J|A|C|S COMMUNICATIONS

Published on Web 07/28/2009

Multiphoton Writing of Three-Dimensional Fluidic Channels within a Porous Matrix

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Surfaces with switchable hydrophilicity are of considerable interest because of their potential applications in, for example, sensors,[1] drug delivery,[2] microfluidics,[3] and colloidal assembly.[4g,i] Modulation of hydrophilicity has been triggered by light irradiation,[4] temperature,[5] electric potential,[6] electric field,[7] pH,[8] and solvents.[9] Here we demonstrate that three-dimensional (3D) microfluidic channels can be formed by writing a hydrophilic pathway within the interior of an otherwise hydrophobic three-dimensionally porous host. Localization of the pattern formation is accomplished by using a multiphoton-based photoacid generation process; this photoacid converts the interior surface of the porous host from hydrophobic to hydrophilic.

Multiphoton-initiated chemistries have been used to define high-resolution 3D structures, including microchannels, micropumps, cantilevers, plasmonic devices, and photonic crystals, for use in microfluidic, biomedical, microelectromechanical, and photonic systems.[10] The use of a tightly focused pulsed laser source enables 3D patterning because, for a two-photon process, the probability of photochemistry is proportional to the square of the incident light intensity. In this way, activation is confined to the focal volume, and sweeping the focal volume in a defined pattern causes a complex structure to be formed.

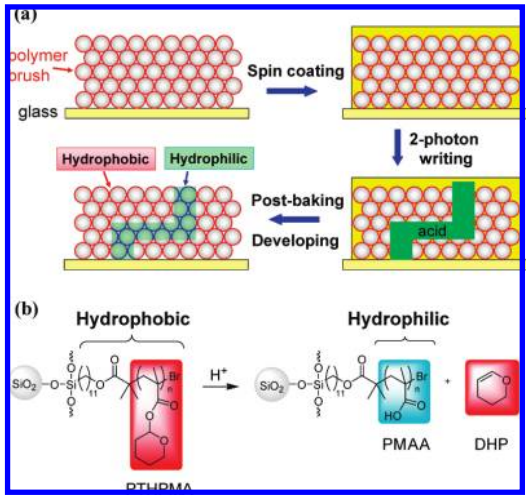

Figure 1. (a) Fabrication process for formation of 3D microfluidic channels in a porous host material. (b) Two-photon-triggered conversion of hydrophobic PTHPMA to hydrophilic PMAA.

The photoactive porous host was formed starting with a silica colloidal crystal (Figure 1a).[11] The silica surface was functionalized with an acid-hydrolyzable polymer brush, poly(tetrahydropyranyl methacrylate) (PTHPMA),[10a,12] through surface-initiated atom-transfer radical polymerization,[13] giving a dry thickness of 5.8 nm (see the Supporting Information for a TEM image). The remaining space within the porous host was infilled via spin coating with a mixture of photoacid generator (octoxyphenylphenyliodonium hexafluoroantimonate), sensitizer (isopropylthioxanthone), and a copolymer of methyl methacrylate and poly(ethylene glycol) methyl ether methacrylate [poly(MMA-*co*-PEGMA)]. The copolymer has the appropriate polarity to dissolve the photoacid generator and sensitizer and additionally is a close refractive-index match to the silica host, minimizing undesirable light scattering during the writing process.

The focal point of a Ti−sapphire femtosecond laser was rastered in a controlled fashion through the sample, resulting in the localized two-photon generation of acid within poly(MMA-*co*-PEGMA). During the postbaking period (65 °C for 1 min), the photoacid hydrolyzed the hydrophobic PTHPMA brush, forming hydrophilic poly(methacrylic acid) (PMAA) (Figure 1b). The poly(MMA-*co*-PEGMA), photoacid generator, sensitizer, and reaction byproducts were subsequently removed from the porous matrix using 0.26 N tetramethylammonium hydroxide in tetrahydrofuran, leaving behind a hydrophobic porous host containing an embedded hydrophilic channel (see the Supporting Information for experimental details).

The embedded hydrophilic channel was imaged via laser scanning confocal microscopy. Water was introduced onto the sample. The hydrophilic channel was written to extend to the surface, allowing the aqueous solution to infiltrate it. To reduce scatter and allow multichannel imaging, the remaining hydrophobic regions of the opal were infiltrated with an oily, fluorescent solution of pyrene in dodecane. This enabled acquisition of fluorescence-mode (Figure 2a) and reflectance-mode (Figure 2b) confocal images of the 3D structure of the channel. The overlay of these images (Figure 2c) shows that water completely filled the hydrophilic channel and dodecane filled only the hydrophobic regions (see the Supporting Information for images of samples infiltrated only with water).

