Defining microchannels and valves on a hydrophobic paper by low-cost inkjet printing of aqueous or weak organic solutions

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We describe a simple and cost-effective strategy for rapid fabrication of microfluidic paper-based analytical devices and valves by inkjet printing. NaOH aqueous solution was printed onto a hydrophobic filter paper, which was previously obtained by soaking in a trimethoxyoctadecylsilane-heptane solution, allowing selective wet etching of hydrophobic cellulose to create hydrophilic-hydrophobic contrast with a relatively good resolution. Hexadecyltrimethylammonium bromide (CTMAB)-ethanol solution was printed onto hydrophobic paper to fabricate temperature-controlled valves. At low temperature, CTMAB deposited on the paper is insoluble in aqueous fluid, thus the paper remains hydrophobic. At high temperature, CTMAB becomes soluble so the CTMAB-deposited channel becomes hydrophilic, allowing the wicking of aqueous solution through the valve. We believe that this strategy will be very attractive for the development of simple micro analytical devices for point-of-care applications, including diagnostic testing, food safety control, and environmental monitoring. © 2015 AIP Publishing LLC.

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I. INTRODUCTION

Recently, microfluidic paper-based analytical devices (μ PADs) have received significant attention because they offer various advantages over microfluidic systems fabricated on polymers, glass, and silica, including easy and rapid fabrication, low cost, and ease of use. Additionally, fluids can wick through (hydrophilic) cellulose through capillary actions, thereby eliminating the necessity for using external fluid pumps. As a result, μ PADs have emerged as a promising platform for point-of-care analytical applications in clinical diagnostics,^{1–3} food safety control,^{4,5} and environmental testing.^{6,7}

Various techniques have been used to fabricate μ PADs, including photolithography,^{8,9} wax printing,^{10–12} inkjet printing,^{13–15} laser etching,^{16,17} plasma treatment,¹⁸ and use of metal/paper masks.^{19–23} Each technique has particular advantages and drawbacks.²⁴ Wax printing is the most commonly used technique for fabricating hydrophilic-hydrophobic contrast materials, because it offers rapid fabrication, good resolution, and the ability to mass prototype. However, this method uses an expensive wax printer to deposit wax onto paper, making it unsuitable for applications in resource-limited settings and impoverished countries. Inkjet printing is relatively a cheap alternative to wax printing that can be classified into two categories. Prior to 2013, strong organic solvent or hydrophobic materials prepared in organic solvents were printed onto hydrophilic paper to create hydrophobic barriers. For example, toluene,¹³ poly(dimethylsiloxane)-hexane solution,¹⁴ and an alkenyl ketene dimer-heptane solution¹⁵ have been used as printing inks for fabricating μ PADs. Unfortunately, the cartridges and printers are easily attacked by organic solvents with strong solvation power (toluene, hexane, and heptane). Thus, when using inkjet printer to prototype μ PADs, inks that do not

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contain strong organic solvents are more compatible and desirable than those that do. Recently, Maejima *et al.*²⁵ demonstrated the patterning of a filter paper by inkjet printing of solvent-free ink. In their work, μ PADs were fabricated by inkjet printing of a hydrophobic ultraviolet curable acrylate composition without organic solvents. Xu *et al.*²⁶ and Rajendra *et al.*²⁷ subsequently presented strategies for fabricating μ PADs on hydrophilic filter paper by inkjet printing of hydrophobic materials dissolved in ethanol or methanol-isopropanol mixtures. Another inkjet printing method creates a desired pattern by printing aqueous etching solution onto a hydrophobic paper. For example, Wang *et al.*²⁸ fabricated hydrophilic areas using an aqueous base solution. Prior to printing of the base solution, the hydrophilic paper was hydrophobically patterned using a mixture of methyltrimethoxysilane and 0.1 M hydrochloric acid at a 4:1 v/v ratio as modification agents. The hydrophobic barriers fabricated by this method resisted penetration by surfactants, glycerol, toluene, and dimethyl sulfoxide (DMSO), showing great potential in a wide range of analytical applications that require surfactants and organic solvents, for example, in cell analysis. However, an expensive, research-grade piezoelectric inkjet printer was used for barrier fabrication, making it unsuitable for applications in resource-limited settings. In this work, we describe a method for fabricating μ PADs by inkjet printing of aqueous solutions using an inexpensive inkjet printer. A native hydrophilic filter paper was soaked in a trimethoxyoctadecylsilane (TMOS)-heptane solution followed by heating, by which cross-linked hydrophobic groups were immobilized onto the cellulose. NaOH aqueous solution was then printed onto the hydrophobic filter paper using a cheap inkjet printer (ip2780), allowing selective wet etching of the hydrophobic cellulose by the etching agent (NaOH solution) to create a hydrophilic-hydrophobic contrast. This method is simple, cost-effective, allows mass production of μ PADs, and can be used to fabricate μ PADs by untrained personnel, at minimum cost.

