Prospective for biodegradable microstructured optical fibers

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We report fabrication of a novel microstructured optical fiber made of biodegradable and water soluble materials that features ~1 dB/cm transmission loss. Two cellulose butyrate tubes separated with hydroxypropyl cellulose powder were codrawn into a porous double-core fiber offering integration of optical, microfluidic, and potentially drug release functionalities.

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As fabrication of microstructured optical fibers (MOFs) matures, there is a growing trend of integrating multiple functionalities into the same fiber. In particular, microstructured polymer optical fibers have recently received much attention, as several preform fabrication techniques have been established that use a variety of moderately priced polymer materials. Thanks to the biofriendly polymer material composition, many microstructured polymer optical fibers having porous structure have been designed with a view to biomedical applications. Furthermore, proper design of the fiber structure can allow other functionalities, such as fluorescence detection enhancement, laser power delivery, and controlled release of pharmaceuticals.

Sensing by using MOFs[1–5] relies on detecting changes in fiber transmission properties when fiber pores are filled with analyte. A number of porous fibers have been developed, featuring judiciously arranged holes,[6–8] randomly placed holes,[9–11] Fresnel fibers,[11] and hollow multilayer fibers.[12–15] Several all-polymer-based hollow photonic bandgap fibers were also recently demonstrated,[8,16] potentially offering operation with gas- or liquid-filled cores. Liquid-filled fibers in a classical hexagonal arrangement for sensing and microfluidics were considered in Refs. 2 and 17–19.

Regardless of the geometry, a crucial step in making MOF biosensors is sensitizing the inner surface of the fiber pores (holes) with a bioactive material to allow selective binding and consequent detection of a biological analyte. Jensen *et al.*[20] and Rindorf *et al.*[21] demonstrated fluorescence detection of selectively captured antibodies and DNA labeled with fluorescent markers. They also found that deposition of a sensing biolayer onto a polymer surface is easier than onto a glass one, thus making polymer fibers better suited for biosensing than glass.

Functionalities of MOFs can be further enhanced by adding a second core. Traditionally, double-cladding/core MOFs were used for directional coupling[22] and dispersion management. Recently such fibers have been also used to enhance the sensitivity of fluorescence microscopy[23,24] by permitting single-mode delivery of the excitation pulse through a smaller core and efficient collection of the signal (fluorescent light) by the larger multimode outer core. Beyond sensing, hollow-core MOFs[12–15] have been demonstrated to deliver tens of watts of laser power almost anywhere in the IR, providing flexible power delivery from the medically important Nd:YAG, Er:YAG, and CO_2 lasers.

An intriguing possibility is to incorporate optical, sensing, and medical treatment functionalities into the same biocompatible fiber to create a highly integrated and self-sufficient medical system. In one possible scheme, the tissue is first exposed to high-power laser light transmitted through the fiber core, and then integrated optical sensors evaluate the results of tissue treatment, while the porous microfluidic structure impregnated with water-soluble pharmaceuticals allows local release of therapeuticals, such as anaesthetics or antibiotics.

In this Letter we present the design and fabrication of a biodegradable polymer optical fiber that simultaneously embodies optical, microfluidic, and drug release functionalities. To the best of our knowledge, this is the first implementation of a multifunctional biodegradable fiber. The porous dual-core fiber structure presents a small inner core (which can be made hollow or filled) suspended in air by low-refractive-index water-soluble particles separating it from the larger outer core [Fig. 1(a)]. Such a geometry potentially permits many of the above-mentioned applications: the double-core structure allows efficient laser power delivery and improved collection of incoming light for passive sensing; the cladding porosity allows microfluidics, biosensing, and slow drug release by the water-soluble microstructure; a hollow core allows injection or slow release of therapeuticals. This geometry can be easily tailored to a given application by controlling the preform design and drawing processes.

The fiber preform [inset, Fig. 1(a)] was prepared by using commercially available cellulose butyrate (CB) tubes (refractive index 1.475) of two different diameters. Values for the inner/outer diameters of the smaller and larger tubes are (1/8)/(1/4) in., and (3/8)/(5/8) in., respectively. The smaller-diameter tube, which forms the inner of the two fiber cores,

