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Electrohydrodynamic Generation and Delivery of Monodisperse Pico-Liter Droplets Using PDMS Microchip

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Abstract

We developed a drop-on-demand microdroplet generator for the discrete dispensing of biosamples into a bio-analytical unit. This disposable PDMS microfluidic device can generate monodisperse droplets of pico-liter volume directly out of a plane sidewall of the microfluidic chip by an electrohydrodynamic mechanism. The droplet generation was accomplished without using either an inserted capillary or monolithically built-in tip. The minimum droplet volume was around 4 picoliters, and the droplet generation was repeatable and stable for at least 30 minutes, with a typical variation of less than 2.0% of drop size. The Taylor cone, which is usually observed in electrospray, was suppressed by controlling the surface wetting property of the PDMS device as well as the surface tension of the sample liquids. A modification of the channel geometry right before the opening of the microchannel also enhanced the continuous droplet generation without applying any external pumping. A simple numerical simulation of the droplet generation verified the importance of controlling the surface wetting conditions for the droplet formation. Our microdroplet generator can be effectively applied to a direct interface of a microfluidic chip to a bio-sensing unit, such as AMS, MALDI-MS or protein microarray-type biochips.

INTRODUCTION

In the past two decades, the dispensing of microdroplets has been used mostly in fields such as aerosol sciences and inkjet printing.^{1, 2} More recently, due to the increasing demand for high throughput analysis of biological samples in bio-analytical applications, the dispensing of microdroplets has been increasingly applied in the automatic pipetting of samples in massively parallel drug discovery, DNA arraying, and mass spectrometry detection with ultra-low sample concentrations.^{3, 4} So far, the most common way to generate microdroplets is to use a pulled glass capillary tip. However, a droplet dispenser using the microfluidic chip format has recently found increasing popularity due to its potential for massively parallel arrayability and scalability of its size. Especially, the latter characteristic reduces the dead volume of the device, which is essential when dealing with an extremely small sample volume. Furthermore, this microchip format facilitates an easier integration of the dispenser into an existing microfluidic chip as a direct interface to various bio-analytical units.

Among the several common actuation methods for a microfluidic-chip-based dispenser, such as thermal resistive heating^{5, 6}, pneumatic actuation^{7, 8}, and electrohydrodynamic (EHD) method⁹⁻¹¹, the EHD method offers several distinctive advantages. First, this type of actuation

does not require complex micro fabrication processes since no moving components, such as a pump, are required. In addition, the EHD technique can produce monodisperse droplets in a wide range of sizes using either electrospray or single droplet generation. Thus, this technique is widely used for sample dispensing on DNA microarrays¹² or for preparing gas-phase ions in mass spectrometry.^{13, 14}

A droplet formation assisted by an electrical field has been theoretically and experimentally studied for over a century.¹⁵⁻¹⁷ The electric field applied between the charged liquid sample and the ground electrode causes the force of electric origin at the air/liquid interface and the liquid bulk. Once the electric field strength is high enough to overcome the interfacial surface tension, the liquid is elongated in the direction of the electric field and breaks up into single micro droplets from the tip. Depending on the field strength, either a spray or monodisperse droplets can be generated.^{18, 20} The Taylor cone, which is typically formed in the electrospray, enables a spray formation with droplets much smaller than the outlet diameter of the capillary.^{20, 21} However, when generating droplets by the EHD mechanism, the formation of the Taylor cone prompts interfacial instability leading to irregular droplet generation.²² Even with an inserted emitter tip to enhance the efficiency and stability of the droplet formation, its fabrication and critical alignment remain challenging.²³⁻²⁵

We have developed a pico-liter monodisperse droplet dispenser as a discrete sample injection interface for Accelerator Mass Spectrometry (AMS) instrument.²⁶ This dispenser generates uniform-size microdroplets with well-defined trajectories instead of a random spray. It is especially suited for the dispensing operation with small amount of original samples, which requires tight volume control. The dispenser can controllably deliver droplets (through air) as far as 1~3cm in the horizontal direction, which greatly facilitates the integration of the droplet dispenser into the AMS or other equipments. For the sake of design and fabrication simplicity, we have developed a PDMS device that generates monodisperse droplets directly out of a plane sidewall of the PDMS chip without using either capillary or monolithically integrated tips. While conventional EHD droplet generation required either pulsatile electric field or external pneumatic pump, our design required no external pumping by modification of the channel geometry. The instability, poor directionality, and diversity in droplet size were effectively suppressed by coating Teflon on the plane sidewall surface of the PDMS chip, where the droplets were generated out of the microchannel end, and reducing the surface tension of the sample liquids. A simple 2-dimensional numerical simulation successfully confirmed the effect of the surface wetting condition on the droplet formation. With this device, we could demonstrate the generation of the pico-liter micro droplets in a stable and repeatable way using various aqueous solutions. During dispensing, a constant generation rate was maintained, with the small droplets being generated at a higher frequency and the larger ones at lower frequency. The minimum size of the droplets was mainly determined by the size of the microchannel opening, which could be altered for specific droplet size needs.

