Polymerized nanotips via two-photon photopolymerization

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Abstract: We present new methods to produce polymerized nanotips via two-photon photopolymerization. By gradually changing the laser power, we fabricate a single polymerized tip with the size of 120nm. When two rectangle anchors with protuberances are close enough, lines with the slimmest part of about 20-30nm and tips with the widths of about 35nm are produced between anchors, which are the best resolution obtained with the resin SCR-500 to our knowledge. As the tips are adhered to larger polymerized structures, they can survive post processing in spite of their small sizes.

OCIS codes: (140.3390) Laser materials processing; (320.7110) Ultrafast nonlinear optics; (220.4000) Microstructure fabrication.

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1. Introduction

Two-photon polymerization has shown its tremendous potential in the field of micro-fabrication [1-7] due to its intrinsic three-dimensional (3D) fabrication capability [1] and sub-diffraction limited (SDL) spatial resolution [8]. Resolution, as a pivotal factor of fabrication, has been studied in different ways such as the ascending scan method [8] using single volume element (voxel), line scanning method [9] using lines etc. Single voxel is too small to survive post processing and people usually study the resolution using lines. To our knowledge, the best resolution of this method is 30nm with photoresist SU-8 by controlling the laser power slightly above the threshold [9].

SU-8 and SCR500 have become popular materials for two-photon microfabrication. SU-8 resist (MicroChem Corp.) is commonly utilized for the fabrication of high-aspect-ratio microstructures via a photochemical and thermal cationic polymerization. This two-step crosslinking procedure needs relatively long and complex processing cycle, which is determined by the choice of solvent and bake condition. The absence of liquid-to-solid transition during laser exposure can minimize the local change in the refractive index, thus creating stable irradiation condition. However, the formation of the microstructures cannot be monitored during fabrication [9, 10]. SCR500 resin (Japan Synthetic Rubber Company) is an unrethane acrylate resin that solidifies via a single-step radical polymerization [2, 5, 8, 11]. The polymerized resin has a slightly higher refractive index after exposure, so the whole fabrication process can be monitored and optimized with adjusting the fabrication parameters. The unexposed liquid resin can be easily washed away by ethanol, leaving a microstructure which is an exact replicate to the pathway of the laser focus.

The SDL spatial resolution of 120nm has been obtained using SCR500 [8]. By introducing a radical quencher to SCR500, and at an optimized concentration the resolution was improved to 100 nm due to the threshold effect. To further enhance the resolution, suspended lines with width of 65nm were fabricated due to the shrinkage of polymer [11].

Without adding radical quencher to SCR500, it is still a challenge to obtain a spatial resolution less than 65nm or even better than 30nm like photo resist SU-8. New measure is also required to preserve the tiny structures like tips for scanning probe microscopy.

In this paper, we present new methods to produce polymerized nanotips by two-photon photopolymerization using SCR500. Different from fabrication by the layer-by-layer accumulation of the sliced multiple CAD data [12], we get a single polymerized tip by gradually changing the laser power. The diameter of the tip is around 120nm, consistent with the resolution reported before [8]. When two rectangle anchors with protuberance were close enough, we fabricate lots of polymerized nanotips with widths around 35nm. This is the best resolution for SCR500. Because the tips are adhered to larger polymerized anchors, most of them survive post processing. Meanwhile, lines with the smallest widths of 20-30nm are polymerized using SCR500.

2. Experiments and results

A Ti:sapphire laser system (Tsunami, Spectra Physics) was used as the light source in this experiment. The 80-fs pulses were at 800nm with a repetition rate of 82MHz. The laser beam was filtered and then focused by an objective lens (100×, 1.35 NA) into a drop of resin SCR 500 on a glass substrate mounted upon a 3D piezoelectric translator. The whole process was *in situ* monitored with a CCD camera.

We fabricated polymerized tips in *y* or *z* direction by gradually decreasing the power while the sample was moved along the *y* or *z* direction, as shown in Fig. 1.We rotated a half wave plate with a spinning stage (Shot 202, Sigma-Koki) before a Glan prism to continuously attenuate the incident power. With the drop of the power, the polymerized structure gradually reduced until the power was below the threshold that was a level of intensity, above which the photochemical reactions became irreversible. Two-photon absorption induced radicals initiated polymerization only at the region where irradiation intensity larger than the threshold

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[8]. Therefore, when the power was below the threshold, the polymerization terminated and a tip was formed. It was obvious that the smallest ends of the tips showed the spatial resolution.

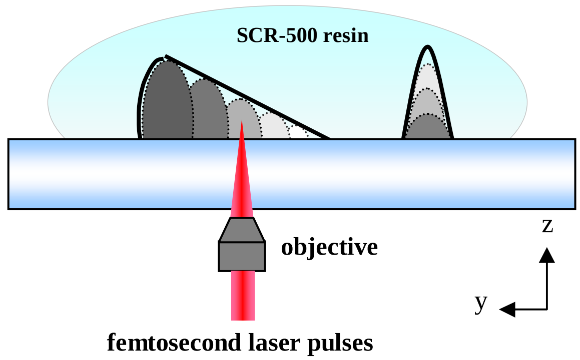

Fig. 1. Schematic of the fabrication of nanotips in *y* or *z* direction by power attenuation. The laser power was decreased by rotating a half wave plate before a Glan prism while the sample was moved along the *y* or *z* direction.

