RSC Advances

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Cite this: *RSC Advances*, 2013, **3**, 18811

Fast prototyping of paper-based microfluidic devices by contact stamping using indelible ink†

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Received 7th May 2013,
Accepted 29th July 2013

DOI: 10.1039/c3ra43825b

www.rsc.org/advances

Here we present a fast and cheap prototyping technique for the realisation of paper-based microfluidic devices simply by using a stamp and indelible ink. The proposed mechanism involves contact stamping of indelible ink to laboratory filter paper using a PDMS stamp, which defines the microfluidic structure. It is a cleanroom and washing steps-free method which provides a reproducible method for the production of functional paper-based microfluidic devices in a single step in less than 10 s. The method is fully characterised and the concept has been applied, as a proof-of-principle, for the realisation of a low-cost colorimetric glucose sensor.

Introduction

This paper describes the development of a single step technology for the realisation of paper-based microfluidic devices, where indelible ink is transferred from a PDMS stamp to laboratory filter paper by contact stamping, generating a microfluidic structure in less than 10 s. The indelible ink acts as a barrier for the liquid, which is forced to move inside the stamped microfluidic structure.

Paper-based microfluidics devices have been identified as excellent candidates for low-cost and easy/ready-to-use analytical platforms for Point of Care (POC) diagnostic devices.[1] The potential application of paper-based microfluidic devices for fast health screening of large number of individuals in developing countries, for instance, where sophisticated technologies are poor or non-existent, has been pointed out.[2,3] Paper-based microfluidics could have a positive impact on monitoring medical disorders such as diabetes and AIDS among others, when early diagnosis is crucial.[4] Moreover, they could also play an important role in the development of sensors for on-site environmental monitoring at the point-of-need.[5] For example, fresh water management is of crucial importance for pre-risk assessment of fresh water streams in developing countries, where poor environmental conditions can cause the development of severe human disorders like cholera.[6]

Another interesting aspect of paper-based microfluidic technology is the high compatibility of nitrocellulose with many chemical reagents and biological relevant substances,[7] making paper a suitable substrate for its integration with different analytical techniques, such as electrochemical,[8] electrochemiluminescence,[9] chemiluminescence[10] and colorimetric.[11] Ideally, the most interesting method of detection would involve a colour or light intensity variation, monitored by means of a mobile phone camera.[12] The coupling of such technologies would open new opportunities toward the realisation of a wireless sensor network (WSN) in the field of chemical and biochemical sensing for environmental and health monitoring.[13]

On the fabrication side, new paper microfluidic fabrication protocols continuously appear in the literature. Shen *et al.*[7] recently summarised the *pros* and *cons* of all these protocols. Photolithography[14] and CO_2 laser treatment[15] techniques, for instance, provide high resolution patterning of paper but, on the other hand, the final devices are not flexible and compatible with lateral flow assays, respectively. Whitesides *et al.*[16] also proposed a FLASH photolithography method where there is no need for a clean room, reducing substantially the production costs. Nevertheless, the use of wax for the hydrophibisation of paper normally needs an extra heating step, for wax diffusion in paper, which ultimately can increase fabrication costs.[17,18]

Here we propose a fast and reproducible, one-step fabrication method for the production of paper-based microfluidic devices on laboratory filter paper. The innovation of this

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† Electronic supplementary information (ESI) available: Video 1, Video 2 and Video 3 show the behaviour of the inked papers when water is drop cast on top, respectively for Black Fountain Pen Ink from Noodler's Ink™, Black 214# *Stamp Ink* from HITT Marking Devices Inc. and Lumocolor© Permanent Universal Ink Black from Staedtler Mars GmbH & Co. KG. See DOI: 10.1039/c3ra43825b

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technique lies on the simplicity of its fabrication method, as it requires only a PDMS stamp, with the designed features, along with the paper and ink. In contrast to the view that printing techniques using standard inks are not suitable for the fabrication of paper-based microfluidic devices,[16] we demonstrate that, by taking advantage of the absorbing capability of filter paper, it is possible to create paper-based microfluidics by simple contact stamping. While the use of indelible ink to create microfluidic structures has been reported previously,[19,20] to the best of our knowledge this is the first time that direct contact stamping of paper-based microfluidics has been performed using commercially available ink.

