Polymer 49 (2008) 2197–2201

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymer Communication

Photoluminescence of poly(thiophene) nanowires confined in porous anodic alumina membrane

Xianglan Liu, Faqiang Xu*, Zongmu Li, Wenhua Zhang

National Synchrotron Radiation Laboratory, University of Science and Technology of China, 42 Hezuohua South Road, Hefei, Anhui 230029, People's Republic of China

ARTICLE INFO

Article history:
Received 21 September 2007
Received in revised form 1 February 2008
Accepted 4 March 2008
Available online 12 March 2008

Keywords:
Poly(thiophene)s
Nanocomposite materials
Photoluminescence

ABSTRACT

Poly[3-(2-methoxyphenyl)thiophene] (PMP-Th) nanowires confined in the nano-channels of porous anodic alumina (PAA) membranes were first prepared through electrochemical deposition in cyclic voltammetry and investigated by photoluminescence (PL) spectroscopy. The morphologies and molecular structures of PMP-Th/PAA nanocomposites were studied with electron microscopy and FT-IR. The maximum absorption in UV–vis spectrum of the PMP-Th/PAA nanocomposites was located at 400–450 nm. The photoluminescence spectra show that the nanocomposites have green luminescence bands with the peaks at 560–570 nm. Compared to the electropolymerized PMP-Th film, the PMP-Th nanowires confined in the nano-channels of PAA membranes exhibit obvious blue-shifts in luminescent spectra and great enhancements in photoluminescence intensity. Further spectral analyses suggest that the PL enhancement could be attributed to Förster energy transfer from oxygen vacancies in PAA to PMP-Th molecules.

1. Introduction

Poly(thiophene)s (PThs) have attracted considerable attention as a novel class of semiconducting polymers because of their good chemical and thermal stabilities as well as great potential in organic light-emitting diodes (OLEDs), nonlinear optical devices, field-effect transistors (FETs), photovoltaic cells, sensors, etc. [1–4]. Though poly(thiophene)s are one of the attractive red luminescent materials, a full-color emission and high emission efficiency are more desirable for the application in full-color emitting device. However, how to modify poly(thiophene)s with chemical or physical methods to exhibit perfect emission property for their use is still a big challenge.

Hybridization of conjugated polymer and inorganic nanomaterials to form nanocomposites has been proved to be an effective method that may change the optical properties of the related materials [5,6]. When the conjugated polymers were blended with inorganic particles, their optical and electronic properties were altered significantly [7,8]. Organic fluorescent molecules adsorbed in porous silica and porous anodic alumina (PAA) show a blue-shift and an enhancement in intensity [9,10]. The changes in the optical properties are usually attributed to the quantum size effect of the inorganic nanomaterials. This idea may be borrowed to design conjugated polymer nanocomposites with special luminescent properties, which may solve the full-color challenge of PThs. Nevertheless, few efforts [11] have been made in this direction. To the best of our knowledge, up to now no study on the luminescent properties of PThs in PAA membranes has been reported. As a kind of poly(thiophene) derivative, poly(phenylthiophene)s have excellent optical property as well as good chemical and thermal stabilities compared to other PThs [1]. However, their fluorescence property still needs to be improved for practical use. In this communication, we investigate in detail the PL spectra of the poly[3-(2-methoxyphenyl)thiophene] (PMP-Th) nanowires confined in the nano-channels of PAA membranes. The nano-confinement leads to a significant blue-shift, at the same time the energy transfer from PAA to polymeric molecules induces a great enhancement in intensity. The corresponding luminescence mechanisms of the nanocomposites are also discussed.

The polymeric molecules can be embedded into media nano-channels by various methods, such as chemical polymerization, electrochemical polymerization, template wetting and sol–gel deposition [12–15]. Since the pioneering work of Martin's group [16] in 1990s, the electrochemical preparation of the nanostructured conducting polymers in nanoporous membranes, which is termed 'template method', is recognized as the most efficient one in controlling the growth of nanostructures and has been widely used to produce conductive polymer nanowires or nanotubes [17]. In most previous reports, constant current deposition [18] and potentiostatic electrodeposition methods [19] are widely used to produce conducting polymer. Although cyclic voltammetry (CV) is mostly applied for electrochemical analysis, such as studies of redox

---

* Corresponding author. Tel.: +86 551 3602127; fax: +86 551 5141078.
E-mail address: fqxu@ustc.edu.cn (F. Xu).

