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Local excitation and collection in polymeric fluorescent microstructures

Franciele Renata Henrique, Cleber Renato Mendonca *

São Carlos Institute of Physics, University of São Paulo, PO Box 369, 13560-970 São Carlos, SP, Brazil

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ABSTRACT

Integrated photonics has gained attention in recent years due to its wide range of applications which span from biology to optical communications. The use of polymer-based platforms for photonic devices is of great interest because organic compounds can be easily incorporated to polymers, enabling modifications to the system physical properties. The two-photon polymerization technique has emerged as an interesting tool for the production of three-dimensional polymeric microstructures. However, for their further incorporation in photonic devices it is necessary to develop methods to perform optical excitation and signal collection on such microstructures. With such purpose, we demonstrate approaches to perform local excitation and collection in polymeric microstructures doped with fluorescent dyes, employing tapered fibers. The obtained results indicate that fiber tapers are suitable to couple light in and out of fluorescent polymeric microstructures, paving the way for their incorporation in photonic devices. We also show that microstructures doped with more than one dye can be used as built-in broadband light sources to photonic circuits and their emission spectrum can be tuned by the right choice of the excitation position.

1. Introduction

In recent years, the development of integrated photonics has been motivated by the need of developing compact and high performance systems for a variety of applications, spanning from on-chip biosensors to telecommunication devices [1–3]. Several fabrication approaches and materials have been exploited in this field, from two-dimension devices in silicon photonics to three-dimensional microstructures in organic and hybrid materials [4,5]. Although silicon photonics presents the clear advantage of compatibility with existing electronic integrated circuits [6], depending on the application, other platforms, such as polymers, offer advantages as ease of functionalization with different organic materials that present specific optical, electrical or biological properties [7–11]. In this direction, the fabrication of polymeric-based microstructures has received a great deal of attention in the last few years [12,13]. Two-photon absorption polymerization [14], for instance, has been shown to be a powerful method to fabricate complex three-dimensional microstructures, which can be embedded with additional materials that confer special properties to the structures, aiming at specific applications [15–20]. For example, microstructures containing single walled carbon nanotubes, with potential applications in electronic and mechanical devices have been demonstrated [21]. In the point of view of optical devices, it has been shown the fabrication by two-photon polymerization of birefringent microstructures [22,23], resonators [24], waveguides [25] and fluorescent microstructures [26,27]. For most of such applications, however, microstructures have been connected to light sources by means of microscope objectives, which have also been used to collect and drive the light signal to analysis instruments. Therefore, more compact approaches are still on demand to perform excitation and collection in polymeric microstructures. Optical fiber tapers [28,29] have appeared as an interesting option for such task, as their diameter suits the size of the microstructures [30]. Besides, tapered fibers are usually produced by a heat-and-draw method, in such a way that their standard end can be attached to light sources or other instruments [31,32].

In this paper we explore possibilities in this direction, by demonstrating localized optical excitation and optical signal collection in polymeric fluorescent microstructures fabricated by two-photon polymerization. Two approaches were employed; in the first one microstructure excitation is performed by the conventional method, i.e. by using objective lenses, while a fiber taper is used to collect the microstructure emission. In the second approach, fiber tapers are used to perform both excitation and collection of the sample emission. By using these approaches in multiple doped microstructures, we were able to demonstrate excitation of a particular fluorophore (dopant) localized in a specific site of the structure, or the excitation of more than one

* Corresponding author.
E-mail address: crmendon@if.sc.usp.br (C.R. Mendonca).

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fluorophore at once. Hence, the local excitation and collection of microstructures emission can be conveniently explored to produce built-in optical sources for photonic devices.

2. Materials and methods

Three-dimensional polymeric microstructures were produced by two-photon polymerization. The employed precursor resin was a mixture of two triacrylate monomers [33]: tris(2-hydroxyethyl) isocyanurate triacrylate (50 wt.%), which gives hardness to the microstructure, and ethoxylated (6) trimethylolpropane triacrylate (50 wt.%), which reduces polymerization shrinkage. The photoinitiator ethyl-2,4,6-trimethylbenzoylphenyl phosphinate, also known as Lucirin TPO-L [34], was mixed to the resin in a proportion of 3 wt.% in excess. To confer emissive properties to the polymeric microstructures, three different dyes were incorporated to the unpolymerized resin: Rhodamine B (0.5 wt.%), Disodium Fluorescein (1.5 wt.%) and Stilbene 420 (0.1 wt.%). The concentration of each dye was chosen to optimize their emission according to their solubility in the resin. After a homogeneous mixture of monomers, photoinitiator and the chosen dye is obtained, a droplet of resin is placed on a glass substrate that is subsequently covered with a coverslip. The resin is confined to the region between the substrate and the coverslip by a 200 μm spacer.

