Cellulose
DOI 10.1007/s10570-013-9991-6

COMMUNICATION

Patterned superhydrophobic paper for microfluidic devices obtained by writing and printing

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Received: 28 January 2013 / Accepted: 5 July 2013

Abstract This work outlines inexpensive patterning methodologies to create open-air microfluidic paper-based devices. A phase-separation methodology was used to obtain biomimetic superhydrophobic paper, hierarchically composed by micro and nano topographies. Writing and printing are simple actions that can be used to pattern flat superhydrophobic paper with more wettable channels. In particular, inkjet printing permits controlling the wettability of the surface by changing the darkness of the printed regions. The difference between capillary forces provides the possibility to control and drive liquid flows through the open path lines, just by titling the piece of paper. Additionally, maintaining a continuous flow, it is possible to direct the liquid at different volumetric rates in a horizontal position along non-linear channel paths printed/written over the surface.

Keywords Superhydrophobicity · Biomimetic · Patterned paper · Open-air microfluidic devices

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Introduction

Superhydrophobic (SH) surfaces are a widespread field in scientific research. By definition, these surfaces exhibit an extreme tendency to repel water droplets and are characterized by an apparent water contact angle (WCA) higher than 150° (Guo et al. 2011; Roach et al. 2008). Non-wettable surfaces were first found in nature with the observation of biological systems: the lotus leaf is the archetypal example of superhydrophobicity (Bhushan 2012; Barthlott and Neinhuis 1997; Neinhuis and Barthlott 1997). Besides non-wettable behavior, water droplets can also easily roll off on the lotus leaf surface, presenting a contact angle hysteresis lower than 10° (Guo et al. 2011; Roach et al. 2008). Barthlott and Neinhuis (1997) (Neinhuis and Barthlott 1997) reported the nano and micro hierarchical organization of the surface topography of the lotus leaf as the principal leading factor of superhydrophobicity. Henceforth, many studies have demonstrated that to produce artificial SH surfaces it is necessary to fulfill two requirements: roughness topography and low surface energy (Bhushan 2012; Bhushan et al. 2009; Jiang et al. 2005). Paper is essentially composed of fibrous cellulose. The hydroxyl groups of this polysaccharide make the material hydrophilic (Zhao and van den Berg 2008). The modification of paper to render the surface more hydrophobic, or even SH, permits extending its applicability. Increasing water resistance could be profitable in order to use paper in devices able to sustain the flow or the presence of water over the surface, such as in microfluidic applications.

Microfluidic devices have been largely reported for biomedical uses (Hsu et al. 2004; You et al. 2012); the reduction of consumption of expensive reagents and the high surface-to-volume ratio are some of the most reported advantages. Different purposes have been suggested for these devices such as cell based-biosensors (Cai et al. 2002) and biochemical analytical systems (Hofmann et al. 2002). Unlike traditional closed-microfluidics, open-air microfluidics (devices that do not present a roof) can overcome problems like bubble trapping, the impossibility to access the surface directly and the complex fabrication techniques employed (You et al. 2012; Xing et al. 2011). There are different strategies to confine the liquid flow that can be used in microfluidic manufacturing; one of the most advantageous is the surface-tension driven force using a selective hydrophobic/hydrophilic contrast (Mark et al. 2010; Zhao et al. 2002). Different processes can be applied to obtain structured surfaces exhibiting patterns with different wettabilities; for instance, Gau et al. (1999) developed an open microfluidic device patterning a hydrophobic silicone rubber or a thiolated gold substrate with more wettable regions, using a thermal vapor deposition of magnesium fluoride (MgF_2) through appropriate masks. Progress in microfluidic devices has been achieved by adapting the special features observed in the lotus leaf (Stratakis et al. 2011; Domachuk et al. 2010; Runyon et al. 2004): Oliveira et al. (2010) suggested the fabrication of open microfluidic devices through the surface modification of a patterned SH polystyrene; Xing et al. (2011) reported an unconventional droplet-driven system on SH-patterned polydimethylsiloxane (PMDS) surfaces using a lithographic methodology. The use of paper to produce such devices could bring new advantages, such as better prices and availability. The possibility of writing and printing on paper permits changing the local wettability on a sub-millimetric scale range.

Among recent works, inkjet and wax printings are the most common methodologies employed to pattern the paper surface (Li et al. 2010, 2012; Lu et al. 2009). Droplet handling and controlling operations using SH paper substrates were first suggested by Balu et al. (2008) through printing hydrophilic patterning domains. However, such processes have never proposed using patterned SH paper in the area of microfluidics. Using a simple phase separation process to fabricate SH paper substrates (Obeso et al. 2013), we present straightforward methodologies to modify the resulting substrates to fabricate inexpensive open-air microfluidic devices.