0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.03.016

characteristics of conducting polymer films [20], it has also been proved recently to be a powerful approach for fabricating conducting polymer films [21]. CV is a dynamic electrochemical method in which the potential applied to the electrodeposition cell is scanned. The polymer grows during the anodic sweep of the potential, while reduces to neutral state in cathodic potential sweep [22]. Thus in this work, the CV method is employed to fabricate PMP-Th nanowire arrays in PAA.

2. Experimental

2.1. Materials

3-Bromothiophene (97%), 2-bromoanisole (97%) and [1,3-bis-(diphenylphosphino)-propane]nickel(II) chloride were purchased from J&K-Acros Corp. (USA). Acetonitrile (HPLC grade) and boron trifluoride diethyl etherate (BFEE) (AR) were supplied by Sinopharm chemical reagent Co., Ltds (China). All the reagents were used as received. The PAA membranes used in this work were fabricated via a typical two-step anodizing electrochemical procedure by anodizing high-purity (99.999 %) aluminum foil at a constant voltage in 0.3 mol/L sulfuric acid and oxalic acid at about 5 °C, respectively. The anodizing voltage was 20 V for sulfuric acid and 40 V for oxalic acid. The average pore diameters of the through-hole PAA template are 30 nm for sulfuric PAA and 60 nm for oxalic PAA (the correlated SEM images are presented in Fig. S1 in Supplementary data). For preparation detail, see the literature [23]. The 3-(2-methoxyphenyl)thiophene (MP-Th) monomer was synthesized according to the similar procedures as reported in literature [24].

2.2. Electropolymerization

The electropolymerization of MP-Th was performed in a three-electrode Teflon cell on a LK98IIB Microcomputer-based electrochemical system (LANLIKE, China). The working electrode was fabricated according to the following procedures. First, an Au layer with a thickness of ca. 200–300 nm was evaporated onto one side of the PAA membrane. Secondly, a copper wafer as a current collector was contacted to the Au layer of the PAA membrane. The resulting electrode was fixed to the bottom of the Teflon cell. The area of the membrane contacted to the reaction solution was ca. 0.3 cm^2. A glassy carbon electrode ($\o = 5$ mm) was placed directly opposite to the membrane as the counter electrode. An Ag/AgCl electrode used as the reference electrode was immersed directly in an electrolyte solution containing 10 mmol/L MP-Th. Referring to the research of Li et al. [25], we chose an mixed solution of acetonitrile and BFEE ($v/v = 1:2$) as the electrolyte. Before electropolymerization all solutions were de-aerated by dry N_2 bubbling and ultrasonically treated for 5 min successively. During the experiment, the cell was maintained at a slight N_2 overpressure. The PMP-Th nanowires were prepared by CV from 0.00 V to 1.20 V (versus Ag/AgCl) at room temperature. The scan rate used was 50 mV/s and the scan finally stopped at 0.00 V. After electropolymerization, the membrane had a red color indicating the existence of PMP-Th. This color is consistent with a previous report: red in undoped state [22]. The reference PMP-Th film was polymerized under the same conditions except that a Pt sheet instead of PAA template 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. Before the spectral measurements of PMP-Th/PAA nanocomposites, the Au layer was removed by abrasive paper and cleaned with ethanol. In the following discussion, PMP-Th/PAA nanocomposites prepared from oxalic PAA and sulfuric PAA were denoted as PMP-Th/PAA-C and PMP-Th/PAA-S, respectively.

2.3. Characterization

The PMP-Th nanowires and the PMP-Th/PAA nanocomposites were characterized by a Jeol JSM-6700F field emission scanning electron microscope (FE-SEM) and a Hitachi H-800 transmission electron microscope (TEM). Fourier transfer infrared (FT-IR) spectra were recorded on a Nicolet MAGNA-IR 750 spectrometer over the range of 4000–400 cm^{-1} using KBr pellets. 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. All the measurements were carried out at room temperature and in ambient air.

