Performing chemical reactions in virtual capillary of surface tension-confined microfluidic devices

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Abstract. In this paper we report a new method of fabrication of surface tension-confined microfluidic devices on glass. We have also successfully carried out some well-known chemical reactions in these fluidic channels to demonstrate the usefulness of these wall-less microchannels. The confined flow path of liquid was achieved on the basis of extreme differences in hydrophobic and hydrophilic characters of the surface. The flow paths were fabricated by making parallel lines using permanent marker pen ink or other polymer on glass surfaces. Two mirror image patterned glass plates were then sandwiched one on top of the other, separated by a thin gap – created using a spacer. The aqueous liquid moves between the surfaces by capillary forces, confined to the hydrophilic areas without wetting the hydrophobic lines, achieving liquid confinement without physical side-walls. We have shown that the microfluidic devices designed in such a way can be very useful due to their simplicity and low fabrication cost. More importantly, we have also demonstrated that the minimum requirement of such a working device is a hydrophilic line surrounded by hydrophobic environment, two walls of which are constituted of air and the rest is made of a hydrophobic surface.

Keywords. Microfluidics; surface tension; wetting; hydrophobic; hydrophylic.

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1. Introduction

Microsystems technology (MST), considered as one of the key technologies of the 21st century, is rapidly replacing traditional large and grandiose machines by smaller, faster and cheaper ones with increased efficiency. In this regard, microfluidics [1], that involves chemistry and physics in the movement of nanolitre to pico-litre quantities of fluids through microchannels, occupies a central position in major application areas of MST. Its potential applications in the fields of biotechnology, pharmaceutical industry, drug delivery, combinatorial chemistry, automated, miniaturized, intelligent pneumatic systems and in information technology such as inkjet printing cannot be overstated [2–4]. For example, the principles of microfluidics have helped to develop the *lab-on-a-chip technology* in aiding biologists to analyse more samples in less time and minimizing cost and power consumption [5,6]. DNA array sorter is an example of a current microfluidic device [7–9]. On the other hand,

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although it seems that the small-sized microreactors cannot be used for industrial scale synthesis, it has been shown that only 1000 microreactors operating continuously could produce 1 kg of material in a day using what is known as the 'scaling out' concept [10].

In general, there exists two different kinds of microchannels; one is a three-dimensional (3D) channel with physical side-walls and the other is a two-dimensional (2D) channel without any physical side-wall. The physics behind the fluid movement inside both kinds of channels is similar. Traditionally, microfluidic devices (3D channels) are fabricated by various methods such as molding, photolithographic processes involving etching and rapid prototyping using poly(dimethyl siloxane) elastomers [11,12]. On the other hand, 2D microchannels are generally designed by chemically altering selective regions of a substrate surface [13]. The fluid flow is induced and controlled in 3D microfluidic channels by several processes like pumping, electro osmosis, capillarity etc., while that in 2D channels are driven by capillary forces.

When a drop of water or any other high surface tension liquid is placed on a solid surface, its initial spherical shape assumes a pancake-like form due to gravity. If the surface is hydrophilic the liquid in the drop would be attracted to the surface, and it will continue to spread into a thin film. Again if the intermolecular interaction energy is higher than that of liquid molecules and solid surface, then the liquid drop will not spread and the solid surface in this case would be called hydrophobic. This is measured by an angle called contact angle between the liquid and the solid surface and is shown in figure 1.

A gradient in surface tension leads to spreading, recoil and movement of a liquid drop on a solid supported surface. Chaudhury and Whitesides [14] showed that careful creation of spatial gradient in surface free energy was capable of causing drops of water to move uphill against gravity. It is well-known that wettability gradient across a surface also leads to spreading, recoil or movement of a liquid drop [15,16].