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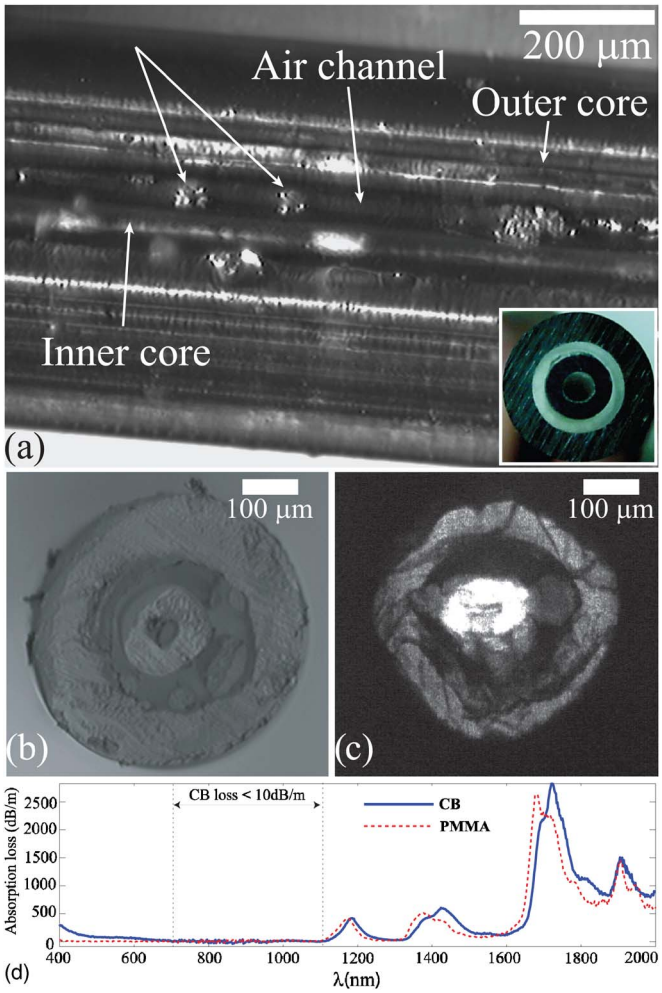

Fig. 1. (Color online) (a) Double-core biodegradable microstructured fiber. The inner core is suspended in air by the powder particles. Inset, preform cross section. (b) Fiber cross section. (c) Power distribution in the fiber cross section after 3 cm of propagation. (d) CB and PMMA material losses.

was sealed at both ends with Teflon tape and placed in the middle of the larger tube that formed the outer core. In the final fiber structure the air hole of the inner tube could be collapsed or left open, depending on the application, by controlling fiber drawing conditions. Space between the tubes was then filled with a polydisperse hydroxypropyl cellulose powder (refractive index of 1.337) to yield a lower-index inner cladding. The glass transition temperatures of CB and hydroxypropyl cellulose are 95 °C and 120 °C, respectively. As the powder has a significantly higher melting temperature than the tubes, it remained in a powder state during the drawing process. The preform was preheated at a temperature of 150 °C for one hour, and the fiber was subsequently drawn at 180 °C. Reminiscently, Kominsky *et al.*[25] used silica powder packed between two silica tubes to draw fiber featuring randomly distributed continuous holes formed by drawn gas bubbles while the powder particles were completely melted.

The biodegradable fiber was drawn down to a diameter of 450 μm [cross section shown in Fig. 1(b)], and a standard cutback measurement was performed at $\lambda = 630$ nm, resulting in a fiber transmission loss between 1 and 2 dB/cm, showing significant variation from one sample to another because of the random realization of the microstructure. A typical distribution of power in the fiber cross section after 3 cm of propagation is shown in Fig. 1(c), where the distortion in the power distribution is due mostly to the imperfect cutting of a fiber end. Powder particles remained intact during the drawing process and are clearly seen in Fig. 1(a) to be supporting the inner core and forming a very porous inner cladding with an effective refractive index close to that of air. In Fig. 1(d) ellipsometric measurements of the material losses of thick samples (~5 mm) of CB and polymethyl methacrylate (PMMA, for comparison) are presented. At $\lambda = 630$ nm, the CB material loss is 0.4 dB/cm, accounting for almost one half of the measured fiber loss. The CB transparency window (material loss < 10 dB/m) is $700\ \text{nm} \lesssim \lambda \lesssim 1100$ nm, for which several medical lasers exist. In this window several meters of CB fiber can be used, long enough for many medical applications. Overall, in the near-IR the CB and PMMA material losses are similar, while in the visible the PMMA transparency window is wider, $410\ \text{nm} \lesssim \lambda \lesssim 1100$ nm.