3. Results and discussion

Fig. 1a shows the bottom surface morphology of the PMP-Th/PAA-C nanocomposite membrane after removing the Au layer. It can be observed that almost every pore is stuffed by PMP-Th nanowires. Fig. 1b exhibits the SEM image of PMP-Th nanowire arrays after dissolving the alumina template with the 0.10 mol/L NaOH solution. From this image, one can see that the aligned nanowires with lengths of 3–5 μm stand on the Au support. Fig. 1c and d demonstrates the TEM images of several typical PMP-Th nanowires, and they indicate that the nanowires have average diameters of about 50 nm and 25 nm close to the pore diameters of the PAAs fabricated from oxalic acid and sulfuric acid, respectively. Thus it can be concluded that the nanowires of PMP-Th are formed in the pores of the PAA. The length of nanowires can be controlled by the total charges passed the cell. If sufficient charge is passed the cell, nanowires could grow as long as the thickness of the template, though the reaction rate may turn lower and lower.

A typical FT-IR spectrum of the PMP-Th nanowires freed of PAA (shown in Fig. S2 in Supplementary data) exhibits the characteristic absorption of PMP-Th. The absorption bands at 1436 cm^{-1}, 1464 cm^{-1} and 1491 cm^{-1} can be assigned to the C=C stretching vibration of the thiophene ring, while the bands at 1578 cm^{-1} and 1600 cm^{-1} can be assigned to the C=C stretching vibrational modes of the benzene ring. The strong absorption at 753 cm^{-1} was attributed to C–H out-of-plane vibration of orthosubstituted benzene and the band at approximately 830 cm^{-1} was associated with the C–H out-of-plane deformation of the 2,3,5-trisubstituted thiophene ring, indicating that the electrochemical coupling of 3-substituted thiophenes occurred preferentially at 2,5-position. Therefore, the α–α linkage is predominant in the polymer chain.

The UV–vis absorption spectra of the PMP-Th/PAA nanocomposites and PMP-Th film on ITO substrate are shown in Fig. 2; curves a and b corresponding to PMP-Th/PAA-C and PMP-Th/PAA-S nanocomposites have absorption bands at about 406 nm and 420 nm, respectively. Whereas in the UV–vis absorption spectra of pristine PAA (Fig. 2d and e), no absorption peaks were observed in this wavelength range. Apparently the absorption peaks at 406 nm and 420 nm should originate from π to π^* transition of PMP-Th molecule in PAA. Subtracting the contribution of PAA, the absorption spectra of PMP-Th/PAA is similar to that of PMP-Th film (Fig. 2c) in line shape, indicating that PMP-Th nanowires have filled the nanopores of PAA with a better extended π-conjugation along the polymer backbone. Furthermore, the absorption peak position of the PMP-Th/PAA nanocomposites shows significant blue-shift by comparison with that of the PMP-Th film at around 500 nm. This

