Research Article | Vol. 26, No. 10 | 14 May 2018 | OPTICS EXPRESS 13408
Optics EXPRESS

Optical waveguiding properties of colloidal quantum dots doped polymer microfibers

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Abstract: QDs-doped polymer microfibers are fabricated through direct drawing method. By adding the polymethylmethacrylate into polystyrene, the surface quality and flexibility of microfiber are improved. Under direct excitation by the focused laser, the polymer microfibers doped with different quantum dots emit different colors and act as an optical waveguide. The waveguide properties of the microfiber are studied in detail. It is found that refractive index of the substrate and diameter of microfiber are the most important factors that affect the optical loss of this waveguide. The microfiber does not produce significant polarization after being deposited on the substrate. Moreover, exciting the QDs-doped polymer microfiber through a blue LED is demonstrated. This structure may find widespread applications in integrated photonic devices.

OCIS codes: (130.5460) Polymer waveguides; (230.5590) Quantum-well, -wire and -dot devices.

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#327398 https://doi.org/10.1364/OE.26.013408
Journal © 2018 Received 2 Apr 2018; revised 2 May 2018; accepted 7 May 2018; published 9 May 2018

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1. Introduction

Polymer fibers, as an optical waveguide structure created by organic materials, have received continuous attention in recent years due to their excellent properties, such as simple preparation, low cost, high optical transparency and flexibility [1–4]. More specific properties of polymer fibers are exhibited when their diameter decreases to a few micrometers or even nanometers, including tight optical confinement, high fraction of evanescence fields, and more flexible structure [5–7]. Therefore, polymer micro or nanofibers have been considered as a promising component for integrated photonic devices. Photonic devices fabricated by polymer micro or nanofibers such as a coupler and microresonator have been demonstrated [3]. In addition to these structure, good processability of the polymer materials makes it easily be doped. Dye molecules [5,8,9], noble metal nanoparticles [10–14], or quantum dots-doped polymer fibers have been investigated recently [15–22], which show fascinating optical properties.

As a quasi-zero-dimensional nano-semiconductor light-emitting material, quantum dots (QDs) have various characteristics such as adjustable emission wavelength, high quantum yield and photochemical stability. Owing to the small volume, the QDs doped in polymer microfiber do not introduce big optical loss to the microfibers. Lights can generate and then propagate inside the QDs-doped polymer microfiber, which form the active waveguide structure with high emission efficiency, low optical loss and good stability. Compared with bare polymer microfiber, extra light source and coupling structure are not required with QDs-doped polymer microfibers, which can make the integrated photonic devices more compact.

Electrospinning and direct drawing are the main methods to fabricate QDs-doped polymer microfibers [2,4,16,17,21]. Compared to electrospinning, direct drawing method is easier and with lower cost. A variety of polymer, such as poly(trimethylene terephthalate) (PTT) [18], poly(methyl methacrylate) (PMMA) [19,21], polystyrene (PS) [20], polyacrylamide (PAM) [5,23], poly(vinyl alcohol) PVA can be used to fabricated the polymer microfiber. However, different physical properties of these polymers can affect the surface quality and mechanical properties of the microfibers [24]. In order to improve the flexibility of polymer microfibers, a mixed PMMA and PS has been used herein. Optical properties of polymer microfiber with different diameters and holding substrates were studied. Besides the optical properties, how to excite the QDs-doped polymer microfiber is also important. Generally, focused laser for fiber taper are usually used [5,6,16,25], while they may not be suitable for miniaturized integrated photonic devices, because the laser system has a large volume, and the fiber taper coupling system is complex. Here it is demonstrated that excitation of QDs-doped polymer microfiber

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can be realized through a blue light emitting diode (LED), which will be possible to apply in integrated photonic devices.

2. Experimental setup and results

2.1 Fabrication of QDs-doped polymer microfiber

The QDs-doped polymer microfiber with diameters ranging from several micrometers to tens of micrometers were fabricated by direct drawing method as reported previously [4,5]. First, PS was dissolved in toluene with concentration of 11 wt%. Then, a certain percentage of PMMA was added into the solution, the weight ratio between PMMA and PS is 1:0.7. In experiment, it was found that the polymer microfiber drawn directly from PS was easily broken due to its bad mechanical properties. As a highly flexible polymer, PMMA has a wide range of applications. While polymer microfibers were difficult to mold when using PMMA alone. Therefore, the PMMA was introduced into PS in our experiment to improve the mechanical flexibility and surface quality of polymer microfiber. After that, CdSe/CdS core-shell QDs (0.3 wt%) with three different sizes were mixed in the solution respectively to form three kinds of solution. The mixture solution was stirred in order to ensure uniform dispersion of QDs.