EXPERIMENTAL SECTION

Fabrication of PDMS Microdroplet Dispenser

We used PDMS to fabricate the microdroplet generator following the general PDMS chip fabrication processes.²⁷ We made a master with SU-8 on a silicon wafer using photolithography and poured PDMS on top of it. Before pouring, we mounted a glass slide vertically to one end of the positive micro channel to obtain a clean side surface around the orifice. After curing PDMS at 60°C in oven, we peeled off the PDMS sheet and cut it into rectangular shapes. Figure 1(a) shows the schematic of the PDMS chip. Two different types of the microchannels were built and directly connected to the circular reservoir of the sample fluid. A straight microchannel (Type I in Figure 1(a)) with a dimension of 15 μm $\times$ 20 μm $\times$ 5 mm (H $\times$ W $\times$ L) and a widened microchannel toward the opening (Type II in Figure 1(a))

with the dimension of $20\ \mu\text{m} \times 25\ \mu\text{m} \times 5\ \text{mm}$ ($H \times W \times L$) were fabricated. The opening of the second microchannel was expanded from $25\ \mu\text{m}$ to $50\ \mu\text{m}$ in width at an angle of 75 degrees, as shown in Figure 1(a). Both microchannels were covered by a separate PDMS plate containing a wedge shape with an inclined angle of 20 degrees. This wedge shape was fabricated by pouring PDMS in between a glass slide inclined by 20 degrees and a silicon wafer as a substrate plate with subsequent curing. This wedge shape was to reduce the surface at the opening of the channel, thus minimizing the contact area between the sample liquid and the side wall. Another reason for using a wedge-shaped top plate was to enable a better observation of the droplet generation process from the top of the device with a CCD camera. This shaping method also allowed us to obtain a transparent PDMS surface through which the microchannel with its opening could be observed from the top. For a proper sealing of the orifice, it was essential that the edge of the cover plate matches that of the bottom plate. Therefore, we aligned them under a stereo microscope before bonding. After bonding, the orifice of the device was coated with Teflon AF 1600 (DuPont, 601S1-100-6) by simply brushing the liquid over the PDMS surface. After applying the liquid Teflon which dries within 1~2 minutes, a negative pressure was briefly applied from the reservoir with a syringe in order to clear any clogging of the channel by the coating material. The coating provided a hydrophobic surface with a contact angle of ~ 110 degrees. To make sure that the channel was open at its end, it was additionally vented after complete drying.

Experimental Setup

Figure 1(b) provides a schematic illustration of the microdroplet generator system. The copper ground electrode had a 1 mm diameter opening in the middle to allow the ejected microdroplets to pass through into a transparent tube with 5 mm inner diameter. The tube was sealed against the counter-bored hole of the copper plate. First, this tube assisted us to visualize the droplets once they passed through the hole in the center of the copper plate. This allowed us to estimate how far each droplet can travel under the applied electric field. Also, the tube can be used to assist the ejected droplets to travel farther if a negative pressure is applied from the other end of the tube. (This was the standard operation mode of AMS system.) A high voltage DC power supplier (Stanford Research Systems, Inc., model P350) was connected between the ground electrode and the PDMS sample reservoir. A syringe needle with a pipette tip was inserted into the reservoir to fill the channel with a sample liquid and to connect it to the power supply. For initial filling of the microchannel with the sample liquid, a syringe pump (Kent Scientific Inc.) was used. The ground electrode and the microdroplet generator were installed on two separate XYZ stages (Thorlabs Inc.) to control the gap size between them and to align the orifice of the microchannel toward the hole in the center of the copper plate. The variation of the electric field was achieved either by adjusting the voltage or the gap between the PDMS chip and the ground electrode. To capture the motion of the droplet, a high speed camera (Redlake Imaging, MotionScope 8000 PCI) was installed directly above the orifice of the device. It enabled a frame rate of up to 8,000 fps. The experimental setup is shown in Figure 1(c).