Figure 2 shows the scanning electron microscopy (SEM) images of the fabricated nanotips in *y* and *z* directions. The sample was moved at a speed of 5μm/s while the power was decreased from 15mW to 5mW within 10s. The power was measured before the objective lens. With the decrease of the power, a polymerized structure dwindled down to a tip. Because the power was reduced below the polymerization threshold (6 mW), the diameter of the tip end showed the resolution. Moreover, tips obtained in this way were parts of larger structures, so they survived developing and other post processing. The diameters of tips in Fig.2 are about 120nm, in agreement with the SDL resolution with SCR-500 reported before [8].

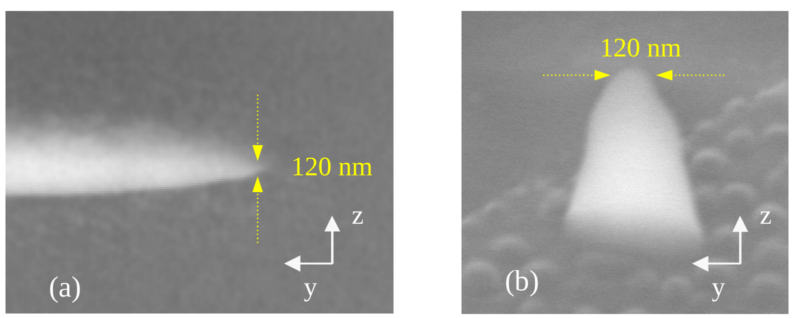

Fig. 2. Polymerized nanotips in the y direction (a) or in the z direction (b). The tips were produced by gradually decreasing the laser power from 15mW to 5mW within 10s while the sample was moved at a speed of 5μm/s along the y or z direction.

When the decrease rate of the power and the sample moving speed were changed, the tiny parts of the preserved tips were always around 100nm. Therefore, a novel method was required to fabricate smaller tips. We occasionally found polymerized nanotips and lines when two juxtaposed rectangles were close enough. Figure 3 shows a tip and a line, where the distance between two rectangles is 350nm. The slimmest part of the line is around 20nm and the width of the tip is around 35nm.

The formation of the lines and tips might arise from the lower-degree polymerized portion around the rectangle structures [11]. There were many radicals around the polymerized structures during the polymerization process [13], resulting in the lower-degree polymerized portion that was usually washed away during development [11]. Due to the fluctuation of laser

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output and the vibration of the ambient, some protuberances were formed in the rectangle structures. When the protuberances approached close, the lower-degree polymerized portion around the protuberances might overlap and enhance each other, so the crosslinking was strengthened to form lines. Because the middles of the lines were too slim, some were broken off during post processing, resulting in tips.

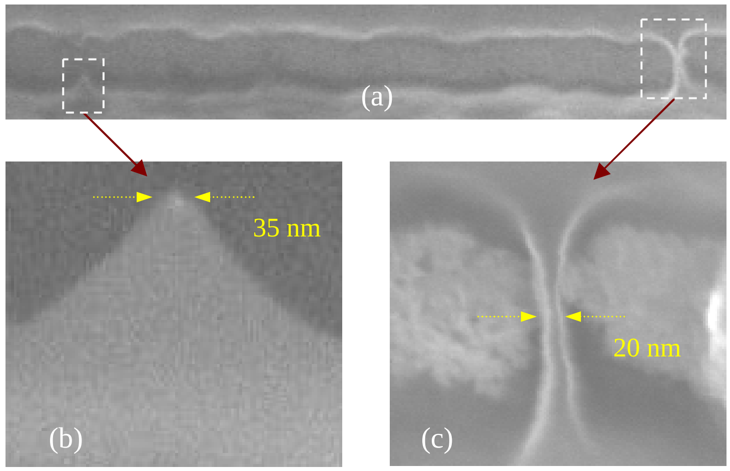

Fig. 3. (a) a tip and a line obtained between two juxtaposed rectangle structures. (b) and (c) are the enlarged image of the tip and the line, respectively.

Based on the above experimental results, we proposed a new method to produce nanotips. We first scanned a large rectangle structures whose one border was modulated to form periodical protuberances every 500nm that were 400nm above substrate glass, as shown in Fig. 4(a). The laser power was 10mW. Then another rectangle anchor with protuberances was juxtaposed oppositely. When the distance between the two anchors was around 500nm, the lower-degree polymerized portion around pairs of protuberances overlapped to form new lines as expected. Because the lines were short and adhered to the thick anchors, most were preserved as shown in the SEM image in Fig. 4(b).