The preparation process of QDs-doped polymer microfiber is shown in Fig. 1(a). The QDs-doped PMMA + PS mixture solution was dropped on the substrate. The sharp metal tip was drawn with a constant speed after immersed into the solution. Then the QDs-doped polymer microfiber formed with rapid solvent evaporation in the air. Here, the diameter of microfiber can be adjusted through changing the size or the drawing speed of the metal tip. Figure 1(b) shows the SEM image of a 9.3 μm polymer microfiber. It can be seen that the polymer microfiber has a uniform diameter and smooth surface without any defects. The insect image shows a clear and sharp edge which can be contributed to the adding of PMMA.

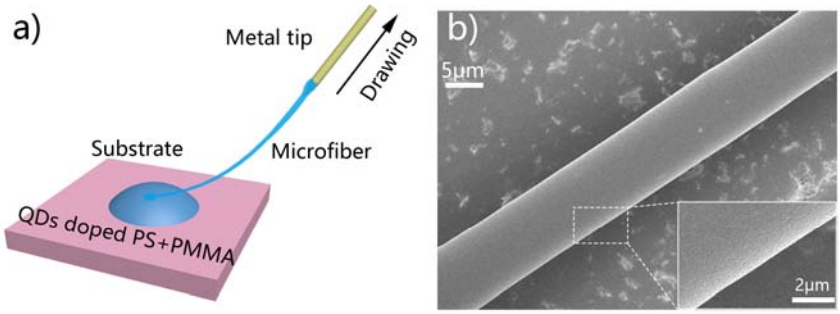

Fig. 1. (a) Schematic diagram of the fabrication of polymer microfiber by direct drawing method. (b) SEM image of a 9.3μm diameter QDs-doped polymer microfiber. Inset: Close-up view of the edge.

2.2 Measurement of optical properties

Figure 2(a) shows the schematic diagram of the optical properties testing. A small section of QDs-doped polymer microfiber was put on a MgF_2 substrate. The refractive of MgF_2 (n = 1.39) is relatively low compared with PMMA (1.49) and PS (1.59). A He-Cd laser beam operating at 325 nm was directly irradiated onto the polymer microfiber. The emitted light propagates along the fiber and scattered to the space at the end of microfiber. The scattered light was collected through a microscope objective and detected by a charge coupled device (CCD). Figures 2(c)-2(e) show the optical image of QDs-doped polymer microfibers under laser excitation. It can be clearly seen that there was a much brighter region in each polymer microfiber, which indicated that the region was excited. The QDs inside the polymer fiber

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was directly excited by the ultraviolet laser on this excited area, and then different QDs emitted different color of lights. It should be noticed that part of the excitation laser also became waveguide mode in the polymer microfiber. However, the excitation light disappeared very quickly with the continued absorption of QDs during propagation. The emitted light was guided by the polymer microfiber and finally scattered. The photoluminescence (PL) was collected at the end of polymer microfiber, which is shown in Fig. 2(b). The emissions from the different QDs-doped polymer microfibers are located at about 480, 560, and 610 nm, respectively, which agree well with those QDs in solution. It means that the incorporation of the QDs into polymer does not affect their optical properties. Moreover, QDs-doped polymer microfiber with desired emission wavelength can be fabricated through changing QDs or even combining several different QDs.