Surface tension-confined microfluidics (STCM) [13] works on the principle that combines wettability gradient across a surface and capillarity in order to guide liquid along what we would like to call – a 'virtual capillary'. Typically, such a capillary is constructed by placing two planar substrates against each other, separated by a spacer, with each substrate consisting of a hydrophilic line surrounded by two hydrophobic lines (or *vice versa*) that serve as barriers and are perpendicular to the long axis of the capillary. In STCM, two of the four walls are primarily made up of air, while the other two are made of either hydrophobic or hydrophilic surfaces. The
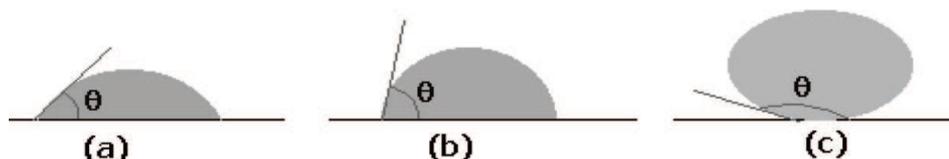
Figure 1. A high surface tension liquid drop that (**a**) wets a solid surface well, i.e. hydrophilic surface, (**b**) wets the surface moderately and (**c**) that does not wet the surface which is called a hydrophobic surface.

edges connecting the alternate walls are made of either hydrophobic or hydrophilic 'ink' lines that depend on the nature of the substrate walls. When the adhesive force of the liquid with the substrate surface is more than that with the edge, the liquid moves along the substrate path by capillary action. The lines at the edges thus act as curbs for the liquid. As a result of this, a well-defined path for liquid movement through the channel is established. The liquid movement in these microchannels is *laminar* and not turbulent and is parallel to the local orientation of the walls of the channel [17–19]. The velocity profile of the movement over the cross-section of the channel is expected to be parabolic with zero velocity at the walls and a maximum velocity at the center of the channel [19]. The liquid fills the wider path more rapidly than the narrower path with maximum limit of the width. The fluid flow also depends on the spacing (height) between the sandwiched surfaces. As spacing is increased, the flow becomes more and more opposed and ultimately ceases when it crosses the limit. The limit of the height and width ratio of the capillary is decided by the surface free energy minimization and a relationship in this regard has been derived by Lam *et al* [13], which is given below (eq. (1)):

$$h_{\max} = w \cos \theta. \tag{1}$$

Here, $h_{\max}$ is the maximum spacing between the two substrate surfaces, w is the width of the channel and θ is the contact angle of the liquid on the substrate.

Although considerable attention has been paid to the development of the three-dimensional mirofluidic devices, the growth with respect to the STCM devices is scant. Originally developed by Oh [15] for capillary electrophoresis it was further designed by Lam *et al* [13] in which they demonstrated fluid flow in both hydrophobic as well as hydrophilic substrates. However, their work was limited to fluid flow in microchannels and no real chemical reaction in these channels was performed. This is important as the simplicity and versatility of the STCM demands further progress in terms of being able to pursue chemical reactions in these channels for various applications mentioned above.

In this article, we report for the first time the performance of a few common laboratory chemical reactions inside such capillaries of STCM. The substrate is of glass slides with lines of ink of permanent marker pen (colored) or clear nail polish. Two such slides placed one against the other and separated by a spacer makes the device. We also show that a sandwich of a glass slide and the polycarbonate part of a commercially available compact disc (CD) with lines drawn on the glass slide is enough to make a working device. This means a hydrophilic line surrounded by hydrophobic parts of the capillary is enough for aqueous solution to flow through the channel and make chemical reactions happen.

We have successfully demonstrated some well-known chemical reactions in these microfluidic devices consisting of single channel and parallel multiple channels separated by virtual walls. We have also studied the cases where a single reagent enters from one common end of a V-shape channel and then reacts individually with two other reagents independently entering into those channels from the other ends. Visible interferometric technique was used to measure the height of these channels. Further, we also show that the product formation in these channels could be followed by visible spectroscopy, the results of which were found to be the same as those studied in bulk. Also, the ease of changing the dimensions of the

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channels by changing the width and the height (using different thickness spacers) is an important factor in the functioning of these devices.

2. Materials

Glass slides, compact disc (CD), permanent marker pen ink, ORLY base coat (nail polish), piranha solution (3:1 conc. H_2SO_4 and 30% H_2O_2), 25 μm teflon spacer, brown tape, web camera (Creative, Model No. PD 1001), ferric chloride ($FeCl_3$), ammonium thiocyanate (NH_4SCN), potassium iodide (KI), lead acetate ($Pb(CH_3COO)_2$), potassium chromate (K_2CrO_4), mercuric chloride ($HgCl_2$) and silver nitrate ($AgNO_3$).

