Three-dimensional fabrication of optically active microstructures containing an electroluminescent polymer

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Microfabrication via two-photon absorption polymerization is a technique to design complex microstructures in a simple and fast way. The applications of such structures range from mechanics to photonics to biology, depending on the dopant material and its specific properties. In this paper, we use two-photon absorption polymerization to fabricate optically active microstructures containing the conductive and luminescent polymer poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV). We verify that MEH-PPV retains its optical activity and is distributed throughout the microstructure after fabrication. The microstructures retain the emission characteristics of MEH-PPV and allow waveguiding of locally excited fluorescence when fabricated on top of low refractive index substrates. © *2009 American Institute of Physics*.
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Since its introduction in 1997,[1] two-photon polymerization has proven to be a suitable technique to fabricate three-dimensional microstructures, with applications in optical circuitry,[2] optical data storage,[3] three-dimensional micromechanical actuators,[4–6] birefringent microstructures,[7] photonic crystals,[3,8] and biomedical devices.[9–12] Two-photon polymerization enables the fabrication of three-dimensional microstructures because the polymerization is restricted to the focal volume of the laser beam, where the photon flux density is high enough that two photons can be simultaneously absorbed in a single event.[13] By scanning the focus of the laser beam in three dimensions, complex microstructures can be fabricated.[13,14] While the majority of studies reported to date explore undoped microstructures, which are passive and therefore of limited use in technological applications, more recently, some reports deal with doped microstructures, which possess enhanced optical and biological properties.[7,11,15–21]

In this paper, we report on two-photon polymerization of microstructures containing the polymer poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV).[22–24] We use a guest-host strategy in which the host consists of two triacrylate monomers. The guest material is MEH-PPV, a polymer known for its conductivity,[24] electroluminescence,[22,23] and nonlinear optical properties.[25–28] The microstructures are freestanding and preserve the luminescence properties of MEH-PPV. Our results show that MEH-PPV is distributed throughout the microstructure and not just at the surface. We also demonstrate waveguiding of MEH-PPV fluorescence in 100 μm long microstructures fabricated on mesoporous silica substrates. The microstructures hold promise for photonics applications, such as microlight emitting diodes (microLEDs) and microwaveguides.

We fabricate microstructures by two-photon absorption polymerization of an acrylate-based resin containing MEH-PPV. The resin consists of a mixture of two triacrylate monomers: tris(2-hydroxyethyl) isocyanurate triacrylate (30% by weight), which increases the hardness of the microstructure, and ethoxylated(6) trimethylolpropane triacrylate (70% by weight), which reduces shrinkage upon polymerization. We initially prepare an ethanol solution containing these two triacrylate monomers, to which we add MEH-PPV (up to 1% by weight). We stir this solution for 1 h to fully mix the components. Ethanol is then eliminated by evaporation at room temperature for 24 h, yielding a viscous liquid. Finally, we add to this liquid the polymerization photoinitiator ethyl-2,4,6-trimethylbenzoylphenylphosphinate, commercially known as Lucirin T-POL[29,30] (3% by weight), mixing it for 1 h prior to use.

To increase adhesion of the microstructure to the glass substrate, we treat the surface of a microscope slide with (3-acryloxypropyl)trimethoxysilane. Then we place a drop of the resin inside a spacer located on the surface-treated microscope slide and place a cover slip on top of the spacer. The resin is polymerized using 130 fs pulses at 800 nm from a Ti:sapphire laser oscillator operating at 80 MHz. For fabricating the microstructures, we use an average power of 40 mW, measured before the 0.65 numerical aperture objective, which focuses the laser beam into the sample, yielding a laser fluence of nearly 30 mJ/cm^2. A motorized stage moves the sample in the axial z direction and a pair of galvano mirrors scans the laser across the resin in the x-y direction. After fabricating the desired microstructure, we place the sample in ethanol to wash away any unpolymerized resin. In addition, we fabricate waveguides using the same approach described before. However, in this case, we use mesoporous silica films as substrates, which have a low refractive index