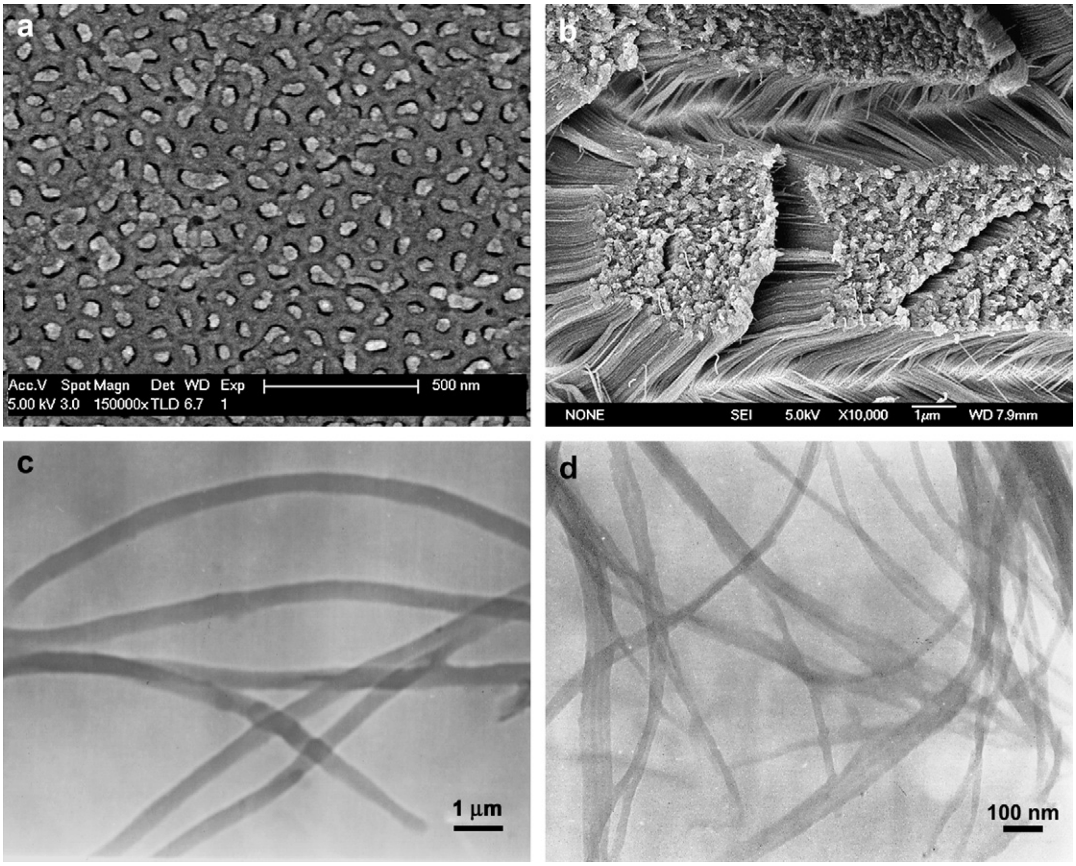

Fig. 1. SEM images of (a) the bottom image of PMP-Th/PAA-C after removing the Au layer and (b) PMP-Th nanowire arrays after the PAA being partially dissolved by NaOH solution. TEM images of the PMP-Th nanowires liberated from (c) oxalic PAA and (d) sulfuric PAA. The average diameters of PMP-Th nanowires are about 50 nm and 25 nm, respectively.

demonstrated that the effective conjugation length in the PAA becomes shorter with respect to PMP-Th film. Short effective conjugation length results in large optical energy gap. Correspondingly, a blue-shifted PL spectrum is observed by comparison with the PMP-Th film.

Fig. 3 displays the PL spectra of the PMP-Th/PAA nanocomposites and PMP-Th film electrochemically deposited on Pt sheet under the same polymerization conditions. An emission band centered at 610 nm is observed from PMP-Th thin film as shown in Fig. 3a. However, the PL spectrum of PMP-Th/PAA-S nanocomposite (Fig. 3b) exhibits a strong band at 570 nm. For the PMP-Th/PAA-C nanocomposite (Fig. 3c), the PL spectrum shows a strong band at 560 nm with a weak shoulder at 450 nm attributed to the PAA membrane [23]. It is apparent that the emission spectra of PMP-Th/PAA nanocomposites show notable (about 40–50 nm) blue-shifts compared to the PMP-Th film on Pt sheet. Specifically, the blue-shift of PMP-Th/PAA-S with small diameters is little than that of PMP-Th/PAA-C with large diameters. Another remarkable feature on the PL

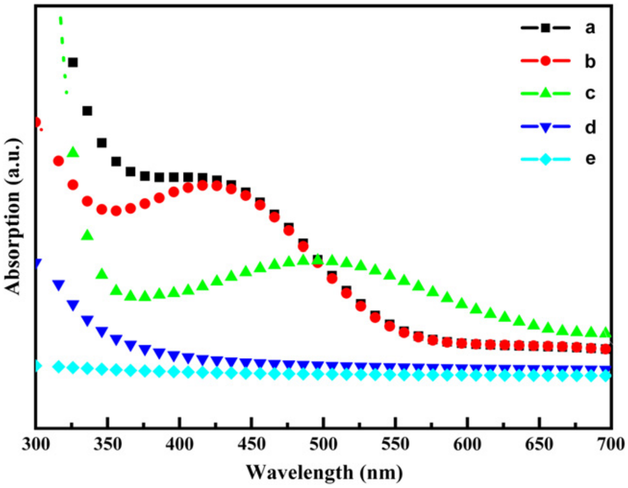

Fig. 2. UV–vis absorption spectra of (a) PMP-Th/PAA-C, (b) PMP-Th/PAA-S, (c) PMP-Th film electropolymerized on ITO, (d) oxalic PAA, and (e) sulfuric PAA.