3. Methods

In the present set of experiments, we have used a simple, flexible and inexpensive method to fabricate microfluidic devices of glass slides. Microscope glass slides were cut into approximately 25 mm × 25 mm sizes and then dipped in freshly prepared piranha solution for about half an hour. They were then cleaned with water and air-dried. The treatment makes the slides more hydrophilic. Hydrophobic patterning of desirable circuit was done on the hydrophilic glass slides by using a permanent marker pen or by using commercially available 'ORLY bonder base coat' nail polish using a paintbrush. In order to make the device, hydrophobic patterning was imprinted on two glass slides such that one is a mirror image of the other. This was followed by placing one slide against the other with a spacer in between and they were then clamped tightly. The spacer used was either a commercially available 25 μm teflon spacer or a brown tape. A photograph of such a device is shown in figure 2.

A glass capillary, a micropipette tip or a cotton thread was used in order to introduce different reagents on the two ends of a microchannel. The product formation
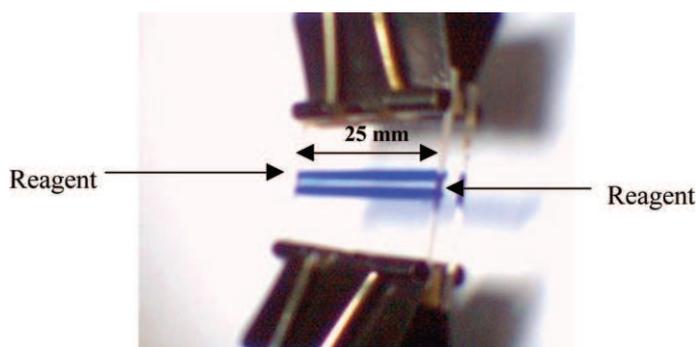
Figure 2. A photograph of a typical microfluidic device, made of a sandwich of two hydrophobically patterned glass slides separated by a brown tape spacer and fixed together by two clamps.

was observed visually and recorded using a web camera. For example, when a drop of water was spotted on one end of the channel, water wetted the two surfaces and quickly filled the hydrophilic regions reaching the other end of the channel. The flow was smooth and fast. In order to demonstrate some well-known chemical reactions, aqueous solutions of ferric chloride, ammonium thiocyanate, potassium iodide, potassium chromate, lead acetate and silver nitrate were prepared in water and used for different experiments that are described in the experimental section. Further, V-shaped channels were fabricated for the reaction of one reagent with two other reagents independently.

The same idea of designing microfluidic device was extended when the polycarbonate part of a commercially available compact disc (CD) was used instead of one of the patterned glass plates. One side of a CD is grooved and the other side is smooth. We have used one (ink) patterned glass slide on which the smoother side of the CD (hydrophobic surface containing no ink marks or groove) was sandwiched. The solutions were introduced into the channels in the same way as above.

The height of the hydrophobic lines and the spacing between the glass plates were measured using interferometric method [20]. For the measurement of height of the lines, optically flat quartz plates were used instead of glass slides. For this purpose, a device was made of two patterned quartz plates as above, but without the presence of any spacer. Visible spectrum of the device was recorded and the heights of the lines were calculated from the absorption maxima and minima using a procedure reported earlier. The heights of regular glass fluidic devices (with spacers) were measured in the same way using visible spectroscopy-based interferometry.

4. Results and discussion

The microfluidic devices of our design primarily consisted of glass slides patterned with permanent marker pen ink in the form of parallel lines (hydrophobic) surrounding parts of a hydrophilic glass slide. Two such patterned slides, where one pattern is a mirror image of other, were then sandwiched and separated by a spacer. The advantage here is that, on the one hand, the width and spacing of these lines could be arbitrarily changed using appropriate pen and printing device, while on the other hand the height could also be changed easily by changing the spacer. In a typical device of the present set of experiments, the height of a hydrophobic line was about 2–4 μm, while the height of the channel was about 25–30 μm when teflon spacer was used and about 40 μm when a brown tape was used. Additionally, as described in the experimental section, an STCM device is relatively simple to fabricate and easy to use. In addition, such a device could, in principle, be dismantled and reused with ease. When compared to the fabrication procedure of three-dimensional devices its simplicity is truly remarkable. As the virtual wall of the STCM is primarily made of air, the bubble formation in the capillary is prevented and we have not observed any bubble formation in any of the reactions we have performed. Typically, we have added the reagent solutions in sequence from two ends of a microchannel. There are three possibilities of the mechanism of reagent mixing. If the volume of the first reagent were larger than the volume of the channel, which would be the case in many systems, then the liquid would

