Three-dimensional microfabrication for photonics and biomedical applications

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We use two-photon absorption polymerization to fabricate microstructures containing compounds with interesting properties for optical and biomedical applications. Our investigations open the door to new applications in data storage, waveguides manufacturing, organic LEDs, optical circuitry and scaffold for bio-applications.

Introduction

Two-photon absorption polymerization is a powerful tool in the fabrication of complex three-dimensional micro- and submicron-structures. The nonlinear nature of the multiphoton absorption process essentially confines the polymerization to the focal volume of the ultrashort laser, allowing the fabrication of microstructures with complex geometries by moving the laser focus three-dimensionally through the resin. In the last few years, two-photon polymerization (2PP) has been applied to the fabrication of photonic crystals, optical devices and 3D micromechanical actuators[1]. However, majority of the structures reported until now are passive elements, whose properties cannot be externally controlled, thus hindering their applications. In this way, it is desirable to look for new resin formulations containing active components, which still can be polymerized using two-photon absorption.

In order to explore the possibilities in this direction, we propose here the preparation of blends in a guest/host scheme. For the polymeric host we used an acrylate resin, in which organic dyes or even other polymers with interesting properties can be incorporated as guest. Aiming to show the potential of this approach, we present here the fabrication by 2PP of an optically inducible birefringence structure, a microstructure containing conjugated polymers for organic LEDs or polymeric microcircuiting, and an interconnected microstructure for biomedical applications.

Results and Discussion

The host resin employed here consists of tris(2-hydroxyethyl)isocyanurate triacrylate, which gives hardness to the polymeric structure, ethoxylated(6) trimethyl-lolpropane triacrylate, which assists in decreasing the structure shrinkage upon polymerization, and ethyl-2,4,6-Trimethylbenzoylphenylphosphinate, which acts as the polymerization photoinitiator[2]. Two distinct compounds were used as the guest material: (i) the organic dye Disperse Red 13, an azochromophore which is known to exhibit photoinduced birefringence due to a reversible *trans-cis-trans* isomerization[3]; (ii) the conjugated polymer poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV)[4], whose interesting optical and electrical properties attracts considerable attention mainly for its application as organic LEDs.

We induce the two-photon absorption polymerization with a Ti:sapphire laser oscillator that produces 130-fs pulses at 800 nm. To fabricate structures we use an average laser power of 20 mW, measured before the 0.65 NA objective that focuses the laser beam into the sample. The sample was positioned in the axial *z*-direction using a motorized stage, and the laser beam was scanned in the resin x-y-direction with a set of galvano mirrors. The entire system is computer-controlled, which allows the fabrication of reasonable complex 3D structures. After the fabrication process, the unpolymerized resin is washed away with ethanol and dried at room temperature.

A scanning electron micrograph of a typical three-dimensional microstructure containing DR13 is shown in Fig. 1a. The optical birefringence was induced in the fabricated structures by irradiating the samples with an Ar^+ ion laser at an irradiance of 10 W/m^2. After several isomerization cycles, an excess of chromophores is created in the direction perpendicular to the laser polarization, causing birefringence. Figure 1b shows the induced birefringence in two fabricated structures. The sample is placed under an optical microscope between crossed polarizers and its angle was varied with respect to the polarizer angle. As shown in Fig. 1b, the structure is visible when the angle between the sample axis and the polarizer is an odd multiple of 45°; at even multiples of 45° the structure is not visible. This birefringence can be completely erased by irradiating the sample with circularly polarized light. This optically inducible/erasable birefringence can be used for optical storage devices and for manufacturing waveguides and optical switches, whose action can be controlled by external means by applying light with appropriated intensity, wavelength and polarization.

