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Laser-treated hydrophobic paper: an inexpensive microfluidic platform

Girish Chitnis,^{ae} Zhenwen Ding,^{be} Chun-Li Chang,^{ae} Cagri A. Savran^{acde} and Babak Ziaie^{*cde}

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We report a method for fabricating inexpensive microfluidic platforms on paper using laser treatment. Any paper with a hydrophobic surface coating (*e.g.*, parchment paper, wax paper, palette paper) can be used for this purpose. We were able to selectively modify the surface structure and property (hydrophobic to hydrophilic) of several such papers using a CO₂ laser. We created patterns down to a minimum feature size of $62 \pm 1 \mu\text{m}$. The modified surface exhibited a highly porous structure which helped to trap/localize chemical and biological aqueous reagents for analysis. The treated surfaces were stable over time and were used to self-assemble arrays of aqueous droplets. Furthermore, we selectively deposited silica microparticles on patterned areas to allow lateral diffusion from one end of a channel to the other. Finally, we demonstrated the applicability of this platform to perform chemical reactions using luminol-based hemoglobin detection.

Introduction

Litmus impregnated paper strips for pH indication has been around for several hundred years (on one account it was developed by the French chemist J. L. Gay-Lussac). Commercially available diagnostic tests for diabetes and pregnancy are also paper-strip-based assays (dipstick). Such chemical detection systems offer several important advantages such as ease of use, disposability, and low cost. Microfluidic structures on paper have the potential to enhance such paper-based detection techniques. Patterning paper to create hydrophilic–hydrophobic structures for microfluidic platforms used in medical diagnostic tests has been pioneered by Whitesides and co-workers.¹ In their original work, they used SU8-soaked chromatography paper which was subsequently patterned by lithography to create microfluidic channels for medical diagnostics.^{1–4} Their method attracted a considerable attention due to its simplicity, low cost, and disposability.^{5,6} In later works, they explored plotting hydrophilic/hydrophobic patterns on filter paper using hexanes-dissolved PDMS.⁷ Most recently, wax printing was used by Lu *et al.* to define hydrophobic barriers and fabricate millimetre scale microfluidic channels on paper.^{8,9} Similar work was also performed in parallel by the Whitesides group.¹⁰ Another similar printing technique was demonstrated by Li *et al.* where they

chemically bonded hydrophobic agent to cellulose to create hydrophobic barriers.¹¹ All of the methods mentioned above create a hydrophilic pattern on un-treated paper by depositing hydrophobic polymers (SU8, PDMS, wax, *etc.*). Hydrophilic pattern creation can also be achieved by etching away or dissolving previously deposited hydrophobic agents to expose the underlying hydrophilic paper. This approach has been implemented by utilizing oxygen plasma¹² or inkjet printing of solvents on hydrophobic paper.¹³

In this paper, we report on an alternative method for fabricating inexpensive microfluidic platforms on hydrophobic papers. Any paper with a hydrophobic surface coating (*e.g.*, parchment paper, wax paper, palette paper) can be used for this purpose. We employed selective surface modification using a CO₂ laser to create hydrophilic patterns on several such papers. Laser modification is known to alter the wettability of the engineering materials by causing structural and chemical changes to the surface;¹⁴ however, this treatment has never been performed on paper. In contrast with the methods described by the Whitesides group which start with a hydrophilic plain paper and are predominantly additive, our approach is subtractive and can selectively convert hydrophobic areas to hydrophilic ones in a single step process. Since the hydrophobic agent is already present throughout the thickness of the paper, our method does not require heat treatment after patterning to create islands of hydrophilic patterns, as is the case in the wax printing technique. This is especially advantageous in applications where one only needs to have a patterned hydrophilic surface. For example, many detection methods in biochemistry, such as ELISA, require arrays of hydrophilic dots or microzone plates.¹⁵ Other advantages of this method include its higher resolution ($62 \pm 1 \mu\text{m}$) and greater robustness (surface-treated hydrophobic papers are structurally and mechanically stronger than regular paper and can be handled more easily without being torn). Although

