NOVEL NON-EQUILIBRIUM ELECTROKINETIC MICROMIXER WITH NANOPOROUS MEMBRANE FABRICATED BY LASER POLYMERIZATION TECHNIQUE

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ABSTRACT

We propose a non-equilibrium electrokinetic (EK) mixer with a nanoporous membrane fabricated on a microfluidic chip by laser polymerization technique. A non-equilibrium EK mixer had an array of nanochannels to generate a vortex using ion depletion and consequent electroconvection [1]. The nanochannels, however, require expensive and complicated fabrication processes. On the other hand, the laser polymerization technique has proved that nanoporous membranes are readily fabricated on a chip and can be used for microdialysis [2] or sample preconcentration [3]. Here, we show for the first time that a nanoporous membrane in-situ fabricated on a microchip can be used for a non-equilibrium EK mixer.

KEYWORDS

Non-equilibrium micromixer, nanoporous membrane, electroconvection, ion depletion.

INTRODUCTION

A non-equilibrium EK micromixer uses unique phenomena caused by ion concentration polarization across nanochannels with selective ion permeability due to Debye layer overlap. When the electric field is applied across the nanochannel, the ion concentration is higher at one side and lower at the other side. If the concentration approaches zero on the depletion side, the system reaches a limiting current. When the voltage is increased further, significant overlimiting current can be observed due to a strong convective mixing called electroconvection. We found that this phenomenon can be realized with a nanoporous membrane.
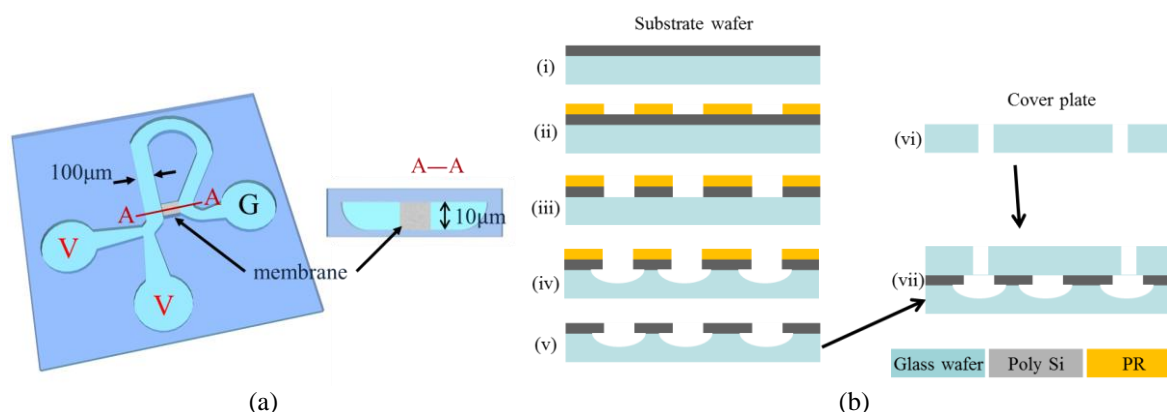
EXPERIMENTAL SETUP

Figure 1. (a) Schematic of an EK mixer with a nanoprous polymer membrane and (b) chip fabrication process.

A glass microfluidic chip was prepared to have a higher electric field across the nanoporous membrane than across the microchannel (Figure 1a). It has two inlets and one outlet, and the width and height of the main channel are 100 μm and 10 μm. The chips were fabricated with borosilicate glass (BOROFLOAT® 33) by using the process depicted in Figure 1b: the LPCVD deposition of an 500 nm-thick, amorphous poly-silicon layer on the glass substrate (i), photo-resist (AZ4620) patterning (ii), developing (ii), poly-silicon etching with a reactive ion-etch (iii), wet-etching of the glass substrate with buffered oxide etchant (iv), and PR removal (v). Finally, a cover plate made of borosilicate glass with holes (vi) was bonded with the etched substrate by anodic bonding process (vii). Then, we in-situ fabricated a zwitterionic nanoporous polymer membrane on a microchip by using a phase separation polymerization technique with an optically-shaped UV laser beam (Figure 2). The laser beam is 355 nm in wavelength and is optically conditioned to become a sheet with 100 μm thickness. The pore size of the membrane is known to a few nanometers [2, 3]. Mixing solutions were prepared with 5 mM KCl solution with and without electrically neutral Rhodamine B. They were introduced into a micromixer using an electroosmotic flow induced with electrodes located in the reservoirs of the inlets and outlet.
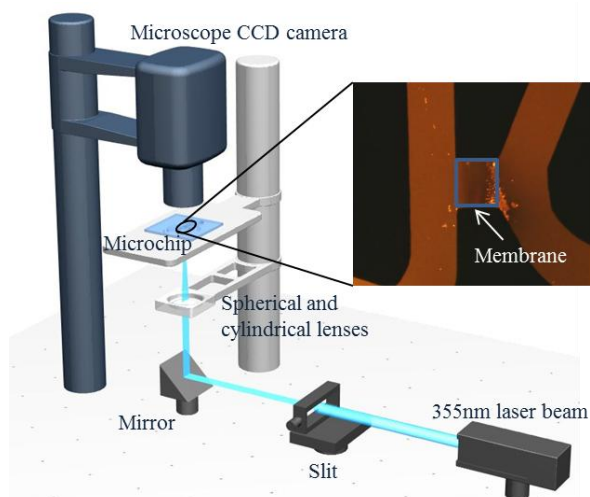
Figure 2. Schematic of the optical setup for in-situ laser polymerization using phase separation