Although μ PADs offer a cheap and promising platform for designing portable, low-cost, and simple biochemical sensors, the autonomous nature of fluid wicking on paper cellulose poses difficulties in various analytical applications, especially when complex, multiple-step assays are conducted on a μ PAD. Thus, integrating valves on μ PADs are important for their development in various applications. To date, three strategies have been developed for fabricating valves to control fluid on μ PADs. The first strategy is to design geometries with channels of differing width, length, and shape. For example, Fu *et al.* demonstrated a method for controlling fluid transport using a geometry comprising a network and dissolvable barriers.²⁹ The second strategy is to use chemicals in the flow path to adjust flow rates.^{30–32} Lutz *et al.* demonstrated controlled delays of fluid flow by adding sugar solutions with different concentrations onto channels.³⁰ The third method is to use mechanical means to connect or disconnect channels, thus to maintain or stop fluid wicking in the paper cellulose. A successful and promising demonstration was described by Toley *et al.*³³ In their work, a toolkit of paper microfluidic valves and methods for automatic valve actuation was developed, using movable paper strips and fluid-triggered expanding elements. In this work, we developed a new strategy for fabricating valves on μ PADs by inkjet printing a surfactant, whose solubility in water varies sharply with temperature, onto a hydrophobic paper. A hexadecyltrimethylammonium bromide (CTMAB) solution prepared in ethanol was printed onto the hydrophobic paper and used to manipulate fluid flow by adjusting the temperature. At low temperature, CTMAB is insoluble in aqueous fluid so the paper surface remains hydrophobic, preventing the wicking of fluid through the hydrophobic cellulose. At high temperature, however, CTMAB dissolves in aqueous fluid, lowering the surface tension between the hydrophobic surface and fluid to allow the latter to wick through the CTMAB-deposited valve.

II. EXPERIMENTAL

A. Chemicals and apparatus

All chemicals used were of analytical grade unless mentioned otherwise, and demineralized water was used throughout. TMOS was purchased from Aladdin Industrial Co. (Shanghai, China). 0.3% (v/v) TMOS-heptane (containing 5% ethyl acetate) was used to

hydrophobically pattern the native hydrophilic filter paper. Then, 0.1 mol l^{-1} NaOH solution (containing 30% glycerol and 2.0% triton X-100) was used as etching ink to fabricate hydrophilic channels on the hydrophobic filter paper. The etching ink was prepared by dissolving 0.2 g NaOH in 25 ml water, followed by adding 15 ml glycerol and 1.0 ml Triton X-100, and then diluting to 50 ml with water. A 2.0% CTMAB-ethanol solution, prepared by dissolving 1.0 g CTMAB in 50 ml ethanol, was used as printing ink to fabricate valves on the hydrophobic paper. The ink was filtered through a $0.45 \mu\text{m}$ filter membrane before use. The inkjet cartridge was modified by removing the sponge from within the cartridge (modified cartridges are also available and affordable on the second-hand market). The inks were loaded into the cartridge with a plastic syringe. $0.067 \text{ mol l}^{-1} \text{ Fe}^{3+}$ was prepared by dissolving 1.6 g $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 50 ml H_2O (containing 2 ml concentrated HNO_3). $0.2 \text{ mol l}^{-1} \text{ SCN}^-$ was prepared by dissolving 1.0 g KSCN in 50 ml H_2O . An inkjet printer (ip2780, Canon, Japan) with a printing resolution of $4800 \times 1200 \text{ dpi}$ was used to print NaOH and CTMAB solutions. The volumes of single droplet of black and color inks are 25 and 5 pl, respectively, for the ip2780 printer. A contact angle meter (JC20001, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd., Shanghai, China) was used to measure contact angles, based on the sessile drop method, using a $6 \mu\text{l}$ water drop. A heater (YH-946B) was used to control the temperature.