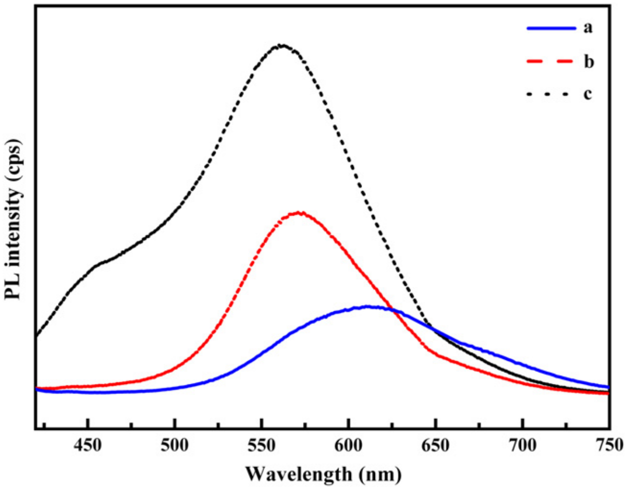

Fig. 3. Photoluminescence spectra of PMP-Th film electropolymerized on Pt sheet (a), PMP-Th/PAA-S (30 nm) nanocomposite (b) and PMP-Th/PAA-C (60 nm) nanocomposite (c). The excitation wavelength is 390 nm.

spectra is that the PL intensities of PMP-Th nanowires are greatly enhanced compared to the PMP-Th film with the suppression of the emissions from PAAs in the PMP-Th/PAA nanocomposites. In addition, the PL enhancement is more significant for PMP-Th/PAA-C than PMP-Th/PAA-S (this behavior will be discussed later).

Currently, there are two mechanisms to explain the fluorescent blue-shift of the nanocomposites: size confinement effect [26] and chemical interaction between two media [27]. In the PMP-Th/PAA nanocomposite systems, the blue-shifts are not due to chemical interaction, because the FT-IR spectrum (see Fig. S2 in Supplementary data) shows no evidence indicative of chemical bonding between the polymeric chains and the PAA. Considering the nanometer pore sizes of the alumina templates and comparing the behavior of the polymeric molecules in thin film, it is reasonable to attribute the blue-shifts to the nano-size effect. After the PMP-Th molecules were buried into the nanometer-sized holes, the interaction between the molecules is reduced compared to that of the molecules in the thin film. Such an isolation in nanometer scale results in a decrease of the band gap, which leads to the blue-shift as observed in the PL spectra. It is unexpected that the PL blue-shift of the sample fabricated with sulfuric PAA is smaller than that prepared with oxalic PAA because the pore size of oxalic PAA doubles that of the sulfuric PAA as shown in the SEM images. This means that the smaller the diameter is, the less the blue-shift is. This seems to be opposite to the rule of quantum size effect [28]. Martin et al. [29] have found that conjugated polymer can be aligned in polycarbonate membrane with small diameter pores (tens of nanometer). Furthermore, McGehee and coworkers [30] have also reported that when the nanopores of PAA are smaller than 60 nm in diameter, the orientation of polymer chains improved rapidly. The alignment of polymer chains results in the increase of the conjugated length; as a direct consequence, the band gap greatly decreased. Herein the less blue-shift may be attributed to the higher portion of ordered polymer chains in the PMP-Th nanowires in sulfuric PAA.

The PL intensity enhancement with the PMP-Th embedded in the PAA can be explained by comparing the PLE spectra of PAA, PMP-Th thin film and PMP-Th/PAA. As shown in Fig. 4, the PMP-Th thin film exhibits a broad excitation transition at ∼450 nm (curve a), while a differently strong band at 360 nm can be observed for the PMP-Th/PAA nanocomposite (curves b and c). The two spectra of oxalic PAA and sulfuric PAA have the similar line shapes under our experiments (Fig. 4d and e) and exposed a same PLE band at 360 nm by deconvoluting the spectra with Gaussian function, which has been attributed to the oxygen vacancies [31,32]. It is noticeable that the PMP-Th/PAA nanocomposite film and the PAA have a very similar PLE band at 360 nm. Taking into account the disappearance of the PAA photoluminescence in the PMP-Th/PAA nanocomposite, we propose that the carriers were photogenerated in oxygen vacancies in the PAA membrane, and then mostly recombined in the PMP-Th molecules. The two processes should be linked by an energy transfer. Generally, Förster energy transfer could take place from PAA to embedded nanomaterials and induce an energy shift of optical transition [33]. In order to realize an efficient Förster energy transfer, two requirements have to be fulfilled [34]: (a) sufficient spectral overlap between the emission of the wider band-gap substance and the absorption of the narrower band-gap substance, and (b) a Förster interaction range from several to tens of nanometers, where the first one is the essential condition. In this study, the PL spectra of PAAs almost completely overlap with the UV–vis absorption spectrum of the PMP-Th thin film on ITO as shown in Supplementary data (Fig. S3). Moreover, as shown in Fig. 1a, the PMP-Th nanowires almost cram the nanopores of PAA and the surface of these nanopores is full of oxygen vacancies [35]. Therefore, the two requirements for Förster energy transfer are completely met here. We thus conclude that there is a substantial energy transfer between the PAA and PMP-Th nanowires. The Förster energy transfer process is probably from oxygen vacancies, acting as a donor, to PMP-Th, acting as an acceptor. Normally, energy transfer could bring out effective increase of PL efficiency. Since a large number of oxygen vacancies exist around PMP-Th in the PAA, the energy transfer is expected to be efficient enough to greatly enhance the PL intensity. It is well known that the PL intensity of the PAA formed in sulfuric acid is much weaker than that in oxalic acid because of the lack of oxygen vacancies in the sulfuric PAA [22]. So the Förster energy transfer efficiency is lower in the PMP-Th/PAA-S nanocomposite than that in the PMP-Th/PAA-C nanocomposite. This has been confirmed in Fig. 4 by the weaker intensity of the 360 nm PLE band of PMP-Th/PAA-S with respect to that of PMP-Th/PAA-C. As a result less enhancement in the PL intensity of PMP-Th/PAA-S sample was observed.

