



Patterning of wettability for controlling capillary-driven flow in closed channels

Muireann O'Loughlin, Craig Priest*, Mihail N. Popescu, John Ralston

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia

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ABSTRACT

Glass capillaries are prepared with well-defined regions of tuneable wettability on the interior walls using an inexpensive and simple approach. A homogeneous layer of hydrophilic TiO₂ nanoparticles is adsorbed on the capillary wall and chemically hydrophobized using octadecyltrihydrosilane (OTHS). The hydrophobic OTHS monolayer is then patterned by spatially-selective removal of the OTHS via TiO₂-catalysed decomposition by ultraviolet irradiation. By patterning the capillaries with hydrophilic-hydrophobic rings, modulated penetration of a liquid (glycerol, in this study) can be achieved. For given wettability contrast, the penetration dynamics and equilibrium rise heights are very sensitive to the characteristic length-scale of the pattern, and may offer greater, time-dependent sampling control in fluidic devices.

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1. Introduction

Precise control of liquid flow within microchannels is central to the function of microfluidic systems [1]. Chemical, biological and medical applications of microfluidics require transport, positioning and mixing of liquid samples [2], which are generally carried out using active control through mechanical pumping [3,4], electro-wetting [5], electroosmosis [6], or external magnetic fields [7]. These techniques require additional energy sources or equipment, such as mechanical pumps and power supplies, which significantly increases the size, cost, and complexity of the microfluidic device. Large, expensive equipment is not always feasible for microfluidic applications, especially where portability is required, which has increased the popularity of passive actuation methods [8]. In this article, we demonstrate the fabrication of periodic millimetre-scale wettability patterns on the inner walls of capillaries to passively control microfluidic sampling via capillary-driven penetration of liquids.

Altering the wettability of the bounding surfaces to drive and control liquid flow within microchannels is an alternative approach to mechanical pumping and valving. Chemical patterning of wettable and non-wettable patches on the walls of channels enables controlled pressure drops, gated flow regions, and control of flow pathways. Recently, several studies have reported methods to control liquid flow in microchannels using wettability-patterned surfaces [1,9–14]. For example, Liang et al. fabricated a thermally active coating for glass, consisting of a cross-linked poly(*N*-isopropylacrylamide) layer. The authors showed that the wettability

(contact angle of water) of this surfaces could be modified from a strongly hydrophilic to a weakly hydrophilic one when the temperature was varied within a 30 °C range [12]. In other work, Suk and Cho have shown that patterning hydrophobic and hydrophilic stripes on planar surfaces and aligning them in a slit-like geometry (parallel plates) can lead to a surface pattern induced control over the speed of capillary-driven flow [1]. Caprioli et al. developed a photoactive capillary through which the contact angle of water in a cyclic olefin copolymer microchannel could be varied by up to 20° via ultraviolet illumination [9]. By using chemical patterning to imprint wettable lanes on a non-wettable background substrate, Zhao et al. achieved surface directed liquid flows in microchannels [14]. Using similar methods, pressure sensitive switches and gas-liquid microreactors without mechanical controls can be created [15–19].

Most of the methods proposed so far for patterning hydrophobic and hydrophilic regions on the inner walls of microchannels first modify the surfaces in the selected areas and then require mild or contact bonding techniques to seal the device [20–22]. These exposed surfaces (as well as the open channels) can be easily modified using a host of methods because they are directly accessible [23,24]; however, once bonded there is little flexibility left for further modification of the chemical pattern and/or wetting properties. Moreover, the precise alignment of the patterned features at the small scales typically encountered in microfluidics upon bonding the device can be difficult and the risk of contamination of, or damage to, the patterned surface chemistry remains significant.

In contrast, methods which allow *in situ* modification of capillaries or bonded channels have a number of advantages. There are no bond-alignment issues or concerns about maintaining the integrity of the chemistry during bonding. All the microchannel

* Corresponding author. Fax: +61 (0)8 8302 3683.

E-mail address: Craig.Priest@unisa.edu.au (C. Priest).

walls can have the same chemistry, which is important in some applications, e.g., Laplace pressure valves [25]. Furthermore, some post-bonding patterning techniques allow the reuse of microfluidic devices that are expensive or difficult to fabricate. In these cases, the internal surface functionality is designed in such a way that it can be chemically stripped from the channel walls under flow and retreated accordingly. For a recent review of post-bonding methods for microchannel patterning see Ref. [26]. The simplest strategy for chemical patterning inside sealed channels involves the use of multiphase laminar flow [27]. However, for this method the number of pattern designs is severely limited by the number of flow profiles that can be generated within a given channel geometry.

Here we use an *in situ* modification method to chemically pattern the inner walls of capillaries for the modulation of spontaneous liquid penetration. The method has no requirement for special instrumentation or harsh processing conditions, allows the pattern geometry and wettability contrast to be easily tuned, and is compatible with *in situ* “erase and re-draw” of the pattern. Our approach to prepare capillaries with well-defined patterns on the inside wall is to coat them with hydrophilic TiO₂ nanoparticles, apply a second, hydrophobic coating with self assembled monolayers (SAMs) of octadecyltrihydrosilane, and carry out a simultaneous photocatalytic patterning and wettability tuning of the patches by selective UV irradiation through a photomask for various exposure times. As a proof-of-principle for liquid manipulation, we fabricate capillaries with chemically patterned rings of contrasting wettability and analyse the changes in the capillary rise of glycerol with respect to that in untreated capillaries with homogeneous inner walls. This study builds upon previous work by Takei et al. [28], who studied Laplace valves with contact angles from 9° to 168° to valve flow of liquid in microchannels. Here, we have employed a more modest wetting contrast (contact angles below 90°) to achieve modulation of capillary-driven flow, rather than creating Laplace valves that stop the meniscus completely. Based on the method of Takei et al., we show that the wettability can be fine-tuned with a typical precision of 3° in a reasonable manner and use periodic patterns (rings) to control the kinetics of the liquid penetration in the various regions of the capillary.