Materials and methods

The microfluidic platform was fabricated using standard laboratory filter paper (Whatman© grades 1 and 595), which adsorbs the ink through its full thickness and defines the borders and so the flow channels of the microfluidic structure. Three different inks were examined: Black fountain pen ink from Noodler's Ink™ (*Product Code*: *19001*), Black 214 *Stamp Ink* from HITT Marking Devices Inc. and Lumocolor© Permanent Universal Black Ink (kindly provided by Staedtler Mars GmbH & Co. KG). Lumocolor© ink viscosity was reduced by using a solvent mixture made of a 1 : 1 v/v ethanol-n-propanol, 10 : 1 ink-solvent mixture. The main attractive characteristics of the listed inks are their hydrophobic nature when dry, and short drying times.

The contact stamping is performed using PDMS stamps (10 : 3 *w*/*w* monomer-curing agent), cured at 60 °C for 8 h. In order to control the volume of ink transferred from the PDMS stamp to the filter paper, the inking of PDMS is performed using a stone ink-pad (2″ × 4″ rectangle from HITT Marking Devices©). Based on the company specifications, the ink-pad is capable of providing a constant ink flow from the porous stone when in contact with the stamp. Moreover, the ink-pad can be used with solvent/acid based industrial inks, which cannot be employed with standard pads. The PDMS stamp was incorporated onto a custom made rectangular prism made of aluminum and a layer of a black ceramic material (see Fig. S1, ESI†). The dimensions of the prism are 4.35 × 5.1 × 7.6 cm (H × W × L) with a total weight of 440 grams. The stamping device (PDMS stamp/rectangular prism) will be referred to as PDMS stamp from now on.

The PDMS negative molds were fabricated through a micromiller (CAT3D, Datron, UK) using 4 mm thick PMMA (poly methyl methacrylate) master as substrate, although other materials could be employed. First, a 3 mm flat endmill was used to shave off 300 μm of material in order to flatten the PMMA surface. Following this, a 600 μm deep pocket of suitable *x* and *y* dimensions was milled out. Using flat endmills of appropriate dimensions, the required negative mold was milled out starting from the bottom of the pocket. All designs were performed using Solid Works© Student version 2012 and converted to the final toolpaths using AutoDesk© HSMxpress.

The inking process was performed by gently pushing the PDMS stamp three times against the ink saturated stone pad. This step was followed by exposing the inked PDMS to air for 5 s, in order to remove any air bubbles formed on top of the PDMS stamp. The presence of air bubbles on the surface of the inked PDMS occurs as a consequence of the air that is expelled from the pores of the stone during the inking process. Finally the PDMS stamp was placed in contact with the laboratory filter paper for three seconds, without the application of any force.

The glucose paper based assay was performed by spotting 2 μL of a fresh phosphate buffered saline (PBS) solution (pH = 7.4) containing 67 U mL^{-1} of glucose oxidase (GOx), 100 U mL^{-1} of Horseradish peroxidase (HRP), 0.3 mM Trehalose, 6 mM 4-Aminoantipyrine (4AAP) and 12 mM is 4-Hydroxybenzoic acid (HBA). All the chemical were purchased form Sigma-Aldrich and used as received. Functionalised paper-based microfluidic devices were dried at RT and used the same day. Photographs of the paper-based microfluidic devices were taken using a Canon PowerShot G7 camera in a controlled light intensity area. After transferring the images to the computer, the analysis of the sensing area colour change was performed using a script and functions on Matlab R2007b© (The MathWorks, Inc., MA, USA).

