Supporting Information

Characterization of Microstructures Fabricated by Two-Photon Polymerization Using Coherent Anti-Stokes Raman Scattering Microscopy

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S1. CARS microscopy in the range between 2800 cm^{-1} and 3000 cm^{-1} of three-dimensional microstructures fabricated by TPP

The test sample consisted of a pair of truncated cones with square cross-sections. They were fabricated by means of TPP by stacking in the z direction square patterns with smaller and smaller diameters. A separation between the different stacks of 3 μm was selected. The laser average power (as measured after the microscope objective), stages velocity, and excitation wavelength used for the fabrication process were 8 mW, 10 μm/s, and 775 nm, respectively. The excitation beam was focused into the photoresist with a 40X, 0.75NA objective lens. The final dimensions of the microstructures were 27 μm for the height and 50 μm for the sides. A scanning electron micrograph of this sample is shown in Figure S1(a), where the sample was tilted in order to better reveal the microstructures three-dimensionality. The particles on the substrate are contaminants deposited during the sputtering process required to coat the sample with a thin film of gold for recording the scanning electron micrograph.

Prior to imaging by scanning electron microscopy, the test sample was investigated by CARS microscopy. The Stokes and pump beams were set at 1064 nm and 813 nm, and average powers of 10 mW and 5 mW (as measured at the sample) were used, respectively. This corresponds to a Raman shift of 2902 cm^{-1}, hence on resonance with the stretching mode of the carbon/hydrogen bonds of the polymer. The collinear beams are focused in the sample by a 40X, water immersion objective with 1.15NA. Using a raster-scanning pattern, xy images of the sample were recorded by collecting the forward–generated CARS signal. A stack of these images in the z direction were recorded by changing the position of the focal plane axially every 0.5 μm. A three-dimensional volume rendering was then obtained by interpolating the various xy images. This process was accomplished by using the Volume Viewer plug-in available with the image processing software ImageJ (http://rsbweb.nih.gov/ij/index.html). The result is show in Figure S1(b) where a magnification and tilted view similar to the ones employed for Figure S1(a) were chosen for comparison.

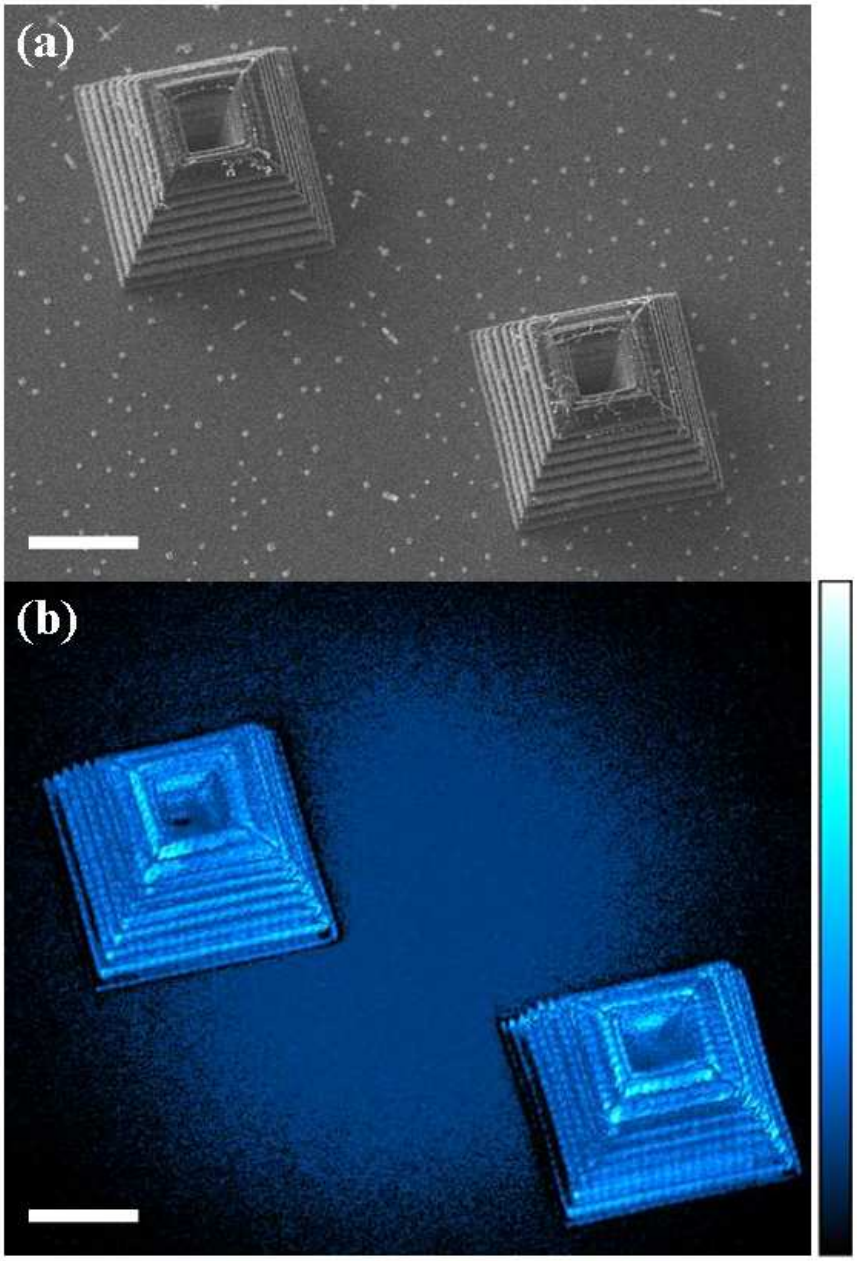

Figure S1. (a) Scanning electron micrograph of microstructures fabricated by TPP. (b) 3D volume rendering of the CARS signal collected from the same microstructures at 2902 cm^{-1}. The central round-shaped pattern is due to the non-resonant part of the signal arising from the substrate (glass coverslip). Color lookup table for figure S1B is shown on the right. The scale bar for both images is 25 μm.

