

VOC-FREE INKJET PATTERNING METHOD FOR THE FABRICATION OF “PAPERFLUIDIC” SENSING DEVICES

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ABSTRACT

A direct inkjet patterning method for paperfluidic devices using a hydrophobic UV-curable composition has been developed. Patterns are printed on the surface of untreated filter paper. After UV-curing, hydrophobic barriers are formed. To prevent liquid from leaching through the bottom of the device, a uniform layer of the same ink is printed on the backside of the paper, followed by UV-curing. Patterns are stable against surfactants and retain functionality for at least one month when stored at room temperature. The suitability for paperfluidic sensing is demonstrated on the example of a pH sensor.

KEYWORDS: Microfluidic, Chemical Sensor, UV-Curing, Printing

INTRODUCTION

For environmental analysis or clinical diagnostic tests in low resource settings (e.g. developing countries), affordable and easy to use sensing systems are desired. Whitesides and coworkers have started to use paper as the substrate for the fabrication of microfluidic devices (paperfluidics) [1]. Liquid flow in paper is entirely capillary force driven, eliminating the need for external pumping. The fabrication of the devices basically requires two steps: the creation of a microfluidic pattern on the paper, and the deposition of the reagents necessary to perform (bio)chemical sensing. A variety of patterning methods has been developed so far (photolithography [1], cutting [2], wax printing [3] and flexography [4], among others).

We have first demonstrated that inkjet printing is a useful technology for the fabrication of paperfluidic devices. Only inkjet printing can be used to fabricate a complete sensing device, since it allows both the patterning of the paper substrate, and the deposition of the necessary reagents. As one example, a device for the determination of pH, total protein and glucose has been demonstrated [5]. Furthermore, inkjet-printed lateral flow immunosensing has been shown for a model immunoassay. In a final step, chemical sensors and immunosensors, all fabricated by inkjet printing, have been integrated on a single piece of paper. A first example, combining two model immunoassays with one chemical assay (pH), has been realized [6].

So far, we have relied on inkjet etching for the patterning of the microfluidic structure on paper [5, 6]. The entire paper has first to be converted into a hydrophobic substrate by soaking in a solution of poly(styrene) in toluene. Then, inkjet printing of toluene locally removes the hydrophobic polymer, creating flow channels and sensing areas by restoring the originally hydrophilic paper substrate. A serious drawback of this approach is the requirement of a volatile organic compound (VOC). Besides the environmental impact, the use of toluene requires a customized inkjet printer. Furthermore, the entire paper substrate has to be pretreated to render it hydrophobic, and therefore, all hydrophilic areas of the patterned device have been exposed to polymer and solvent, with unknown influence on sensing chemistries.

The objective of the present work is to overcome these disadvantages, while keeping the advantages of the inkjet printing technology. A VOC-free inkjet printable hydrophobic UV-curable ink composition has been developed, which after curing results in hydrophobic barriers surrounding the microfluidic channels and sensing areas. In this way, the areas of the paper coming into contact with sensing reagents and samples are not affected by polymer and solvent.

EXPERIMENTAL

Inkjet printing was performed on an unmodified EPSON PX-101 (Epson, Suwa, Japan) inkjet printer, where the original ink cartridges had been removed and replaced by refillable cartridges (Daiko, Tokyo, Japan). The composition of the UV-curable ink is given in Table 1. Monomer (Wako Pure Chemical Industries, Osaka, Japan), crosslinker (TCI, Tokyo, Japan) and initiator (Wako) were used as received, except for temperature endurance tests, where the ink was prepared after inhibitor removal by treatment with 5% (w/w) aqueous NaOH solution. Patterns for printing were created with Microsoft PowerPoint on a personal computer and printed in the “Envelope” mode of the printer on Advantec 5C (Advantec, Tokyo, Japan) filter paper (1 μm pore size). For better paper feeding in the printer, the circle-shaped filter paper was attached to a sheet of copy paper using clear tape. Immediately after each printing step, UV-curing was performed for 60 s at a power of 600 mW/cm² (measured at 365 nm) under a Lightningcure LC-6 UV spot light source (Hamamatsu Photonics, Hamamatsu, Japan).