As sample fluids for droplet generation, DI water and various aqueous solutions, commonly used in biological applications, were tested to assess their applicability for electrohydrodynamic droplet generation. Physicochemical properties of the aqueous solutions used are summarized in Table 1.²⁸ Each tested solution contained a cosolvent of 0.1 volume percent.

Characteristics of Electrohydrodynamic Microdroplet Generation and Delivery

The generation of a microdroplet is controlled mainly by two dimensionless numbers: the gravitational Bond number, $Bo^G = \rho g R^2 / \sigma$, which is the ratio of the gravitational force ($\rho g R^2$) and surface tension (σ) on the droplet, the electrical Bond number, $Bo^E = \epsilon R / E^2 / \sigma$, which is the ratio of the electrical force ($\epsilon R / E^2$) and surface tension (σ). Here, ρ represents the sample

liquid density; g the constant of gravitational acceleration; R the microdroplet radius; σ the interfacial tension at the air-water interface; ε the sample liquid permittivity; and $\mathbf{E}$ the applied electric field. The diameter of the microdroplet was less than 100 μm and the applied electric field was less than 25,000 V/cm. Consequently, the value of Bo^G is on the order of $O(10^{-3}\sim 10^{-2})$ and Bo^E on the order of $O(1\sim 10)$, so that the gravitational force is negligible. Therefore, dispensing the droplets either in a vertical or horizontal position does not greatly influence the droplet generation, at least for the launching of the droplets. The traveling distance of the single droplet can be calculated by $\sqrt{r_{tube}/2g} \times v_0$ while the droplet falls by $r_{tube} = 2.5$ mm, which is the half diameter of the tube, before touching the surface of the extension tube. With the initial velocity, v_0 , which we obtained as 3 m/sec for DI water using the single frames taken with a high-speed camera, the travel distance of droplet was about 3 cm. Such a droplet travel distance is certainly adequate for our specific application (coupling of the droplet dispenser to AMS instruments), and should be long enough for many other microfluidics-detector integrations. Additionally, in our case, an inert gas flow (e. g. He) is maintained from the chip to the AMS instrument, which will help delivering the droplets farther.

THEORETICAL MODELING

Electrohydrodynamical Generation of a Microdroplet with Two Surface Wetting Conditions

We conducted a two-dimensional numerical simulation with COMSOL Multiphysics 3.2a (COMSOL Inc.) to investigate the effect of surface conditions on droplet generation. For the simulation, we applied the incompressible Navier-Stokes module ($\mathbf{u}$) governed by the Navier-Stokes equations and the continuity equation, and electrostatics module (V) by the Poisson equation. In addition, we included the convection and diffusion module (ϕ) governed by the convection-diffusion equation to apply the Level Set Method.^{29, 30} The Level Set Method is a numerical technique for tracking fluid interfaces or shapes of two different densities (in our case, liquid and air). The advantage of the Level Set Method is that one can perform numerical computations involving curves and surfaces on a fixed grid without having to parameterize these objects. Also, the Level Set Method makes it very easy to follow shapes which change topology, for example when a shape splits in two, develops holes, or the reverse of these operations. All these make the Level Set Method a great tool for modeling time-varying objects, like inflation of an airbag, or a droplet generation. Figure 2 shows the computational domain, which was non-dimensionalized with the initial droplet diameter, R_0 . When applying the Level Set Method, the setting of the initial interface condition is of relevance. The function was defined so that the level set function was zero at the high density fluid/low density fluid interface, greater than zero for the low density fluid, and less than zero for the high density fluid.^{29, 30} In this simulation, the sample liquid was represented by the high density fluid and the air by the low density fluid. The Level Set function in this simulation was $\min[-x, \sqrt{(x + 0.1R_0)^2 + y^2} - 0.4R_0]$ for the non-coated PDMS surface and $\min[-x, \sqrt{(x + 0.3R_0)^2 + 2y^2} - 0.4R_0]$ for the Teflon-coated PDMS surface. The physicochemical parameters including viscosity, permittivity, and surface tension coefficient were set so that the following condition was met: $Bo^G = 10^{-2}$ and $Bo^E = 4$. These values were close to those of DI water. The computational domain was filled with the two fluids because the Level Set Method tracks the fluid interface of two different densities. Since the region of our interest, the orifice, was far off from the top, bottom and the left boundary, we expected no significant influence of these boundary conditions on the fluid interface. Therefore, we assumed that all boundaries have no slip conditions for the sake of the simplicity. For the electrostatics, $\partial\Omega_1$ and $\partial\Omega_2$ have the boundary condition of $V = 0$ and V_0 , respectively. All the other boundaries were set to zero charge/symmetry conditions. Insulation/symmetry conditions were set to all boundaries in the convection and diffusion module.