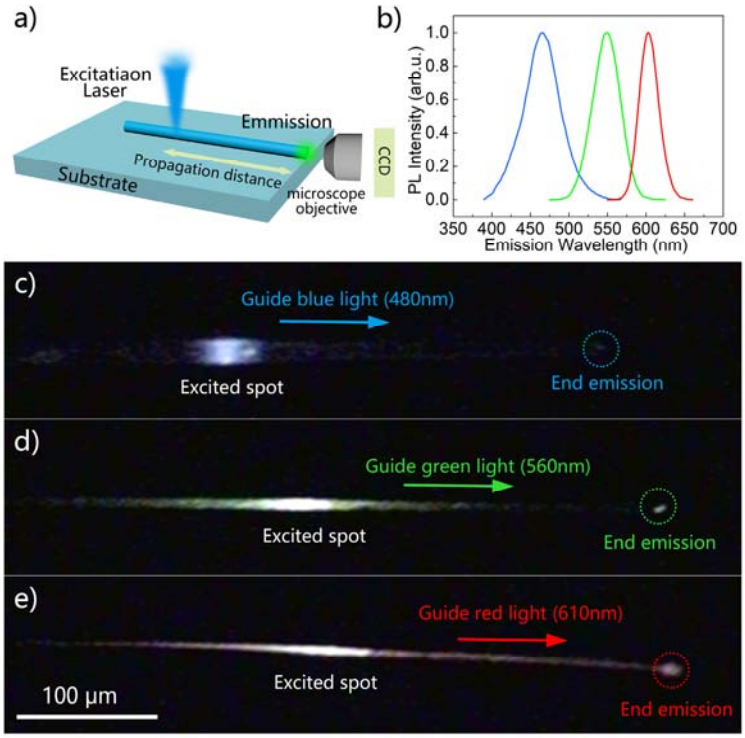

Fig. 2. (a) Schematic diagram of the experimental step. The microfiber supported with substrate is excited by focused laser. (b) PL spectra measured at the end of microfiber. The blue, green, red emission peaks correspond to the three microfibers in (c) (d) (e). (c) - (e) Optical image of three polymer microfiber doped with different quantum dots excited by 322nm focused laser.

To further study the optical properties of QDs-doped polymer microfibers, polarization characteristic of the emission light was investigated. QDs-doped polymer microfiber with the emission peak at 550 nm was selected and placed on the MgF_2 substrate. Figure 3(a) shows the PL spectra of QDs-doped polymer microfiber, which was directly excited by excitation laser with two different polarization directions. Here, P represents that the direction of polarization of the excitation laser is parallel to the substrate. Conversely, V represents that the direction of polarization of the excitation laser is vertical. As shown in Fig. 3(a), the PL intensity of P direction is slightly stronger than the V direction. It should be pointed out that the power of the excitation laser and the propagation distance are kept the same when the direction of polarization changed. The propagation distance refers to the distance from the excited spot to the end of polymer microfiber as the Fig. 2(a) shows. The existence of the

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substrate breaks the circular symmetry of surrounding around the polymer microfiber. As a result, the substrate has a different influence on the light with different directions of polarization. From the PL spectra in Fig. 3(a), it can be seen that the V direction light has a slightly larger optical loss. That means the interaction between substrate and V direction light is stronger, which can also be predicted. Furthermore, the polarization properties of different diameters of polymer microfiber were investigated. The integrated PL intensities of polymer microfiber with two different diameters are shown in Fig. 3(b) as function of propagation distance. Diameters of polymer microfiber 1 and 2 are 27 and 21 μm, respectively. It was found that smaller diameter polymer microfiber showed a faster rate of intensity decay for both P and V polarized light. However, the PL intensity decay rates of the two polarization directions basically keep identical in a single polymer microfiber. Therefore, it can be concluded that within a certain diameter range, the polarization effect caused by the substrate is very small.

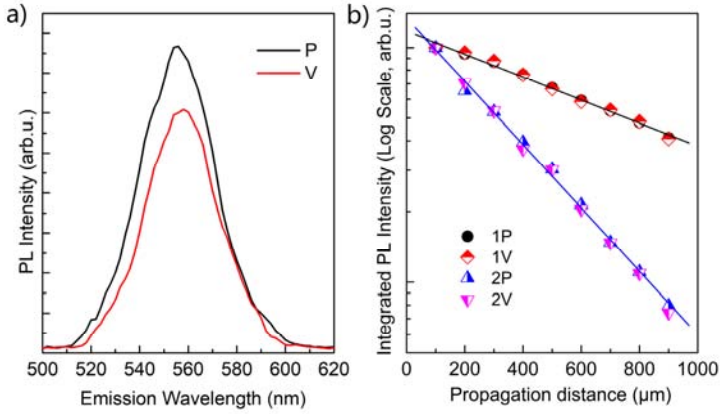

Fig. 3. (a) PL spectra of the microfiber excited by the laser with different polarization directions. P represents parallel to the substrate, V represents vertical to the substrate. (b) The polarization-related integrated PL intensity of sample 1 and sample 2 as a function of propagation distance.