Materials and methods

We used a 7.5 % (w/v) poly(hydroxybutyrate) (PHB) (Biomer) in chloroform solution to soak pieces of commercially available cartridge paper (Pontus®), previously treated with chloroform (Sigma-Aldrich), to remove any additives. After 6 h, the PHB-soaked paper surfaces were rapidly immersed in a coagulation bath composed by 85/15 (v/v) of ethanol (Pancreac) and water for 12 h. In the end, the samples were dried at room temperature.

Wettability measurements were performed with an OCA 15+ goniometer from DataPhysics (Germany) using the sessile drop method. The shape and WCA values were recorded using the SC20 software, 5 s after depositing a 3-µl water drop (HPCL grade) onto the sample surfaces. At least five measurements were carried out for each condition. All results are presented as mean and standard deviation. The surface morphology was accessed by scanning electron microscopy (SEM) analysis using a Leica Cambridge S-360 SEM [Leica Cambridge (UK)]. All samples were pre-coated with a thin conductive layer of sputtered gold. Different magnifications were used with an accelerating voltage of 5 kV.

We wrote different paths onto SH surfaces, using either coal pencils and water-based markers, purchased from UNO®, or a commercially available Inkjet Printer (Epson Stylus SX105). To study the liquid behavior onto the patterned SH substrates, we dispensed colored water solution (a couple of hundreds of microliters) onto the open-channel/path domains and carefully tilted the substrate. Additionally, different volumetric flows of colored water were also pumped along hydrophilic channels patterned on the SH paper surfaces using a peristaltic pump. These substrates were patterned using the inkjet printer, with a mid intensity color, and shaped as curved open lines.

The representative images were taken with a Panasonic photographic digital camera (Lumix FS14).

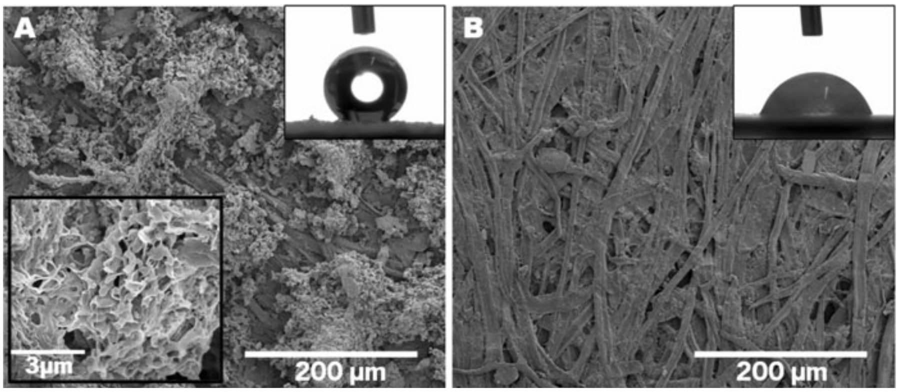

Fig. 1 Representative SEM images of **a** the SH paper surface and the corresponding magnification, and **b** commercial cartridge paper used to prepare the substrates. The *inset* images show representative profiles of 3-μl water droplets over the surfaces

Results and discussion

During the modification of the surface of the paper with PHB, the thermodynamic of the system (PHB solution and coagulation bath) was destabilized by the mass transfer occurring on the interface between the solvent and the non-solvent (Zhang et al. 2008; Yuan et al. 2007; van de Witte et al. 1996). This triggered a liquid-liquid demixing and the consequent polymer separation, forming both poor and rich polymer phases; the PHB-rich phase aggregates around the polymer nuclei precipitated in the PHB-poor phase (Zhao et al. 2005; Wei et al. 2010). This leads to the formation of PHB asperities distributed over all the surface of the paper; see Fig. 1a. In the magnification of Fig. 1a, it is possible to distinguish some sub-micrometer sphere-like structures deposited on the surface. The rough structure of SH paper, hierarchically organized at nano- and micro-scales, is quite distinct from the smooth fiber structure of the original commercial cartridge paper; see Fig. 1b. The insets of the figures reveal a WCA of 155.8° ± 2.84° for the rough paper surface and 70.5° ± 2.51° for the original paper. The SH paper presents a contact angle hysteresis of 1.1° ± 0.10°. The low adhesion of the water droplets to the SH surfaces suggests that the Cassie-Baxter model would be the most adequate to explain the repellency properties of the obtained substrate. Following this model, we consider that the liquid is suspended by air pockets, which are trapped between the rough structures (Cassie and Baxter 1944). The area fraction of the liquid–solid contact is given by:

$$f = \frac{\cos\theta^* + 1}{\cos\theta + 1} \quad (1)$$

where θ^* is the WCA of the rough paper surface and θ is the WCA of smooth PHB surface. Taking $\theta = 87.0°$, we can estimate $f = 0.084$.

