Optical waveguiding in an electrospun polymer nanofiber

Yuya Ishii*, Ryohei Kaminose1, and Mitsuo Fukuda1
1Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan

E-mail: yishii@ee.tut.ac.jp

Abstract. Optical waveguides with nanometer diameters are needed to realize nanometer-scaled optical circuits, which promise high-speed and high-capacity information processing. In this work, we fabricate polymer nanofibers with uniform diameters, containing an organic dye. Fluorescence microscopy observations and photoluminescence measurements demonstrate optical waveguiding in the nanofiber.

1. Introduction
To achieve high-speed and high-capacity information processing, optical circuits are attracting much attention as a substitute for electronic circuits [1, 2]. An optical waveguide is an essential element in optical circuits, and several nanometer ranged optical waveguides have been developed, such as silicon waveguides [1, 3], highly-drawn silica wires [4], and lithographic patterned polymer waveguides [2]. Electrospun polymer fibers have diameters in the nanometer range, high aspect ratios [5, 6], and show mechanical flexibility. Thus, the fibers are prime candidates for small waveguides. To date, only several groups have reported waveguiding properties inside electrospun nanofibers [7, 8].

In this work, we fabricate electrospun polymer nanofibers containing an organic dye, and demonstrate optical waveguiding in the fiber.

2. Experimental details
2.1. Materials
Nile Blue A perchlorate (NBA, Fig. 1) and poly(methyl methacrylate) (PMMA, average $M_w \sim 350,000$) was purchased from Sigma-Aldrich and used as received. $N,N$-dimethylformamide (DMF) and chloroform were purchased from Wako Pure Chemical Industries, Ltd. and used as received.

* To whom any correspondence should be addressed.
2.2. Electrospun fibers

To produce composite nanofibers by electrospinning, the different materials first need to be dissolved [9]. PMMA and NBA were dissolved in a mixture of DMF and chloroform (DMF:chloroform = 7:3 volume ratio). The PMMA concentration is varied to give 6, 8, and 10 wt% solutions and the NBA concentration is $1 \times 10^3$ mol·l$^{-1}$ for the PMMA volume. The solution of PMMA/NBA was loaded into a glass syringe equipped with a stainless steel needle (0.3 mm in diameter) and syringe pump (KDS-100, KD Scientific Inc.). The PMMA/NBA solutions are ejected from the needle tip at constant rates (Table 1). A high-voltage power supply (HVU-30P100, Mecc Co., Ltd.) applied a high voltage to the needle, and a grounded silicon plate collector was placed 15 cm below the tip of the needle to collect the fibers. All electrospinning experiments were performed in air at room temperature with a humidity of 35–48%.

**Table 1.** Electrospinning conditions for each PMMA/NBA solution.

| PMMA concentration (wt%) | Feed rate (ml·h$^{-1}$) | Applied voltage (kV) |
|--------------------------|------------------------|----------------------|
| 6                        | 0.30                   | 4.5                  |
| 8                        | 0.32                   | 3.8                  |
| 10                       | 0.35                   | 3.5                  |

2.3. Characterization method

Shapes and diameters of the fibers were characterized using field-emission scanning electron microscopy (FESEM, SU8000, Hitachi) and fluorescence microscopy (BX-51, Olympus). The average fiber diameter was calculated from 100 SEM images of individual fibers (2 images per 50 individual fibers). Note that the standard deviation in fiber diameters among electrospun fibers is about two times larger than that within an individual fiber [10].

Photoluminescence (PL) spectra were measured with a spectral analyzer (USB4000, Ocean Optics), which was connected to the fluorescence microscope via an optical fiber. Excitation light was supplied by a halogen light source (U-LH100-3, Olympus) through a 510–550 nm bandpass filter. The PL spectra from the samples were collected through a sharp-cut filter ($\lambda > 590$ nm). The circular detection area had a diameter of 20 $\mu$m.

The absorption spectra of dilute solutions were measured with a UV-Vis spectrophotometer (U-4100, Hitachi). To prepare a dilute solution, NBA was dissolved in ethanol at a concentration of 4.26 mg·l$^{-1}$.

