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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 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 micro-mechanical actuators,4–6 birefringent microstructures,7 photonic crystals,8,9 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.1 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: 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-POL25,26 (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/cm². 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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fabricated by two-photon polymerization. Figure 1 shows
the microstructure are displayed in Fig. 1. The fluorescence
spectra of the microstructure and of an emission spectrum
of a film containing MEH-PPV are obtained using 540 nm excitation
wavelength. We collect the fluorescence spectrum of microstruc-
tures through an exit port of the microscope using a portable
spectrometer.

The confocal microscopy images of the microstructure
fabricating 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 di-
rection 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
top view bright-field image of the microstructure. Figure
1(c) shows the fluorescence image of the same microstruc-
ture. 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 con-
tained in the microstructure. The noise observed in the
microstructure spectrum is due to the low intensity of the
fluorescence signal because the microstructure has dimen-
sions of only a few micrometers. We also fabricated micro-
structures 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 lin-
early 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 fluores-
cence intensity.

To verify that the MEH-PPV is distributed throughout
the microstructure, we obtained fluorescence confocal mi-
croscopy images of a pyramidal microstructure with a
squared base of 120 × 120 μm² at different z levels (Fig. 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, contain-
ing 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 micro-
structure 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 con-
ventional 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 ab-
sorption of two photons, localizing polymerization to the fo-
cal region and allowing the fabrication of three-dimensional
microstructures. The MEH-PPV containing microstructure in
Fig. 1(a) exhibits excellent integrity and good definition, in-
dicating 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 microstruc-
ture, as demonstrated by the characteristic fluorescent emis-

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).

FIG. 2. (Color online) Fluorescent confocal microscopy images of planes separated by 16 μm in a pyramidal microstructure (squared base of 120 × 120 μm²).

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, 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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