To create wettable open-air channels on the SH paper, we developed simple methods to pattern the surface, based on the writing possibilities offered by paper. Figure 2 presents the WCA of the different strategies explored, and the correspondent insets show

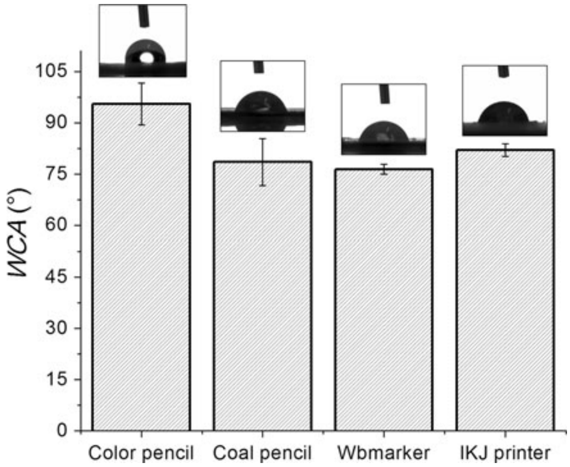

Fig. 2 WCA of a 3-μl water droplet dispensed on the different patterned domains of SH paper-based substrates with the corresponding representative profiles. A colored pencil, coal pencil, water-based marker (Wbmarker) and inkjet printer (IKJ printer) were used to create the patterned regions

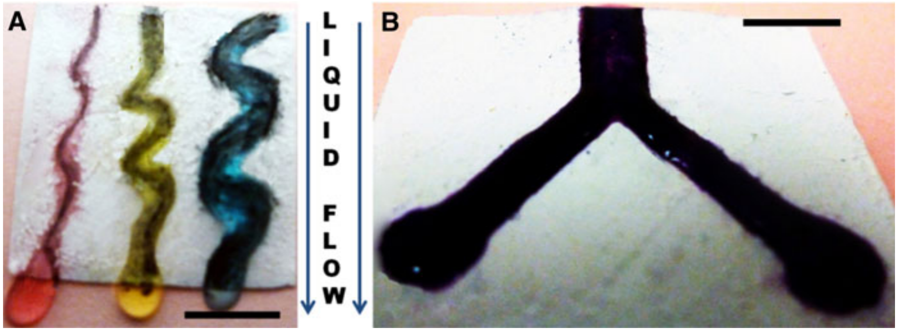

Fig. 3 Representative images of colored water flowing along wettable lines: **a** *curved lines* written with a coal pencil onto **a** the SH paper substrate with distinct widths; **b** *branched line* written with water-based marker on a SH paper substrate. The *scale bars* are 10 mm

the representative images of the interfacial drop-surface contact.

The wettabilities of the written areas using coal pencils and water-based markers are able to create a significant contrast with the surrounding SH areas. Figure 3 shows representative images of the open lines written with different shapes and widths. When colored water flows along the channel, the liquid is constrained between its limits. In Fig. 3a, it is possible to distinguish liquid flows along complex patterned paths with different widths produced with a coal pencil: the width of the stream increases with the width of the printed line. The more acute the curves of the path are, the higher the possibility of the liquid crossing the limits of the written line is. The definition of the water stream is within the millimetric scale range. The irregularities that are detected should be related to the presence of graphite microparticles that are released outside the main lines during the writing. Such residues are hydrophilic and contribute to the irregular wetting observed. For the patterning with a water-based marker, we tested the behavior of the liquid onto a branched-like geometry. This process enabled increasing the wettability of the written regions again (Fig. 2). As a consequence, the liquid flows along the patterning without wetting the remaining area (Fig. 3b). We believe that not needing masks or specific equipment, the simplicity, speed, energy saving and low cost are important advantages when comparing this with traditional patterning techniques.

Inkjet printing has already been described in the literature as suitable to create patterned paper surfaces (Abe et al. 2008, 2010; Li et al. 2010; Khan et al. 2010), mainly using solutions, solvents and proteins as modifying agents. We extend in this work with this simple approach to printing SH paper, which after modification presents a WCA of 82.0° ± 1.89° upon patterning with a mid-color intensity. The liquid ink is distributed at small volume rates through a piezoelectric material in an ink-filled reservoir behind a nozzle. The piezoelectric material changes the form when a voltage is applied to the equipment, providing a pressure in the fluid able to propel it from the nozzle. We used solvent inks in which the main ingredient is a volatile organic compound. Due to the solvent evaporation, it is possible to deposit the ink conveniently on the SH surface. Using different color grades, from lightest to darkest, it is possible to control the wettability: with the use of darker colors the surface becomes more wettable; see Fig. 4. We compared the liquid flow on straight lines (Fig. 5a) and curved lines (Fig. 5b), induced by the effect of gravity. It can be seen that even with the curved lines, the liquid can follow the patterned paper reasonably. Additionally, we investigated the ability of the patterned SH paper substrates to enable different volumetric flows moving along a curved hydrophilic path. In this case, the flow