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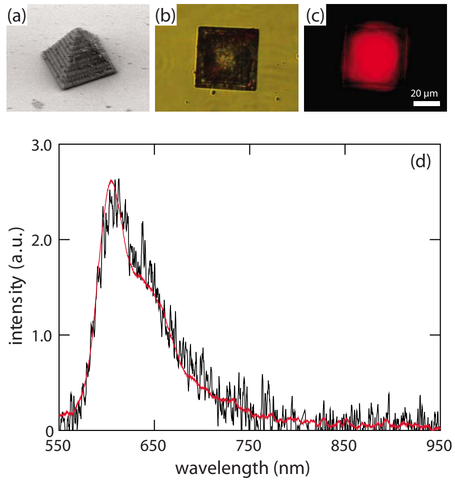

FIG. 1. (Color online) (a) Scanning electron microscopy of a pyramidal microstructure containing MEH-PPV. Fluorescence microscopy image of the pyramid (top view) with laser excitation at 532 nm (b) off and (c) on. (d) Emission spectrum of the microstructure (black line) and of a film with the same composition (red line).

(n=1.185) throughout the visible spectrum.[31]

We obtain the fluorescence spectrum and fluorescence microscopy images of the microstructures by exciting them with a neodymium doped yttrium aluminum garnet cw laser operating at 532 nm and an average power of 1 mW. To obtain the fluorescence microscopy images, we use a color filter in front of the camera to block the excitation light at 532 nm. We collect the fluorescence spectrum of microstructures through an exit port of the microscope using a portable spectrometer.

The confocal microscopy images of the microstructure containing MEH-PPV are obtained using 540 nm excitation light (40× objective). We collect the emission at 570 nm from x-y planes of the microstructure separated in the z direction by 16 μm.

Figure 1(a) shows scanning electron microscope image of a 40 μm square-base pyramid containing 1% MEH-PPV fabricated by two-photon polymerization. Figure 1(b) shows a top view bright-field image of the microstructure. Figure 1(c) shows the fluorescence image of the same microstructure. The fluorescence spectra of the microstructure and of an approximately 100 μm thick film with the same composition as the microstructure are displayed in Fig. 1(d). The spectra have the same shape, confirming that the fluorescence observed in Fig. 1(c) arises from the MEH-PPV contained in the microstructure. The noise observed in the microstructure spectrum is due to the low intensity of the fluorescence signal because the microstructure has dimensions of only a few micrometers. We also fabricated microstructures down to 4 μm long side, which presents the same features of the fluorescence spectrum showed in Fig. 1(d). We observed that the fluorescence intensity decreases linearly with the MEH-PPV content as the microstructure size diminishes. For microstructures of a given size, we measured a maximum variation of approximately 20% in the fluorescence intensity.

To verify that the MEH-PPV is distributed throughout the microstructure, we obtained fluorescence confocal microscopy images of a pyramidal microstructure with a squared base of 120×120 μm^2 at different z levels (Fig. 2).

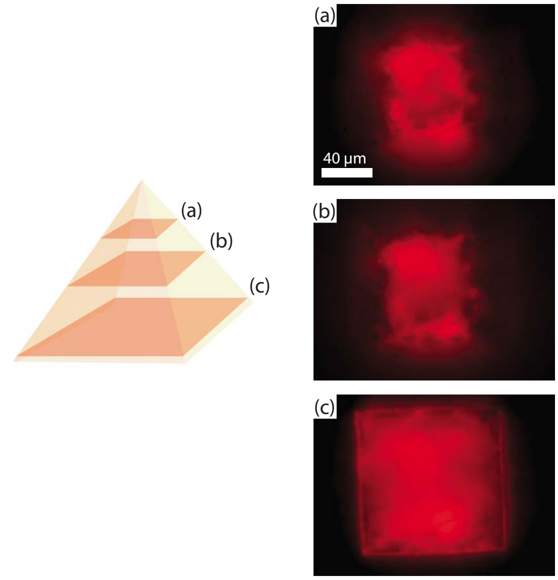

FIG. 2. (Color online) Fluorescent confocal microscopy images of planes separated by 16 μm in a pyramidal microstructure (squared base of 120 ×120 μm^2).

The sequence of fluorescence images represent layers of the pyramidal microstructure separated by 16 μm each.

