

Fabrication of Photoluminescent Dye Embedded PMMA Nanofiber and its Fluorescence Resonance Energy Transfer

Kyung Jin Lee, Joon Hak Oh, Younggeun Kim, and Jyongsik Jang*

Hyperstructured Organic Materials Research Center and School of Chemical Engineering, Seoul National University, Shinlimdong 56-1, Kwanakgu Seoul 151-742 (Korea).
 jsjang@plaza.snu.ac.kr

Introduction

The solid state optical nanostructures, which can be the promising materials for diverse applications, have been extensively studied.^[1] The nano-confined organic dyes might undergo energy transfer, resulting in enhancement of fluorescent signal at low dye concentration.^[2] The FRET has been extensively studied from the theoretical viewpoints to practical applications, especially as the emitting layer for light emitting diode (LED).^[3] Most researches related with energy transfer have been conducted using chromophores-embedded thin films due to the distance dependent character of the energy transfer.^[4] In addition, the chromophores confined in nanodimension such as micelle, mesoporous silica or carbon, zeolite, and nanoparticles have also been investigated as the energy transfer system. However, there has been no report concerning the fabrication of polymer nanofiber embedded with multiple organic dyes for FRET application.

Herein we report on the fabrication of organic dyes embedded polymer nanofiber via vapor deposition polymerization and subsequently dipping in organic dye solution using anodic aluminum oxide (AAO) membrane. Having demonstrated the feasibility of FRET application, we were prompted to apply it to embed the photoluminescent dyes such as coumarin 6 (Cm6) and rhodamine B (RhB) into poly(methyl methacrylate) (PMMA) and observed the FRET properties in this system.

Experimental

The porous AAO membrane with 100 nm of pore diameter and 60 μm of thickness was placed in reaction vessel equipped with a sealing apparatus and monomer loading reservoir. The reaction chamber was evacuated until the vacuum pressure was reached at 10–2 torr. Then, the heptane solution containing 2,2 azo-bis-(2,4-dimethylvaleronitrile) as a radical initiator was injected into the vessel. The AAO membrane was wetted by radical initiator solution. Consecutively, methyl methacrylate monomer was introduced and the reaction chamber was located in 70 °C for 6 h. The AAO template was taken out from the reaction vessel and soaked into the organic dye solution, which was prepared with dissolving a variable amount of Cm6 and RhB in methanol. The treated AAO membrane was dried at room temperature and polished by fine sand-paper in order to prevent the pore blocking of AAO membrane. A vapor deposition polymerization was performed to encapsulate the organic dyes with polymer without any deterioration of organic dyes. The AAO membrane was etched by sodium hydroxide solution (3M) and PMMA-dyes-PMMA nanofiber was precipitated.

Results and discussion

The prepared PMMA nanotubes by VDP had remarkably smooth outer surface and the wall thickness is reasonably uniform. The uniform thin wall and open channel accommodate foreign materials such as organic dye into the inner pore of polymer nanotube. Figure 1 displays confocal laser scanning microscopy (CLSM) images of PMMA-Cm6-PMMA and PMMA-RhB-PMMA nanofibers. The excitation wavelength of laser was 488 nm and 543 nm, respectively. The CLSM images confirmed the green and red emissions of 1D nanocomposites and the emitting position was restricted within PMMA nanofiber. The organic dyes could be effectively impregnated into the 1D nanostructure of PMMA without phase separation, and were not removed by the etching process. The PMMA layer plays a role of protection of organic dyes from environmental condition.

Figure 2 represents photoluminescence spectra of PMMA/Cm6/PMMA and PMMA/Cm6/RhB/PMMA nanofiber with different weight ratio of Cm6 and RhB excited at absorption λ_{max} (maximum

absorption wavelength) of Cm6. The characteristic photoluminescence band of Cm6 is detected at 500–550 nm (black circle). As the concentration of RhB increases, the emission peak of RhB increases gradually at 550–600 nm. On the other hand, the emission intensity of Cm6 decreases owing to the energy transfer from Cm6 to RhB. In the case of RhB/Cm6 weight ratio of 0.04, the fluorescence intensity of RhB (560 nm) (red diamond) was drastically enhanced by ca. 10 times compared with fluorescence intensity of single dye doped PMMA nanofiber (pink triangle). Considering that the weight ratio of acceptor/donor is below 0.1 for efficient FRET,^[5] the FRET occurs effectively in the PMMA nanofiber. The PMMA layer has no interference with emission flux of both dyes due to its optically transparency. The FRET observation in this system provides crucial evidence that the photoluminescent dyes are confined in nanodimension of polymer nanofiber.

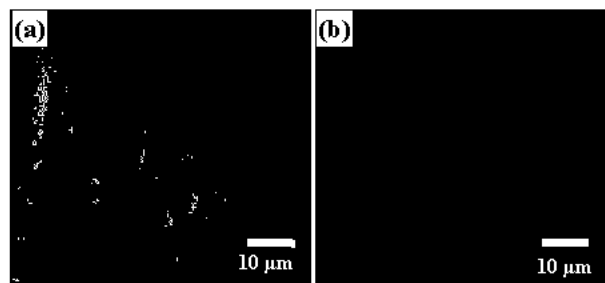


Figure 1. CLSM images of (a) PMMA-coumarin 6-PMMA nanofiber excited at 488 nm laser and (b) PMMA-rhodamine B-PMMA nanofiber excited at 543 nm.

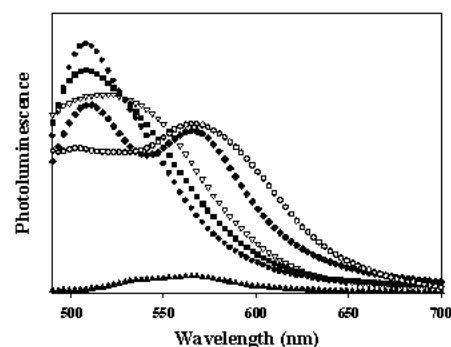


Figure 2. Photoluminescence spectra of PMMA-Cm6-PMMA (●) and PMMA-Cm6-RhB-PMMA (■, ▽, ◆, ○); weight ratio of RhB and Cm6 is 0.004 (■), 0.02 (▽), 0.04 (◆), and 0.08 (○) and the photoluminescence spectrum of PMMA-RhB-PMMA (▲); The absolute amount of RhB in PMMA-RhB-PMMA was same as that of PMMA-dual dyes-PMMA whose weight ratio of RhB/Cm6 was 0.04.

Conclusions

The PMMA nanotubes and organic dyes embedded PMMA nanofibers were successfully fabricated using VDP and sequential dye dipping method. In the case of dual dye system, the effective FRET was observed due to their restricted dimension and spectral overlaps between donor and acceptor. This synthetic method might be expanded to allow the fabrication of 1D polymer nanocomposites, which include metallic, inorganic, and organic polymer materials.

References

- [1] I. Rasnik, S. A. McKinney, T. Ha, *Acc. Chem. Res.* **2005**, *38*, 542.
- [2] L. Wang, R. Yan, Z. Huo, L. Wang, J. Zeng, J. Bao, X. Wang, Q. Peng, Y. Li, *Angew. Chem. Int. Ed.* **2005**, *44*, 6054.
- [3] T. -H. Kim, D. -H. Yoo, J. H. Park, O. O. Park, *Appl. Phys. Lett.* **2005**, *86*, 171108.
- [4] M. Berggren, A. Dodabalapur, R. E. Slusher, Z. Bao, *Nature* **1997**, *389*, 466.