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Microchannels Constructed on Rough Hydrophobic Surfaces

A microchannel was constructed between two glass slides, taking advantage of their surface properties. The channel geometry was defined by a line that was previously printed on the slide surface using a highly water-soluble liquid [2-(2-ethoxyethoxy)ethanol] as the ink. Water, which acted as the working fluid flowed along this line. Although the channel did not have any sidewalls, the water was fixed along the printed line due to the large contact-angle hysteresis of the slide surface whose properties were rough and hydrophobic. Such roughness was more advantageous over smoothness due to the large contact-angle hysteresis of water and the good wettability of the ink. Using a syringe pump, the water was able to continuously flow through a 1 mm wide and 0.13 mm deep channel without flooding.

Keywords: Microchannel, Surface, Contact angle, Rough hydrophobic surfaces

Received: January 31, 2008; *accepted:* May 22, 2008

DOI: 10.1002/ceat.200800060

1 Introduction

Miniaturized systems for chemical/biochemical analysis and synthesis have attracted much attention in recent years [1–3]. These systems often have small pipes called microchannels in which various chemical processes, such as reaction, extraction, and separation, are carried out [4]. Such a channel can be constructed on a glass substrate using micromachining techniques, e.g., photolithography and etching [5]. A working fluid, such as water, is confined in the channel by the top and bottom layers, and two sidewalls when the channel has a rectangular cross-section. Thus, the channel is normally described as a pipe with a small cross-sectional area.

However, some groups have recently reported surface-directed channels that are not pipes [6–13]. These channels were constructed between parallel top and bottom glass slides separated by a spacer. The slide surface was chemically treated to make it hydrophobic generally, but hydrophilic along a narrow line. Such a contrast in the surface properties enabled water to be confined along this line. Therefore, water introduced from the end of the line flowed along the line, and a channel filled with water was formed. As a consequence, this type of channel did not have any sidewalls.

The advantages of these surface-directed channels over the pipe-type channels can be summarized as follows. Surface-directed channels can be constructed without etching the glass

substrates with hydrofluoric acid, which is a dangerous chemical. Since the etching process is removed, one can cut the manufacturing costs and save time. In addition, although small pipes are easily clogged, surface-directed channels may be free of clogging because they have no sidewalls.

A type of surface-directed channel that can be constructed using an inkjet printer has been devised by the current author [14, 15]. This channel was constructed using the following procedure. Two glass slides, which had rough and hydrophobic surfaces, were prepared. A line that would eventually act as the channel was printed on each surface by an inkjet printer using a highly water-soluble liquid as its ink. The glass slides were stacked with a thin spacer inserted between them. Water injected between the slides flowed along the printed line. Thus, a channel filled with water formed along the line. In addition, this channel could be easily erased by rinsing the slide surface with acetone or methanol, and another channel could be reconstructed using the same slide. Therefore, this type of channel is referred to as a “refreshable microfluidic channel.”

The formation mechanism of the refreshable channels seems to be similar to that of surface-directed channels. However, because the ink used in the above procedure is a highly water-soluble liquid, the printed line soon disappears after the channel is filled with water. The question of how to fix the water along a line that has already disappeared has to be answered? Some other mechanism should be considered and this factor is studied in this work. The reasons why a rough surface is used and the required surface properties are explained. In addition, a method is devised to cause the water to flow without flooding, even though the channel does not have any sidewalls.

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2 Experimental

Two glass slide pieces as shown in Fig. 1a) were ground with an abrasive (220-mesh aluminum oxide), and treated with octadecyltrimethoxysilane (ODS) in order to make the slide surfaces hydrophobic [15]. The surface texture parameters, R_a (the arithmetical mean deviation of the roughness profile) and RSm (the mean width of the profile elements) of the slide were 1.70 μm and 77 μm , respectively. These parameters were measured using a stylus instrument (SJ-201R, Mitutoyo, Kawasaki, Japan) according to method JIS B 0601:2001.

As shown in Fig. 1a), a line typically having dumbbell-shaped ends was printed on each slide using an inkjet printer (PM-G730, EPSON, Suwa, Japan), which was equipped with an ink cartridge filled with 2-(2-ethoxyethoxy)ethanol (EE) as the ink. This line later became the channel. The line printed on the bottom slide was elongated outward by 3 mm from the

top slide edge. This seemed to be useful to successfully fill the channel with water.

