DNA optical nanofibers: preparation and characterization

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Abstract: We demonstrate the preparation and characterization of DNA optical nanofibers. The prepared DNA optical nanofibers with strong strength and high flexibility are tested. Coupled with silica fiber tapers, their optical characteristics including light transmission performance, group delay and chromatic dispersion are experimentally investigated. The visible and near infrared light waveguiding properties of the DNA optical nanofibers with and without R6G doping are also studied. It is expected that the DNA optical nanofibers may be potential for building the miniaturized biomedical photonic devices.

OCIS codes: (060.2280) Fiber design and fabrication; (310.6628) Subwavelength structures, nanostructures.

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1. Introduction

DNA materials can be used to fabricate drug delivery system, biomedical devices and bioelectronics due to their bioabsorbable and biodegradable nature [1]. Besides, DNA has the double helix structure and hence possesses unusual optoelectronic characteristics, such as enhanced photoluminescence and lasing characteristics [2–4]. DNA complexed with cationic surfactant cetyltrimethylammonium chloride (CTMA) is thermally and optically stable, which makes it suitable for applications in photonics, optoelectronics and sensing [2–5]. Recently, the development of DNA-based devices in nanoscale attracts increasing attention [1–4]. DNA-CTMA has been used to fabricate the optoelectronic devices [6], optical image correlation device [7] and low loss waveguide [8].

Up to date, most of these devices were fabricated by eletrospinning and lithography. DNA photonic wire has been demonstrated [9], whereas effort to fabricate DNA optical fiber based on DNA material suffered some difficulties [10]. For example, surface stiffness, flexibility and strength are the issues that should be considered. In comparison, direct drawing is a simple but more effective method to fabricate prototype photonic devices, such as waveguide, high sensitive sensor, splitter and all optical display [11–13]. Using this method, we have successfully fabricated the DNA optical microfibers (fibers in micrometer scale) and the devices [14]. The fabricated DNA optical microfibers often suffer from the poor uniformity and strong irregular roughness due to the residual impurities in the purified DNA materials. These cause serious light scattering and mainly attribute to the high loss (6 dB/mm), much higher than that of the molecular beam deposited DNA film (~0.02 dB/mm) described in [3]. Compared with the microfiber, the nanofiber has smaller size and higher surface-to-volume ratio. When the diameters of optical fibers decrease down to sub-microscale or even nanoscale (close to the diffraction limit of the guided light), some interesting phenomena including large evanescent fields and large waveguide dispersions have been obtained [15–19]. These phenomena have excited a lot of research issues for developing the compact photonic components after combining the functionalized materials such as chemical indicators, laser dyes and semiconductor nanowires [12,20–22]. Because of the large evanescent fields, the nanofibers have been widely investigated as the sensors and the compact photonic devices, such as the sensor of monitoring the gas concentration change with the ppm-level sensitivity, a single-cell endoscopy by injecting a "small" nanofiber into a cell, the connector of being

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directly coupled with the plasmonic nanowire, the ultracompact splitters and all-optical full-color displays [12,13,21,22]. The large waveguide dispersion of the nanofiber was widely used in supercontinuum generation [23]. Hence it is necessary to develop DNA optical nanofibers (fibers in nanometer scale) and study their properties.

In this paper, we demonstrate the preparation of DNA optical nanofibers. The DNA material purification method is improved by use of the filter with the nanoscale pore. DNA optical nanofibers were fabricated by simple drawing. Transmission loss, group delay (GD) and chromatic dispersion (CD) of DNA optical nanofibers were experimentally investigated. Since DNA-CTMA can greatly enhance fluorescent efficiency and R6G has the high quantum efficiency [3–5], R6G doped DNA optical nanofiber was fabricated and the visible and near-infrared light waveguiding properties were studied.

2. Preparation of DNA optical nanofibers

DNA-CTMA was homemade by mixing salmon sperm DNA (Sigma-Aldrich) and CTMA (MW = 320, Sigma-Aldrich) solution. The details are described as follows. First, salmon sperm DNA was dissolved in ddH_2O, and then the DNA solution was decolorized by active carbon and filtered with the normal filter membrane. Second, CTMA solution was added into the preceded DNA solution continuously until there is no more precipitation, which is similar to the method described in [5]. Third, the DNA-CTMA layer was dissolved in 1-butanol (MW = 74.12, Sigma-Aldrich) and purified with the 0.45 μm syringe filters (Millipore). Finally, an additional step of using LiposoFast-Basic with the 50-nm-pore membrane (Avestin) was used to filter the DNA-CTMA suspension again.