^aSchool of Mechanical Engineering, Purdue University, West Lafayette, IN, 47907, USA

^bDepartment of Physics, Purdue University, West Lafayette, IN, 47907, USA

^cSchool of Electrical and Computer Engineering, Purdue University, West Lafayette, IN, 47907, USA. E-mail: bziaie@purdue.edu; Tel: +1 765-494-0725

^dWeldon School of Biomedical Engineering, Purdue University, West Lafayette, IN, 47907, USA

^eBirck Nanotechnology Center, Purdue University, West Lafayette, IN, 47907, USA

microchannels patterned using laser writing do not allow movement of aqueous reagents along a channel, we demonstrate that this can be easily achieved by additional coating of silica microparticles.

Materials and methods

The microfluidic platform can be fabricated on several commercially available surface-treated hydrophobic papers. These include, but are not limited to, parchment paper (Reynolds® Parchment Paper, ~50 μm thick), wax paper (Reynolds® Cut-Rite® Wax Paper, ~30 μm thick), and palette paper (Canson® Palette Paper, ~70 μm thick). Parchment paper is made by coating silicone on a compressed fiber sheet to achieve a hydrophobic, heat-resistant surface. Wax and palette paper use wax and plastic, respectively, as the coating material. All further discussions are with respect to parchment paper but are equally applicable to other kinds of papers with minor variations.

Parchment paper was spread, placed on the laser platform, and surface treated using a computer-controlled CO_2 laser cutting and engraving system [Universal Laser System, Inc. Professional Series, maximum power 120 watts, maximum speed 2 mm ms^{-1} , wavelength 10 μm , Continuous Wave (CW) mode]. The desired pattern was generated using CorelDraw (Corel Corporation) and printed onto the parchment paper by raster-scanning the laser beam across the surface. To avoid completely cutting through the paper (instead of selective surface modification), the laser power and scanning speed had to be carefully selected. Higher laser power and lower scanning speed resulted in complete removal of surface and bulk material (*i.e.*, paper) to create through-paper defects. For the parchment paper selected in our experiments (50 μm -thick silicone coated), the laser source was controlled at 15% of its maximum power and was operated at a maximum scanning speed. Even for other types of paper, namely wax and palette paper, we achieved successful surface treatment with the parameters mentioned above. X-ray photoemission spectroscopy (XPS) analysis (Kratos Ultra DLD XPS system) was performed on laser-treated regions of parchment paper to understand its chemical composition before and after treatment. Also, SEM (Field Emission SEM, Hitachi S-4800) images were taken to observe changes in surface micro-structure.

After the treatment, the patterned areas were coated with silica microparticles to enhance directional wettability of the surface (as explained in the next section, this is only necessary if one desires to allow diffusion of a water droplet from one end of a channel to the other). Silica particles (average size 9–13 μm) were obtained from Sigma-Aldrich®. Water suspension of these silica particles (concentration 1 g ml^{-1}) was prepared using a vortex mixer at 3000 rpm. This suspension was poured on top of the laser-treated parchment paper. Treated hydrophilic areas retained the suspension and the silica particles were left behind once water evaporated. The treated paper was then shaken vigorously to dislodge loosely attached particles.

Results and discussion

Fig. 1 shows laser treatment of parchment paper with a large variety of geometries and dimensions. Fig. 1(A) shows SEM image of high resolution array of lines (60 μm wide and 80 μm