Results and discussion

Ink selection

During the evaluation of the most suitable ink for the stamping process, the three selected inks (see above) were tested by simply drop casting 1 μL of each onto Whatman© filter paper grade 1. The Noodler's Ink™ sample was found to be unsuitable for stamping the filter paper for two reasons. Firstly, a yellowish ring (most probably due to separation of components in the ink) formed around the outer rim of the ink spot (see Fig. S2, ESI†) and secondly, despite its hydrophobic nature, this ink did not coherent hydrophobic barriers in the paper (see Video 1 ESI†). For these two reasons it was decided not to use Noodler's™ Black Ink for further experiments. In contrast, neither the Black 214 nor the Black Lumocolor© showed this yellowish ring after being drop cast on paper.

After the ink stains were dried at room temperature for 5 min (enough time to assume that the solvent of the inks is completely evaporated), the hydrophobicity of the two inked papers was then characterised by placing a 2 μL drop of DI water on top. Black 214 is described by the manufacturer as a ''*waterproof ink with excellent adhesion*'', while Black Lumocolor© ink is similarly claimed to be a water- and weather-proof ink with drying time of seconds. However, Black 214 did not make the paper hydrophobic enough, displaying similar behaviour to Noodler's™ Black Ink. Furthermore, a yellowish substance leached out from the inked area just after the DI water droplet was absorbed by the

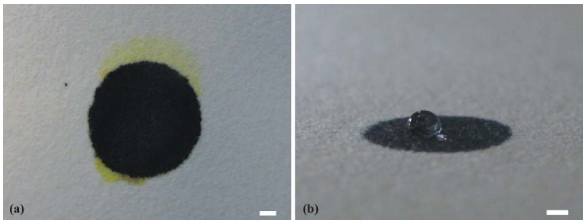

Fig. 1 Whatman filter paper grade 1 spotted with 1 μL of (a) Black 214 and (b) Black Lumocolor© inks. The two pictures show the different behavior of the paper upon placing a 2 μL DI water droplet on top of the ink spots. Coloured components can be clearly seen leaching from the Black 214 sample as the droplet is absorbed and passes from the centre to the outer edge of the droplet by capillary action. In contrast, the droplet sits in a stable manner on top of the Black Lumocolor spot and is still clearly visible after 5 min (scale bar: 1 mm).

paper during testing, Fig. 1(a). In contrast, Black Lumocolor© ink makes the stained regions of the paper very hydrophobic, as the water droplet was able to sit on top of it for several minutes without being absorbed, as shown in Fig. 1(b). These results demonstrated that only the Black Lumocolor© ink is capable of making stained areas of paper suitably hydrophobic, and therefore it was selected for the fabrication of the paper-based microfluidic devices. Videos 2 and 3 of the ESI show the behaviour of the papers when water droplets are placed on inked-regions.

It is well known that a functional paper-based microfluidic device will be produced only if the patterned hydrophobic barrier (normally polymers) penetrates the entire thickness of the paper to the distal surface, otherwise the liquid flow may continue beneath the microfluidic borders making the paper-based microfluidic channel inoperative.[16] Therefore, while these initial tests had confirmed that Black Lumocolor© ink provides a sufficient hydrophobic barrier, it was particularly important to establish if the stamping process was capable of generating a continuous barrier that could fully retain water across the entire thickness of the paper. Fig. 2 (a) and (c) show stamped rings generated using a PDMS stamp with an internal diameter of 3 mm and outer diameter of 4.1 mm, where two different viscosities of Black Lumocolor© ink were used. The ring shown in Fig. 2 (a) was generated using Black Lumocolor© ink as received by Staedtler Mars GmbH & Co. KG, while the ring in Fig. 2 (c) was stamped using a 10 : 1 v/v solution of the Black Lumocolor© ink and a thinning solvent (see materials and methods), in order to obtain a less viscous formulation, without losing substantial ink hydrophobicity for the pattering of paper.