B. Fabrication of μPADs

The μPAD fabrication process consisted of three steps. In the first step, a native hydrophilic filter paper was immersed in a 0.3% TMOS-heptane solution followed by heating at 100°C for 2 h and then held overnight (Figures 1(a) and 1(b)). During this process, Si-OH groups were produced by hydrolysis of TMOS in ambient water, TMOS was thereby immobilized onto cellulose via a reaction between Si-OH groups in TMOS and C-OH groups on cellulose. Simultaneously, the hydrolyzed TMOS may crosslink through self condensation of the silanol groups.^{34,35} Hence, hydrophobic paper with a water contact angle (WCA) of 127° was produced. In the second step, 0.1 mol l^{-1} NaOH solution was printed onto the hydrophobic paper (three printing passes on each side), by which a digitally designed pattern was transferred onto the hydrophobic paper (Figure 1(c)). In the third step, the printed paper was heated for 15 min at 85°C , allowing selective etching of the hydrophobic cellulose by the etching agent. Thus, a hydrophobic-hydrophilic contrast was generated on the filter paper (Figure 1(d)). The patterned paper could be used for analytical applications after washing sequentially with 0.01 mol l^{-1} HCl and H_2O for 2 min each.

FIG. 1. Schematic diagram illustrating the fabrication of μPADs by inkjet printing of etching agent. (a)–(d) Cross sections of a native filter paper (a), hydrophobic paper obtained by immersing the native paper in a TMOS solution, followed by heating (b), hydrophobic paper deposited with etching agent by inkjet printing (c), and hydrophilic-hydrophobic contrast obtained by etching (d). (e) Image captured after spraying water onto paper (A5 size) fabricated with 28 flower-shaped μPADs .

FIG. 2. Design of hydrophilic reservoirs (a) and valves (b).

C. Fabrication of valve on μ PAD

μ PADs with valves were fabricated by two steps of inkjet printing. In the first step, hydrophilic circle reservoirs ($\Phi = 6.0$ mm, 12 mm apart) (Figure 2(a)) were fabricated by inkjet printing of NaOH solution onto a hydrophobic filter paper, prepared as described above. Specifically, 0.1 mol l^{-1} NaOH (containing 30% glycerol and 2.0% triton X-100) was printed onto the hydrophobic filter paper for six printing passes (three printing passes on each side), followed by sandwiching between two glass slides and heating at 85°C for 15 min. The paper was then washed sequentially with 0.01 mol l^{-1} HCl and H_2O for 2 min each. In the second step, a valve ($6.5 \text{ mm} \times 2 \text{ mm}$) (Figure 2(b)) was fabricated by performing six printing passes (three printing passes on each side) onto the hydrophobic gap between these two reservoirs, using a 2.0% CTMAB-ethanol solution as printing ink. The device was then air dried for 8 min, to evaporate the ethanol. The two hydrophilic reservoirs were thus connected by the channel valve. To study the effect of temperature on the flow rate in the CTMAB-deposited channel, a μ PAD with two hydrophilic reservoirs ($\Phi = 10$ mm) connected by a CTMAB-deposited channel (2 mm wide and 80 mm long) was fabricated using the two-step printing approach.

III. RESULTS AND DISCUSSION

A. Effects of printing times

We studied the effect of printing times on the water contact angle (WCA) on the NaOH-patterned surfaces. As shown in Figure 3(a), the WCA on the patterned surface decreased with increased printing times. This may have been caused by an increased amount of etching agent deposited on the paper with increased printing cycles. WCA decreased to 0° on the patterned paper when six printing passes were performed. The water flow rate through the

FIG. 3. (a) Effect of printing times on water contact angle. NaOH concentration: 0.1 mol l^{-1} (containing 30% glycerol and 2.0% triton X-100). (b) Water flow distance in the patterned channel as a function of time. Channel width: 2 mm; printing passes: 6.