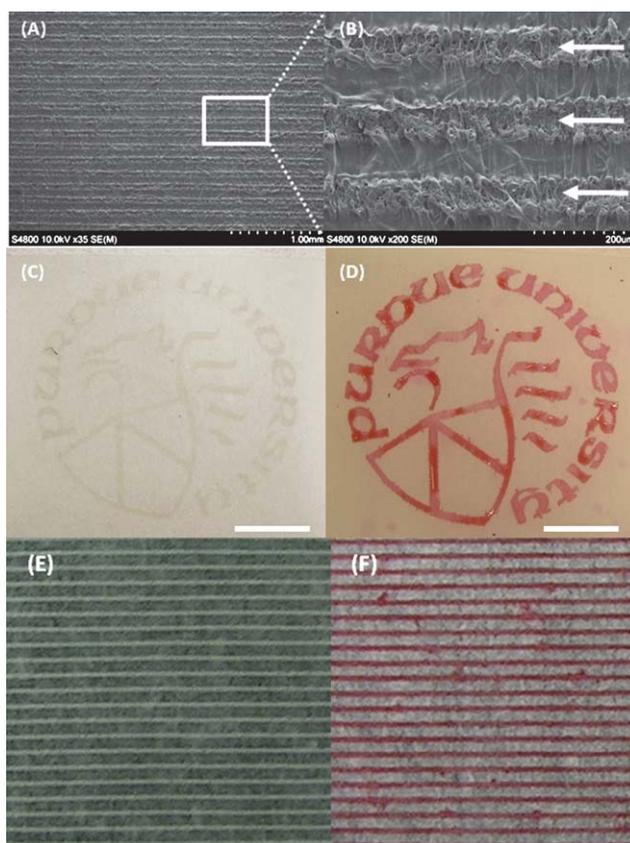


Fig. 1 Laser treatment (15% of maximum power and 100% speed) on parchment paper with different geometries and dimensions; (A) SEM image of an array of lines (width 60 μm and 80 μm separation), (B) close up image of the white box in (A) (arrows show the laser-treated areas), (C and E) laser-treated Purdue Logo and array of lines on parchment paper, and (D and F) patterned liquid on laser modified parchment paper with Purdue logo and array pattern (line width 60 μm and separation 250 μm). (Scale bar: 10 mm; red dye was added to improve the contrast.)

separation). Fig. 1(B) shows a close up image of the white box in Fig. 1(A). Laser treatment of parchment paper changes surface property of its silicone coating, transforming hydrophobic areas to hydrophilic ones. Contact angle measurements showed that the laser treatment reduces the contact angle from 115° to 20°. Fig. 1(C and E) shows laser-treated paper with a Purdue logo and array of lines (60 μm wide 250 μm separation). Fig. 1(D and F) shows the treated papers after dipping in colored (red) water. As can be seen, water was deposited only on laser-patterned areas leaving untreated regions completely dry. We also tested wax and palette papers under similar conditions to create hydrophilic patterns. Fig. 2 compares all three patterned surfaces before (Fig. 2(A, C and E)) and after the droplet assembly (Fig. 2(B, D and F)). In order to test the long-term stability of the hydrophilic areas, a laser-patterned parchment paper was tested after three weeks of its treatment showing no visible difference in surface properties.

To understand the mechanism of hydrophobic–hydrophilic conversion of laser-treated parchment paper, we performed high resolution imaging and spectroscopic analysis. Fig. 3 shows SEM images of treated and un-treated samples. The fibers in parchment paper are clearly visible and protected by the surface