flow through the channel to the other end to fill up the channel. When the second reagent solution is added at the other end, it would push the liquid back as well as mix with the first reagent. The final product position in the channel would be dependent on the volume of the second reagent solution, the larger the volume, the more visible would be the product formation from the end of the channel towards the beginning (more with larger volume). Even if bubble is formed during mixing or transferred from the parent solution there is always the possibility of escape into the virtual wall. However, here the danger of overflow cannot be completely discarded. In another situation, which might be the case in the present set of experiments, if the quantity of liquid delivered is small then the microchannel can be filled up to arbitrary length by the first liquid solution. When the second reagent solution is added from the other end then there is the possibility of formation of bubble at the meet point of the liquids. Our observations, however, suggest that the bubble formation – even if it had taken place – did not sustain and we observed product formation mostly or nearly the mid-point of the channel. Our experiments clearly demonstrate the technical advantage of STCM devices over their conventional counterpart. Also, all the experiments were performed under the condition of ordinary capillary action and thus power requirement was not there.

As a first example, we show the performance of the reaction of $FeCl_3$ (added first) and NH_4SCN to produce $Fe(SCN)_3$ in a microchannel as shown in figure 3a. The product can easily be identified from its red color formed near the centre of the channel. As seen in the figure, the reagent liquids as well as the product were all in the channel and there was no evidence of overflow beyond the channels. In a typical experiment we have started with somewhere around a few hundred nanolitres of each liquid. The volume of the product formed, as observed by the naked eye, was as low as 30 nl. The results clearly demonstrate the feasibility, ease of operation and observation of the product formation of a common chemical reaction as well as the power of the method using STCM of the present design.

Next, we show that a patterned glass slide and the polycarbonate part of a CD can, when sandwiched appropriately, work as a microfluidic device and the same chemical reactions can be performed as well. In other words, a hydrophilic line surrounded by hydrophobic barrier, air and opposite hydrophobic surface is enough to
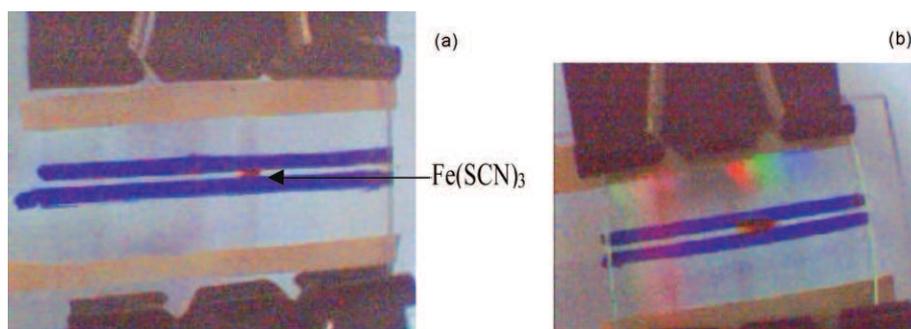
Figure 3. (a) Red colored $Fe(SCN)_3$ formed in microchannels by the reaction between $FeCl_3$ and NH_4SCN. (b) A microfluidic device fabricated by sandwiching patterned glass slide and the polycarbonated part of a CD.
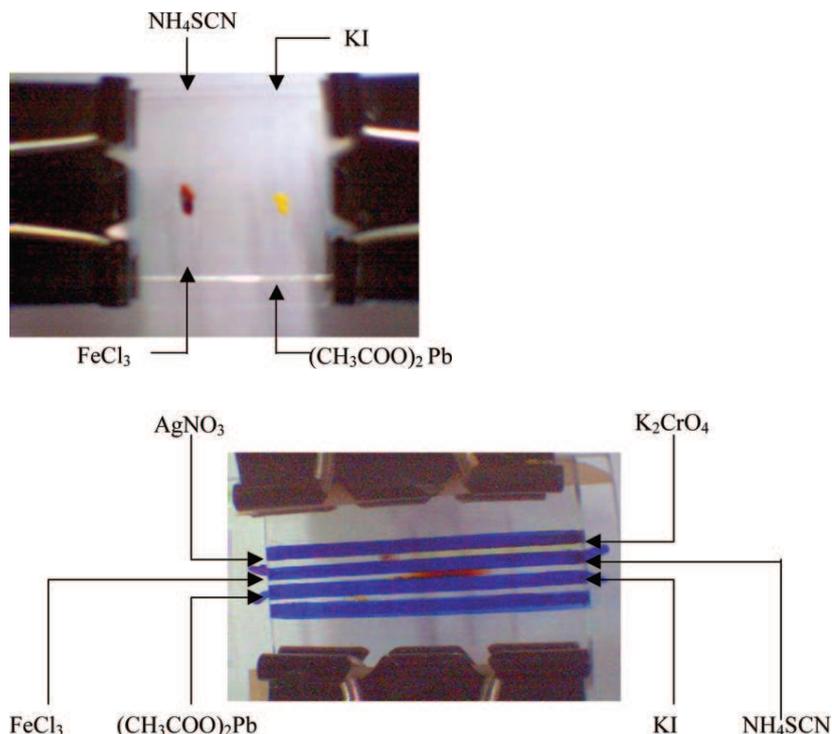
Figure 4. (**a**) Two distinct reactions in two parallel channels. (**b**) Demonstration of multiple reactions in the mocrofluidic device containing channels with common side walls.