The two inset pictures on the top right of Fig. 2 (a) and (c) show the reverse (distal) side of the stamped ink rings. Comparing these two images, it appeared that the transferred ink ring on the reverse side of the paper was not as effective for the commercial ink formulation. In fact, the inset of Fig. 2(a) shows the ink was not completely absorbed throughout the thickness of the paper, since a less intense and somewhat patchy black colour ring can be seen when compared to the inset picture of Fig. 2(c). Performing contact stamping with the ink as provided does not ensure appropriate fabrication conditions. On the other hand, using only a 10 : 1 v/v

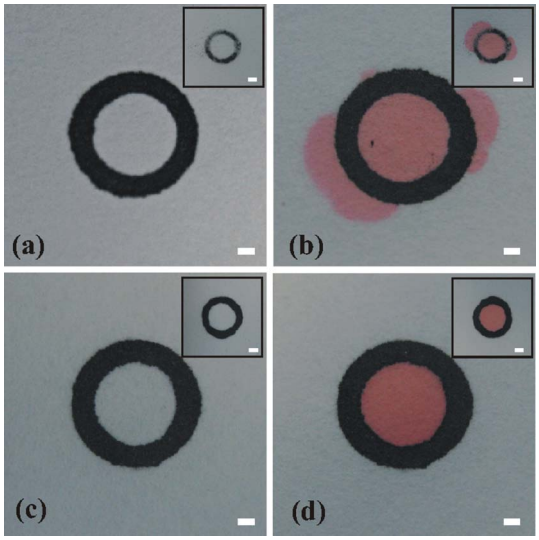

Fig. 2 Rings stamped in Whatman filter paper grade 1 using Black Lumocolor© ink of two different viscosities: used as received from Staedtler Mars GmbH & Co. KG (a, b) and diluted 10 : 1 to decrease viscosity with the thinning solvent (c, d). Pictures b and d show the rings after the addition of 4 μL of red food dye aqueous solution was placed inside the rings. Insertion pictures show the reverse side of the inked paper (scale bars: 1 mm for the main pictures and 2 mm for inset pictures).

formulation of ink/thinning solvent§, suitable contact stamping fabrication conditions achieved a continuous barrier against the diffusion of water from the interior region is provided.

This is verified by comparing Fig. 2 (b) and (d) where, upon the addition of 4 μL of a red food dye water solution, the liquid can be contained inside the stamped ring just when the less viscous ink formulation is employed.

Contact stamping performance

In order to explore the functionality of the paper-based microfluidic devices made using this technique, a series of open straight channels (L × W = 6 × 1.5 cm) were stamped on paper using several PDMS stamps with varying dimensions. In order to define the open channel structures on paper, a pair of borders of equal width was employed. For instance, the channel border pairs were varied from 200 μm to 1200 μm, in steps of 100 μm. This range of border widths was chosen to find the minimum channel border width required to make effective fluidic structures. In addition, Whatman grade 1 and 595 laboratory filter papers were employed throughout these experiments, in order to understand if their different flow rates (respectively medium and medium fast) influence the ink stamping effectiveness.

Two main parameters were considered to be particularly critical for the realisation of useful paper-based microfluidic

§ Experiments using higher volume ratio of ink/thinning solvent, *e.g.* 10 : 2 and 10 : 3 v/v, still provided a hydrophobic barrier against water but, at the same time, higher percentage of border width variation of the transferred ink features were observed. On the other hand, lower volume ratios, did not generate a proper hydrophobic barrier.