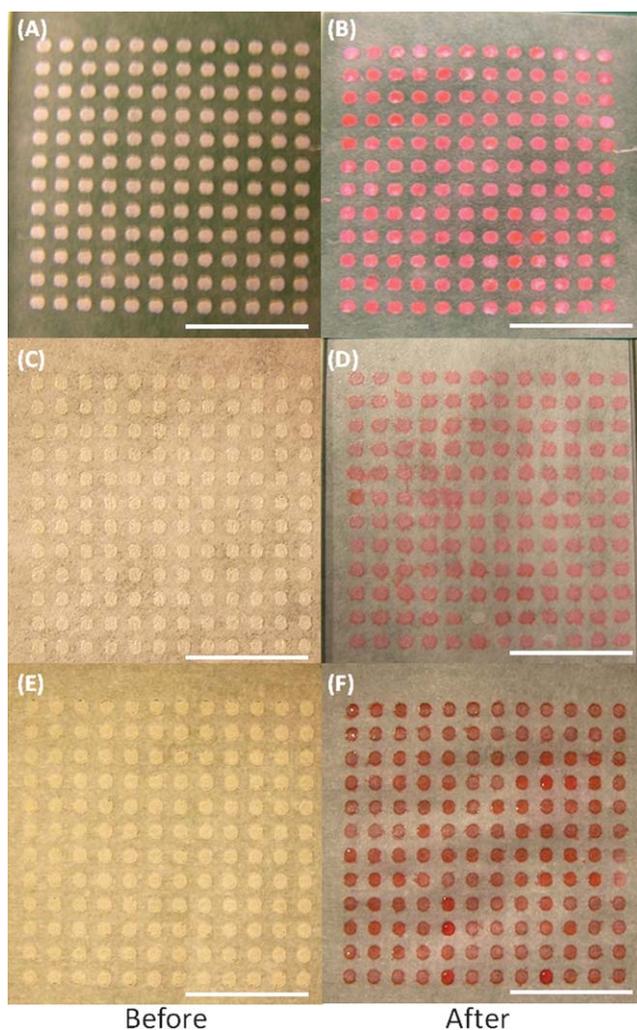


Fig. 2 Comparison of laser treatment on various hydrophobic papers before and after dipping in aqueous red dye. (A and B) Wax paper, (C and D) palette paper, and (E and F) parchment paper. (Scale bar: 10 mm; red dye was added to improve the contrast.)

coating on the non-treated areas (Fig. 3(A–C)). Since all the fibers are coated by silicone, the parchment surface is natively hydrophobic. Once the surface is laser-treated (Fig. 3(D–F)), the top silicone layer is modified increasing the surface roughness (Fig. 3(D)). In higher magnifications (Fig. 3(E and F)), one can easily see micro/nano-scale cobweb structures on the surface. Although it may appear that these are the exposed cellulose fibers, nanoscale diameter of these fibers does not support this hypothesis. SEM of the untreated area clearly shows underlying cellulose fibers, which are about 10 μm in diameter. Hence we believe that these structures are formed due to the melting and re-solidification of the silicone coating during the surface treatment. This porous structure could be helpful in providing a space to trap aqueous reagents for microfluidic applications.

Laser treatment is also known to cause changes in chemical properties of the substrate. Fig. 4 shows raw and processed data from the treated and un-treated parchment paper. The data were processed using CasaXPS software to separate closely overlapping peaks. Comparison of C1s spectra of untreated and laser-treated regions (Fig. 4(A and C) respectively) clearly reveals

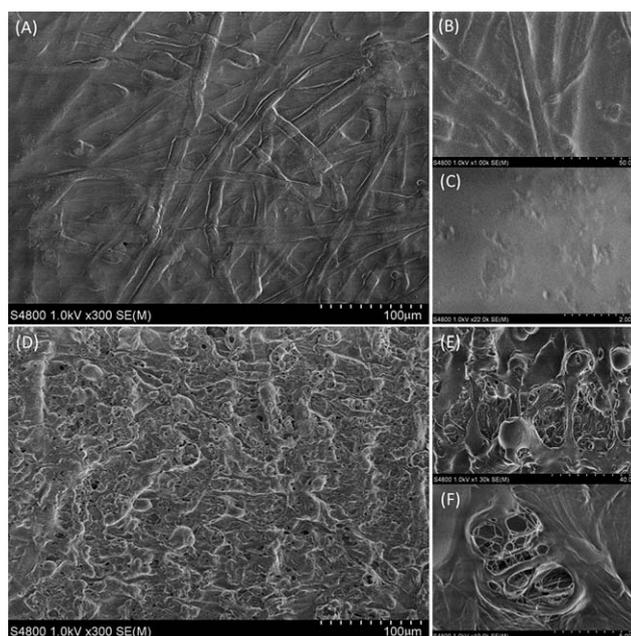


Fig. 3 Top-view SEM images of laser treated parchment paper under different magnifications. (A–C) Area without laser treatment, and (D–F) laser treated area.