Initially, the microchannel was filled with sample liquid, which was represented by the high density fluid, and a droplet was formed at the exit of the microchannel. The droplet dangling

at the exit of the microchannel had a contact angle that depends on the surface condition. We assumed a contact angle of approximately 90 degrees for the non-coated PDMS surface and 110 degrees for the Teflon-coated PDMS surface. We started the simulation with two different droplets on two different surfaces, but with the same initial liquid volume. The interface between liquid and air experienced strong electrical body forces ($\rho_E \mathbf{E} - |\mathbf{E}|^2 \nabla \epsilon / 2$) and we assumed that only the interface had electrical charges. This was realized with the Dirac-Delta function at the interface. The domain was discretized into 6,998 triangular elements after the convergence test and the region near the droplet had denser meshes as shown in Figure 2.

RESULTS AND DISCUSSION

To generate monodisperse microdroplets directly out of the PDMS device, we investigated the effect of three different parameters on the droplet formation: the hydrophobicity of the surface at the opening of the channel, the surface tension of the sample liquid, and the channel geometry.

Effect of Ultra-Hydrophobic Surface Conditions

Both the computational and the experimental results of our droplet generation are shown as a function of the dimensionless time unit for DI water in Figure 3. The dimensionless time unit was obtained by dividing with the total travel time of the droplet from the ejector to the ground electrode. In the case of the non-treated PDMS surface, the initial contact angle was approximately 90 degrees in Figure 3(a), while it increased to 110 degrees in the case of the Teflon-coated surface, shown in Figure 3(b). This difference in the contact angle is due to the lower surface wettability after the Teflon coating of the side wall around the orifice. In the case of the non-coated PDMS device, a large residual droplet built up and prevented a formation of equally-sized droplets, as shown in Figure 3(a). In addition, the Taylor cone was formed at the end of the residual droplet on the sidewall when an electrical field was applied. This generated additional droplets with diameters at least two orders of magnitude smaller. However, its frequency fluctuated, which caused an unstable droplet formation and uncontrolled dispensing of the sample. In contrast, the droplet did not spread out from the opening to the side wall on the ultra-hydrophobic surface, as shown in Figure 3(b). Rather, it maintained its ellipsoidal shape. In the single frames of Figure 3(b), one can clearly see monodisperse droplets generated out of the orifice without the Taylor cone. The numerical simulation also proved the possibility of generating droplets without creating a long tail of sample residue behind the traveling droplets.

Figure 4 shows DI water droplet generation as a function of the gap between the opening of the straight microchannel (Type I in Figure 1(a)) and the ground electrode. By adjusting the gap size, we controlled the applied electric field strength on the droplets. The electrical body force exerted on the air/liquid interface is $\rho_E \mathbf{E} - |\mathbf{E}|^2 \nabla \epsilon / 2$. From a simple algebraic calculation, the first term is $O(10^2)$ and the second term is $O(10^0)$. Therefore, the size and the frequency of the droplet generation depend linearly on the electrical field strength, as validated by the experimental results in Figure 4(f). Since the relatively high surface tension of DI water pulled up the liquid from the channel after shooting the first droplet, the following droplets were automatically generated without any external mechanical pumping. The generation was repeatable and stable for 1.5 hours with a typical droplet size variation of less than 2.0%. However, when the field is increased too much (corresponding to 70 μm of droplet size or less), increased electric field led to the formation of the Taylor cone on the top of a residual droplet, which did not break off completely from the PDMS surface, as shown in Figure 4(c)~4(e). Only a small portion of the droplet broke off from the opening leaving a larger amount of the liquid on the surface.