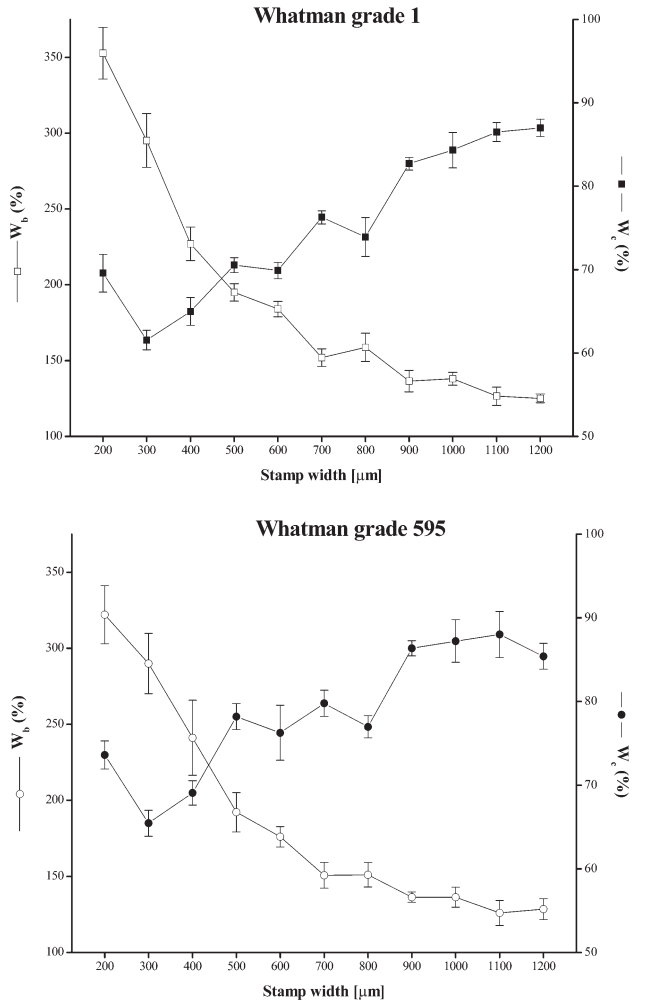

Fig. 3 Percentage of border width variation (W_b) and final channel width (W_c) for open straight channels with different border width on Whatman grade 1 (top) and grade 595 (bottom) filter papers (n = 5).

devices, such as the width of the stamped borders and the final width of the microfluidic channel. Fig. 3 shows the percentage increment of the stamped border width (W_b - left hand side y axis) and the percentage of the achieved channel width (W_c - right hand side y axis) *versus* the width of the employed PDMS stamp. W_b and W_c can be defined as follows:

$$\%W_b = (W_{sb}/W_{PDMS}) \times 100$$

$$\%W_c = (W_{sc}/W) \times 100$$

where W_{sb} is the stamped border width on the paper, W_{PDMS} is the width of the border of the employed PDMS stamp, W_{sc} is the stamped channel width on the paper obtained using a stamp channel width of W, in this case 1.5 cm (schematic representation Fig. S3, ESI†).

The results show that W_b decreases as the stamp width increases. For instance, for both paper types, a 200 μm border of the PDMS stamp, produced features on paper that were over 300% the initial value, *i.e.* >600 μm. Larger channel border pairs produced wider stamped features in absolute terms, but smaller in relative terms. This effect can be explained as the ink loaded on the PDMS stamp, when in contact with the paper, is preferentially absorbed by the fibers of the paper perpendicularly to the applied stamp pressure in an isotropic manner along the paper-air interface. However, this behaviour is less pronounced when the border stamp width is increased. In fact from 900 μm onward a plateau region (between ~137% and ~125%) can be observed for both paper types. In this case the loaded ink still spreads along the paper-air interface, but an increasing proportion of it is also absorbed through the paper thickness, as more ink is available.

As consequence of the increase of the feature border width W_{sb} on paper, the final size of the microfluidic channel width is affected as well, *i.e.* W_c in Fig. 3. In particular as W_{PDMS} increases, the decrease on the stamped channel width is less pronounced. Moreover, this effect gradually levels off when the PDMS stamp is > *ca.* 900 μm. This result is particularly critical if paper-based microfluidic devices of well defined channel widths are required. Therefore during fabrication of paper-based microfluidics using this approach, the effective channel reduction factor has to be taken into account when designing the microfluidic structure. An interesting outcome of these results is that no substantial differences in the behaviour of the two different paper grades was observed, except for slightly higher reproducibility of the features generated with the Whatman grade 1 paper, as the average of the standard deviation is 8.36% and 11.35% for Whatman grade 1 and 595, respectively (smaller error bars, Fig. 3). Therefore, for the rest of the experiments, only Whatman grade 1 was used.