additional oxidation peaks in the treated regions. In fact, peaks corresponding to both C–OH (at 286.8 eV) and O=C–OH (at 288.6 eV) are prominent in treated regions. Similarly, Si2p spectrum of the treated region (Fig. 4(D)) shows the presence of Si–O bond (peak at 103.7 eV), which is not observed in the case

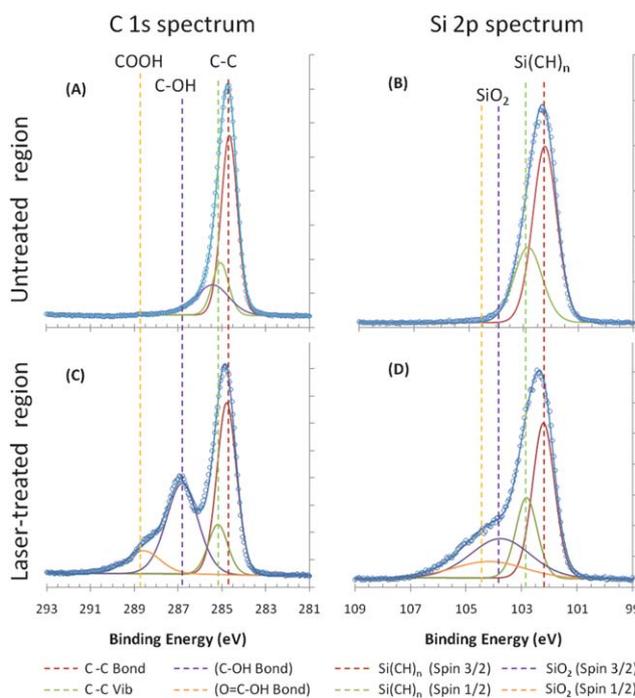


Fig. 4 XPS surface analysis high resolution spectra; (A) untreated region C 1s spectrum, (B) untreated region Si 2p spectrum, (C) laser-treated region C 1s spectrum, and (D) laser-treated region Si 2p spectrum.

of untreated regions (Fig. 4(C)). Peak observed at 102.2 eV is due to Si–C bonds present in the silicone.¹⁶ Apart from these major peaks, a smaller peak observed in C1s spectrum of untreated region (Fig. 4(A)) is most probably due to some external contamination. Although exposed cellulose fibers can also contribute to increased level of oxidized carbon in the treated region, higher level of oxidized silicon (Si–O) definitely proves surface oxidation due to chemical reactions with atmospheric oxygen. Overall it is clear that laser treatment results in significantly more number of hydrophilic –OH, =O groups at the surface. A combination of a highly fibrous structure formed due to melting/re-solidification and chemical surface modification allows the retention of water in the treated areas.

Although laser-treated paper can retain water on its surface, it was observed that it does not allow the lateral diffusion/flow. For many microfluidic applications, it is critical to be able to move the liquid along the channel. To achieve such property, a layer of silica microparticles was deposited on the treated areas. These