NaOH-patterned channel (2 mm in width) obtained by six printing passes was investigated using a ruler, stop watch, and a smart mobile phone. Figure 3(b) shows that water flow rate decreased with time and distance, perhaps because of fiber swelling. The effects of fiber swelling on water flow rate would be two-fold: (1) the liquid would be absorbed into the fiber wall, thus less liquid could be transported through the capillary channels and (2) the size of capillary pores would be reduced, leaving less space for liquid transport.¹⁵

B. Resolution of fabrication

The resolution of channels fabricated by the NaOH-printing method was characterized by printing six straight channels (200, 400, 600, 800, 1000, and 1200 μm wide, respectively) with a common reservoir. Colored solution was added onto the common reservoir, allowing the solution to wick through the channels of differing width. Figure 4(a) shows that this method could be used to fabricate μPADs with a relatively good resolution and a channel with a width of 600–700 μm could be fabricated. The width of channel as actually etched is usually larger than the width set for printing in the software. The actual widths of etched channel for 600, 800, 1000, and 1200 μm designed in software were 700, 817, 1051, and 1225 μm , respectively. Furthermore, the pattern could be readily varied on demand by designing these in the software, which is, in contrast, challenging for methods that use metal or paper masks. We used the ink-jet printing method to print a traditional Chinese paper cut pattern of a double Phoenix, which is usually used in weddings in China, to demonstrate this feature. As shown in Figure 4(b), the pattern was displayed after spraying water onto the printed paper through penetration of water into the NaOH-etched cellulose. The patterned paper was stable for at least 2 months when stored at 4 °C.

C. Hydrophobic-hydrophilic transformation of CTMAB-printed channels

The second objective of this work was to develop a simple strategy for fabricating valves on μPADs by inkjet printing. Surfactants are amphiphilic organic compounds that usually contain both hydrophobic groups (their tails) and hydrophilic groups (their heads), and which can be used to reduce the surface tension between a hydrophobic surface and a fluid. CTMAB is a surfactant whose solubility in water decreases markedly with decreasing temperature. At a low temperature, CTMAB deposited onto the hydrophobic paper was insoluble in an aqueous fluid, and therefore, a CTMAB-printed flower-shaped pattern remained hydrophobic and prevented the wicking of fluid through the CTMAB-deposited cellulose (Figure 5(b)). At a high temperature, however, CTMAB had increased solubility in water so the fluid penetrated into the

FIG. 4. (a) Image illustrating the fabrication resolution by printing six straight channels with a common reservoir. The channel width is in the range of 200–1200 μm . The image was captured by adding a Rhodamine B solution onto the common reservoir. (b) A traditional Chinese paper cut pattern produced by inkjet printing NaOH solution onto a hydrophobic filter paper. The image was captured after spraying water onto the NaOH-printed hydrophobic paper. Printing passes: 6; NaOH concentration: 0.1 mol l^{-1} (containing 30% glycerol and 2.0% triton X-100).

FIG. 5. Photographs of a hydrophobic paper sheet with a flower-shaped pattern before (a) and 10 min after (b) spraying with water at low temperature ($<15^{\circ}\text{C}$), and then heating for 0.5 min (c) and 3 min (d) at 50°C . The flower-shaped pattern was fabricated by inkjet printing a 2.0% CTMAB-ethanol solution onto hydrophobic paper. Printing passes: 6.

hydrophobic filter cellulose (Figures 5(c) and 5(d)). This unique feature of CTMAB was used to fabricate temperature-controlled valves on μPADs through inkjet printing of CTMAB onto a hydrophobic paper. The CTMAB-patterned paper was stable for at least 1 month when stored at 4°C .

D. Operating principle of CTMAB-printed valve

The μPAD used for proof-of-concept demonstration consisted of two hydrophilic reservoirs connected by one CTMAB-deposited valve (Figure 6(a)). The device was fabricated as described in Sec. II C. The CTMAB-deposited channel was used as a valve to manipulate the flow of aqueous fluids from one hydrophilic reservoir to the other, by adjusting the temperature. Figure 6(b) illustrates an enlarged microscopic event occurred when the aqueous fluid from one reservoir wicked through the CTMAB-deposited valve at a high temperature. Because of the increased solubility of CTMAB in water at a high temperature, CTMAB was dissolved at the fluid front, thereby reducing the surface tension between the fluid and the hydrophobic cellulose there and hence the aqueous fluid penetrated the hydrophobic filter cellulose. Therefore, the hydrophobic tails of dissolved CTMAB molecules penetrated and remained within the hydrophobic layer of the filter cellulose, while the hydrophilic heads extended out of the hydrophobic layer, generating a hydrophilic layer on the surface of the hydrophobic cellulose. In this way, the fluids wicked and the fluid front advanced continuously at a high temperature through the CTMAB-deposited valve.