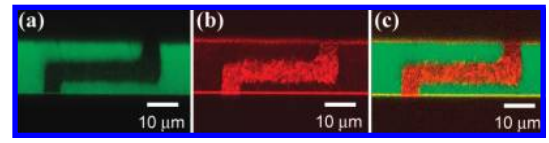

Figure 2. Laser scanning confocal microscope cross sections of two-photon-written hydrophilic channels after back-filling with water (dark/reddish) followed by a fluorescent oily solution (green). (a) Fluorescence channel displaying the hydrophobic (unexposed) regions of the sample, which contained pyrene in dodecane. (b) Reflectance channel displaying the hydrophilic region after back-filling with water. (c) Two-channel overlay of (a) and (b).

To investigate the minimum feature size and resolution of the hydrophilic pattern, rectangles with widths ranging from 0.8 to 25 μm (all were 10 μm long) running through the thickness of the porous host were written using laser powers of 20, 30, and 40 mW. Water containing an aqueous dye, trisodium 8-hydroxypyrene-1,3,6-trisulfonate (HTPS), was introduced onto the sample. Figure 3a shows that at a power of 20 mW, the feature width was less than

10.1021/ja904554m CCC: $40.75

1 μm greater than the target width. The narrowest features (0.8, 1, and 2 μm) did not appear at this writing power. At a power of 40 mW (Figure 3b), the feature width was 2.5−4 μm larger than the defined width. The increase in width is due to both the increase in the effective spot size at higher powers and the higher concentration of the photoacid, which diffuses to some extent away from the region in which it is formed, leading to an expanded zone of deprotection of the PTHPMA. The fact that hydrophilic channels narrower than ~2.5 μm did not appear is perhaps a function of the diffusion length of the photogenerated acid. Because acid diffuses away into the surrounding areas for smaller feature sizes, below a certain exposure dose there is no longer a sufficient acid concentration within the exposed regions to make the polymer brush hydrophilic.

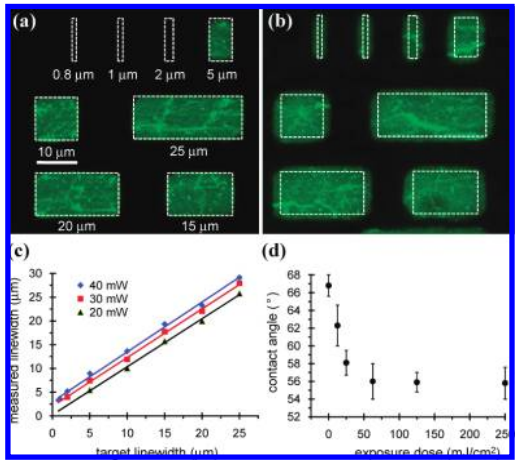

Figure 3. (a, b) Laser scanning confocal microscope fluorescence images of two-photon-patterned hydrophilic features after back-filling with HTPS-containing aqueous solution (green) and dodecane (dark), showing the exposed regions (white dashed rectangles) and resulting features (green) formed using powers of (a) 20 and (b) 40 mW. (c) Measured line width vs targeted line width for various writing powers (using 780 nm radiation). (d) Relationship between the exposure dose at 351 nm and the water contact angle for a planar film.

Wetting of the hydrophilic channels and exclusion of water from the hydrophobic regions is driven by the change in contact angle of the polymer brush upon photoacid activation. As a model system, PTHPMA was grown off a glass slide. Its contact angle was 66.8 ± 1.2°. The slide was coated with the photoacid generator, sensitizer, and polymer mixture, exposed to 351 nm laser radiation (both UV and pulsed IR result in the same photoacid generation), and developed following the same procedure as for the porous matrix. Figure 3d shows that the water contact angle decreased to 56.0 ± 2.0° after a dose of 62.5 mJ/cm^2 and then remained constant for higher doses. The required dose of ~62.5 mJ/cm^2 agrees with previous work in a related photoresist system.[12]

In conclusion, we have demonstrated a facile method for fabricating 3D microfluidic channels by using two-photon-activated chemistry to locally switch the interior surface of a porous solid from a hydrophobic state to a hydrophilic state. These 3D structures can be infilled selectively with water and/or hydrophobic oil with a minimum feature size of only a few micrometers. We envision that this approach may enable the fabrication of complex microfluidic structures that cannot be formed via current technologies.