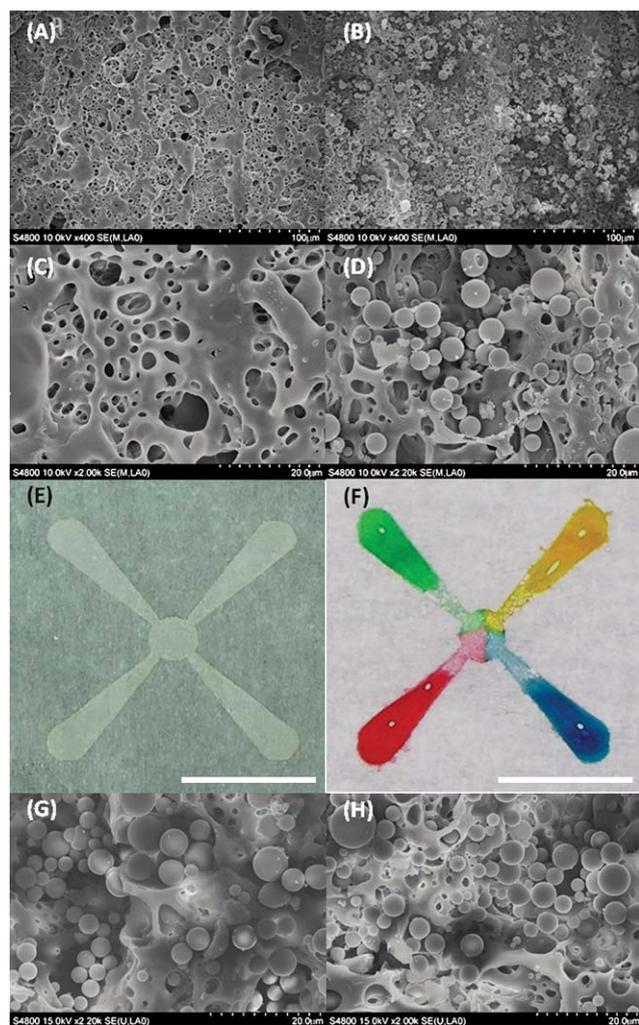


Fig. 5 Silica microparticle deposition on laser-treated areas; (A and C) SEM of a laser-treated area without microparticles, (B and D) SEM of a treated area with microparticles, (E) pattern after silica particle deposition, (F) colored water diffusing towards the center after droplets were placed in the corners (scale bar: 10 mm), (G) SEM of dried sample after water flow, and (H) SEM of dried sample after testing under water.

microparticles get trapped in the porous structure created by laser treatment. The highly hydrophilic nature of silica allows the water to flow along the surface. Fig. 5 shows SEM images of laser-treated areas before (A and C) and after (B and D) silica microparticle deposition. Fig. 5(D) clearly shows microparticles immobilized on top of the highly fibrous/porous structure. Fig. 5(E) shows an optical micrograph of patterned areas after microparticle deposition. Fig. 5(F) shows droplets of colored water that were placed at four corners being mixed in the central region due to diffusion along the channel. SEM image taken after the flow along the surface (Fig. 5(G)) confirms that silica particles adhere well to the surface and do not move along with diffusing water. To further test the robustness of silica particle adhesion, particle-coated sample was shaken (at 2 Hz) under water for one minute. Fig. 5(H) shows the SEM image of the sample after the test, with silica particles still present on the surface.

Laser treatment of paper is a fast and cost effective method to produce microfluidic platforms. The laser machine used in the experiments can raster scan at the speed of 4 ft² per hour. It should be noted that even faster scanning is possible with other laser systems. Hydrophobic papers used in this method are commercially available and they are manufactured in bulk. A laser machine does not have any consumables. Hence to produce hydrophilic patterns, the only cost is that of the paper (less than \$0.10 per ft²). Such inexpensive platforms can be very useful in many biomedical applications involving microzone plates such as detection assays (*e.g.* ELISA). In such applications capillary flow is not required but the reagent should bind to the surface. Even in cases where one needs capillary flow, cost of silica is also not very significant (\$0.10 per g). Based on a conservative estimation that 1 g of silica is needed to produce 1 ft² of capillary flow enabled patterns, the total material cost is less than \$0.20 per ft².

A demonstration indicating an application of such platforms was performed using luminol (3-aminophthalhydrazide, Sigma-Aldrich) chemiluminescence assay, commonly used in forensics for detection of blood. The luminol stock solution was prepared by adding 160 mg luminol and 1.2 g potassium hydroxide (KOH) in 40 ml 3% hydrogen peroxide solution. The luminol solution was patterned on the laser-treated surface to create an array of uniform droplets. After carefully placing this paper on a planar surface, blood solution (mice blood diluted in de-ionized water) was sprayed on the array. As blood mixed with the luminol solution at each spot of the array, chemiluminescence was