Effect of Surface Tension

We tested the droplet generation of various aqueous solutions to lower the surface tension of the sample liquid. For this test, we used the straight microchannel (Type I). Figure 5 shows the single droplets of 0.1% acetic acid solution, which is a common solvent for biological applications. The electric field strength was changed by varying the voltage while keeping the gap constant at 1 mm. A syringe pump was used at a flow rate of 1 $\mu\text{L}/\text{min}$ for initial filling and it was remained connected to the droplet generator after it was turned off. In the case of acetic acid, lower surface tension of the liquid made the surface-tension-driven droplet regeneration process (after shooting previous droplets) inefficient. Therefore, external pumping was required to produce microdroplets with the straight microchannel end (Type I). However, since the required pressure for droplet generation was rather small, residual pressure from the syringe pump (mainly used for initial filling) was adequate to maintain continuous droplet generation. In this case, the estimated flow rate of the pumping was $\sim 0.1 \mu\text{L}/\text{min}$. Due to the lower surface tension of 0.1% of the acetic acid solution compared to that of DI water (approximately 70 dynes/cm), the formation of droplets was observed without any sample residue at the orifice even in the case of extremely small droplets of 21 μm . In Figure 5(f), the size of the droplet of 21 μm in diameter corresponds to a liquid volume of 4.2 pico-liters. This shows that a minimum size of the droplet close to the size of the microchannel can be achieved when using acetic acid solution.

Effect of Microchannel End Geometry

The dispensing operation using cosolvents in previous sub-section could be carried out only for less than a minute without external pumping. This result is mainly due to the fact that the drag force along the inner surface of the microchannel in front of the orifice reduces the electrical body force on the droplet surface. One way to overcome this problem is to increase the electric field. However, this can cause undesired electrospray formation. To avoid this problem, we used a different type of the microchannel whose opening widens toward the end of the microchannel (type II in Figure 1(a)). We expected to achieve several benefits with this type of microchannel geometry. While coating the sidewall of the orifice with Teflon, we realized it can penetrate into the inside of the channel because of the widening angle of the channel and thereby, can coat the inner surface of the channel. This in turn reduces the drag force inside the channel and as a result, a higher electrical body force can be applied to pull out the sample liquid from the inside of the channel and form the droplet. Also, the widening of the channel imposes less flow resistance due to the higher cross section area. In addition, the level of liquid, h , in a hydrophobic vertical channel increases proportionally to the inner diameter of channel, r , according to the equation, $\Delta h = (2\pi\sigma\cos\theta/\rho g)\Delta r$. Depending on the hydrophobic/hydrophilic condition, the sign of the term $\cos\theta$ changes. In the hydrophobic channel, for instance, Δh increases with higher Δr while in the hydrophilic channel the opposite occurs. This explains why the liquid moves from the straight channel toward the widened opening under atmospheric pressure if the channel is hydrophobic. Therefore, the angled sidewall of the channel orifice creates additional surface tension to pull out the liquid from the microchannel, allowing efficient, continuous auto-regeneration of the droplets even with liquid of lower surface tension.

In order to check a pumpless droplet generation in the device, we disconnected the syringe pump from the droplet generator after initial filling, and waited for an hour to equilibrate the pressure inside the microchannel. This pumpless, channel-geometry-enhanced droplet generation lasted for about 30 minutes and the results obtained with various aqueous solutions are shown in Figure 6(a). For many different aqueous solutions, monodisperse droplets could be generated without external pumping.

To prove that the droplet generation with the generator of Type II was only by the electrohydrodynamic actuation, we conducted a control experiment. In this experiment, all the conditions remained unchanged except the voltage difference being set to zero, therefore, the driving force was purely pneumatic (mainly due to surface tension). As shown in the supplementary video (TypeII.avi), the droplets were generated only in the presence of the applied voltage. When the voltage was turned off, the droplet did not take off from the end of microchannel. Instead, its size kept increasing because the widened opening pulled the liquid from the inside of the microchannel. This also proved that the droplet generation using Type II generator had the drop-on-demand (DOD) characteristic. One can control the droplet generation by turning on/off the applied voltage. Although the EHD droplet generation without any external pumping shown in Figure 4(a)~(b) and Figure 6(a) resembled that of the dripping mode¹¹, this result of the control experiment shows a new mode of the EHD droplet generation by modifying the surface wetting property and geometry of the droplet generator.