Figure 3(a) shows a 100 μm long waveguide, containing MEH-PPV, illuminated in its central region by a focused laser at 532 nm (top view). The MEH-PPV fluorescence is guided through the microstructure and scatters at both microstructure ends. Because of surface roughness, some light scattering occurs along the waveguide. Figure 3(b) shows no waveguiding of a microstructure fabricated on top of a conventional glass slide (top view). In the left hand side of Fig. 3, we display a schematic (side view) of the microstructure excitation and the corresponding waveguiding.

The fabrication method used in this work involves absorption of two photons, localizing polymerization to the focal region and allowing the fabrication of three-dimensional microstructures. The MEH-PPV containing microstructure in Fig. 1(a) exhibits excellent integrity and good definition, indicating that the presence of MEH-PPV does not affect the fabrication process, provided we use laser power below 40 mW. Furthermore, MEH-PPV is retained in the microstructure, as demonstrated by the characteristic fluorescent emis-

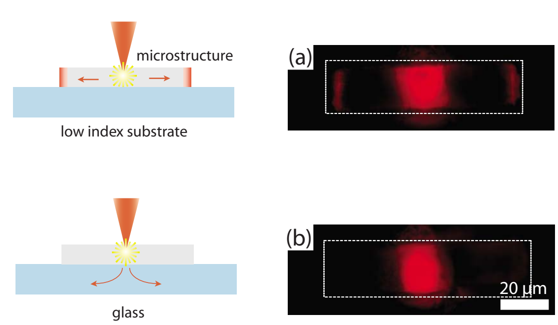

FIG. 3. (Color online) Fluorescence optical microscopy image (top view) of a MEH-PPV-containing microstructure fabricated on a mesoporous silica substrate (a) and on a conventional glass substrate (b). In (a), the light is guided through the microstructure ends when it is excited at its center. For the microstructure on glass substrate no fluorescence waveguiding is observed (b). In the left hand side of the figure we display a schematic (side view) of the microstructure excitation and the corresponding waveguiding.

sion observed in Fig. 1(c) and its corresponding spectrum [Fig. 1(d)]. Such a result implies that the MEH-PPV retained in the microstructure is not degraded during the microfabrication, which is desirable for application in optical devices. For laser powers above 40 mW, we observe generation of bubbles during microfabrication, which ruins the quality of the final structure.

The fluorescence confocal microscopy images in Fig. 2 show that MEH-PPV is distributed throughout the microstructure and not only at its surface. The microstructures preserve their luminescent properties, although the images at each z level reveal nonuniform distributions at different planes of the microstructure. This nonuniformity could be caused by the moderate solubility of MEH-PPV in the acrylic based-resin. To improve the solubility and distribution of MEH-PPV in the acrylic resin, one could reduce the amount of dopant, although this would decrease the fluorescence intensity of the microstructure.

When the microstructures are fabricated on top of low-refractive index substrates, we observe waveguiding of MEH-PPV fluorescence [Fig. 3(a)]. The low refractive index,[31] the homogeneity, and the flatness of the mesoporous silica minimize the waveguiding losses in the acrylic-based waveguides by preventing parasitic scattering and coupling into the substrate. On the other hand, we do not see waveguiding in Fig. 3(b) because this microstructure lies on a conventional glass substrate, leading to light coupling into the substrate. The light scattering observed along the waveguides arises from surface roughness and inhomogeneity of the microstructure, which can be decreased by improving the stages and objectives in the microfabrication setup. Ultimately, microstructures fabricated on top of mesoporous silica substrate could be used for photonics applications, such as microLEDs and microwaveguides.

In conclusion, we present an approach for fabricating three-dimensional microstructures containing the luminescent polymer MEH-PPV using two-photon absorption polymerization. The microstructures present good definition and structural integrity, which is required for photonics devices. Fluorescence microscopy images show that MEH-PPV is retained in the microstructure after the fabrication and that its optical properties are preserved. Fluorescence confocal microscopy images show that the MEH-PPV is distributed not only at the surface, but throughout the bulk of the microstructure, which enhances the luminescence properties of the microstructures. In addition, we demonstrate waveguiding of the MEH-PPV emission in 100 μm long microstructures fabricated on top of porous silica substrates, revealing the feasibility of fabricating photonics devices such as microLEDs and microwaveguides.

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