induce flow of an aqueous solution through the channel for the study of chemical reactions. This is shown in figure 3b, where $FeCl_3$ (added first) and NH_4SCN were reacted to produce red colored $Fe(SCN)_3$. Also, there was no apparent indication of overflow of liquids through the barriers supporting the fact that the minimum requirement of a microfluidic channel is a hydrophilic line surrounded by hydrophobic environment in which air-gap can take part as the virtual walls. This is quite significant as far as the design of a microfluidic device is concerned as this would mean a simple print out of a design with hydrophilic or hydrophobic lines surrounded by hydrophobic or hydrophilic environment (respectively) which is enough for the device to carry out reactions at the microscale.

Next we show that two separate sets of reactions in two parallel channels could be performed in the same microfluidic devices. This is shown in figure 4a. The channels were drawn in glass slides using the same method as described before for the case of two glass slides. The difference here is that the hydrophobic lines were drawn using transparent Orly base coat. As is evident from the picture, the red colored $Fe(SCN)_3$ from $FeCl_3$ and NH_4SCN is well-separated from the yellow colored PbI_2, produced from the reaction of $Pb(OOCCH_3)_2$ and KI. It is important to note that there was no overflow or mixing of the two reactions. The hydrophobic lines truly acted as virtual walls in separating fluids flowing through microchannels.
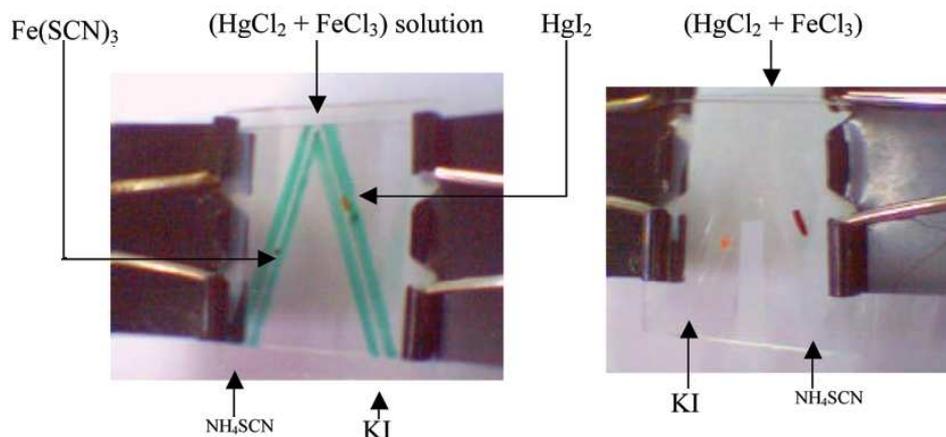
Figure 5. Detection of multiple reagents from a solution using a V-shaped channel device.