The characteristics of this droplet generation are determined by four dimensionless numbers, gravitational Bond number Bo^G , electrical Bond number Bo^E , Reynolds number Re , and Weber number We . Here, the Reynolds number ($\rho v_c R / \mu$) and the Weber number ($\rho v_c^2 R / \sigma$) represent the ratio of inertial forces to viscous forces and the ratio of inertial forces to surface tension, respectively. For calculation, we used $R = 50 \mu\text{m}$ and $v_c = 5 \text{ mm/sec}$ which was taken from the volumetric flow rate ($0.1 \mu\text{L/min}$) inside the microchannel. The numbers of both 0.1 % aqueous solutions and pure cosolvents are summarized in Table 2. All solutions used in this work have similar values of Re which in fact does not influence the generation characteristics significantly. Since the permittivity difference term ($\sim \nabla \epsilon$), which is included in the second term of electrical body force, is negligible, the permittivity in Bo^E does not play an important role in the droplet generation either. In contrast to Re and Bo^E , Bo^G and We of the 0.1 % aqueous solutions are about 3 ~ 10 % higher than those of DI water. By further increasing these numbers with higher solvent concentration, for instance with 1% and 10% aqueous solutions, we could not observe any monodisperse droplets even with the widening channel end (Type II device). These results showed that the aqueous solution with Bo^G and We of 3 ~ 10 % higher than those of DI water had the proper surface tension under the given experimental conditions to generate the monodisperse droplet without an external pumping. However, it may be possible to achieve similar operation with solvents with larger Bo^G and We (heavier, more viscous solvents), either by optimizing the orifice design and/or additional charging of the liquid. To find the optimum solvent concentration for stable droplet generation, a further experimental investigation is required.

We also demonstrated that formic acid droplets with a diameter of $50 \mu\text{m}$ traveled into the tube through the hole of the copper plate, as shown in Figure 6(b). In our experiment setup, the travel distance of the droplet was approximately 3 cm when a vacuum was applied from the end of the tube (corresponding to a gas flow rate of 360 mL/min). This flow rate was not high enough to have an effect on the pressure gradient inside of the microchannel. Although the generation with and without the negative pressure was qualitatively similar, the vacuum assisted to extend the travel length of the droplets in the tube. This result suggests the possibility that our droplet generator can be used to dispense droplets with a sample volume in the range of pico-liter into an analytical sensing device. Droplets of other cosolvents, listed in Table 1, were also successfully injected into the tube.

CONCLUSIONS

In this study, we demonstrated an electrohydrodynamic generation and dispensing of monodisperse droplets directly out of a plane sidewall of a PDMS chip without using any integrated capillary or monolithically built-in tip and without external pumping. Under an applied typical electric field of around $25,000 \text{ V/cm}$, the Taylor cone, which is commonly

observed in the EHD method and hinders accurate control of the size and generation frequency, was completely removed after we coated the surface of the orifice area with Teflon. The numerical simulation also proved the effect of surface wetting condition on the formation of the microdroplets. However, the EHD force has multiple components and originates from different aspects of the electric property. To explore the inner connection between the EHD forces and the droplet generation more accurately, a more detailed theoretical study is necessary. Various aqueous solutions commonly used in the biological applications were tested and the microdroplets with approximately the same size as that of the channel opening could be generated with the cosolvents. With widening channel end, the generation of the droplets was repeatable and stable for more than 30 minutes without any external pumping. Optimal conditions for the operation have been identified, in terms of several dimensionless number for aqueous solutions used. We were able to produce the monodisperse microdroplets with a typical size of 20 μm , which corresponds to a sample volume of 4 pico-liters, and delivered them through air as far as 3cm horizontally. Such capability would be highly useful for various microchip-world integration projects, such as microchip-AMS, microchip-MALDI, and microchip-microarray for example. This simple design of the device enables cost-effective fabrication of this disposable device, with minimal requirements for fabrication capability. The microfabrication method using PDMS also enables us to build high-density nozzle array for multi-sample injections. Future work will demonstrate the applicability of such a multi-sample dispenser for direct delivery of pico-liter samples to a sensing unit.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Figure 1.

(a) Schematic illustration of two types of microdroplet generators; Type I with a straight channel and Type II with a widening exit at the end of the channel. The bottom PDMS plate had the microchannel and the cover PDMS plate had an inclined angle of 20 degrees. (b) Schematic of the experimental system. The vacuum was applied to increase the travel length of the droplet in the tube. The assembled system is shown in Figure 1(c). The PDMS microchip incorporated three individual droplet generators.

Figure 2. Numerical analysis domain and boundaries of the microdroplet generator. The electric field was applied between $\partial\Omega_1$ and $\partial\Omega_2$. The region near the orifice of the droplet generator was further discretized.