For pH sensing, bromothymol blue (BTB) and thymol blue sodium salts (TB) were lipophilized by ion exchange with trimethylstearylammmonium chloride and tridodecylmethylammmonium chloride, respectively, similar to a previously described method [6]. The lipophilized pH indicators and methyl red (MR) were separately encapsulated into poly(styrene-block-vinylpyrrolidone) nanoparticles (Aldrich, Japan) [6, 7]. The resulting aqueous particle suspensions of BTB, TB and MR were mixed in a 3:2:6 volume ratio (total 1.21 mL), followed by the addition of 0.1 M NaOH solution (0.04 mL), and dilution with water (1.75 mL). The final pH-sensitive ink was obtained by adding 10 % (v/v) glycerine (viscosity control) and 30% (v/v) 2-propanol (surface tension control). The resulting inkjet ink contained a total of 0.48 % (w/w) of polymeric particles.

Table 1. Chemical composition of the inkjet printable UV-curable ink

Function	Chemical Compound	Weight%	Remarks
Monomer	Octadecyl acrylate	59.5	Melting point 32 °C
Crosslinker	1,10-Decanediol diacrylate	25.5	Boiling point 181 °C (2 mm Hg)
Initiator	Benzoyldimethylketal	15.0	

RESULTS AND DISCUSSION

The components of the UV-curable ink have been selected to fulfill three main criteria: low volatility (VOC-free), high hydrophobicity and inkjet printability. In order to achieve a high hydrophobic barrier function, an octadecyl-substituted acrylate monomer ($\log P_{ow} = 9.45$) was chosen. The 1,10-decanediol diacrylate simultaneously acts as a crosslinker, as a non-flammable and non-volatile solvent for the solid monomer and the photoinitiator, and as a viscosity adjustment agent. The viscosity of the mixture of monomer and crosslinker was 8.73 mPas at 26 °C.

A schematic outline of the inkjet-based paper patterning process is shown in Figure 1a. The printing and curing of the pattern on the paper surface and of the homogenous layer on the backside of the paper have been achieved in two separate steps. The outline of the microfluidic structure is defined by the printed line pattern on the surface of the paper, which is transformed into the hydrophobic barrier enclosing the microfluidic channels and sensing areas.

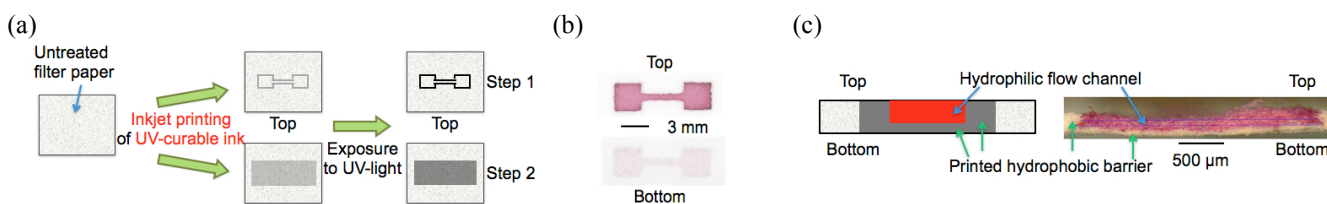


Figure 1: (a) Schematic representation of the patterning process: in the first step, the pattern is printed on the surface of the paper, followed by UV curing. In the second step, a uniform layer of the same ink is printed on the opposite side of the paper, followed by UV curing; (b) Photographs of an inkjet printed pattern on filter paper (colored by food dye solution); (c) Cross-sectional views of an inkjet printed microfluidic channel in filter paper. Left: schematic drawing. Right: optical micrograph.

Figure 1b shows an example of a printed simple model pattern after the application of 3 μL of water colored with a red food dye (amaranth). The bottom view indicates that the liquid does not completely penetrate the thickness of the paper and that the uniform layer of ink printed on the back of the paper acts as a bottom cover for the microfluidic structure. In order to confirm the structure of the channel, a cross-sectional cut through the center of the microfluidic channel connecting the two square areas was analyzed under an optical microscope (Fig. 1c). The approximate depth of the paperfluidic channel measured within the uncertainty of the paper roughness was $137 \pm 9 \mu\text{m}$ ($n=10$), while the thickness of the bottom cover layer was found to be $60 \pm 8 \mu\text{m}$ ($n=10$). A good linear relationship was observed between the nominal line width set in PowerPoint for printing the patterns and the experimentally measured width of the resulting hydrophobic barrier (Fig. 2a), making the inkjet-based patterning method very controllable and reproducible. Because of the capillary force driven spreading of the ink in the paper immediately after printing, the resulting barrier width is inevitably larger than the set printing width. In a further experiment, the minimally required nominal printing width setting to prevent the aqueous sample from leaking was evaluated. Based on the results shown in Figure 2b, it can be concluded that a nominal printing width of 1.0 mm guarantees a complete containment of the aqueous liquid.