RESULTS

In order to examine the generation of ion-depletion and electroconvection across a nanoporous membrane, we applied an equal voltage to two microchips: one with non-porous membrane and with nanoporous membrane. Upon the application of voltage across the channel, we found that an electroosmotic flow (EOF) occurs on both microchips However, a flow mixing occurs only on the microchip with a nanoporous membrane. Figure 3 compares fluorescence images on flows near a membrane with and without nanopores. Two inlet flows are vividly distinct downstream of the non-porous membrane (Figure 3a), indicating that there is no flow mixing by electroconvection but only slow diffusion across the interface of the two streams. In contrast, the two inlet flows are thoroughly mixed for the microchip with a nanoporous membrane (Figure 3b). This implies that the nanopores of membrane is ion-selective and generate ion-depletion and electroconvection.
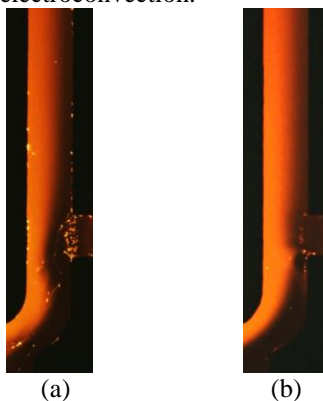

(a)   (b)

Figure 3. Fluorescence images without nanopores and EOF only (a), and with nanoporous membrane and electroconvection (b). A KCL solution of 0.1 mM and 250V were used in both cases.

After confirming that the nanoporous membrane is ion-selective, we investigated the development of flow mixing with time. Figure 4 shows consecutive flow images after the onset of EOF. Initially, when there is no flow, the fluorescent dye is spread in the entire channel due to diffusion. Upon the application of voltage, the two inlet flows upstream of the membrane starts to become distinct because of the introduction of inlet-flows by EOF. The two inlet flows are vividly distinct after 400 ms. Chaotic vortex flows generated by the electroconvection seem to occur near membrane where non-uniform fluorescence region is observed after 200 ms. Downstream of the membrane, it is hard to observe any difference in the fluorescent intensity at any time, implying that the two distinct flows are well mixed.

Finally, we examined the effects of applied voltage on the mixing index that is calculated with Eq. 1

$$\text{Mixing index} = \frac{\int |I(x) - I_{diff}(x)| dx}{\int |I_{100\%}(x) - I_{diff}(x)| dx} \quad (1)$$

where $I(x)$ is the fluorescent intensity 300 μm downstream of the membrane, $I_{diff}(x)$ is the intensity 300 μm upstream of the membrane, and $I_{100\%}$ is the intensity for perfect mixing. The mixing index becomes 1 for perfect mixing and 0 for non-mixing. Figure 5 exhibits the mixing index with respect to applied voltages across the channel. In a voltage range of 25 through 400V, mixing indices are fairly high: higher than 0.9 regardless of the applied voltage. However, the high mixing index at a low voltage (below 150V) is probably due to the effects of molecular diffusion that is dominant because EOF is weak at the voltages. The mixing index is relatively low in a voltage range of 150 to 250V where, we believe, EOF is strong while both electroconvection and molecular diffusion are weak relatively. With a

voltage higher than 250 V, mixing index becomes almost one, indicating the occurrence of electroconvection.

CONCLUSIONS

We developed a non-equilibrium EK micromixer with a nanoporous membrane. We found that a nanoporous membrane is ion-selective and is able to induce ion-depletion and electroconvection across it, leading to effective flow mixing upon the application of a moderate range of voltage. Further investigations are required like the effects of buffer solution properties on mixing, types of nanoporous membranes proper for mixing, and etc.
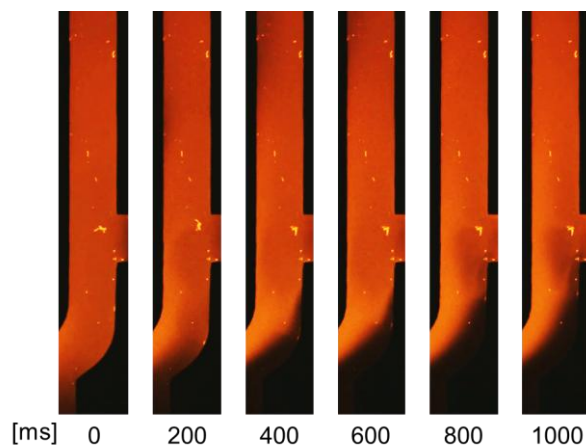

Figure 4. Consecutive flow images with a time interval of 200 ms after the onset of 250V.
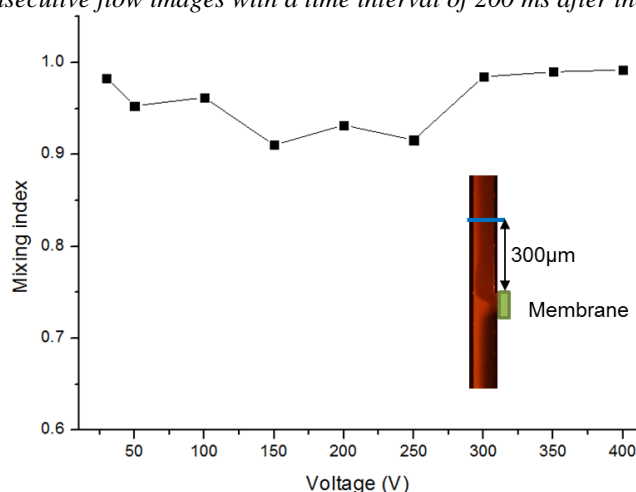

Figure 5. Mixing index comparison for various applied voltages. The mixing index was calculated 300 μm downstream of the membrane.

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