S2. CARS microscopy in the range between 1500 cm^{-1} and 1800 cm^{-1} of three-dimensional microstructures fabricated by TPP

With experimental conditions identical to the ones described in section S1, the word "CARS" was written several times onto a glass surface by means of TPP. A scanning electron micrograph presenting a tilted view of three of these microstructures is shown in Figure S2(a). Before washing away the unpolymerized part of the photoresist that surrounds these microstructures, CARS microscopy was performed on this sample at 1628 cm^{-1} and 1643 cm^{-1}. Because of the characteristic dispersive line shapes of CARS spectra, the CARS signal of the unpolymerized photoresist is stronger than the CARS signal of the polymerized photoresist at 1628 cm^{-1}, while the situation is inverted at 1643 cm^{-1} (see figure 3(b) in manuscript). By acquiring a stack of images in the z direction by CARS microscopy and by implementing the Volume Viewer plug-in of ImageJ (http://rsbweb.nih.gov/ij/index.html), three-dimensional rendering of the CARS signal originating from these microstructures were obtained. Figures S2(b) and S2(c) were recorded at 1643 cm^{-1} and are top and side views of the word "CARS", respectively. Figures S2(d) and S2(e) were instead recorded at 1628 cm^{-1} and are top and side views of the word "CARS", respectively. For clarity, the intensity scale in figures S2(b-e) was set to a threshold so to render close to zero small signals.

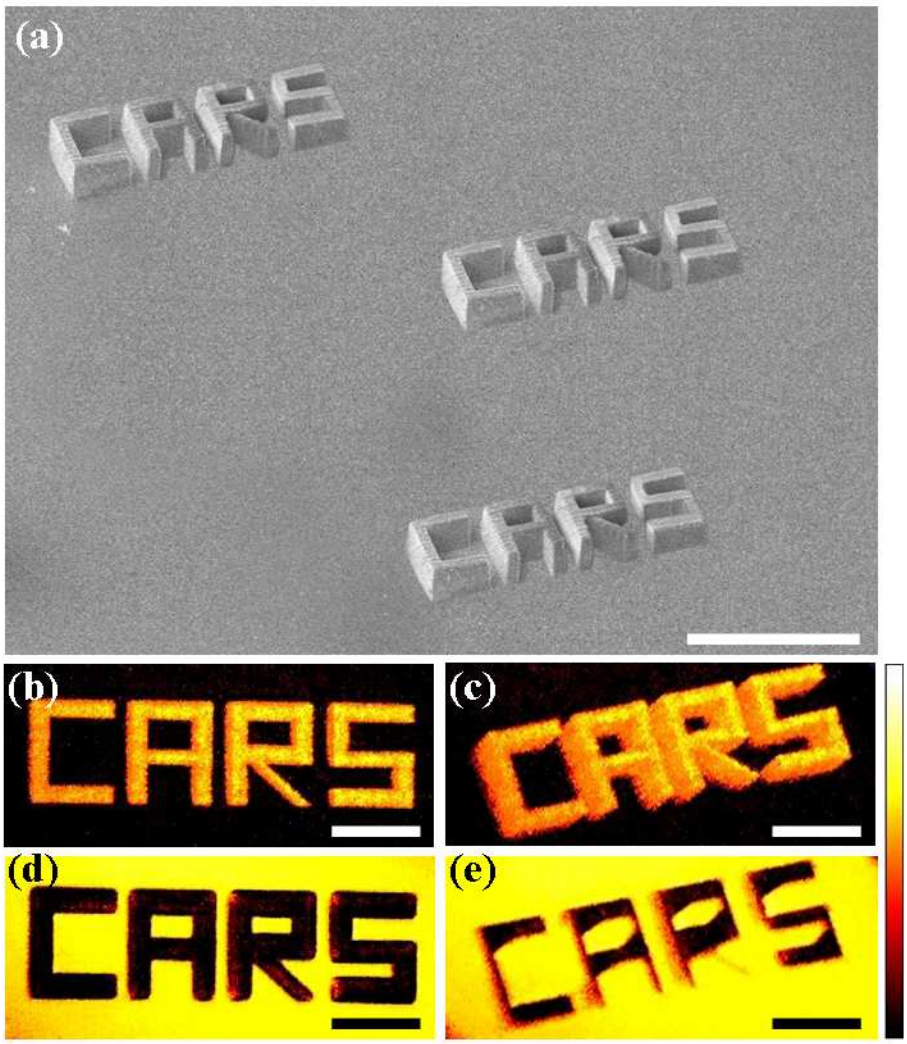

Figure S2. (a) Scanning electron micrograph of a set of "CARS" words fabricated by TPP onto a glass surface. The sample was tilted during imaging to reveal the depth of the microstructures. The scale bar is 40 μm. CARS microscopy was performed on this sample before washing away the bath of unpolymerized photoresist in which it was immersed. (b) Top and (c) side views of the volume rendering of CARS signal generated at 1643 cm^{-1}. (d) Top and (e) side views of the volume rendering of CARS signal generated at 1628 cm^{-1}. The scale bar in all four images (b, c, d, and e) is 20 μm. The color lookup table of CARS images is shown on the right.