It is important to appreciate that functional fluidic channels were not obtained for all conditions used in these experiments. As mentioned previously, when smaller microfluidic borders are used, most on the ink spreads along the top surface of the paper, without penetrating completely to the reverse side, which allows liquid to leak across the boundary of the defined fluidic channel (for example, see the inset image, Fig. 2(b)). Therefore the volume of ink that can be loaded onto the surface of the PDMS stamp during the inking step is crucial for producing functional structures. Higher volumes of ink are retained with increasing the PDMS stamp width and it was observed that only stamps with borders ⩾1100 μm have an acceptable performance.

Fig. 4 shows a set of video frames recorded when 20 μL of an aqueous solution of a red food dye was placed at the right end of a channel. No leakage was observed over the entire length of the channel, demonstrating the applicability of this technique for the fabrication of paper-based microfluidic devices.

Stamping of cheap paper-based microfluidic glucose sensors

Since the first development of paper-based microfluidic devices, the main explored application has been in the field of clinical diagnosis, where the demand for low cost, robust and reliable systems is very high. As proof of concept, a colorimetric glucose sensor was designed and fabricated using contact stamped paper- based microfluidic device composing of a straight channel of dimensions 10 × 2 mm (L × W) followed by a circular sensing area of a diameter of 1.9 mm.

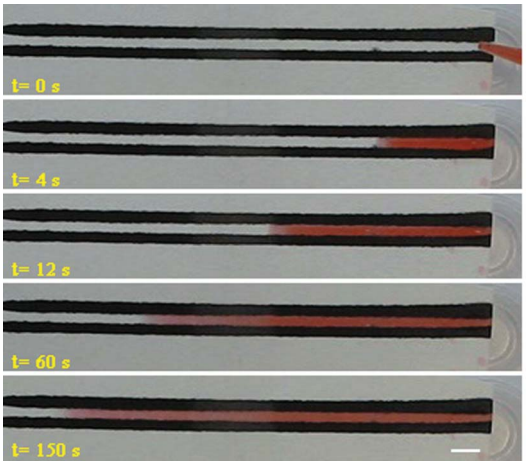

Fig. 4 Sequence of video frames from a μPAD formed on Whatman grade 1 paper tracking the movement of 20 μL of a red food dye solution. Stamping conditions: PDMS stamp border width 1100 μm, Black Lumocolor© ink thinned formulation, average flow speed = 1.3 mm s^{-1} (scale bar: 3.5 mm).

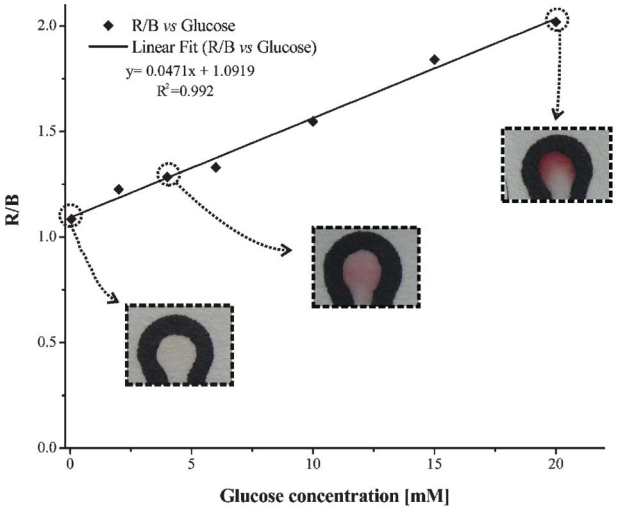

Fig. 5 Calibration curve of the colorimetric paper-based microfluidic glucose sensor device.

