanowires have a better extended π -conjugation along the polymer backbone. Moreover, the absorption peaks of the PMP-Th nanowires are distinctly blue-shifted compared to those of the PMP-Th thin film, which suggests that the effective conjugated length of PMP-Th nanowires becomes shorter. When the diameter of nanowires decreased from 80 nm to 60 nm, the absorption peak gradually shifted from 440 nm to 416 nm. However, when the PMP-Th nanowires diameter reduced to 40 nm, the absorption peak shifted to 430 nm. Therefore, the size of PAA nanopores has a clear influence on absorption peak position of the PMP-Th nanowires. Correspondingly, blue-shifts in emission spectra should also be observed by comparison with the emission of the PMP-Th thin film.

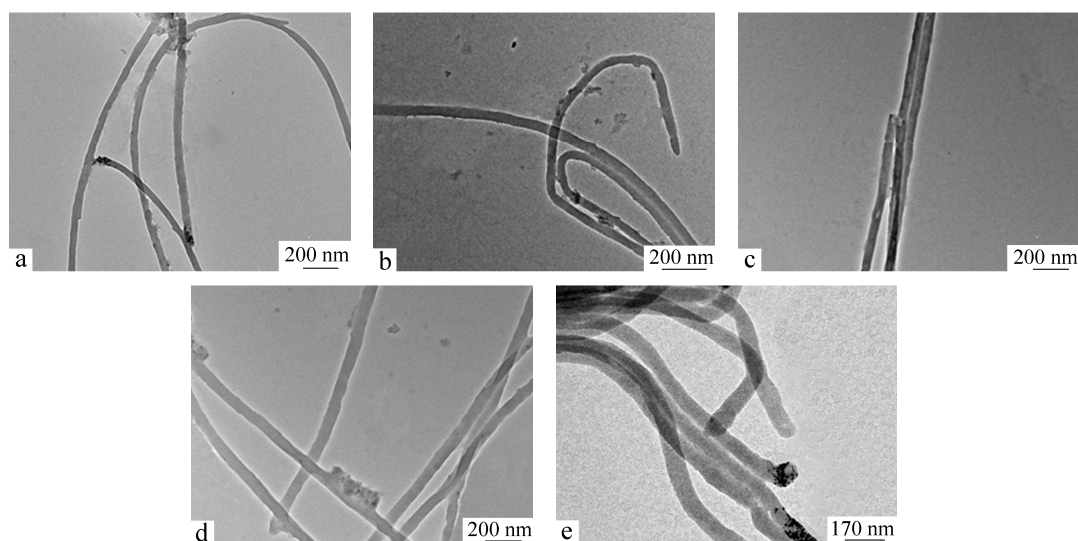


Fig. 2 TEM images of PMP-Th nanowires liberated from PAA with nanochannels size of (a) 40 nm, (b) 50 nm, (c) 60 nm, (d) 70 nm and (e) 80 nm

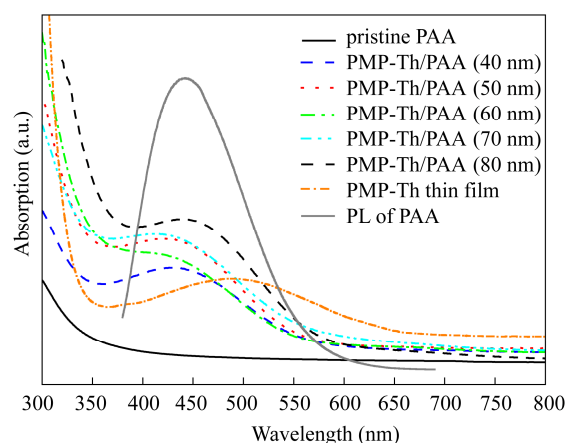


Fig. 3 UV-Vis absorption spectra of PAA, PMP-Th thin film and PMP-Th nanowires in PAA with various diameters

The PL spectrum of pristine PAA is also presented to indicate its overlap with the absorption spectra of PMP-Th nanowires, which was excited by radiation of 390 nm.