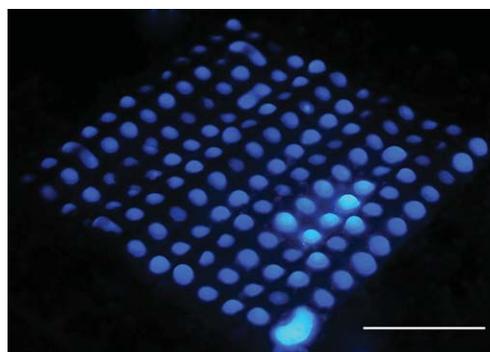


Fig. 6 Demonstration of luminol fluorescence experiment on parchment paper based microfluidic platform. (Scale bar: 10 mm.)

triggered due to the catalytic action of the iron in the hemoglobin. Fig. 6 shows blue luminescence which could be easily seen in a dark room. The few water bridges observed in Fig. 6 are due to sprayed droplets landing in between two adjacent luminol spots.

Conclusions

In conclusion, we reported a simple and inexpensive method to selectively pattern hydrophilic surfaces on hydrophobic paper by laser treatment. Using computer-controlled CO₂ laser, we created a high resolution two-dimensional pattern on the hydrophobic surface of parchment paper. XPS analysis indicated a change in the surface chemical property through inclusion of atmospheric oxygen, hence creating hydrophilic groups on the surface. Laser treatment also modified the surface physically due to melting and re-solidification of silicone to create micro/nano-hybrid structure, which enabled the trapping of aqueous reagents. Furthermore, these hydrophilic patterns were coated with silica microparticles to allow lateral diffusion along the fabricated microchannel. Finally, we used surface modified parchment paper to perform a luminol chemiluminescence assay. We expect this method to have a wide variety of applications ranging from microfluidics to rapid medical diagnostics.

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References

- 1 A. W. Martinez, S. T. Phillips, M. J. Butte and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 2007, **46**, 1318–1320.
- 2 A. W. Martinez, S. T. Phillips, B. J. Wiley, M. Gupta and G. M. Whitesides, *Lab Chip*, 2008, **8**, 2146–2150.
- 3 A. W. Martinez, S. T. Phillips, E. Carrilho, S. W. Thomas, H. Sindi and G. M. Whitesides, *Anal. Chem.*, 2008, **80**, 3699–3707.
- 4 A. W. Martinez, S. T. Phillips and G. M. Whitesides, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 19606–19611.
- 5 W. Zhao and A. van den Berg, *Lab Chip*, 2008, **8**, 1988–1991.
- 6 W. Zhao, M. M. Ali, S. D. Aguirre, M. A. Brook and Y. Li, *Anal. Chem.*, 2008, **80**, 8431–8437.
- 7 D. A. Bruzewicz, M. Reches and G. M. Whitesides, *Anal. Chem.*, 2008, **80**, 3387–3392.
- 8 Y. Lu, W. Shi, J. Qin and B. Lin, *Anal. Chem.*, 2010, **82**, 329–335.
- 9 Y. Lu, W. Shi, L. Jiang, J. Qin and B. Lin, *Electrophoresis*, 2009, **30**, 1497–1500.
- 10 E. Carrilho, A. W. Martinez and G. M. Whitesides, *Anal. Chem.*, 2010, **81**, 7091–7095.
- 11 X. Li, J. Tian, G. Garnier and W. Shen, *Colloids Surf., B*, 2010, **76**, 564–570.
- 12 X. Li, J. Tian, T. Nguyen and W. Shen, *Anal. Chem.*, 2008, **80**, 9131–9134.
- 13 K. Abe, K. Suzuki and D. Citterio, *Anal. Chem.*, 2008, **80**, 6928–6934.
- 14 J. Lawrence and L. Li, in *Laser Modification of the Wettability Characteristics of Engineering Materials*, Professional Engineering Publishing, 2000.
- 15 E. Carrilho, S. T. Phillips, S. J. Vella, A. W. Martinez and G. M. Whitesides, *Anal. Chem.*, 2009, **81**, 5990–5998.
- 16 R. Nordberg, H. Brecht, R. G. Albridge, A. Fahlman and J. R. Van Wazer, *Inorg. Chem.*, 1970, **9**, 2469–2474.