We also show the performance of three separate reactions in three different parallel and side-by-side channels with common walls. This is shown in figure 4b. The product formed from all the three reactions can be easily seen in the figure. This result further establishes the ability of such a device in carrying out multiple reactions in a microfluidic device with common walls.

We pursued further in the design of channels such that the reagents present in one solution can react with two separate reagents in two separate channels. This was achieved by designing a V-shaped channel structure such that the common end of V was used to introduce the solution containing two reagents, namely $HgCl_2$ and $FeCl_3$. Through the other ends KI and NH_4SCN were separately introduced in the two arms of V. As seen in figure 5, the product formation (HgI_2 and $Fe(SCN)_3$) in the two channels indicate the feasibility of studying the presence of multiple reagents in a sample solution. The same can be seen even more prominently with Orly base coated channels.

Finally, we demonstrate that the same microfluidic channels can be used to study the product formed using visible spectroscopy. In order to achieve this we performed the reaction of $FeCl_3$ with NH_4SCN in microchannels as well as in an optical cuvette with the same starting concentration of the reagents in aqueous solutions. The results are shown in figure 6.

As is clear from the graph, both the products in two separate cases gave similar visible spectra with characteristic peak of $Fe(SCN)_3$ occurring at about 460 nm. Thus a microfluidic device is good enough to carry out chemical reactions as well as to perform *in situ* spectroscopic analysis of the formed product.

5. Conclusions

In this paper we have reported the development of a simpler way of fabricating two-dimensional microfluidic devices. The basis of the confined fluid movement in

Virtual capillary of surface tension-confined microfluidic devices
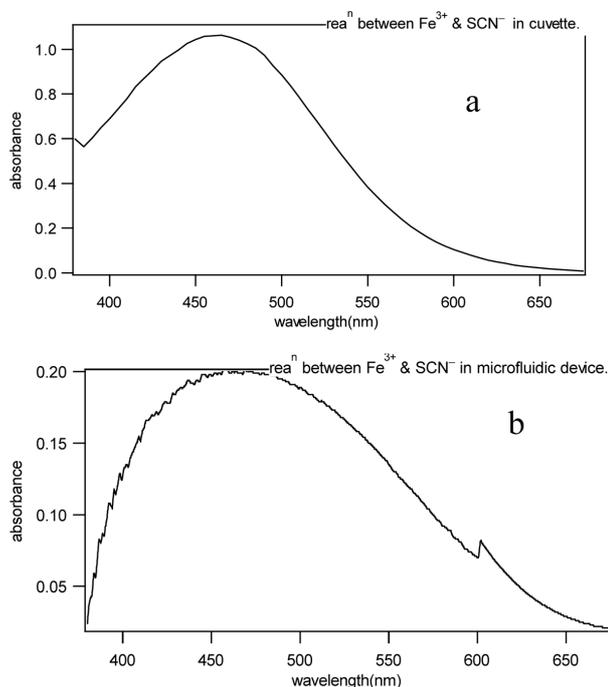
Figure 6. Visible spectra of the product $Fe(SCN)_3$ (from $FeCl_3$ + KSCN) recorded in a cuvette (**a**) and in the present microfluidic channel (**b**) respectively.

these devices is the surface tension, which guides the fluid to move selectively in either of the hydrophilic or hydrophobic region because of their different wetting property. The simplicity and low fabrication cost is the strength of our method, which can be employed to fabricate microfluidic devices both inside and outside a laboratory. By suitably printing hydrophobic lines on hydrophilic surface, a working device could be made. The heights of these lines as well as the channels were measured by visible spectroscopy applying the principles of interferometry. Using these microfluidic devices we have demonstrated some well-known chemical reactions primarily using reagents of a few hundred nanolitre volumes. We have also reported the development of a minimal requirement of a single line constituting a channel to carry out chemical reactions. The same principle has been used to carry out multiple reactions in different channel configurations. Finally, visible spectroscopic method has been used to follow the product formation in these channels and compared with that in the bulk.

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