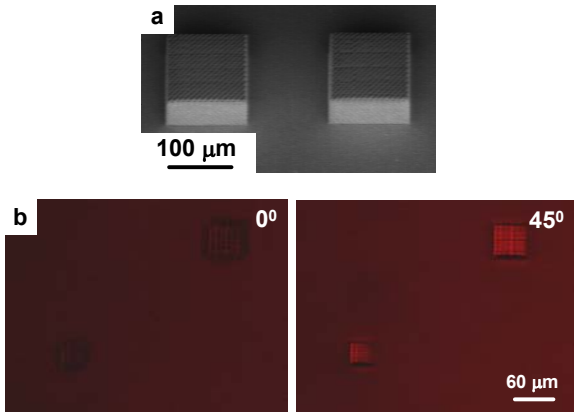

Figure 1 – **a:** Scanning electron micrograph of solid squares structure fabricated by 2PA polymerization. **b:** Polarization microscopy for sample like the ones shown in a. The angle between the polarizer and sample is shown in the top right corner of each image.

Figure 2a shows scanning electron micrographs of a three-dimensional microstructure fabricated using the acrylic-based resin containing the conjugated polymer MEH-PPV. The microstructure in Fig. 2a show excellent integrity and good definition.

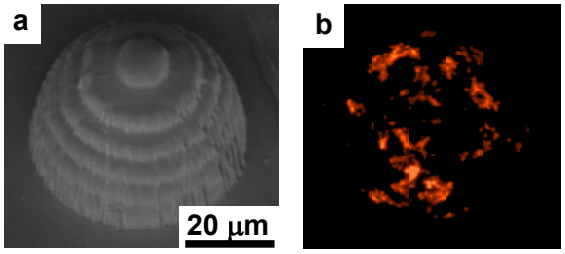

Figure 2 – a: Scanning electron micrograph of the polymeric blend containing the acrylic-based resin and MEH-PPV. **b:** fluorescence microscopy of the polymeric blend.

In Fig. 2b is shown a fluorescence microscopy image of the resin doped with MEH-PPV, excited at 543 nm. The structure exhibits fluorescence at approximately 600 nm, characteristic of MEH-PPV, indicating that the conjugated polymer preserves its properties in the polymeric blend. It can also be seen that the MEH-PPV distribution in the polymeric blend is not uniform; however we believe that more homogeneous distributions can be achieved by changing the preparation method. In this way, the approach employed here is a promising alternative for the fabrication of microstructures containing conjugated polymers for application in polymeric-based displays, luminescent plastics and organic or plastic circuits. Although the structure shown in Fig. 2a has dimensions of the order of tenths of microns, much smaller structures can be fabricated, allowing for instance the manufacture of pixel for displays.

Fabrication using 2PP has also been proposed as a way to create 3D scaffolds for biological applications. Figure 3 presents scanning electron micrographs of a three-dimensional interconnected microstructure fabricated using the pure acrylic-based resin. The inset of this figure displays a detail of the interconnected structure, which again presents excellent integrity and good definition. Therefore, tailor-made scaffolds for tissue engineering and bone reconstruction can be fabricated in short time using 2PP, once they are promising for the rational confinement of cells in 3D. The addition of drugs (e.g. growth factors, antibiotics, etc) or biopolymers to the material used for the microfabrication is also feasible, opening a lot of opportunities in advanced drug delivery and tissue regeneration systems.

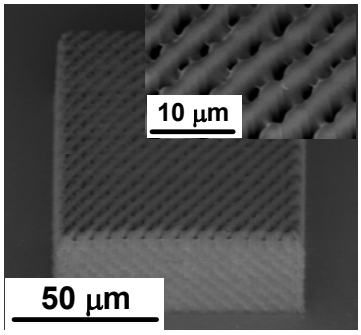

Figure 3 - Scanning electron micrograph of an interconnected structure for biological applications. The inset shows a detail of the structure.

Conclusion

To summarize, we use 2PP to fabricate microstructures containing the azochromophore DR13 and the conjugated polymers MEH-PPV, with potential applications for optical storage, optical switches, organic LEDs, etc. Besides, the fabrication of 3D scaffolds for biological applications was also presented. This work was carried out with the financial support from FAPESP (Brazil), the National Science Foundation under contract DMI-0334984 and the Army Research Office under contract W911NF-05-1-0471

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