To obtain more information about the properties of this waveguide, three different diameters of polymer microfiber were used to conduct a diameter-dependent measurement. Through changing the location of the excited spot, the integrated PL intensity with different propagation distances were measured, which is shown in Fig. 4(a). It can be clearly seen that, when the propagation distance increases, the PL intensity decreases exponentially. Moreover, the thinner polymer microfiber has a higher decay rate. The experimental data can be fitted well by Beer-Lambert law:

$$I = I_0 e^{-\alpha x}. \quad (1)$$

In this equation, I is the measured PL intensity in the end of polymer microfiber, I_0 is the PL intensity in the initial position, x is the distance between the initial position and the end of microfiber, α is the absorption coefficient. The absorption coefficient of these three microfibers are 13.0 cm^{-1}, 19.2 cm^{-1}, 26.6 cm^{-1}, respectively. Here, we consider that is related to the self-absorption of QDs and the optical loss of the polymer microfiber. The diameter of the microfiber and the choice of substrate are all the factors that affect the optical loss. The PL intensity was all measured from microfibers on MgF_2 substrate and the concentration of the QDs is kept the same. Therefore, it can be concluded from Fig. 4(a) that the optical loss increases with decreasing diameter of the polymer microfiber. This result can also be supported by the optical image in Figs. 2(c)-2(e). When the polymer microfiber has a larger diameter, it shows very weak surface scattered light between the excited spot and the

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end of microfiber. With the diameter decreases, there has a stronger surface scattered light, which indicates a larger optical loss.

In addition to the diameter of polymer microfiber, the substrate is also an important factor affecting the properties of the waveguide. Therefore, the substrate-dependent measurement was conducted. The polymer microfiber with a diameter of 25 μm was placed on four different substrates. It should be pointed out that the air substrate means that the microfiber is suspended in the air. The refractive index of these substrates are 1.0 (air), 1.38 (MgF_2), 1.55 (quartz), and 3.5 (silicon). Figure 4(b) shows the integrated PL intensity as a function of propagation distance in the case of four different substrates. It can be seen that the PL intensity measured in different cases all decrease exponentially with the propagation distance. Through fitting the experimental data, the absorption coefficient in these four cases are 7.8 cm^{-1} (air), 12.6 cm^{-1} (MgF_2), 16.8 cm^{-1} (quartz), and 21.8 cm^{-1} (silicon), respectively. For the suspended polymer microfiber, optical loss is caused by surface scattering. With the increase of refractive index of the substrate, optical loss caused by substrate will increase. When the refractive index of the substrate is high, light propagating in the microfiber will leak into the substrate or scatter at the interface, resulting in bigger optical loss.

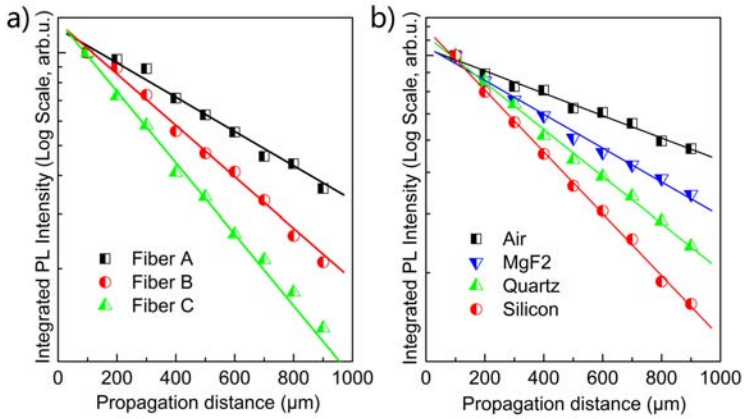

Fig. 4. (a) The integrated PL intensity of three different diameters microfiber as a function of propagation distance. The diameter of this three micorfibers are 27μm (A), 23μm (B), 19μm (C), respectively. (b) The integrated PL intensity of microfiber supported by four kinds of substrates as a function of propagation distance.

2.3 Excite QDs-doped polymer microfiber by LED

It is known that integrated photonic devices require the components to have small volume. Therefore, the focused laser system is not suitable for exciting QDs-doped polymer microfiber for this application. Recently, the fiber taper was used to excite QDs-doped polymer microfiber [5,6]. In this method, a fiber taper should place in parallel and close contact with one end of microfiber. The excitation light in the fiber taper will be introduced into the microfiber due to the coupling of the evanescent field. The coupling efficiency of the excitation light is high, but it is closely related to the diameter of microfiber and taper, the close contact and the length of the coupling region. In practical applications, it is very difficult to operate and control due to the tiny size of fiber taper and polymer microfiber. In addition to these two methods, it is shown herein to excite the QDs-doped polymer microfiber directly through a blue LED. This method is smaller in size and can be simply implemented. The excitation mechanical is similar with that of focus laser excitation. The light irradiates onto the surface of the microfiber and excites quantum dots inside. But it will have higher excitation efficiency because the contact area of light and microfiber is larger. During the