3. Results and discussion

The optical microscopy images of the electrospun fibers deposited on silicon plate collectors are shown in Fig. 1. The PMMA/NBA fibers electrospun from the 6 wt% solutions have a beaded-fiber morphology. With increasing concentration, the number and size of the beads on the nanofibers is reduced, and uniform fibers are obtained from the 10 wt% solution. This homogenization of fiber...
diameters results from increased solvent distribution over the polymer molecules [11]. To suppress the loss of light from inside the fiber, uniform fibers are required. Thus, we use the fibers spun from the 10 wt% solutions to probe the waveguiding properties inside these fibers.

The inset in Fig. 3 shows an FESEM image of PMMA/NBA electrospun fibers. Uniform fibers with nanometer diameters are obtained. We measured the fiber diameters from 100 SEM images (Fig. 3). The average diameter of the fibers was 600 nm with a standard deviation of 70 nm.

We cut some nanofibers with a knife, and obtained the optical and fluorescence microscopy images (Fig. 4). The fibers exhibit bright and uniform PL [Fig. 4(b)], which demonstrates the homogeneous incorporation of the NBA molecules. The isolated fiber shown in Fig. 4(c) bends upwards and the end face of the fiber is clearly observed. PL from the end face of the fiber [point B in Fig. 4(c) and (d)] is more intense than that from the middle of the fiber [point A in Fig. 4(a) and (b)]. We measured the PL of the fiber at points A and B (Fig. 5). The PL intensity at point B is approximately 9.5-times higher than that at point A. This high PL intensity at the end face of the fiber is due to the integrated NBA PL and clearly demonstrates that waveguiding occurs in the nanofiber. Figure 6 shows the normalized PL spectra of the fiber at points A and B. The PL at point B is red-shifted compared to that at point A. This is due to re-absorption effects. The NBA absorption spectrum overlaps with the PL spectrum in the range 590–690 nm (Fig. 6). Although the average diameter of the fibers is 600 nm, the NBA PL occurs at wavelengths >600 nm, and waveguiding occurs inside the fiber because of the higher refractive index of PMMA (n=1.49 at 633 nm) [12] compared to air.

**Figure 3.** Distribution of diameters in NBA/PMMA fibers electrospun from the 10 wt% NBA/PMMA solution. We measured the diameters from 100 different fibers. The diameter interval for fibers is 5% of the average fiber diameter. Inset: FESEM image of the fibers. The scale bar is 3µm.

**Figure 4.** Optical [(a) and (c)] and fluorescence [(b) and (d)] microscopy images of PMMA/NBA electrospun nanofibers. Middle [(a) and (b)] and end face [(c) and (d)] fibers are shown. At points A and B, PL spectra are measured.
4. Summary
We have fabricated uniform PMMA/NBA electrospun nanofibers by adjusting the concentration of PMMA/NBA solutions. Fluorescence microscopy images and PL spectra of the fiber demonstrate optical waveguiding in the nanofibers.

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References
[1] Jalali B and Fathpour S 2006 *Journal of Lightwave Technology* **24** 4600
[2] Ma H, Jen A K Y, and Dalton L R 2002 *Adv. Mater.* **14** 1339
[3] Liang D and Bowers J E. 2010 *Nat. Photon.* **4** 511
[4] Tong L, Gattass R R, Ashcom J B, He S, Lou J, Shen M, Maxwell I, and Mazur E 2003 *Nature* **426** 816
[5] Li D and Xia Y 2004 *Adv. Mater.* **16** 1151
[6] Ishii Y, Sakai H, and Murata H 2011 *Nanotechnology* **22** 205202
[7] Liu H, Edel J B, Bellan L M, and Craighead H G 2006 *Small* **2** 495
[8] Camposeo A, Di Benedetto F, Stabile R, Neves A A R, Cingolani R, and Pisignano D 2009 *Small* **5** 562
[9] Ishii Y and Murata H, 2012 *J. Mater. Chem.* **22** 4695
[10] Ishii Y, Sakai H, and Murata H 2009 *Thin Solid Films* **518** 647
[11] Ramakrishna S, Fujihara K, Teo W-E, Lim T-C, and Ma Z 2005 *An Introduction to Electrospinning and Nanofibers* (Word Scientific)
[12] Tanio N and Irie M 1994 *Jpn. J. Appl. Phys.* **33** 3942