Given the potential for *in vivo* applications that is due to the general biocompatibility of a cellulose material, it is important to understand the effects of water exposure on the fiber microstructure and fiber optical transmission. Particularly, since the powder particles in the porous cladding are made of water dissolvable hydroxypropyl cellulose, we expect dramatic changes in the fiber properties after water exposure. We used the setup illustrated in Fig. 2(a) to measure optical transmission through the fiber immersed in deionized water. The fiber passes through a capillary embedded in the window of a receptacle (recipient) such that one fiber extremity remains dry while the other extremity is immersed in water. Light from a He–Ne laser is coupled by a lens into the dry end. Two caches and an iris ensure that only light transmitted from the fiber reaches the detector. The cache within the receptacle hides only half of the output window, leaving a clear viewpoint so that a time-lapse camera can take photographs of the light side scattered by the fiber [Fig. 2(b)]. The experiment begins when the receptacle is filled with water, immersing the fiber. Figure 2(c) shows the typical variation of a transmitted power over the course of 26 h. In the first hours of an experiment, while the fiber becomes filled with water, we typically observe an increase in the fiber transmission. Transmission levels off eventually, once the fiber is filled. On removing the fiber from the receptacle, inspection under a microscope confirms the dissolution of the powder particles after 1 day of submersion. We suspect that the intake of water increases fiber transmission because water ($n = 1.33$) substitutes for air ($n = 1$) in the porous inner cladding formed by powder particles ($n = 1.337$), thus increasing the uniformity of the microstructured cladding and reducing the side scattering.

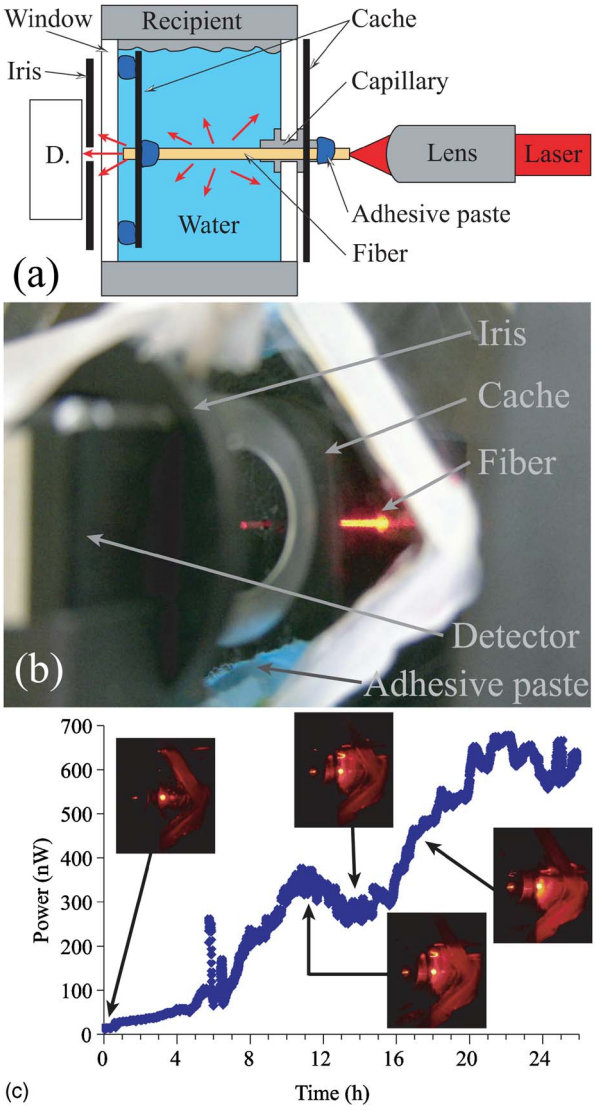

Fig. 2. (Color online) (a) Schematic of a water immersion setup. (b) Photograph of a setup. (c) Variation of transmitted power as a function of time. Insets, stills from a time-lapse camera showing the side-scattered light.

In conclusion, we have demonstrated fabrication of a novel microstructured polymer optical fiber from two types of biodegradable cellulose that have different glass transition temperatures. The resulting fiber has a porous double-cladding structure in which the inner core is suspended in the middle of an outer cladding by the intact powder particles. The inner core is a cellulose tube with a hole that can be collapsed, for laser delivery, or left open, for potential drug delivery. We have also shown that transmission through the fiber first increases when it is filled with water, leveling off when fiber is filled completely and the microstructure is dissolved. Finally, we believe that the use of monodisperse particles with a judicial choice of particle size could allow further tailoring the properties of such fibers for a variety of applications.

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