Compared with our previous work [14], the additional step can remove the impurities larger than tens of nanometers by the manual extrusion of the suspension through a polycarbonate membrane of the defined pore size in this work. Otherwise, the impurities with diameters close to or below 0.45 μm can't be filtered out. In consequence, the diameter of DNA optical fiber should be in micrometer scale and the DNA fiber will suffer the poor uniformity as shown in Fig. 1(a). In fact, such impurities and the irregular roughness result in very strong light scattering as shown in Fig. 1(b). The above-mentioned factors explain why the DNA fibers we made had relatively high loss [14]. The impurities mainly consisting of the active carbon with diameters greater than 50 nm in DNA solution were extruded, which results in the reduced loss of DNA optical fiber described as below.

DNA optical nanofibers were fabricated at room temperature by directly drawing the DNA-CTMA solution with a silica optical fiber taper. Compared with our previous method [14], the DNA solution was used before it becomes viscous. Under these conditions, the DNA-CTMA molecules in 1-butanol solution can be self-assembled into DNA optical nanofiber with diameter down to ~300 nm and length up to tens of centimeter. Thanks to the improved purification of DNA-CTMA, the light scattering of the DNA optical nanofibers fabricated by the improved method decreases greatly, as shown in Fig. 1(c) and 1(d), in comparison with that of the previous DNA optical microfiber (see Fig. 1(b)).

The strength and the surface smoothness of DNA optical nanofibers were studied by scanning electron microscope (SEM) with gold sputtering and transmission electron microscope (TEM), respectively. A DNA optical nanofiber with the diameter being ~300 nm is shown in Fig. 2(a). Figure 2(b) illustrates a DNA optical nanofiber loop fabricated by micromanipulation. The TEM images (Fig. 2(c) and Fig. 2(d)) show the good smoothness of DNA optical nanofibers. The roughness of the previous microfiber shown in Fig. 1(a) disappears completely from the surface of the nanofiber because the crude impurities were removed. Interestingly, it is found that DNA optical nanofibers with diameters up to 600 nm can be easily cut off when they are exposed to the TEM electron beam with the normal voltage, which indicates that the electrons penetrate through DNA-CTMA more easily than other polymers. In contrast, other polymer nanofiber, such as the poly(methyl methacrylate) (PMMA) nanofiber, is hardly cut off when its diameter is larger than 200 nm. As a result, the

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electron diffraction pattern cannot be obtained for the nanofibers with diameters above 200 nm because the electrons cannot penetrate through them.

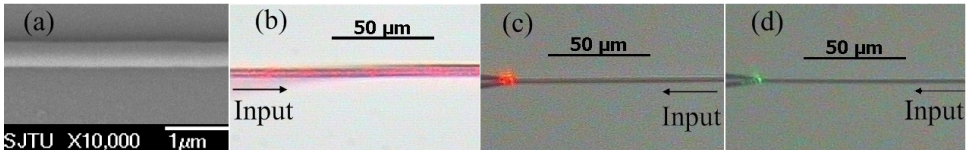

Fig. 1. Images of DNA optical fibers prepared by two methods. (a) SEM image of ~500 nm DNA fiber and (b) the microscope image of part of DNA optical microfiber loop with 632-nm light transmission prepared by previous method [14]. Microscope images of a 650-nm-diameter DNA optical fiber with (c) 632-nm light transmission and (d) 532-nm light transmission prepared by the improved method.

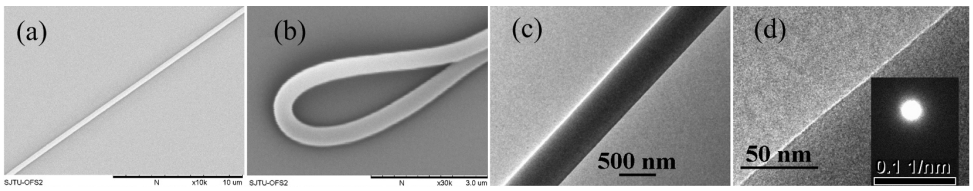

Fig. 2. Electron microscope images of DNA nanofibers prepared by the improved method. (a) SEM image of a 300-nm-diameter DNA optical nanofiber, (b) SEM image of a 480-nm-diameter DNA optical nanofiber loop, (c) TEM image of a 500 nm DNA nanofiber, (d) TEM of a 420 nm DNA nanofiber and the electron diffraction pattern (inset).