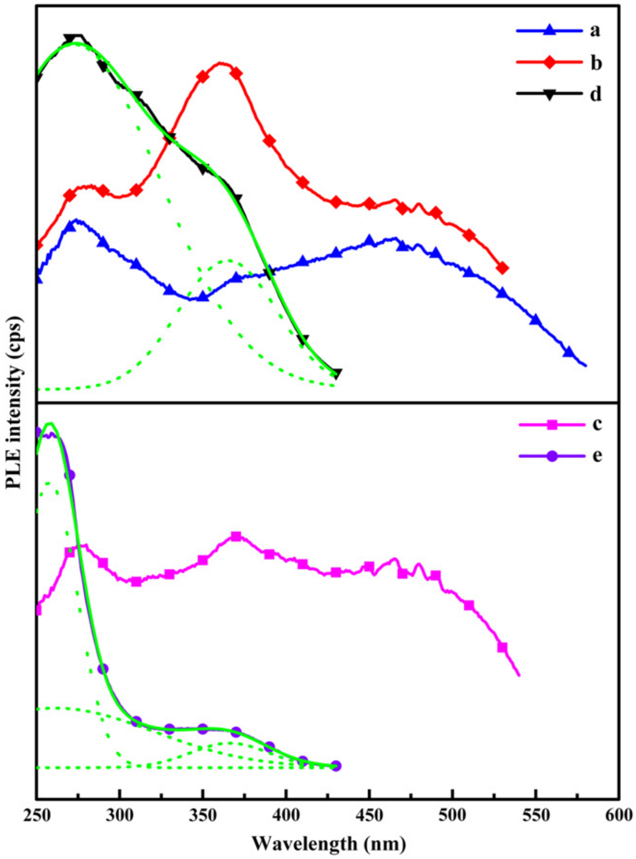

Fig. 4. PLE spectra of (a) PMP-Th film electropolymerized on Pt sheet, (b) PMP-Th/PAA-C nanocomposite, (c) PMP-Th/PAA-S nanocomposite, (d) PAA film prepared in oxalic acid, and (e) PAA film prepared in sulfuric acid. The experimental PLE spectra of these as-prepared PAA films have been deconvoluted by Gaussian functions (dotted curves).

4. Conclusion

In summary, we have investigated for the first time the PL properties of PMP-Th/PAA nanocomposites with different pore sizes. An obvious blue-shift in PL spectra and enhancement in PL intensity are observed. The confinement of the nanopores of PAA contributes the blue-shift, which weakens the intermolecular interaction. Furthermore, blue-shift shows unique size dependence. A little blue-shift is obtained in small pore size resulting from the high portion of the ordered polymeric chains in the small pore compared to that in the large one. From the PLE spectral analyses, we can propose that the efficient Förster energy transfer from the oxygen vacancies in the PAAs to the polymer molecules is responsible for the PL enhancement of the PMP-Th/PAA nanocomposites. The observed modifications in PL spectra of PMP-Th suggest that there is significant potential for modifying the luminescent properties of PThs by isolating the polymer chains in the PAA nanopores. But further optical studies, such as the polarized PL arising from the orientation of polymer chains and the effect of PAA on the PL properties in the nanocomposite, are needed for more systematic analysis and explanation.

