Multiphoton Polymerization in Three-Dimensional Photonic Crystals

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INTRODUCTION

Three-dimensional (3D) photonic bandgap (PBG) materials have recently generated great interest for their potential for photonic applications and have been postulated as the basis of a number of optical devices.1,3 A prime advantage of 3D PBG devices is the potential to transport and modulate light in a compact structure. This will be critical for the on-chip integration of many optical components. The realization of most PBG-based devices requires the incorporation of aperiodic defect structures within 3D PBG materials. While this has been accomplished, for example, via layer-by-layer lithographic techniques, such approaches are tedious and expensive, placing practical limitations on the number of layers achievable.4,6 One alternative, facile route to 3D periodic structures is colloidal self-assembly. However, there is no inherent method for the incorporation of predetermined and engineered defect structures within self-assembled photonic crystals.

We have been making considerable strides in the multiphoton polymerization of high resolution 3D features within colloidal crystals. Multiphoton polymerization can be used to fabricate intricate 3D features with submicron resolution on account of the nonlinear sensitivity of the photoinitiation step to photon flux.7 Multiphoton polymerization has been demonstrated for the fabrication of various 3D structures with submicron resolution, including 3D woodpile structures,8,9 micromachines,7 and sustained release devices.10

However, prior to our work,11 multiphoton polymerization had not been demonstrated within colloidal crystals as a route to fabricate embedded defects.

EXPERIMENTAL

Multiphoton polymerization and confocal imaging were performed on a laser scanning confocal microscope (Leica, DMIRBE microscope and SP-2 scanhead) outfitted with an electro-optic modulator and a Ti:sapphire laser (Spectra Physics Tsunami, ~60 fs pulses, 82 MHz repetition rate) operated at a wavelength of 780 nm. The estimated pulsewidth at the objective was ≤ 100 fs. The 514 nm line of an argon ion laser was employed for the fluorescence confocal imaging. All experiments were carried out using a 63x oil-immersion objective (Leica) with a numerical aperture of 1.32. The samples presented in Figs. 1 and 2 were created using a Norland Optical Adhesive (NOA-81) as the monomer/initiator system. The synthesis and characterization of the two-photon properties of the dye used to generate Figs. 3 and 4, AF350, was described elsewhere12 and was donated by the U.S. Air Force Research Laboratory. Briefly, a stock solution of AF350 in toluene was prepared at 0.96 w/w. The monomer used was trimethylolpropane triacrylate (TMPTA) (Aldrich) from which the inhibitor was removed prior to use with inhibitor removal beads (Aldrich). Approximately 0.1 w/w solutions of AF350 in TMPTA were made before each use from the stock solution of dye in toluene; the toluene was removed by rotovappping. For fluorescence imaging in colloidal crystals, the colloidal crystal was back-filled with a DMF rhodamine solution. Colloidal crystals were formed through sedimentation or in flow cells,13 on glass or PVC coverslips.

RESULTS AND DISCUSSION

Early on, we demonstrated the multiphoton polymerization of an acrylate monomer within a colloidal crystal, using 9-fluorenone-2-carboxylic acid as the initiator (Fig. 1).11 The beam is rastered throughout a particular scan volume while the electro-optic modulator is used to regulate the power of the beam, selectively exposing the regions to be polymerized. Using this approach, we are able to rapidly write three-dimensional structures in NOA-81 as shown in the cross-section of Fig. 1b. The resulting polymer is thermally stable to about 300 °C, enabling a high refractive index contrast selenium-air inverse opal with embedded features to be created. This was accomplished following our published procedure for the melt imbibing of selenium into colloidal crystals15 followed by the subsequent etching of the silica colloids (Fig. 2).

![Figure 1](image1.png)

Figure 1. a) Schematic procedure for multiphoton writing within a photonic crystal. b) Fluorescence confocal image of a polymer feature within a colloidal crystal. The polymer is bright because it is preferentially stained by the dye.

![Figure 2](image2.png)

Figure 2. a) Fluorescence confocal image of a polymer feature within a colloidal crystal. b) SEM micrograph of the same feature after infiltration with selenium and etching of the original silica colloidal crystal. The feature was written at the substrate colloidal crystal interface to facilitate imaging via SEM. The inset is a high magnification image of the outlined region.
However, because of the low multiphoton cross-sections of the initiators in our first system, it was not very reliable, and reproducible feature generation was difficult. The required laser intensities were very close to the damage threshold of the system, and thus many samples contained significant beam damage. More recently, we have been using a dye developed by the Air Force Research Laboratory, AF350.12 This dye is much more efficient than the previous systems, and enables the writing of significantly more complex features. With this system, beam damage is generally not a problem, and features as small as 150 nm across can be formed (Fig. 3). These features were created through a point by point exposure mode.

**Figure 3.** Submicron multi-photon polymerized voxels formed by a series of point-by-point exposures.

High resolution features have also been created within a colloidal crystal (Fig. 4). For this SEM image, the silica-based colloidal crystal has been removed by etching with an aqueous hydrofluoric acid solution to enable observation of the polymer structure created through two-photon polymerization. Again, these features were created by rastering the beam throughout the scan volume while using the electro-optic modulator to regulate the power, exposing only those regions to be polymerized.

**Figure 4.** High resolution free standing polymer structures formed by two-photon polymerization within a silica colloidal crystal. The colloidal crystal has been etched with an aqueous hydrofluoric acid solution. The feature in the top right fell over because it is so thin. In a colloidal crystal this is not a problem because the colloidal crystal will support the polymer structure.

**CONCLUSIONS**

Multiphoton polymerization within colloidal crystals potentially extends the viability of this class of photonic crystals for PBG-based device fabrication and the elucidation of new optical physics. Because the creation of a 3D periodic structure has been accomplished through the self-assembly of colloidal particles, only the embedded defect structures need to be created using multiphoton polymerization. Multiphoton polymerization will enable the creation of PBG devices from self-assembled colloidal crystals, and in general, is a powerful approach to add functionality to self-assembled materials.

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**REFERENCES**