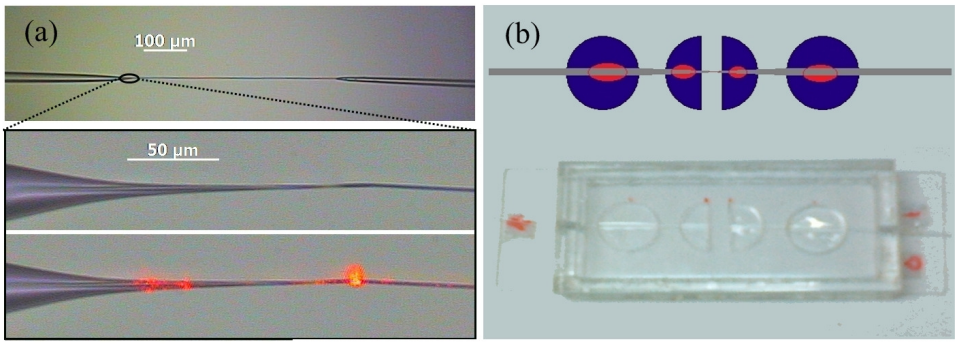

Fig. 3. Images of a DNA optical nanofiber coupled with silica fiber tapers. (a) The microscope image of a 540-nm-diameter DNA nanofiber coupled with silica fiber tapers (up) and its magnified view of the marked zone (middle), light transmission at 632.8 nm wavelength (down). (b) Schematic diagram of a DNA optical nanofiber coupled with silica fiber tapers is fixed with UV curable fluoropolymer (red) (up) and the picture of a packaged DNA optical nanofiber encapsulated with PMMA box on the glass slide (down).

In order to obtain the efficient light coupling, the two ends of a DNA optical nanofiber were coupled with the home-made abrupt silica tapers with submicrometer- or nanometer-order waist. A standard silica single-mode fiber (SMF) was heated by the arc discharge via a fiber splicer (Ericsson FSU975) and drawn to the desired shape by controlling the heating time and the drawing length. Compared with the conventional drawing technique using a flame [16], it ensures the silica taper possessing cleanness and strong suppression of air convection currents near the silica nanofiber. It ensures the formation of the abrupt silica fibers with tips below 100 nm (confirmed by SEM).

As shown in Fig. 3(a), two silica fiber tapers were used as the input and output ports coupled with a DNA optical nanofiber, whose diameter was characterized by SEM. The diameter of the taper changes from several microns to below 100 nm along the tapering direction, which ensures that the mode field diameter (MFD) of a DNA optical nanofiber is

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among the maximum and the minimum of the silica taper MFD. Provided the MFD of a DNA optical nanofiber matches well with those of silica tapers, high-efficient coupling occurs.

The microscope images of light transmission at 632.8 nm wavelength are illustrated in Fig. 1(c) and Fig. 3(a) for 650-nm-diameter and 540-nm-diameter DNA optical nanofibers, respectively. The experimental results show that the total loss (including coupling and transmission loss) is ~10 dB. DNA optical nanofiber coupled with silica fiber tapers was packaged in order to avoid the environmental influence, as shown in Fig. 3(b). Silica fiber tapers coupled with a DNA optical nanofiber were fixed on the MgF_2 surface and then a PMMA box was employed to seal the coupled DNA optical nanofiber.

3. Characterization of DNA optical nanofibers

The experimental setup to characterize DNA optical nanofibers is depicted in Fig. 4. A tunable laser at 1550 nm range is intensity modulated through an amplitude modulator (AM) driven by a radio frequency (RF) signal, and then launched into the DNA optical nanofiber sample (S). The light phase change (Δφ) induced by the sample is measured by a network analyzer. The relative group delay can be calculated by [24].

$$\Delta\tau_{\Delta\lambda} = \frac{\Delta\varphi}{\omega_m}, \tag{1}$$

where ω_m is the angular frequency of the RF signal.