The slides were then stacked using a 0.13 mm thick spacer, and Teflon tubes (inner/outer diameter = 0.1/0.4 mm) were inserted into small notches previously created at both ends of the top slide, Fig. 1b). These Teflon tubes were connected to two syringes installed on a syringe pump (ESP-64, Eicom, Kyoto, Japan) as shown in Fig. 1c). Water injected into the notch flowed along the printed line and a channel filled with water formed. When water continuously flowed through the channel, one syringe sucked up the water from one end of the channel, and the other syringe simultaneously supplied water to the other end.

3 Results and Discussion

3.1 Mechanism for Fixing Water Along the Desired Line Despite the Lack of Sidewalls

In order to clarify the mechanism for fixing water along the desired line despite the lack of sidewalls, the advancing and receding contact angles, θ_A and θ_R , respectively, were measured using water drops on both rough and smooth glass surfaces previously treated with ODS. The data is summarized in Tab. 1. Based on these data, one can predict the condition under which water filling a straight channel does not slip down when the piled glass slides are set upright, Fig. 2. Since the gravitational force working on the water in the channel must be lower than the surface tension along the three-phase contact line, this condition can be written as Eq. (1):

$$wLd\rho_{\text{water}}g\sin\alpha < 2L\gamma_{\text{water}}(\cos\theta_R - \theta_A) \quad (1)$$

where w , L , d are the width, length, and depth of the channel, respectively. In addition, ρ_{water} is the water density ($1.0 \cdot 10^3 \text{ kg/m}^3$), g is earth's gravity (9.8 m/s^2), α is the tilt angle (90° in this case), and γ_{water} is the water surface tension ($7.3 \cdot 10^{-2} \text{ Nm}$) [16]. If $w = 3 \text{ mm}$, $d = 0.13 \text{ mm}$, and the glass slide has an ODS-treated rough surface (see Tab. 1 for the θ_A and θ_R values of this surface), Eq. (1) is satisfied, and predicts that the water can resist slipping down. In fact, this prediction can be confirmed by constructing such a channel, as shown in Fig. 2b). On the basis of Eq. (1), one can say that the water in the channel is fixed along the desired line due to the difference between θ_A and θ_R , i.e., due to contact-angle hysteresis.

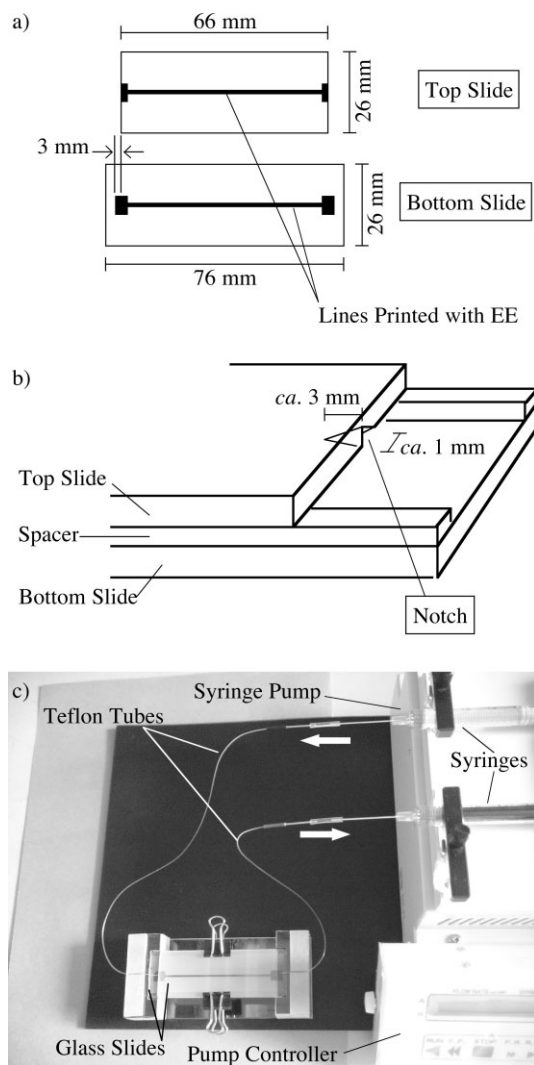


Figure 1. (a) Top and bottom glass slides, (b) the notch into which a Teflon tube was inserted, and (c) the entire apparatus, including the glass slides and syringe pump.