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experimental operation, the polymer microfiber was just simply placed on top of the surface of the LED and ensure that it was located in the center of the LED light. The schematic diagram of LED-excited structure is shown in Fig. 5(a). A single QDs-doped polymer microfiber is deposited on the surface of the blue LED. One end of the microfiber is in the center of the blue light, where the QDs are excited. The red light propagates along the microfiber and emit in another end, which is suspended in the air. Figure 5(b) shows the optical image of the LED excited structure. It can be seen that, with the current injection increases, the blue LED light gradually brightens. At the same time, a weak red emission emerges in the end of microfiber. Figure 5(c) shows the emission spectra measured at the end of microfiber. Through increasing the forward voltage of LED, the emission intensity increases. The inset shows the I-V curve of the blue LED. The integrated EL intensity of blue LED and QDs-doped polymer microfiber are shown in Fig. 5(d) as a function of inject current. When the current injection increases, the emission from blue LED and QDs-doped polymer microfiber increase simultaneously. It is worthwhile mentioning that the emission intensity of QDs-doped polymer microfiber is linear related to the EL intensity of LED. This excited method may be applied in future integrated photonic devices due to its simple structure.

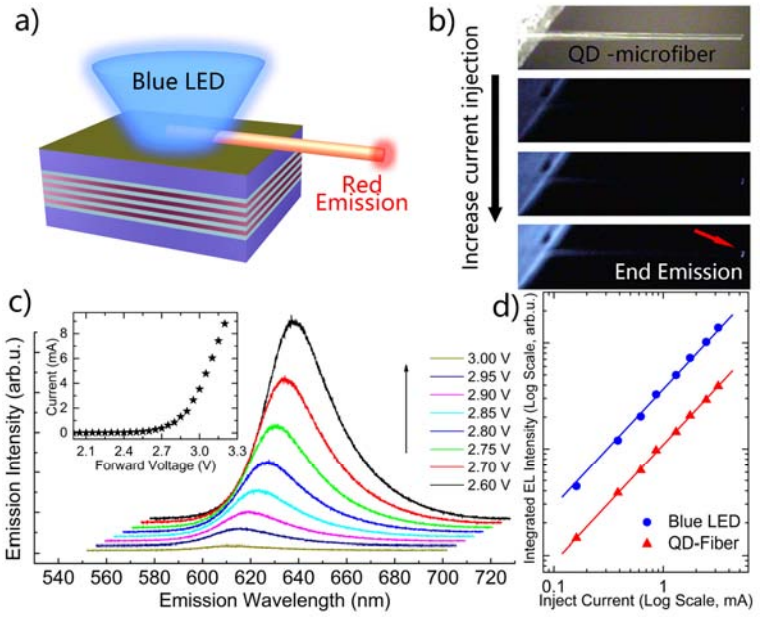

Fig. 5. (a) Schematic diagram of the LED excite structure. (b) Optical image of the DQs-doped polymer microfiber excited by LED. The red arrow points to the end emission light. (c) The emission spectra measured from the end of microfiber change with the forward voltage of LED. Inset shows the I-V curve of LED. (d) The integrated EL intensity of blue LED and QDs-doped polymer microfiber as a function of inject current.

3. Conclusion

In conclusion, we have fabricated the QDs-doped-polymer microfiber. The surface quality and flexibility were optimized through the mixture of PMMA and PS. Under excitation by focused laser, the QDs-doped polymer fiber emitted light and can be severed as a waveguide. Through changing the size of quantum dots, different wavelength emissions have been achieved. On the MgF_2 substrate, the polymer microfiber has not exhibited strong polarization characteristics. It is shown that both the diameter of microfiber and refractive index of the substrate influence the optical loss. Finally, the QDs-doped polymer microfiber was

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successfully excited by blue LED. This simple structure holds a great potential on the integrated photonic devices in the future.

Funding

National Natural Science Foundation of China (11574130 and 11404161), Shenzhen Science and Technology Innovation Committee (Projects Nos.: KQJSCX20170726145748464, JCYJ20150930160634263, and KQTD2015071710313656). R. C. acknowledges the support from National 1000 plan for Young Talents.