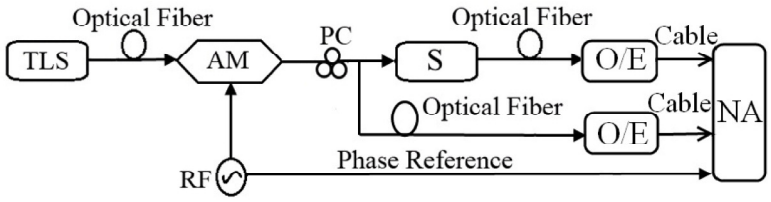

Fig. 4. Schematic diagram of the experimental setup. TLS: tunable laser source, AM: amplitude modulator, PC: polarization controller, S: sample (DNA optical nanofibers), O/E: photoelectric converter, NA: network analyzer, RF: radio frequency signal.

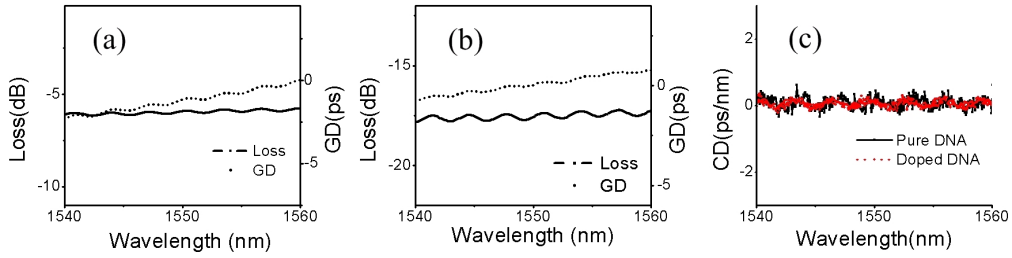

Fig. 5. Transmission spectrum and GD images of DNA optical nanofibers. (a) 1% R6G doped 540-nm-diameter DNA optical nanofiber, (b) 600-nm-diameter DNA optical nanofiber, (c) Calculated CD of DNA optical nanofibers.

Two different DNA optical nanofiber samples after packaging were characterized. The normalized measurement was employed using the silica fiber with the matched length of the measured sample package before every characterization, which can eliminate the influence of silica fiber and the taper. The results are plotted in Fig. 5(a) and Fig. 5(b), respectively. The first one was doped by 1% R6G with a 540 nm diameter and the other one was fabricated from the pure DNA material with a 600 nm diameter. There is a difference in the total loss between these two samples, which is perhaps due to the incomplete coupling situations. The normalized dispersions of DNA optical nanofibers with or without R6G doping are both

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negative in the wavelength range of 1540-1560 nm, which is indicated by the GD curves. The deduced CD value [24] is shown in Fig. 5(c), which is almost close to zero.

It is noted that there are more or less periodic fluctuations for both samples in the loss, GD and CD measurements (see Fig. 5). As described in [25], it can be attributed to the interference between two optical modes (the fundamental mode of LP_{01} and a higher order mode, such as approximate LP_{02}). The working mechanism is discussed as follows. The fundamental mode in the core of the silica SMF (see Fig. 3(a)) excites multiple higher order modes in the transition region of silica SMF taper. First, they suffer the phase difference inside the two tapers. Second, since the DNA optical nanofiber being in nanometer scale supports the only fundamental mode, the excited higher order modes in silica SMF taper leak out to the environmental air and only part of the leaked light is coupled back into the other silica SMF taper. In consequence, interference with low amplitude occurs between the efficient propagation of the fundamental mode (in silica fiber tapers and DNA optical fiber) and the inefficient propagation of the higher mode (in silica fiber tapers and air), respectively. This phenomenon works like a Mach-Zehnder (MZ) type multi-mode interference [26]. It can be further confirmed by the fact that the amplitude of the fluctuations and the period are quite similar to each other as silica fiber tapers and the length of the two DNA optical nanofibers were almost the same.

4. Conclusion

We have demonstrated the preparation of DNA optical nanofibers originated from highly purified DNA materials with the 50-nm-pore membrane. Compared with DNA optical microfibers prepared by the previous method, the DNA optical nanofibers prepared by the improved method greatly reduce light scattering and have better smoothness. The properties of strength, flexibility of the optical nanofibers are verified. The characteristics of DNA optical nanofibers, such as propagation loss, GD and CD, were experimentally investigated. The GD curves indicate that the normalized dispersions of DNA optical nanofibers are negative. The periodic fluctuations of the experimental results are discussed. Thanks to high luminous efficiency of DNA material [1,5], DNA optical nanofibers might be potential candidate in applications to the compact light-emitting device, the novel fiber laser or the sensor in nanometer scale. The strong evanescent field may provide high sensitivity for the biomedical sensors.

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