To perform the polymerization a Ti:Sapphire laser oscillator was employed, emitting 100 fs pulses at 790 nm with a repetition rate of 86 MHz. The beam is focused into the resin by a 0.25-NA objective. Two galvanometric mirrors scan the laser beam in the *x* and *y* axes, while a translation stage moves the sample in the z direction, in order to produce three-dimensional structures. The average laser power, measured after the objective, used for the microstructures fabrication was 12 mW. All microstructures were fabricated with a translation speed of 60 μm/s. After the polymerization process is completed, the unpolymerized resin is washed away with ethanol leaving only the microstructures attached to the glass substrate. Multiple doped microstructures are produced in sequential steps; at first the resin containing one of the dyes is placed on the substrate and two-photon polymerization is performed. After the unpolymerized resin is washed away and the substrate dried, a droplet of the resin containing the second dye is placed over it. The sample is carefully repositioned, with a typical alignment precision of ±3 μm, and the second structure is fabricated in the desired position. Once again the unpolymerized resin is washed away with ethanol. For triple doped microstructures the process is repeated.

Fiber tapers with diameters around 1 μm were produced by a heat-and-draw approach, in which a butane torch heats a conventional optical fiber until it reaches silica softening temperature. At the same time a translation stage stretches the fiber symmetrically. The fiber tapers produced remain attached to the standard fiber end. To perform the optical connection between the doped microstructures and excitation sources, as well as with signal analysis systems, two different approaches were developed, as illustrated in Fig. 1. In the first one (Fig. 1a), the substrate containing the microstructures is placed on an inverted microscope. The laser beam responsible for the microstructure excitation is aligned to an entrance port of the microscope and focused on the sample through the microscope objective. In our experiments an Ar-ion laser (514 nm) and a HeCd (442 nm and 325 nm) were used as excitation sources. The excitation laser power used at the sample position was kept at approximately 1 mW for all wavelengths used. When excitation is carried out in the UV (325 nm), in order to avoid undesirable losses of the excitation light through the microscope optics, we externally adapted UV-optics and a 5-cm lens to focus the excitation light on the sample. The same microscope platform, however, has been used for sample positioning and imaging. The image of the microstructure under excitation is obtained using a CCD camera attached to the microscope. The microstructures emission was acquired by positioning the end of the fiber taper (diameter $\sim$ 1 μm) in the proximity of the microstructure, using a micromanipulator that allows three-dimensional movements with micrometric resolution. The standard end of the tapered fiber was connected to a spectrometer, enabling the measurement of the microstructures emission spectrum. In the second optical connection approach, illustrated in Fig. 1b, a fiber taper is used to locally excite the microstructure. In this case the Ar-ion laser was coupled to the conventional end of the tapered fiber. The tip of the fiber taper was positioned next to the microstructure by means of a micromanipulator, allowing individual/local excitation. As in the previous approach, a fiber taper connected to a spectrometer was used to collect the microstructures emission.

3. Results and discussion

Fig. 2a displays the emission spectrum, collected through the fiber taper, of a Rhodamine B doped microstructure excited using an Ar-ion laser at 514 nm, according to the configuration illustrated in Fig. 1a. As it is shown in the inset of Fig. 2a, the microstructure at the top-right corner was individually excited by aligning the microscope objective with the sample. In the inset it is also possible to observe the fiber taper that acquires the emission. In Fig. 2b, the fiber taper responsible for collecting the emission was positioned, and kept fixed, in the Fluorescein side of a double doped microstructure (containing Rhodamine B and Fluorescein), which was subjected to excitation at 442 nm from the HeCd laser. When the structure was excited in the Rhodamine B side (bottom inset of Fig. 2b), which is accomplished by aligning the 442 nm laser beam on the microscope objective, only the Rhodamine B spectrum was observed (bottom curve of Fig. 2b). When excitation is performed on the Fluorescein side of the microstructure (upper inset of Fig. 2b), the characteristic emission appears at approximately 500 nm, as observed in the upper curve

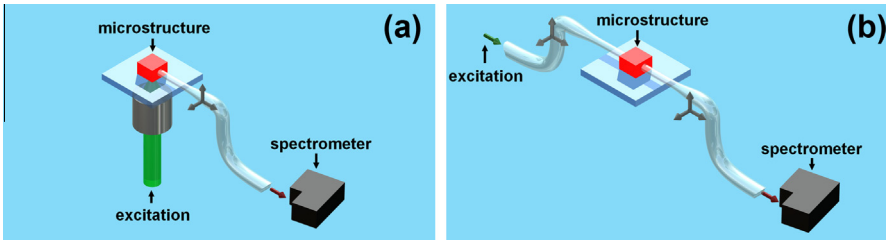

Fig. 1. Illustration of the optical connection methods used. (a) Excitation is performed by a microscope objective, while the microstructure emission is collected by the fiber taper tip. (b) The excitation light is coupled to the conventional end of the fiber taper and directed to the microstructure, whereas the emission is collected by a fiber taper. In both approaches the fiber tapers are positioned by micromanipulators and the conventional end of the collection fiber is connected to a spectrometer.