The paper is organised as follows. Section 2 describes the materials and methods used to fabricate and design chemically patterned capillaries. The fabrication and characterization of the patterned capillaries and several proof-of-principle experiments showing modulation of liquid penetration in these patterned capillaries are discussed in Section 3. The conclusions stemming out of this work and a few remarks on the potential developments are presented in Section 4.

2. Experimental

2.1. Fabrication of patterned capillaries

A dispersion of titanium dioxide (Anatase, 15 wt%, 15 nm) particles in water was purchased from Nanostructured and Amorphous Materials. The zeta potential of the titanium dioxide nanoparticles was measured using a Malvern Zetasizer Nano. To determine the isoelectric point of the TiO₂ nanoparticles a standard zeta potential versus pH sweep was carried out. Electrolyte solution (10⁻² and 10⁻⁴ M analytical grade KCl, with a pH adjusted using analytical grade KOH or HCl solutions) was circulated through the cell and the zeta potential as a function of the pH was measured. From these results an optimal pH for TiO₂ nanoparticle adsorption was chosen (pH = 4), see Results and Discussion section for details.

Precision borosilicate glass capillaries from Friedrich and Dimmock (radius 450 μm) were used as substrates. The inner and outer radii were measured for each capillary used to minimize any uncertainty in the further data analysis. Using optical microscopy, we checked the values of the radius along the length, including both ends, of the capillary, and found no significant differences between measurements at various points, therefore we infer that the inner and outer radii are constant, within ±3 μm, along the whole length of the capillary.

To clean the capillaries before experiments, 8 ml of 2 M potassium hydroxide (90%, Chem-Supply Australia Laboratory Reagent) was flowed through the capillary at a rate of 1 ml/min using a syringe pump. This was followed by rinsing with the same amount of ultra pure water (pH of 5.6 ± 0.1, resistivity of 18.2 MΩ · cm, and surface tension 72.8 mN/m at 22 °C, NANOpore Diamond Barnstead system) at the same volumetric rate. Finally, the capillaries were dried in N₂. This treatment resulted in a completely hydrophilic surface (water contact angle of 0°). Coating of the capillaries with TiO₂ nanoparticles was carried out immediately after cleaning. The TiO₂ colloidal dispersion was introduced into the capillary using a syringe pump (KD Scientific) at a rate of 200 μm/s. The dispersion remained in the capillary for 10 min and was refilled six times to maximise adsorption of the TiO₂ particles via electrostatic attraction on the capillary wall. The capillaries were then annealed for 5 h (see Fig. 4, Section 3).

Surface imaging of both TiO₂ coated and bare capillaries, respectively, was performed with a NanoScope III atomic force microscope (AFM; Digital Instruments, Santa Barbara, CA) in tapping mode (results presented in Results and Discussion section). Ultrasharp silicon SPM cantilevers (NT-MDT, Moscow) were used to obtain topographic information about the surfaces. Root-mean-square (rms) roughness and the actual surface area were obtained using the AFM software. A scanning electron microscope (PHILIPS XL30 FEGSEM) was also used to image both TiO₂ coated and bare surfaces. The samples were mounted on a stub with double-sided conductive tape and coated with carbon to avoid surface charging (which would interfere with the secondary electron imaging).

Time of Flight Secondary Ion Mass (ToF-SIMS) analysis of the chemically patterned OTHS-TiO₂-glass plate was carried out using a PHI TRIFT V nanoToF ToF-SIMS equipped with a 30 keV Au⁺ liquid metal ion gun, using “bunched” instrument settings to optimise mass resolution. Positive and negative ion ToF-SIMS spectra were acquired while maintaining a primary ion dose less than 10¹² ions/cm² to ensure static SIMS conditions. An electron flood gun and neutralisation 10 keV Ar⁺ gas gun were used for dual charge. Samples were analysed under vacuum, typically of 2 × 10⁻⁶ Pa or better. Positive and negative ion ToF-SIMS spectra were calibrated to the CH₃⁺, C₂H₅⁺ and C₃H₇⁺ peaks and CH⁻, C₂H⁻ and Cl⁻ peaks, respectively, before further analysis. Five spots were analysed on each of the sample used in this study.

Titania-treated surfaces were hydrophobized using OTHS (octadecyltrihydrosilane, 97% Sigma Aldrich) to change the wettability. Freshly cleaned TiO₂-coated capillaries were immersed in a fixed concentration (10⁻³ M) of OTHS in cyclohexane (A.R. grade, 99%, Chem-Supply Australia) and left overnight (24 h) at room temperature. The contact angle of water on such surfaces was measured to be 90° ± 3°, which confirmed that a hydrophobic surface was obtained. Since the self-assembled monolayer (SAM) of OTHS on titania is chemically stable and mechanically robust [29], we were able to proceed with a final step of cleaning by washing thoroughly with cyclohexane and drying under a stream of high purity nitrogen without affecting the OTHS coating.

TiO₂ is a well-known photocatalyst for the oxidation of organic compounds by ultra-violet radiation [30–33]. We have used this property to partially or fully remove, in a controlled way, the OTHS

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