Engineering stop gaps of inorganic-organic polymeric 3D woodpile photonic crystals with post-thermal treatment

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Abstract: A method is reported for improving the spatial resolution and engineering the stop gaps of the inorganic-organic 3D woodpile photonic crystals (PhCs). The approach is based on the two-photon polymerization (2PP) of an inorganic-organic hybrid material and a post-thermal treatment (PTT) process. The effects of PTT on polymerized 1D, 2D and 3D structures have been characterized. Ultimately, the feature size of the suspended rods has been reduced to ~33 nm and the spatial resolution of inorganic-organic 3D woodpile PhCs has been improved from ~150 nm to ~86 nm. The approach is also demonstrated as a powerful tool to engineer the stop gaps of 3D PhCs. In particular, a combination of PTT and the threshold fabrication technique leads to the stop gap of a 3D woodpile PhC that can be tuned over a large wavelength range of ~318 nm from the near-infrared to visible region.

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References and links
1. Introduction

Direct laser writing (DLW) is an effective and flexible approach to inducing two-photon polymerization (2PP) in various photoresists and has been intensively studied for the fabrication of three-dimensional (3D) arbitrary micro-structures including 3D photonic crystals (PhCs) [1-10]. The use of all-organic materials such as SCR and SU-8 [1,5] can not only produce 3D PhCs with stop gaps in the near-infrared (NIR) wavelength range [4-7], but also serve as templates for further preparations of “inverted” PhCs with high refractive index [11,12]. Though the feature size of the two-dimensional (2D) polymerized rods can be reduced down to less than 30 nm by employing pre-treatment methods [13-15], their poor thermal and mechanical stability [13,16,17] makes them less applicable for fabricating 3D PhCs and 3D templates of high quality [18]. These problems do not exist in all-inorganic materials which have improved thermal and mechanical stability, such hybrid materials have been successfully applied in the fabrication of functional 3D PhCs [19-22]. However the incorporation of the inorganic part in the polymerized structures has limited the fabrication resolution to approximately 150 nm [20].

Here we use a post-thermal treatment (PTT) method to improve the spatial resolution of the 3D 2PP fabrication in an inorganic-organic hybrid material. Ultimately, the feature size of the suspended rods is reduced to ~33 nm and the spatial resolution of 3D woodpile PhCs is improved to ~86 nm. Moreover, the PTT process can efficiently engineer the stop gaps of the...
PhCs. A combination of PTT and the threshold fabrication technique leads to the stop gap of a 3D woodpile PhC that can be tuned over a large wavelength range of 318 nm from the NIR to visible region.

2. Experimental details

Film samples for material characterizations were prepared by illuminating spin-coated photosensitive resins on cover glass with a UV lamp, followed by washing with 4-methyl-2-pentanone and rinsing with isopropanol [9,19]. The photosensitive resin we used is Ormocer®, which is a kind of the silicate-based inorganic-organic hybrid material. The polymerized structures are stable upon heating at temperature ($T$) up to 270°C [23]. Before the PTT process, the polymerized films (and all the following samples fabricated by 2PP) were hard-baked at 150°C for 3 h. Then the samples were put onto a hot plate under certain temperature for the PTT process. After each heating process, the samples were naturally cooled down to room temperature for measurements. The absorption spectra of the polymerized films were characterized with a Fourier-transform IR spectrometer (FTIR, Thermo Nicolet) in conjunction with an infrared microscope (Continuum).

![Absorption spectra of the polymerized films upon heating at temperature 300°C for different heating time.](image)

Fig. 1. Absorption spectra of the polymerized films upon heating at temperature 300°C for different heating time. Spectra are normalized and translated for better view. The schematic on the right side is based on the observed changes in absorbance of organic functional groups.