To further study the effect of temperature on the flow rate in the CTMAB-deposited channel, a new configuration in which there were two hydrophilic reservoirs (10 mm in diameter) connected by a CTMAB-deposited channel (2 mm wide and 80 mm long) was fabricated by

FIG. 6. (a) Schematic of the μPAD valve design, consisting of two reservoirs connected by one channel valve. (b) Enlarged microscopic diagram illustrating the operating principle of the CTMAB-deposited valve.

FIG. 7. Average flow rate within 2 min as a function of temperature in the range of 27–80 °C.

two-step printing on a hydrophobic filter paper. The flow rate was studied by adding water onto one hydrophilic reservoir at different temperatures in the range of 27–80 °C. As shown in Figure 7, the flow rate in the CTMAB-deposited channel decreased dramatically with a decrease in temperature. Additionally, we investigated the flow of aqueous fluids along the CTMAB-deposited channel at a low temperature, which was achieved using a semiconductor cooling device. The results showed that the valve was closed and water was confined into the hydrophilic reservoir at a low temperature. Although a sharp switching temperature was not obtained because of difficulties in obtaining a specific low temperature with a semiconductor cooling device, we concluded that the temperature has marked effect on the flow rate through

FIG. 8. Time-sequence images illustrating the chromogenic reaction occurred between Fe^{3+} and SCN^- controlled using a CTMAB-deposited valve by adjusting the temperature. (a)–(c) μPAD images obtained after adding 5 μl of Fe^{3+} (a), which was then air dried for 10 min, followed by adding 10 μl of KSCN solution onto the other reservoir (b). The KSCN solution was then air dried for 30 min (c) at a low temperature ($<15^\circ\text{C}$), respectively. (d)–(k) Time-sequence images obtained after adding 5 μl Fe^{3+} (d), which was then air dried for 10 min at low temperature ($<15^\circ\text{C}$), followed by adding 10 μl of KSCN solution onto the other reservoir and heating at 60 °C for 3 (e), 12 (f), 30 (g), 33 (h), 36 (i), 41 (j), and 88 s (k), respectively.

the valve. The valve could be switched from the “off-state” to the “on-state” by using simple cooling and heating devices.

E. Chromogenic reactions controlled by a CTMAB-deposited channel valve

As a proof-of-concept demonstration, a chromogenic reaction between Fe^{3+} and SCN^- was conducted on a μPAD consisting of two hydrophilic reservoirs connected by a valve (designed as shown in Figure 6(a)). 5 μl of $0.067 \text{ mol l}^{-1} \text{ Fe}^{3+}$ was added onto one hydrophilic reservoir and then air dried for 10 min at a low temperature ($<15^\circ\text{C}$), followed by addition of 10 μl of $0.2 \text{ mol l}^{-1} \text{ SCN}^-$ onto the other reservoir. At a low temperature ($<15^\circ\text{C}$), both Fe^{3+} and SCN^- solutions were confined within their individual hydrophilic reservoirs, therefore no chromogenic reaction was observed even 30 min after spotting the SCN^- solution (Figures 8(a)–8(c)). However, the CTMAB-deposited channel was made hydrophilic by increasing the temperature (60°C), allowing the spotted SCN^- solution to wick through the channel (valve) to the reservoir containing Fe^{3+} , thereby generating a red-colored complex owing to the chromogenic reaction between Fe^{3+} and SCN^- (Figures 8(d)–8(k)).

IV. CONCLUSIONS

We described a novel, simple and low-cost strategy for prototyping of μPADs and valves fabricated by inkjet printing of aqueous and weak organic solutions using an inexpensive (290 RMB Yuan) inkjet printer (ip2780). Being free of any expensive equipment, reagents, and trained personnel, this strategy could be used for mass prototyping of valves and μPADs by the untrained personnel with minimum cost, which is very attractive for impoverished countries and resource-limited settings. In addition, aqueous and weak organic solutions were used as printing inks, thus the cartridges and printers were not easily damaged. Our study also provides a new tool to manipulate fluid in μPADs by adjusting the solubility of surfactants in water. We anticipate this strategy may considerably expand the applications and capabilities of μPADs . One limitation of this presented valving method is that the valve switching is not reversible when the whole channel becomes penetrated and wetted with aqueous fluids. This may be owing to a “water bridge” being generated across the CTMAB-deposited channel at a high temperature, thereby inducing aqueous fluids to flow along the valve, even at a low temperature.

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