Figure 3. Numerical simulation and experimental results of the droplet generation with DI water from (a) a non-coated PDMS surface and (b) a Teflon-coated surface of droplet generator Type I as a function of the dimensionless time unit.

Figure 4.

Generation of droplets with DI water as a function of the gap between the generator orifice and the ground electrode at a voltage of 2,500 V without any external pumping. The microchannel was 15 μm deep and 20 μm wide (Type I). At $t = 0.0$ sec, the droplet started to form at the end of the microchannel, as shown on the left side. With decreasing gap distances, the droplet sizes reduced from 108 μm to 30 μm . At $t = 0.125$ msec, the droplet were partially detached from the generator flying to the ground electrode, as shown on the right side. The rest of the droplet was still visible at the orifice of the droplet generator. In the case of Figure 4(e), the droplet diameter could not be determined because of its non-spherical shape. All images were captured at 8,000 fps. The variation of the drop size was less than 2.0%, as shown in Figure 4(f). (See the videos of the droplet generation in supplementary materials)

Figure 5.

Generation of droplets with 0.1% acetic acid solution as a function of the electrical field strength at a gap of 1 mm with an external pumping. The microchannel was 15 μm deep and 20 μm high (Type I). At $t = 0.0$ sec, the droplet started to form at the end of the microchannel, as shown on the left side. With increasing voltages, the droplet size reduced from 150 μm to 21 μm . At $t = 0.125$ msec, the droplet was completely detached from the generator flying to the ground electrode, as shown on the right side. All images were captured at 8,000 fps. The variation of the drop size was less than 2.0%, as shown in Figure 5(g). (See the videos of the droplet generation in supplementary materials)

Figure 6.

(a) Microdroplet generation of various cosolvent solutions with the PDMS microchip of Type II (20 μm deep $\times$ 50 μm wide) at $t = 0.0$ sec. One can see the droplet formation at the end of each microchannel without any external pumping. (b) Magnified view of the tube (view A) behind the ground electrode shows injected formic acid droplets on the tube wall at $t = 10$ sec. (See the videos of (a) the droplet generation and (b) the droplet injection in supplementary materials)

Table 1

Physicochemical properties of various 0.1 % aqueous solutions and DI water. The values of the pure organic solvents are shown in parentheses.

	Density, ρ (g/cm ³)	Surface tension, σ (dynes/cm)	Permittivity, ϵ/ϵ_0	Viscosity, μ (cp)
Acetic acid	1.001 (1.049)	70.37 (27.80)	78.34 (6.15)	1.003 (1.290)
Formic acid	1.002 (1.220)	71.19 (36.60)	78.52 (58.00)	1.004 (1.804)
Methanol	0.998 (0.810)	67.16 (22.61)	78.47 (32.63)	1.011 (0.597)
Ethanol	0.995 (0.791)	67.16 (22.75)	78.45 (24.30)	1.005 (1.200)
Acetonitrile	0.999 (0.949)	70.75 (29.13)	78.48 (37.50)	--- (0.360)
DI water	1.000	73.05	78.54	1.002

Table 2

Dimensionless numbers which represent the characteristics of the droplet generation for various 0.1 % aqueous solutions and DI water. The values of dimensionless numbers of the pure organic solvents are shown in parentheses. Major physicochemical properties are σ , $\varepsilon/\varepsilon_0$, μ , and ν_c . For calculation, we used $R = 50 \mu\text{m}$ and $\nu_c = 5 \text{ mm/sec}$ which was taken from the volumetric flow rate ($0.1 \mu\text{L/min}$) inside the microchannel.

	$Bo^G (\times 10^{-3})$	Bo^E	$Re (\times 10^{-2})$	$We (\times 10^{-4})$
Acetic acid	3.49 (9.25)	3.08 (0.61)	2.50 (2.03)	1.77 (4.72)
Formic acid	3.45 (8.17)	3.05 (4.37)	2.50 (1.69)	1.76 (4.17)
Methanol	3.64 (8.78)	3.23 (3.98)	2.47 (3.39)	1.86 (4.48)
Ethanol	3.63 (8.52)	3.23 (2.95)	2.47 (1.65)	1.85 (4.35)
Acetonitrile	3.46 (7.98)	3.07 (3.53)	--- (6.88)	1.77 (4.10)
DI water	3.35	2.97	2.50	1.71