Luminescence Studies

The evolution of emission from PMP-Th nanowires in PAA was investigated as a function of nanowire diameter, as displayed in Fig. 4. For comparison, the emission spectrum of PMP-Th thin film is also presented. It can be seen that the emission peaks of PMP-Th nanowires with various diameters are centered at 580–562 nm, while the emission peak of PMP-Th thin film is located near 610 nm. The blue-shift of emission peak (about 30–48 nm) was observed for the PMP-Th nanowires and the emission spectra of nanowires confined in the PAA appeared size dependent. The maximum emission wavelength gradually shifts from 580 nm to 562 nm as the nanowires diameter decreases from 80 nm to 60 nm. Surprisingly, when the diameter decrease further to 40 nm, the emission peak gradually shifts back to 580 nm.

In order to investigate the effect of PAA on the luminescence properties of PMP-Th nanowires, the PAA template was completely dissolved by alkaline solution, and the emission spectra of PMP-Th nanowires dispersed in aqueous solution were measured. As shown in Fig. 5, the variation tendency of the peak position in emission spectra is similar to that of nanowires confined in PAA. This result suggests that the PAA has no or

little influence on the peak position of nanowires. That is to say, the nanowire diameter is an important parameter for the blue-shift. When the PMP-Th molecules are deposited into the nanochannels, the polymer chains may become twisted, so the interaction between the molecules is reduced compared to that of thin film. As the size of nanowires decreases from 80 nm to 60 nm, the polymer chains become more twisted and thus the effective conjugated length becomes shorter. Shorter effective conjugated length means larger energy gap. Therefore the blue-shift phenomenon appeared in the PL spectra (Fig. 4). However, when the diameter of polymer nanowires is smaller than 60 nm, the PL blue-shift is reduced. This seems to be opposite to the rule of quantum size effect^[22]. In previous reports of Martin^[23] and McGehee^[24], the orientation of polymer chains in small size nanopores improves rapidly, especially when the diameter of nanopores is smaller than 60 nm. The self-alignment of polymer chains results in a stack of polymer backbone, which provides much longer effective conjugated length. As a direct consequence, the band gap greatly decreased. Herein, the less blue-shift may be due to the higher orientation of PMP-Th nanowires in PAA with smaller diameter.

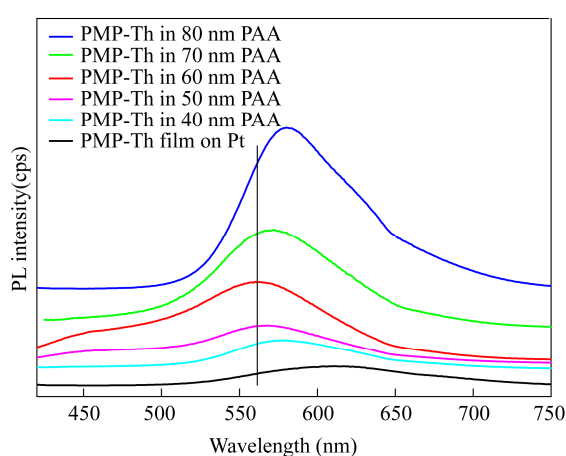


Fig. 4 Photoluminescence spectra of PMP-Th thin film electropolymerized on Pt and PMP-Th nanowires in PAA film with nanochannels diameter ranging from 40 nm to 80 nm. The excitation wavelength is 390 nm. The vertical line means the maximum PL position of PMP-Th nanowires in PAA with 60 nm nanochannels.

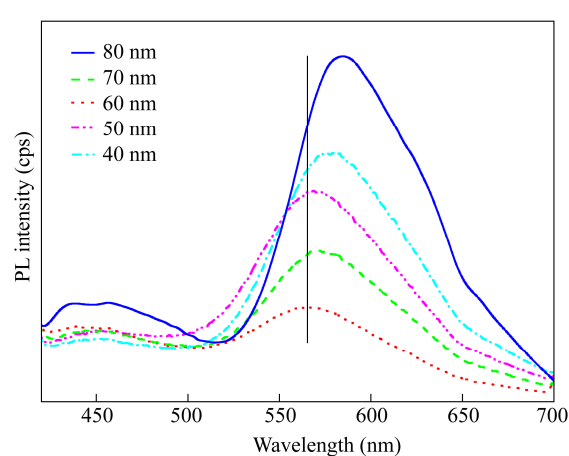


Fig. 5 Photoluminescence spectra of PMP-Th nanowires released from PAA with different sizes. The excitation wavelength is 360 nm. The vertical line means the PL band position of PMP-Th nanowires released from PAA with 60 nm nanochannels.