Acknowledgment. This material is based on work supported by the U.S. Department of Energy, Division of Materials Sciences, under Award DE-FG02-07ER46471 through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana−Champaign. We thank D. V. Gough, and Dr. D. G. Yu for experimental assistance. J.-T.L. gratefully acknowledges partial support from the Ministry of Education of the ROC (Taiwan).

Supporting Information Available: Detailed experimental procedures and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Xia, F.; Ge, H.; Hou, Y.; Sun, T.; Chen, L.; Zhang, G.; Jiang, L. *Adv. Mater.* **2007**, *19*, 2520.
(2) (a) Gupta, P.; Vermani, K.; Garg, S. *Drug Discovery Today* **2002**, *7*, 569. (b) Jiang, J.; Tong, X.; Morris, D.; Zhao, Y. *Macromolecules* **2006**, *39*, 4633.
(3) Beebe, D. J.; Moore, J. S.; Yu, Q.; Liu, R. H.; Kraft, M. L.; Jo, B. H.; Devadoss, C. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 13488.
(4) (a) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Nature* **1997**, *388*, 431. (b) Yu, Y.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145. (c) Feng, X.; Feng, L.; Jin, M.; Zhai, J.; Jiang, L.; Zhu, D. B. *J. Am. Chem. Soc.* **2004**, *126*, 62. (d) Kocer, A.; Walko, M.; Meijberg, W.; Feringa, B. L. *Science* **2005**, *309*, 755. (e) Lim, H. S.; Han, J. T.; Kwak, D.; Jin, M.; Cho, K. *J. Am. Chem. Soc.* **2006**, *128*, 14459. (f) Lim, H. S.; Kwak, D.; Lee, D. Y.; Lee, S. G.; Cho, K. *J. Am. Chem. Soc.* **2007**, *129*, 4128. (g) Piech, M.; George, M. C.; Bell, N. S.; Braun, P. V. *Langmuir* **2006**, *22*, 1379. (h) Brown, A. A.; Azzaroni, O.; Huck, W. T. S. *Langmuir* **2009**, *25*, 1744. (i) George, M. C.; Mohraz, A.; Piech, M.; Bell, N. S.; Lewis, J. A.; Braun, P. V. *Adv. Mater.* **2009**, *21*, 66.
(5) Crevoisier, G. B.; Fabre, P.; Corpart, J. M.; Leibler, L. *Science* **1999**, *285*, 1246.
(6) Lahann, J.; Mitragotri, S.; Tran, T.; Kaido, H.; Sundaram, J.; Choi, I. S.; Hoffer, S.; Somorjai, G. A.; Langer, R. *Science* **2003**, *299*, 371.
(7) (a) Vallet, M.; Berge, B.; Vovelle, L. *Polymer* **1996**, *37*, 2465. (b) Krupenkin, T. N.; Taylor, J. A.; Schneider, T. M.; Yang, S. *Langmuir* **2004**, *20*, 3824. (c) Beni, G.; Hackwood, S. *Appl. Phys. Lett.* **1981**, *38*, 207.
(8) (a) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988**, *4*, 921. (b) Matthews, J. R.; Tuncel, D.; Jacobs, R. M. J.; Bain, C. D.; Anderson, H. L. *J. Am. Chem. Soc.* **2003**, *125*, 6428.
(9) Minko, S.; Muller, M.; Motornov, M.; Nitschke, M.; Grundke, K.; Stamm, M. *J. Am. Chem. Soc.* **2003**, *125*, 3896.
(10) (a) Zhou, W. H.; Kuebler, S. M.; Braun, K. L.; Yu, Y. T.; Cammack, J. K.; Ober, C. K.; Perry, J. W.; Marder, S. R. *Science* **2002**, *296*, 1106. (b) Maruo, S.; Fourkas, J. T. *Laser Photonics Rev.* **2008**, *2*, 100.
(11) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132.
(12) Taylor, G. N.; Stillwagon, L. E.; Houlihan, F. M. *Chem. Mater.* **1991**, *3*, 1031.
(13) (a) Zhao, B.; Brittain, W. J. *Prog. Polym. Sci.* **2000**, *25*, 677. (b) Prucker, O.; Ruhe, J. *Macromolecules* **1998**, *31*, 592. (c) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33*, 14. (d) Prucker, O.; Ruhe, J. *Macromolecules* **1998**, *31*, 602. (e) Tu, H.; Heitzman, C. E.; Braun, P. V. *Langmuir* **2004**, *20*, 8313.

JA904554M