The choosing of temperature for PTT is critical. Here the temperature we used for PTT is 300°C, where the thermal gravimetric analysis curve of Ormocer® shows a slow weight loss of less than 1% and the overall structures are stable under heating for 10 hours (h) [24,25]. In fact, our PTT experiments under 300°C showed the best performance on PhC engineering among the tests with temperatures ranging from 150°C to 450°C. The reason is that at this temperature, some organic parts of the polymerized structures starts to be decomposed slowly while the inorganic part is well preserved, behaved as backbones to support the whole structure. As shown in Fig. 1, at 300°C, C-H groups belonging to alkyl terminations of Ormocer® molecules are decomposed and Si-OH group are formed [25]. Meanwhile, the methacrylic phase is further polymerized as depicted by the decrease in absorbance of C=O and C=C groups. As a consequence, the structures result more condensed with improved mechanical stability. Meanwhile, the refractive index of the polymerized films, measured with Becke line method [10], was 1.554±0.002 before PTT and increased to 1.566±0.002 at the PTT time of 3 h and then remained nearly unchanged from 3 h to 48 h.

The micron-scale samples in the article were fabricated with 2PP method, in which femtosecond pulses (~200 fs) operating at wavelength 580 nm were focused into the photosensitive resin with an oil immersion objective (Olympus, numerical aperture 1.4, 100×) [10,21]. A serial of one-dimensional (1D) and 2D structures were fabricated with variable exposure power and fabrication speed for comparison purposes. 3D woodpile PhCs of different rod spacing were fabricated with various exposure power under a constant fabrication speed of 60 μm/s [21]. The transmission spectra (>900 nm) of the woodpile PhCs
in the stacking direction were characterized with a pinhole-assisted FTIR [10]. The
transmission spectra of PhCs which had a stop gap below wavelength 900 nm were measured
with a CCD (Pixis 100, Princeton Instruments): a broadband light source (Oriel Apex QTH
Source) was focused into the PhCs by an apochromatic objective and the transmitted signals
were then collected by another apochromatic objective, dispersed by a spectrograph (Acton
Spectropro 300i), and finally detected by the CCD. A small aperture was inserted before the
back aperture of each objective to confine the divergence angle to 10° with respect to the
stacking direction of the PhCs.

3. Results and discussions

3.1. PTT effects on 1D and 2D inorganic-organic structures

To study the effects of PTT on polymerized structures, firstly, we heated a laser-generated
thin film for 3 h at temperature 300°C. As shown in Figs. 2(a, b), after 3-h PTT the surface
roughness of the polymerized film is improved significantly by 45% from 10 to 5.5 nm, which
is similar to the thermal annealing effects on other polymers [26]. Meanwhile, the maximum
height of the features is reduced.

![Fig. 2. (a, b) AFM images of the top surface of a laser-generated thin film (a) before and (b) after 3-h heating at 300°C.](image)

The effect of PTT on the height of the polymerized structures was then tested on an array
of the fabricated parallel rods with ascending heights (Fig. 3(a)). The truncated rods were
heated with several steps and the sample was characterized by an atomic force microscope
(AFM) after each process. As shown in Figs. 3(b-d), both the height (H) and width (W) of the
rods are significantly reduced after PTT, different for rods with different initial heights (Fig.
3(d)). In particular, the amount of reduction reaches 79% for a 69.6-nm-high rod, of which the
height is reduced to 14.4 nm after 36-h PTT (see another sample in the inset of Fig. 3(e)). The
plots of the height ratio (H/H0), where H0 is the height of the rod before PTT, as a function of
the heating time reveal that the lower the rod, the larger the reduction (see Fig. 3(e)).
However, the exponential decay behavior of the plots shows that the lower rod has a decay
speed slower than that of the higher one after 3 h. This is because the lower rods have larger
surface-to-volume ratios, which leads to faster heat dissipation and slower PTT effects in the
case of thermal conduction.

We further studied the effect of PTT on the suspended rods fabricated between two solid
supporters. Figures 4(a-b) show the SEM images of the rods with a length of ~1.5 μm before
and after 3-h PTT, respectively. One can see that the width of the rods is significantly reduced
without cracks (the nonuniform sizes of the rods were induced by the stretches from the solid
supporters [27]). For comparison, we plot the rod width before and after 3-h PTT as a function
of the fabrication speed and power in Figs. 4(c-d), respectively. It can be seen that the rod
width is monotonically reduced but thicker rods are reduced by a larger percentage than the
thinner ones. This is because the thicker rods have a smaller surface-to-volume ratio that
results in slow heat dissipation, which makes the PTT effect more efficient. One important
feature of the rods after 3-h PTT is that the suspended thin rods can preserve a good
mechanical property such as rods with a long length of ~5.5 μm shown in Fig. 4(e), while the
reported all-organic polymer structures are less robust under such high temperature (300°C). Furthermore, it is found that the minimum rod width of ~50 nm with 2PP by direct laser writing can be efficiently reduced to ~33 nm with PTT for only 3 h, as shown in Figs. 4(f-g).