Acknowledgements

The authors thank Professor Liangbin Li for his helpful suggestion. This work was supported by National Natural Science Foundation of China (Grant no. 10505019).

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2008.03.016.

References

[1] Li Y, Vamvounis G, Holdcroft S. Macromolecules 2002;35:6900.
[2] Robitaille L, Leclerc M, Callender C. Chem Mater 1993;5:1755.
[3] Ong R, Wu Y, Liu P, Gardner S. J Am Chem Soc 2004;126:3378.
[4] Huynh WU, Peng X, Alivisatos AP. Adv Mater 1999;11:923.
[5] Nguyen TQ, Wu JJ, Doan V, Schwartz BJ, Tolbert SH. Science 2000;288:652.
[6] Le Rendu P, Nguyen TP, Lakehal M, Ip J, Tiginyanu IM, Sarua A, et al. Opt Mater 2001;17:175.
[7] Smilowitz L, Sariciftci NS, Wu R, Gettinger C, Heeger AJ, Wudl F. Phys Rev B Condens Matter 1993;47:13835.
[8] Wu JJ, Gross AF, Tolbert SH. J Phys Chem B 1999;103:2374.
[9] Levitsky IA, Liang J, Xu JM. Appl Phys Lett 2002;81:1696.
[10] Jia R, Shen Y, Luo H, Chen X, Hu Z, Xue D. Appl Surf Sci 2004;233:343.
[11] Qi DF, Kwong K, Rademacher K, Wolf MO, Young JF. Nano Lett 2003;3:1265.
[12] Menon VP, Lei J, Martin CR. Chem Mater 1996;8:2382.
[13] Nakayama M, Yano J, Nakaoka K, Ogura K. Synth Met 2002;128:57.
[14] O'brein GA, Quinn AJ, Iacopino D, Pauget N, Redmond G. J Mater Chem 2006;16:3237.
[15] Guo RL, Ma XC, Hu CL, Jiang ZY. Polymer 2007;48:2939.
[16] Van Dyke LS, Martin CR. Langmuir 1990;6:1123.
[17] Demoustier-Champagne S, Stavaux PY. Chem Mater 1999;11:829.
[18] Park DH, Kim BH, Jang MK, Bae KY, Lee SJ, Joo J. Synth Met 2005;153:341.
[19] Fu M, Shi G, Chen F, Hong X. Phys Chem Chem Phys 2002;4:2685.
[20] Pringle JM, Forsyth M, MacFarlane DR, Wagner K, Hall SB, Officer DL. Polymer 2005;46:2047.
[21] Alkan S, Cutler CA, Reynolds JR. Adv Funct Mater 2003;13:331.
[22] Otero TF, Larreta-Azelain E. Polymer 1988;29:1522.
[23] Du Y, Cai WL, Mo CM, Chen J, Zhang LD, Zhu XG. Appl Phys Lett 1999;74:2951.
[24] Pei Q, Järvinen H, Österholm JE, Inganäs O, Laakso J. Macromolecules 1992;25:4297.
[25] Li XH, Li YF. J Appl Polym Sci 2003;90:940.
[26] Zhao Q, Xin Y, Huang Z, Liu S, Yang C, Li Y. Polymer 2007;48:4311.
[27] Zheng ZX, Xi YY, Dong P, Huang HG, Zhou JZ, Wu LL, et al. Phys Chem Commun 2002;5:63.
[28] Lee JK, Koh WK, Chae WS, Kim YR. Chem Commun 2002;2:138.
[29] Cui Z, Lei J, Liang W, Menon V, Martin CR. Chem Mater 1991;3:960.
[30] Coakley KM, Srinivasan BS, Ziebarth JM, Goh C, Liu Y, McGehee MD. Adv Funct Mater 2005;15:1927.
[31] Huang GS, Wu XL, Xie Y, Shao XF, Wang SH. J Appl Phys 2003;94:2407.
[32] Huang GS, Wu XL, Siu GG, Chu PK. Solid State Commun 2006;137:621.
[33] Shi YL, Wang J, Li HL. Appl Phys A Mater 2002;75:423.
[34] Ding L, Bo Z, Chu Q, Li J, Dai L, Pang Y, et al. Macromol Chem Phys 2006;207:870.
[35] Huang GS, Wu XL, Mei YF, Shao XF, Siu GG. J Appl Phys 2003;93:582.