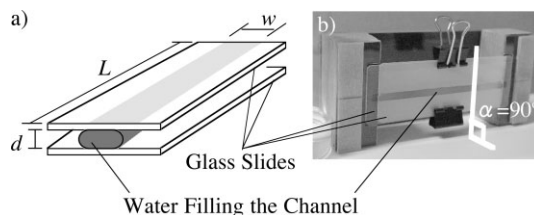


Figure 2. A straight channel constructed between two glass slides that were placed (a) horizontally, and (b) vertically.

Table 1. Advancing and receding contact angles of water.

Surface	Advancing Contact Angle, θ_A (°) ^a	Receding Contact Angle, θ_R (°) ^a
ODS-treated rough surface	112	14
ODS-treated smooth surface	105	80

^a The advancing and receding contact angles were measured by photographing a water drop sliding on the tilted surface.

Eq. (1) also predicts that the water in a channel of the same size will not slip down even if it is constructed on a smooth surface. This prediction was experimentally confirmed. Thus, rough surfaces are not always required to construct such channels. However, as can be seen from Tab. 1, the contact-angle hysteresis of a rough surface is much larger than that of a smooth surface. This indicates that a rough surface is more advantageous than a smooth one for preventing water from slipping down. In addition, a rough surface has another advantage, as described in the next section.

3.2 Advantages of the Use of Rough Surfaces

According to the procedure described in the experimental section, a line was printed on a glass slide using EE as the ink. Lines of 1, 3, or 5 mm width were created, and water was injected into one end of them. When the slide surface was rough, water successfully flowed along these lines, Fig. 3a). However, when the surface was smooth, water did not flow along the 1 mm wide line because it flooded out of the line, Fig. 3b). For the 3 and 5 mm wide lines, water flowed even when the surface was smooth. Thus, although surface roughness was not always necessary, it was preferred when the line width was small.

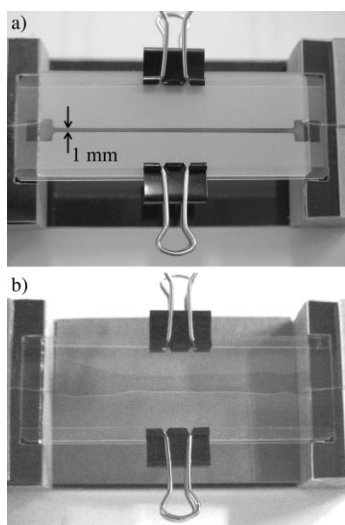


Figure 3. (a) An example of a channel successfully filled with water. The glass slide surface was rough. (b) Flooded channel. The surface was smooth.

The surfaces on which the lines were printed with EE were then observed using a light microscope. As shown in Fig. 4a), EE continuously covered most of the printed area on a rough surface. However, on a smooth surface, dewetting occurred, and the ink existed as small drops, Fig. 4b). Therefore, there seemed to be a relation from which constructing a small-width channel was difficult when the ink dewetted from the surface. A similar relation was also found when various liquid materials were compared as inks. This relation and its possible mechanism have already been reported in a previous paper [15]. Thus, the ink had to be highly wettable on the surface. On the basis of Wenzel's relation [17], a rough texture can enhance wettability with EE. Therefore, using a rough surface is a better choice for constructing the channel.

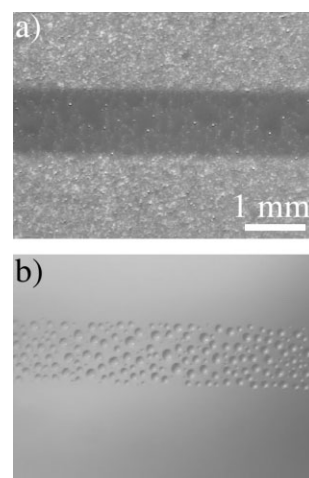


Figure 4. Light microscope images of the printed line on the ODS-treated (a) rough, and (b) smooth surfaces.

3.3 Required Surface Properties

As stated above, the ink should continuously cover the printed area without dewetting. This situation can be illustrated as in Fig. 5, which shows a section perpendicular to the line direction. If the thickness of the ink layer, e , is too small, this layer will decompose into small drops, or the line width, w , will be reduced. In contrast, if e is too large, the ink will flood and widen the line. Since the contact angle, θ , can range from θ_A to θ_R under a condition where the ink continuously covers the area, e can vary with θ . The maximum and minimum values, i.e., e_{\max} and e_{\min} , can be theoretically written as shown in Eqs. (2) and (3):

$$e_{\max} = 2\sqrt{\frac{\gamma_{\text{ink}}}{\rho_{\text{ink}}g}} \sin\left(\frac{\theta_A}{2}\right) \quad (2)$$

$$e_{\min} = 2\sqrt{\frac{\gamma_{\text{ink}}}{\rho_{\text{ink}}g}} \sin\left(\frac{\theta_R}{2}\right) \quad (3)$$