Fig. 3. (a) Schematic of truncated rods on cover glass (side view). (b) and (c) AFM images of the rods before and after 18-h PTT. (d) Corresponding cross-sections of the rods taken from (b) and (c). (e) Height ratio \( H/H_0 \) as a function of the PTT time for rods with different \( H_0 \). The data beyond 3 h are fitted with the exponential decay curve. The fitted decay speeds are 0.162, 0.199 and 0.223 h\(^{-1}\) for rods with \( H_0 \) of 193, 287 and 361 nm. Inset: Cross-sections of rods before and after 36-h PTT.

Fig. 4. (a) and (b) SEM images of rods suspended between two supporters before and after 3-h PTT. (c) and (d) Rod width as a function of the fabrication speed \( (V) \) and power \( (P) \) before and after 3-h PTT. (e) SEM image of suspended rods with a length of ~5.5 \( \mu m \) after 3-h PTT. (f) and (g) SEM images of suspended rods with the minimum feature size survived before and after 3-h PTT.
3.2. PTT effects on inorganic-organic 3D woodpile PhCs

The reliable mechanical properties of the structures after PTT lead to a new way to engineer 3D inorganic-organic PhCs. As the images shown in Figs. 5(a-b), the periodical structures of the PhCs are well preserved after heating at 300°C for 3 and 20 h, respectively, showing a good mechanical strength under PTT. The rod spacing of the woodpile, initially designed and fabricated at 1.1 \( \mu \text{m} \), was reduced to 1.0 \( \mu \text{m} \) after the PTT (Fig. 5(b)). Meanwhile, the measured transmission spectra of a woodpile PhC, as shown in Fig. 5(c), reveal that the center of the stop gap is shifted from 1621 to 1458 nm after 3-h PTT, indicating that the periodicity in the stacking direction is significantly reduced. Moreover, one can notice that the transmission at shorter wavelengths increases, which means less scattering losses of the heated structures due to the improved surface roughness. Another improvement is that unwanted “defects” within the stop gap, induced by the residual stresses inherent in the fabrication process, can be cured by the PTT process that release these residual stresses, as noted in Fig. 5(c).

The blue-shift effect of stop gaps induced by PTT can be applied to tune the stop gaps of PhCs. As shown in Fig. 5(d), the stop gap of a PhC can be continuously tuned from 1596 to 1345 nm with increasing the PTT time, which covers the important telecommunication wavelengths. During this process, the suppression rate of the stop gap reaches a maximum at the heating time of 3 h. On the other hand, the gap/midgap ratio of the stop gap, which is related with the symmetry of the PhC, keeps constant around 7.63% with a small fluctuation of less than 0.37% for heating up to 9 h, indicating the internal symmetry of the PhC was...
perfectly preserved within 9 h. After 9 h, small modifications have been observed (Fig. 5(d)) in the shapes of stop gaps, which indicates the original geometry of part of the woodpile was slightly changed. Nevertheless, the position of stop gaps was consistently shifted towards shorter wavelengths. Figure 5(e) shows the relative blue-shift of the stop gap ($\Delta \lambda_c/\lambda_{c0}$, $\lambda_{c0}$ is the center wavelength of the stop gap before PTT) as a function of the heating time. One can see that the experimental data beyond 3 h fit well an exponential decay curve, which is similar to the change in heights of 2D rods on the cover glass (see Fig. 3(e)). Since the refractive index of the polymerized structures has no noticeable change when the PTT time is longer than 3 h, the value of $\lambda_c$ is proportional to the lattice period in the stacking direction. Thus, the change in $\Delta \lambda_c/\lambda_{c0}$ reasonably reflects the change in the period in the stacking direction and the corresponding fitting relation consistently indicates a smooth reduction in size without much distortions and cracks inside the structure. Meanwhile, in the in-layer plane, a microscope image of the PhC after 38-h heating (inset of Fig. 5(e)) shows the lateral size of the woodpile is reduced by ~16.3 %, similar to the corresponding value of $\Delta \lambda_c/\lambda_{c0}$ (15.7%), which indicates that the overall 3D structure is symmetrically reduced during PTT.