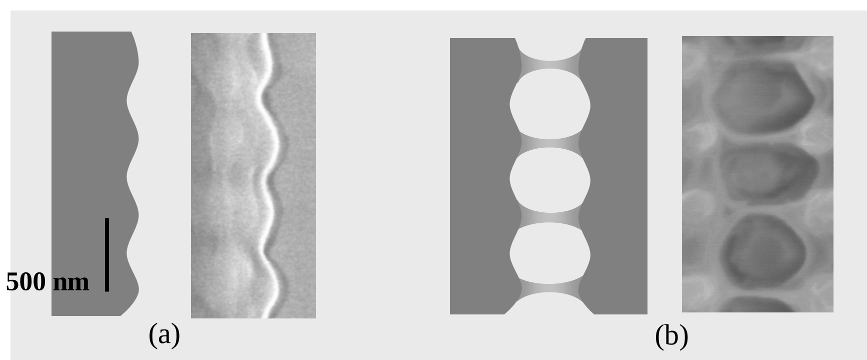

Fig. 4. (a) Schematic of a large anchor with protuberances every 500nm (left) and a SEM image of the polymerized protuberances; (b) Schematic of a series of lines formed between two juxtaposed anchors with protuberances (left) and a SEM image of the produced lines (right).

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Figure 5(a) shows an enlarged SEM image of a newly formed line between two anchors. Its width (~25nm) was much narrower than that of the protuberances. We cut the line with the electron beam, thus a sharp tip with the width of 35nm was obtained as shown in Fig. 5(b).

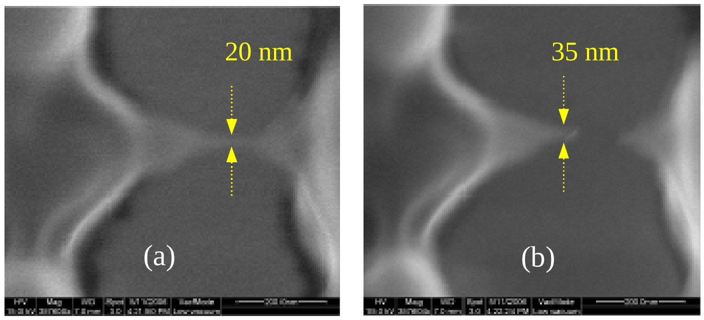

Fig. 5. (a) Enlarged image of a line. The width of the middle of the line is around 20nm. (b) A nanotip obtained by cutting the line with the electron beam.

With the increase of the distance between the rectangle anchors, the reaction of the lower-degree polymerized portions weakened, so the lines became slimmer. Such lines were easily to break off during post processing and sharp nanotips were obtained. When we widened the distance between the rectangles to 800nm, a series of polymerized tips were produced by this method as shown in Fig. 6. The widths of the tip points were from 35 to 50nm. The variance might result from the different sizes of the lines due to the fluctuation of laser output, the vibration from the ambient, and the shrinkage after development. Because the tips were adhered to the polymerized anchors, they survived post processing in spite of their small sizes.

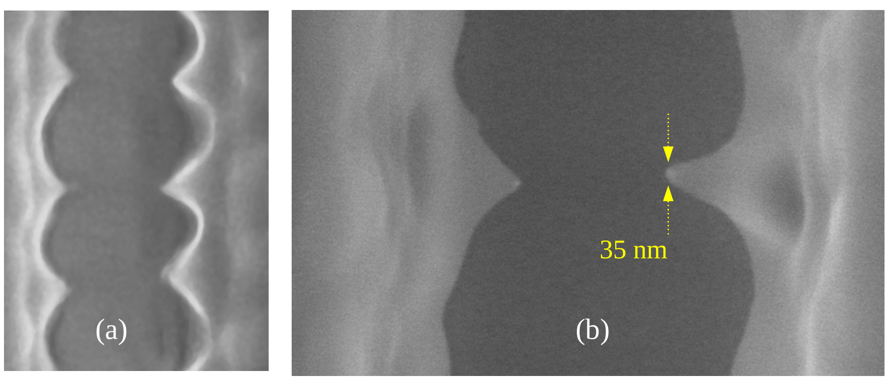

Fig. 6. (a) A SEM image of a series of polymerized nanotips formed between two juxtaposed rectangles at the distance of 800nm; (b) Enlarged image of a pair of nanotips.

When the distances of the two anchors were wider than 1200nm, the lower-degree polymerized portions of the opposite protuberances were too far and too weak to form lines and tips with enough strength to survive post processing, and we only obtained larger protuberances as shown in Fig. 4(a).

3. Conclusion

In summary, we present new methods to produce polymerized nanotips via two-photon photo-polymerization by femtosecond laser pulses using SCR-500. By gradually decreasing the laser power while the sample were moving, we fabricated single polymerized tips with the size of around 120nm. Smaller and sharper tips with widths of ~35nm and lines with the width as small as ~20nm were fabricated when two rectangle anchors with protuberance were close enough, which demonstrated the great potential of two-photon photopolymerizatioin for nanofabrication.

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