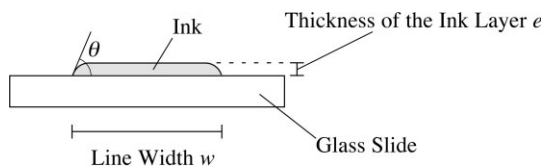


Figure 5. Microscopic illustration of the ink on the glass surface.

where γ_{ink} and ρ_{ink} are the surface tension and the density of the ink, respectively, and g is earth's gravity [18]. Therefore, the requirement of the surface property is that the ink layer on the surface satisfies the following relationship:

$$e_{\min} < e < e_{\max} \quad (4)$$

When EE was used as the ink, $\gamma_{\text{ink}} = 3.4 \cdot 10^{-2}$ N/m, which was measured using the drop-weight method [19], and $\rho_{\text{ink}} = 9.9 \cdot 10^{-2}$ kg/m³. The advancing and receding angles, θ_A and θ_R , respectively, are summarized in Tab. 2, although the receding angle on the rough surface was too small to be measured. Using these values, e_{\max} and e_{\min} were calculated and are also listed in Tab. 2.

The mass of the ink printed on the surface was $7.6 \cdot 10^{-3}$ kg/m², which was measured using an electronic balance. Since the density was $9.9 \cdot 10^{-2}$ kg/m³, the thickness of the ink layer, e , was estimated to be $7.7 \cdot 10^{-6}$ m. Therefore, the smooth surface did not satisfy Eq. (4). This was consistent with the experimental observation that the ink dewetted on a smooth surface, Fig. 4b). Although θ_R could not be measured in the case of the rough surface, it appears to be very low. Therefore, it can be assumed that the rough surface would probably satisfy Eq. (4).

3.4 Mechanism to Cause Water to Flow Through a Channel Without Sidewalls

Similar to surface-directed channels reported by other groups [6–13], the channels used in this study did not have sidewalls. Such channels are likely to flood if one uses a pressure pump to make the water flow. Therefore, Lee et al. [12] used an electrokinetic method and some other groups used capillary action, although the flow appears to have stopped after the channel was filled with water.

Thus, causing water to flow by positive pressure does not seem to be promising. To begin with, since the channel used in this study was not tightly connected to the Teflon tubes, applying positive pressure to the water in the channel was difficult. Therefore, negative pressure was applied as follows. A syringe was used to suck water from one end of the channel, and another syringe simultaneously supplied water to the other end, Fig. 1c). As a result, water continuously flowed through the 0.13 mm deep and 1.0 mm wide channel at flow rates ranging from 1–50 $\mu\text{L}/\text{min}$. This resulted in the successful flow of 2 mL of water flowing at a rate of 50 $\mu\text{L}/\text{min}$ without flooding the channel or leaking water at the joints.

4 Conclusions

A channel filled with water is fixed on a glass surface despite the lack of sidewalls due to the contact-angle hysteresis of the water on the surface. Rough surfaces are more advantageous than smooth surfaces since roughness enhances the contact-angle hysteresis of water and the wettability of the ink that is used to lead the water during the formation of the channel. One can cause a continuous flow of water through the channel using two syringes: The first sucks up water from one end of the channel and the other simultaneously supplies water to the other end.

Acknowledgements

This work was supported by grants from the Japan Securities Scholarship Foundation, and the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grant No. 19510128).

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Table 2. Advancing and receding contact angles of 2-(2-ethoxyethoxy)ethanol.

Surface	Advancing Contact Angle, θ_A (°) ^a	Receding Contact Angle θ_R (°) ^a	e_{\max} (m)	e_{\min} (m)
ODS-treated rough surface	52	Very small ^b	$1.6 \cdot 10^{-3}$	–
ODS-treated smooth surface	41	29	$1.3 \cdot 10^{-3}$	$0.93 \cdot 10^{-3}$

^a The advancing and receding contact angles were measured by photographing a 2-(2-ethoxyethoxy)ethanol drop sliding on the tilted surface.

^b Receding of the three-phase contact line was not observed when the surface was tilted up to 90°. Therefore, the receding contact angle could not be measured, but this indicated that the angle was very small.

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