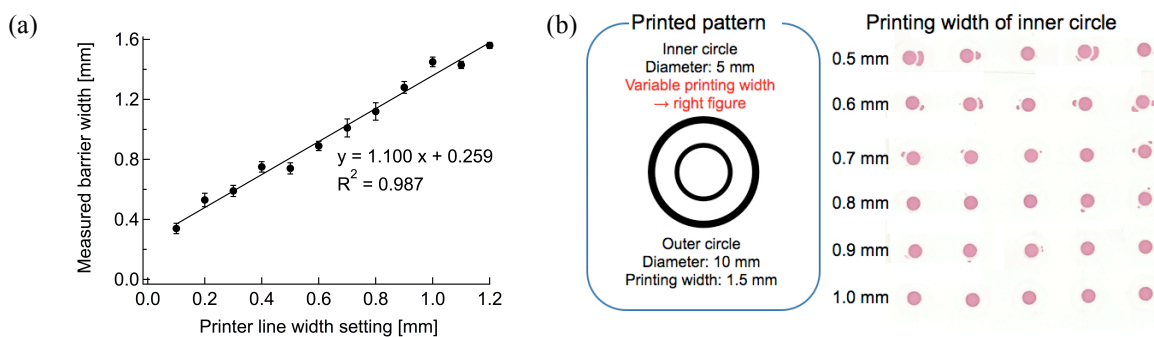


Figure 2: (a) Relationship between the set line printing width and the actually measured width of the resulting hydrophobic barrier (error bars for $n=8$); (b) Minimum required nominal printing width to reproducibly obtain functional hydrophobic barriers (2 μL of aqueous sample were applied to the inner circle).

Given the small amount of ink applied to the paper during printing, it is assumed that the barrier function is caused by hydrophobization of the cellulose fiber network, and not by complete filling of the paper pores with cured polymer. There remains the risk of low surface tension liquids passing the barrier. However, it could be experimentally confirmed that aqueous solutions containing 0.5 mM of nonionic surfactant Triton X-100 (surface tension 31 mN/m) were fully retained by the printed structures.

Furthermore, the thermal stability of the paperfluidic structure was investigated. The printed patterns remained functional for at least one month when stored at room temperature. However, after keeping at 40 °C for 24 h, it was found that aqueous samples were no longer able to pass the narrow channel connecting the two square areas of the printed pattern. It is assumed that the presence of the polymerization inhibitors in the monomer and the crosslinker prevented a complete curing of the printed ink, resulting in a heat accelerated diffusion of free residual hydrophobic compounds until the complete blocking of the microfluidic structure. To overcome this problem, patterning was repeated with inhibitor free inks, resulting in microfluidic structures remaining functional also after storage at 50 °C for 72 h.

Finally, the suitability of the printed paperfluidic structure for chemical sensing was tested for a simple pH sensor. The pH-sensitive ink was inkjet printed into one of the squares of the pattern, while the test buffer solution (4 μ L) was applied to the opposite square. After flowing along the microfluidic channel, the sample induced a pH-dependent color change, which was quantified by digital color analysis using the $L^*a^*b^*$ color space. The corresponding pH-calibration curve is shown in Figure 3.

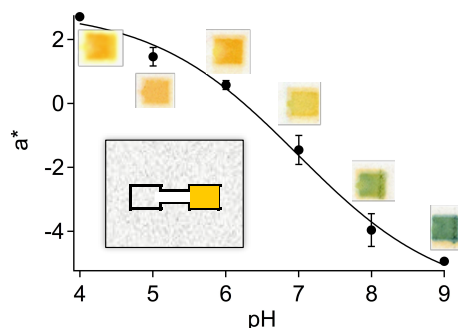


Figure 3: Entirely inkjet-printed paperfluidic pH sensor (inset shows a schematic view of the printed sensor).

CONCLUSION

It has been demonstrated that a VOC-free hydrophobic UV-curable ink composition allows the fast, controllable and reproducible microfluidic patterning of a paper substrate. Besides of being more environmentally friendly and significantly faster compared to inkjet etching, the newly developed patterning approach is to the best of our knowledge the only method so far available for fabricating entire paperfluidic sensors on a single standard manufacturing device. All printing steps, including the deposition of the pH sensing chemistry, have been achieved on an ordinary office inkjet printer.

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