The colorimetric glucose assay was prepared as described in the material and methods section. A red coloured dye (λ_{max} = 510 nm) is generated by the cascade of reactions involving a double enzymes system, where the by-product H_2O_2 of glucose oxidation is used as substrate from HRP along with the two dye precursors, 4-AAP and HBA. The stoichiometry of the chromogenic reaction is as follows:

$$\text{Glucose} + O_2 \xrightarrow{\text{GOx}} \text{Gluconic acid} + H_2O_2$$

$$2H_2O_2 + 4\text{AAP} + \text{HBA} \xrightarrow{\text{HRP}} \text{quinoneimine dye} + 4H_2O$$

The developed detection code allows cropping of the area of interest for a given photograph in order to extrapolate the red, green and blue components of the RGB color space for the area of interest. Once the area is selected, a zeros and ones mask of the whole picture is stored and used as a reference to register the position of the pixels of interest (non-zero values of the mask). Using the mask, the red, blue and green components are obtained for each pixel of the region of interest and stored in R, G and B matrixes. Each matrix keeps the corresponding component information for the whole cropped area. From these data, the mode of each matrix is calculated, which is the value that appears most frequently. Finally, mode values are taken as the three final RGB components of the whole area.[20] Fig. 5 shows the variation in the R/B ratio (red and blue component) for digital images taken of the sensor *versus* concentration of glucose, in the relevant physiological range. A linear model was used to fit the experimental data points, giving a limit of detection of 0.15 mM for the sensor in this particular configuration. The inset pictures show the difference in the colour (red) of the assay obtained with 0.05 mM, 4.0 mM and 20 mM glucose samples. In the current manifestation of the sensor, the red coloured dye generated an even colour across the detection area without leaching beneath the paper-based microfluidic device border, proving the feasibility of the proposed fabrication method and indicating its potential application for a wide range of applications.

Lastly, considering only the price of the materials used *i.e.* paper and ink, we estimate the unit production cost as follows: the laboratory filter paper Whatman grade 1 (VWR international) is ~ €1.74 per sheet (460 × 570 mm), of which only a small portion (15 × 10 mm) was required per unit ~€0.001. Black Lumocolor© costs €30 per litre (commercial value provided by Staedtler Mars GmbH & Co. KG); the volume of ink employed for the stamping of the glucose paper-based microfluidic device was calculated to be ~10 μL, which gives a cost of only ~€0.0003. Therefore the average total cost of production of one single paper-based microfluidic device was estimated to be as little as ~€0.0015.

Conclusions

A fast (10 s), cheap (~€0.0015) and simple method to produce paper-based microfluidic devices by contact stamping using a PDMS stamp has been developed. Black Lumocolor© ink can form effective hydrophobic barriers that constrain the diffusion of water within the boundaries of the ink pattern. The contact stamping performance was characterised using open straight channels, revealing that operative microfluidic device can be obtained only using stamps with borders ⩾1100 μm.

Compared to other reported paper-based microfluidic device fabrication technologies, contact stamping is capable of providing an easy way to produce paper-based microfluidic structures without sophisticated infrastructural requirements. For instance, in developing countries replicas of paper-based microfluidics for diagnostic purpose could be produced by non-especially trained staff employing the contact stamping technique, bearing in mind that only an ink-pad, indelible ink and a PDMS stamp, with the designed features, need to be

provided. Furthermore, for mass production of paper-based microfluidic device sensors similar approaches to the one presented here can be applied, such as the roll-to-roll and pad printing technologies. In this direction, future research will follow towards a more automated printing fabrication process.

Acknowledgements

This work was supported by Science Foundation Ireland under CLARITY CSET award (grant 07/CE/I1147). Thanks to Staedtler Mars GmbH & Co. KG for providing the Lumocolor® Permanent Universal Black Ink.

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