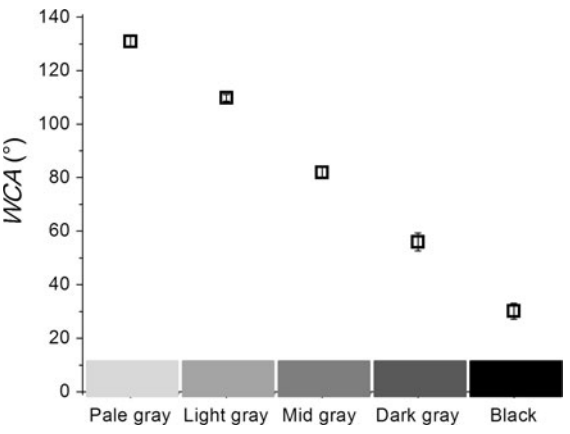

Fig. 4 WCA of a 3-μl water droplet dispensed on printed patterned domains of SH paper-based substrates with different intensities of *gray color*

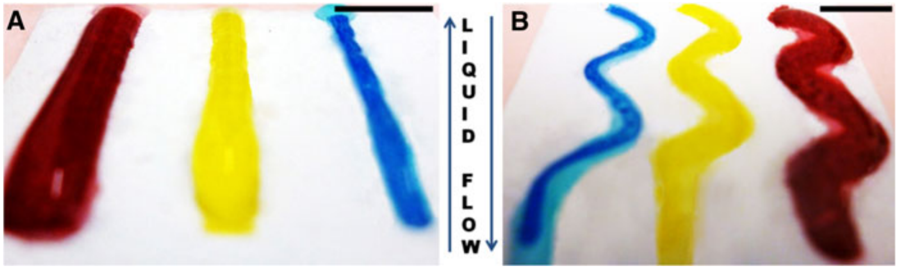

Fig. 5 Representative images of colored water on wettable open **a** *straight curved lines* and **b** *curved lines* with distinct thicknesses printed with an inkjet printer onto an SH paper substrate. The *scale bars* are 10 mm

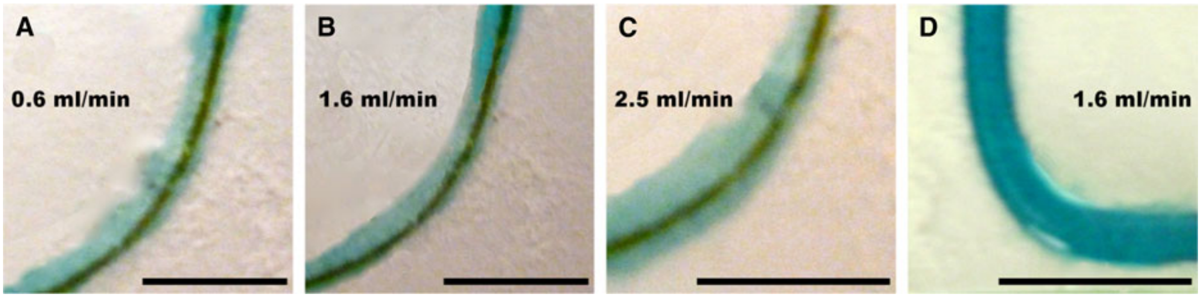

Fig. 6 Streams of colored blue water moving along a hydrophilic channel patterned on an SH paper surface, with different volumetric rates (ml/min): **a** 0.6 ml/min, **b** 1.6 ml/min, and **c** 2.5 ml/min, **d** stream of colored *blue* water moving along a larger hydrophilic channel patterned on an SH paper surface. The *scale bars* are 10 mm. (Color figure online)

of water was controlled by a peristaltic pump. For a flow of 0.6 ml/min (Fig. 6a), or even 1.6 ml/min (Fig. 6b), the liquid follows the wettable path. For a volumetric flow $\geq$2.5 ml/min, we no longer had good spatial control over the liquid flow; see Fig. 6c. All the above-mentioned cases were achieved printing 0.5-mm-wide lines. We applied a 1.6-ml/min volumetric flow onto a 1.5-mm-wide hydrophilic line; as expected, the control of the liquid flow increases with the increase of the line width, as the space available for the water flow is bigger; see Fig. 6d.

Conclusion

Writing and printing are simple and effective tools to pattern SH paper substrates with more wettable domains. For the particular case of using inkjet printing, it is possible to control the wettability of the printed regions by playing with the intensity of the deposited color. By writing or printing wettable lines, it is possible to drive and confine a liquid flow along the predeterminated path. These findings add to the growing body of information on the development of low-cost, straightforward and fast patterning techniques in the microfluidic industry, namely for open-air microfluidics. This could extend the use of paper in the development of new devices for biological and biomedical diagnostics and analysis.

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