It should be emphasized that the measured transmission spectra of the PhCs were very sensitive to the structure geometry. Any effect of PTT, including the influence of the substrate, can be reflected in the changes of stop gaps of PhCs. Deviation of PTT temperature from 300°C would result in no engineering effects ($T<300°C$) or distortions of the stop gaps ($T>300°C$). That is why it is very important to perform the PTT process at 300°C to realize symmetric engineering of PhCs.

3.3. Improving the spatial resolution of inorganic-organic 3D woodpile PhCs

The combination of PTT and the threshold laser writing method [2,3,19] can improve the resolution in fabricating inorganic-organic 3D PhCs and thus realize the operation in the visible wavelength range. As shown in Fig. 6(a), the stop gap of a 700-nm-lattice woodpile PhC, fabricated by the threshold method at a power of 1.3 mW, can be tuned from 1007 to 746 nm after 21-h PTT. For comparison, a PhC with a rod spacing of 800 nm was fabricated along with the 700-nm PhC and experienced the same process. As shown in Fig. 6(b), its stop gap was finally tuned to 831 nm but shows a smoother and deeper gap than that in Fig. 6(a), which reveals that the PhC with a larger lattice constant can maintain better performance for long-time PTT. Moreover, the appearance of a higher order gap [4] at wavelength 531 nm (in Fig. 6(b)) indicates that the symmetry of the woodpile is well preserved. The SEM image depicted in the inset of Fig. 6(c) shows that the width of the rods of the 3D PhC can be

Fig. 6. (a) Measured transmission spectra of a 20-layer woodpile PhC with a rod spacing of 700 nm. The centers of the stop gaps before and after 21-h heating are located at wavelengths 1007 and 746 nm, respectively. (b) and (c) Measured transmission spectra of 20-layer PhCs with rod spacings of 800 and 700 nm after PTT for 21 and 6 h, respectively. The centers of the stop gaps are located at wavelengths 831 and 723 nm, respectively. Inset of (c): SEM image of the PhC in (c). The width of the rod is reduced to ~86 nm.
reduced to \( \sim 86 \) nm, which is reduced by a factor of two compared with the previously reported value of \( \sim 150 \) nm in the inorganic-organic hybrid polymer [20].

Since the PTT speed is related to the surface-to-volume ratio of the initial rods (see Figs. 4(c-d)), we fabricated another 700-nm-lattice PhC with a slightly higher power of 1.35 mW, which results in thicker rods than those of the PhC in Fig. 6(a). It is noted that the stop gap of this PhC, initially at wavelength 1041 nm, is tuned to 723 nm after PTT only for 6 h (Fig. 6(c)). The fast tuning in the stop gap is caused by the more efficient PTT of the thick rods due to their slow heat dissipation, which results in the large speed in the overall size reduction. It should be mentioned that the \( \Delta \lambda / \lambda_0 \) of this PhC reaches \( \sim 30\% \), which is the largest ratio in gap tuning of 3D PhC to our knowledge.

4. Conclusions
In conclusion, we have proposed and demonstrated a PTT method to improve the fabrication resolution of the structures fabricated with 2PP in inorganic-organic hybrid materials. In the cases of the 2D truncated rods on cover glass, the 2D suspended rods and the 3D woodpile PhCs, the limits of the feature size reach \( \sim 14.4, \sim 33 \) and \( \sim 86 \) nm, respectively. This PTT method results structures with high mechanical stability and has been successfully applied to substantially tune the stop gaps of the woodpile PhCs. In particular, a continuous 251-nm-tuning range of the stop gap of a 3D PhC has been achieved. The integration of this PTT method with the threshold fabrication method has resulted in a 3D woodpile PhC operating at visible wavelengths. This work provides a useful option for producing smaller templates for the fabrication of NIR or visible high refractive-index inverse woodpile PhCs [11,12] as well as a constructive platform for promising applications of 3D visible woodpile PhCs. Varying the ratio between organic and inorganic parts in the hybrid polymers provides another dimension to engineer the structures to meet different demands through a temperature-dependent PTT process.

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