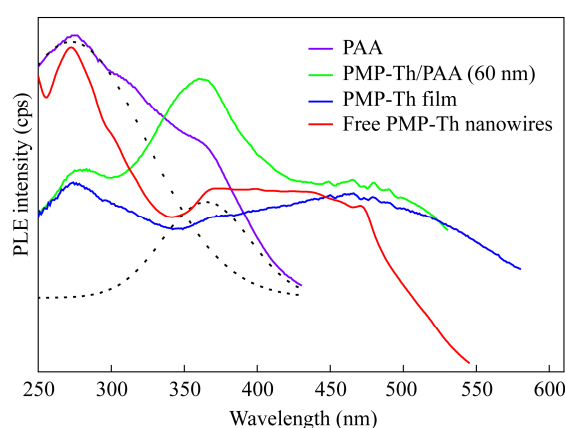


Fig. 6 PLE spectra of PMP-Th thin film, PAA and PMP-Th nanowires in PAA with 60 nm nanochannels, as well as that of the free 60 nm nanowires. The experimental PLE spectra of PAA have been deconvoluted by Gaussian functions (dotted curves).

Another remarkable feature on the emission spectra is that the emission intensities of PMP-Th nanowires in PAA are greatly enhanced compared to the PMP-Th thin film accompanied with the suppression of the emission from PAA at 450 nm^[25]. From the comparison of the PL intensity of PMP-Th nanowires in PAA and free PMP-Th nanowires, we can see that the PAA plays a key role on the modification of the emission intensity. The influence of PAA on the emission intensity in the composite can be disclosed by comparing the photoluminescence excitation (PLE) spectra of PAA, PMP-Th thin film and PMP-Th nanowires in PAA. For analyzing the PLE spectra, we selected the sample fabricated from PAA with 60 nm nanochannels as the representation. As shown in Fig. 6, a broad excitation band at 450 nm was observed for the PMP-Th thin film, while the PMP-Th nanowires in PAA exhibited a strong PLE band at 360 nm. Deconvoluted by Gaussian function, the PLE spectra of PAA exposed an obvious PLE band centered at 360 nm which has been attributed to the oxygen vacancies^[25]. It is noticeable that the PMP-Th nanowires in PAA and the virgin PAA have a very similar PLE band at 360 nm. However, when the PMP-Th nanowires released from PAA, its PLE spectra have the same line shape as that of the PMP-Th thin film. Considering the PL disappearance of the PAA at 450 nm in the composite, we infer that there must be some energy transfer between the PAA and PMP-Th. It is reported that Förster energy transfer could take place between two substances when the emission of the wider band-gap substance and the absorption of the narrower band-gap substance were overlapped^[26, 27]. In this study, the PL spectra of PAA are almost overlapped with the UV-Vis absorption spectrum of the PMP-Th nanowires as shown in Fig. 3. Moreover, as a long range of interaction, the Förster energy transfer range can be of several nanometers even to tens of nanometers^[28]. The nanochannels surface is full of oxygen vacancies which are the emission center of PAA^[29]. When the PMP-Th nanowires were confined in the nanochannels of PAA, it is rational that there is a substantial energy transfer between the PAA and PMP-Th nanowires. The Förster energy transfer process is probably from oxygen vacancies as a donor, to PMP-Th as an acceptor. Normally, energy transfer could bring out effective increase of PL efficiency. Thus, the PL intensity of PMP-Th nanowire is much larger than that of the PMP-Th film and the emission intensity of nanowire increases gradually with the increase of diameter.

CONCLUSIONS

In summary, we have systematically investigated for the first time the emission properties of PMP-Th nanowires of various diameters. A unique size-dependent shift of emission maxima was observed from PMP-Th nanowires with diameters from 40 nm to 80 nm. The tunable emissions are attributed to the change in the degree of confinement of PAA to the polymer macromolecules. Efficient Förster energy transfer from the oxygen vacancies in the PAA to the polymer molecules is identified as being responsible for the enhanced emission from the PMP-Th nanowires in PAA. The evolution of luminescence properties from the PMP-Th nanowires as a function of diameter presents an alternative way to control the emission of polymer nanostructure. This has great potential in the fabrication of novel optoelectronic devices.

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